

# Evaluated Kinetic Data for Combustion Modeling: Supplement II

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This compilation updates and expands two previous evaluations of kinetic data on elementary, homogeneous, gas phase reactions of neutral species involved in combustion systems [J. Phys. Chem. Ref Data **21**, 411 (1992); **23**, 847 (1994)]. The work has been carried out under the auspices of the IUPAC Commission on Chemical Kinetics and the UK Engineering and Physical Sciences Research Council. Individual data sheets are presented for most reactions but the kinetic data for reactions of C<sub>2</sub>, C, ethyl, *i*-propyl, *t*-butyl, and allyl radicals are summarized in tables. Each data sheet sets out relevant thermodynamic data, experimental kinetic data, references, recommended rate parameters with their error limits and a brief discussion of the reasons for their selection. Where appropriate the data are displayed on an Arrhenius diagram or by fall-off curves. Tables summarizing the recommended rate data and the thermodynamic data for the reactant and product species are given, and their sources referenced. As in the previous evaluations the reactions considered relate largely to the combustion in air of organic compounds containing up to three carbon atoms and simple aromatic compounds. Thus the data base has been expanded, largely by dealing with a substantial number of extra reactions within these general areas. © 2005 American Institute of Physics. [DOI: 10.1063/1.1748524]

Key words: chemical kinetics; combustion; data evaluation; gas phase; rate constant.

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## 1. Introduction

This publication is Supplement II to the compilation of critically evaluated kinetic data for combustion reactions published in the *Journal of Physical and Chemical Reference Data*, in 1992.<sup>1</sup> Supplement I was published in the same journal in 1994.<sup>2</sup>

Both of the previous publications in the series were prepared by the CEC Group on Evaluation of Kinetic Data for Combustion Modeling which was established as part of one of the projects within the European Community Energy Research and Development Program. That program has now been completed and the present publication has been prepared with the financial support of the UK Engineering and Physical Sciences Research Council and under the auspices of the IUPAC Commission on Chemical Kinetics of the IUPAC Physical Chemistry Division.

The original compilation was intended for use in computer modeling of the combustion of methane and ethane in air. It also dealt with a number of reactions important in the chemistry of exhaust gases mainly involving NO<sub>x</sub>, and in the combustion of simple aromatic compounds. In Supplement I the coverage was extended to include small unsaturated hydrocarbons and the reactions of a number of radicals particularly important in the combustion of larger hydrocarbons. The coverage of reactions of nitrogen containing species was also extended.

In Supplement II all of the previous material has been updated and a substantial number of new reactions has been added to the data base. They include some reactions of alcohols and dimethyl ether, reactions relating to soot formation, and a considerable number of new reactions within the general areas dealt with previously.

Wherever possible an individual data sheet has been provided for each reaction. However there are some species, important in combustion, for which insufficient data are available to make any useful evaluation and, in those cases (ethyl, *i*-propyl, *t*-butyl, and allyl radicals, atomic C, C<sub>2</sub> radicals), the existing data are presented in Tables with some comment on their quality, if possible.

In Supplement I<sup>2</sup> the policy adopted for updating was to present a new data sheet only for those reactions for which new data had become available since publication of the original evaluation. Thus for complete information on the whole data-base reference to the two publications<sup>1,2</sup> was necessary. A different approach has been used in Supplement II. Here a data sheet is presented for all of the reactions, where possible, whether new data are available or not. In most cases, to limit the presentation of a great deal of old data, only that data which the evaluators have used to arrive at their Preferred Values are tabulated. However, where there are few data for a particular reaction, all of the data are tabulated to allow ready comparison, especially where no Arrhenius diagram is given. Although there is selection in tabulating the data, references are given to all other data, if any, and all of the available experimental results are displayed on any accompanying Arrhenius diagram. Pressure dependences of dissociation and recombination reactions are represented in diagrams of fall-off curves.

Another important feature of Supplement II is a more thorough and extensive review of the thermodynamic data as described in Sec. 3.

The formal cut-off point for the literature searching was Autumn 2001. The Group continued to monitor the literature during the preparation of the manuscript but results published after the cut-off date were only incorporated if they affected significantly the recommendations already made.

## 2. Guide to the Data Sheets

### 2.1. Scope and Reaction Ordering

For each reaction, a data sheet is presented setting out relevant thermodynamic data, rate coefficient measurements, an assessment of the reliability of the data, references, preferred values of the rate coefficients are suggested and, where appropriate, all of the data are displayed on an Arrhenius diagram. The format chosen for the data sheets has been strongly influenced by that used by the IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry.<sup>3</sup> Our format follows theirs closely but we have made more extensive use of graphs because of the need to convey some idea of the quality of the data over a wide temperature range.

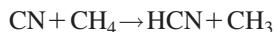
In Supplement I and Supplement II we have departed from this format in presenting data on the reactions of ethyl, *i*-propyl, *t*-butyl, and allyl radicals. The reactions of these radicals are of key importance in modeling the combustion of higher alkanes but in most cases there are insufficient data to warrant production of a full data sheet. For most of the reactions of these species we have therefore presented our recommendations in the form of Tables, with relevant comments on the preferred values, but without detailed display of the data. A similar procedure has been adopted in Supplement II for the reactions of C<sub>2</sub> and C.

The reactions are grouped in order using a system widely adopted in publications of the National Institute of Standards and Technology. The grouping is made on the basis of the attacking atom or radical in the order set out in the following list.

O Atom Reactions  
O<sub>2</sub> Reactions  
H Atom Reactions  
H<sub>2</sub> Reactions  
OH Radical Reactions  
H<sub>2</sub>O Reactions  
HO<sub>2</sub> Radical Reactions  
H<sub>2</sub>O<sub>2</sub> Reactions  
N Atom Reactions  
N<sub>2</sub>O Reactions  
NH Radical Reactions  
NH<sub>2</sub> Radical Reactions  
NH<sub>3</sub> Reactions  
HNO Reactions  
C Atom Reactions  
C<sub>2</sub> Radical Reactions  
<sup>3</sup>CH<sub>2</sub> Radical Reactions  
<sup>1</sup>CH<sub>2</sub> Radical Reactions  
CH<sub>3</sub> Radical Reactions  
CH<sub>4</sub> Reactions  
CHO Radical Reactions  
HCHO Reactions  
CH<sub>2</sub>OH Radical Reactions  
CH<sub>3</sub>O Radical Reactions  
CH<sub>3</sub>CO Reactions  
C<sub>2</sub>H<sub>5</sub>O Radical Reactions  
C<sub>2</sub>H<sub>5</sub>OOH Reactions  
C<sub>3</sub>H<sub>4</sub> Radical Reactions  
C<sub>3</sub>H<sub>5</sub> Radical Reactions  
*i*-C<sub>3</sub>H<sub>7</sub> Radical Reactions  
C<sub>3</sub>H<sub>8</sub> Reactions  
*t*-C<sub>4</sub>H<sub>9</sub> Radical Reactions  
C<sub>5</sub>H<sub>5</sub> Radical Reactions  
C<sub>5</sub>H<sub>6</sub> Reactions  
C<sub>6</sub>H<sub>5</sub> Radical Reactions  
C<sub>6</sub>H<sub>6</sub> Reactions  
C<sub>6</sub>H<sub>5</sub>O Radical Reactions  
C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub> Radical Reactions

$C_6H_5CH_3$  Reactions  
 $p-H_4(CH_3)_2$  Reactions  
 $C_6H_5C_2H_5$  Radical Reactions

Thus, the reaction

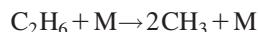


will be found under CN radical reactions. For reactions not classified by this rule, e.g. radical-radical reactions, the rule that species higher on the list take precedence over those lower applies. Thus, the reaction



will be found under OH radical reactions. The same rule applies to reactions between species of a non-radical nature. For the purposes of the classification  $O_2$  and NO are treated as radicals only in their reactions with nonradical species.

An exception to this ordering is the placement of dissociation reactions immediately after their corresponding reverse reaction, the combination of the dissociation products. Thus the data sheet for the reaction



will be found immediately following the data sheet for the reaction



This arrangement is followed wherever a full analysis of the pressure dependence of pairs of such reactions is carried out. In other cases where the data do not justify such a treatment or where only the combination or the decomposition reaction is dealt with, the normal ordering prevails.

## 2.2. Guide to the Tables

Each data sheet begins with a heading giving all the reaction paths considered feasible whether there is evidence for their occurrence or not.

These are followed by the thermodynamic quantities  $\Delta H^\circ$  and  $\Delta S^\circ$  at 298 K and an expression for the equilibrium constant,  $K_c$ , in molecule/cm<sup>3</sup> units, for each of the reaction channels for which there are data available. All thermodynamic data refer to a standard state of 1 bar. The sources of the thermodynamic data are discussed later in this Introduction (Section 2.7 and Section 3).

The kinetic data for the reactions are summarized in a Table under the two headings: (i) Rate Coefficient Measurements, and (ii) Reviews and Evaluations. To keep the size of the compilation within reasonable bounds, in most cases only those rate coefficient measurements which are considered to be of sufficient reliability as to have influenced the derivation of the preferred rate parameters, are recorded in the Table. Similarly only the most recent and/or influential, reviews are recorded. However, where there are few data for a particular reaction, all of the data are tabulated to allow ready comparison, especially where no Arrhenius diagram is given. Where an Arrhenius diagram is presented all of the experimental results are referenced and plotted. Wherever feasible, individual

data points are plotted on the Arrhenius diagram but, to avoid overcrowding on the diagram, the results of a particular study are sometimes given as a line rather than as the individually reported data points.

For bimolecular reactions, the temperature dependence of the rate coefficient is expressed either as  $k = A \exp(-B/T)$  or  $AT^n \exp(-C/T)$  whichever is the more appropriate, where A, n, B, and C are constants. In some cases, the form with C = 0, leading to  $k = AT^n$ , gives the best representation and, occasionally, the rate constant over a wide temperature range is represented as the sum of two exponential expressions. The expressions used for pressure dependent combination and dissociation reactions are discussed in detail later.

Among the Reviews and Evaluations there are a number which are referred to so frequently that, rather than repetitively give their full reference, *in extenso*, we list them among the references in this Introduction and refer the reader back to this list. These reviews are those of the IUPAC Task Group,<sup>3–6</sup> the NASA Panel,<sup>7</sup> and our earlier publications referred to as CEC, 1992<sup>1</sup> and CEC, 1994.<sup>2</sup> The evaluations of the NASA and IUPAC Task Group, subsequent to the publications listed,<sup>3–7</sup> have been published on their respective web sites (<http://jpldataeval.jpl.nasa.gov> and <http://www.iupac-kinetic.ch.cam.ac.uk>)

The tables of data are supplemented by a series of “Comments” summarizing significant features of the experimental studies and reviews. For measurements giving rate coefficient ratios, the absolute value derived from them, and given in the Table, may be different from that quoted in the original paper because the evaluator has chosen to use a value of the reference rate coefficient different from that used by the original author. Such differences are indicated and justified by appropriate entries in the “Comments” section.

Under “Preferred Values” the rate coefficient values recommended for use by modelers are presented as a temperature dependent expression over a stated temperature range. Wherever possible, an attempt has been made to make recommendations for high temperatures even if this requires a considerable extrapolation from the low temperature data and consequent assignment of large error limits. However, in many cases, particularly for reactions likely to have a large activation energy, or where alternative reaction channels may become important, it has not been considered safe to extrapolate much beyond the range of existing measurements.

The preferred values are based almost exclusively on experimental data but in a very few cases estimates have been based on analogous reactions. No attempt has been made to include calculated values of rate parameters but theoretical and empirical estimates have not been ignored. They have often provided valuable background and guidance on whether experimental values are “reasonable.”

The preferred rate constant expression is followed by a statement of the error limits in  $\log k$  at the extremes of the recommended temperature range. Some comments on the assignment of errors are given later in this Introduction (Sec. 2.6).

The section “Comments on Preferred Values” contains a

brief account of how expressions for the preferred values were arrived at and comments on the quality of the available data.

The data sheets conclude with a list of the relevant references and in many cases graphs to illustrate the quality of the data. Where there are few data points for a particular reaction all are recorded but for well-studied reactions, where much data are available, for the sake of clarity, expressions, rather than the original points, are displayed in some cases.

### 2.3. Conventions Concerning Rate Coefficients

It is assumed that all reactions in the compilation are elementary reactions.

The relationship between rate and rate coefficient for a reaction described by a stoichiometric equation such as



is given by

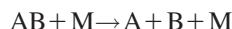
$$\text{Rate} = -(1/2)d[A]/dt = d[B]/dt = d[C]/dt = k[A]^2.$$

### 2.4. Treatment of Combination and Dissociation Reactions

Unlike simple bimolecular reactions such as those considered in Section 2.3, combination reactions



and the reverse dissociation reactions



are each composed of a sequence of different types of physical and chemical elementary processes. Their rate constants reflect this more complicated sequential mechanism, and thus are found to depend on the temperature,  $T$ , and the nature and concentration of the third body, M. In this evaluation, the combination reactions are described by a formal second-order rate law,

$$d[AB]/dt = k[A][B]$$

while dissociation reactions are described by a formal first-order rate law,

$$d[AB]/dt = -k[AB].$$

In both cases,  $k$  depends on the temperature and on [M].

In order to rationalize these representations of the rate constants, we consider the Lindemann-Hinshelwood reaction scheme in which the combination reactions follow an elementary mechanism of the form



while the dissociation reactions are characterized by:



Assuming quasistationary concentrations for the highly unstable species  $AB^*$  (i.e.  $d[AB^*]/dt \approx 0$ ), the rate constant for the combination reaction is given by

$$k = k_1 \left( \frac{k_2[M]}{k_{-1} + k_2[M]} \right)$$

while that for the dissociation reaction is given by

$$k = k_{-2}[M] \left( \frac{k_{-1}}{k_{-1} + k_2[M]} \right).$$

In these equations the terms before the parentheses represent the rate constant of the process initiating the reaction, whereas the expression within the parentheses expresses the fraction of the reaction events which, after initiation, go on to form products.

In the low pressure limit ( $[M] \rightarrow 0$ ), both of these rate constants are proportional to  $[M]$ ; in the high pressure limit ( $[M] \rightarrow \infty$ ) they are independent of  $[M]$ . It is useful to express  $k$  in terms of the limiting low pressure and high pressure rate coefficients

$$k_0[M] = \lim_{[M] \rightarrow 0} dk/[M]/d[M]$$

$$[M] \rightarrow 0$$

and

$$k_\infty = \lim_{[M] \rightarrow \infty} k([M])$$

respectively. With this convention, one obtains the Lindemann-Hinshelwood equation

$$k = \frac{k_0 k_\infty [M]}{k_0 [M] + k_\infty}.$$

For combination reactions, in this equation one has  $k_0 = k_1 k_2 / k_{-1}$  and  $k_\infty = k_1$ ; for dissociation reactions the corresponding relationships are  $k_0 = k_{-2}$  and  $k_\infty = k_{-1} k_{-2} / k_2$ . Since detailed balancing applies, the ratio of the rate constants for combination and dissociation at fixed  $T$  and  $[M]$  is given by the equilibrium constant  $K_c$ , where

$$K_c = k_1 k_2 / k_{-1} k_{-2}.$$

Starting from the high pressure limit, the rate constant,  $k$ , falls off with decreasing third body concentration,  $[M]$ ; the corresponding representation of  $k$  is termed the “falloff curve” of the reaction. In practice, the Lindemann-Hinshelwood expressions do not characterize the fall-off curves completely. Because of the multistep character of the collisional deactivation ( $k_2[M]$ ) and activation ( $k_{-2}[M]$ ) processes, and the energy and angular momentum dependences of the association ( $k_1$ ) and dissociation ( $k_{-1}$ ) steps, as well as other factors, the falloff expressions have to be modified. This can be done by adding a broadening factor,  $F$ , to the Lindemann-Hinshelwood expressions, giving<sup>8-10</sup>

$$\begin{aligned} k &= \frac{k_0 k_\infty [M]}{k_0[M] + k_\infty} F = k_0[M] \left( \frac{1}{1 + k_0[M]/k_\infty} \right) F \\ &= k_\infty \left( \frac{k_0[M]/k_\infty}{1 + k_0[M]/k_\infty} \right) F. \end{aligned}$$

$F$  depends on the ratio  $k_0[M]/k_\infty$  which can be used as a "reduced pressure" measure. To a first approximation,  $F$  is given by:<sup>8-10</sup>

$$\log F \approx \frac{\log F_c}{1 + \left[ \frac{\log(k_0[M]/k_\infty)}{N} \right]^2},$$

where  $N = 0.75 - 1.27 \log F_c$ . For reactions with "rigid activated complexes," where the reaction in the dissociation and the recombination directions has to pass over an energy barrier, the "center broadening factor,"  $F_c$ , generally decreases with increasing molecular complexity of AB and with increasing temperature,  $T$ , before it increases again with increasing  $T$  at very high  $T$ . It can be calculated by unimolecular rate theory;<sup>8-11</sup> alternatively it is often obtained by fitting experimental fall-off curves and sometimes represented by using equations of the form

$$\begin{aligned} F_c &= (1-a) \exp(-T/T^{***}) + a \exp(-T/T^*) \\ &\quad + \exp(-T^{**}/T), \end{aligned}$$

where  $a$ ,  $T^*$ ,  $T^{**}$ , and  $T^{***}$  are constants. If detailed calculations are made it is sometimes found that alternative expressions for  $F_c$  may be more appropriate. At a higher level, asymmetries of the broadening factor,  $F$ , have to be accounted for by adding a term  $a'$  to  $\log(k_0[M]/k_\infty)$  and  $\Delta N$  to  $N$ .  $a'$  is generally in the range  $-0.3 - 0.3$  and  $\Delta N$  assumes different values to the left and right of the center of the fall-off curve, i.e., the position of the minimum of  $F$ . For reactions with "loose activation complexes," where the combination reaction does not have an energy barrier, the situation changes somewhat.<sup>11,12</sup> Here,  $F_c$  is nearly temperature independent over a wide temperature range, and smaller than for systems with rigid activation complexes. Only at very high temperatures does it approach the behavior observed for systems with rigid activation complexes. Asymmetries of the fall-off curves are also observed here at lower temperatures than for systems with rigid activation complexes.

The rate constants for combination and dissociation in this evaluation are often characterized by the three quantities  $k_0$ ,  $k_\infty$ , and  $F_c$ , (and the equations given previously). If an experimental fall-off curve is fitted using these quantities, changes in  $F_c$  also change the values of  $k_0$  and  $k_\infty$ . Therefore, a fall-off representation requires that all three parameters,  $k_0$ ,  $k_\infty$ , and  $F_c$ , be specified which is done wherever possible throughout this evaluation. It should also be noted that unimolecular rate theory allows for at least semiquantitative prediction of  $k_0$ ,  $k_\infty$ , and  $F_c$ , (e.g., see Ref. 8).

In a few instances, rate constants for a particular reaction have been measured under conditions where they are almost certainly pressure dependent but where the measurements are

not of sufficient quantity and/or quality to enable them to be analyzed to give values of  $k_0$ ,  $k_\infty$ , and  $F_c$ . In such cases, in the present evaluation, an expression for  $k$  may be recommended with some limits placed on the range of pressures over which it applies. It should also be noted that, to avoid ambiguity, the subscripts denoting infinite and zero limiting rate constants have, in places been written as superscripts, e.g.,  $k_1^\infty$ ,  $k_1^0$  rather than  $k_{1\infty}$ , and  $k_{10}$ .

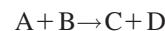
For combination reactions the dependence of  $k_0$  and  $k_\infty$  on the temperature is represented in the form

$$k \propto T^n$$

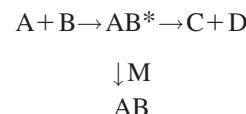
except for cases where it has been established that there is a an energy barrier in the potential. This form of temperature dependence has been chosen because it often gives a better fit to the data over a wider range of temperature than the Arrhenius equation. Obviously, the relevant values of  $n$  are different for  $k_0$  and for  $k_\infty$ .  $k_0$  values are given for selected third bodies, preferentially, wherever possible, for M=N<sub>2</sub> and O<sub>2</sub>.

## 2.5. Treatment of Complex-Forming Bimolecular Reactions

Bimolecular reactions may follow a "direct" pathway

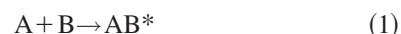


and/or involve complex formation



possibly followed by subsequent reactions of AB.

We designate the rate constants of the individual steps as in Section 2.3,



Assuming a quasistationary concentration of AB\* (i.e.,  $d[AB^*]/dt \approx 0$ ), a Lindemann-Hinshelwood type of analysis leads to

$$d[AB]/dt = k_S[A][B]$$

$$d[C]/dt = k_D[A][B]$$

$$d[A]/dt = (k_S + k_D)[A][B],$$

where

$$k_S = k_1 \left( \frac{k_2}{k_{-1} + k_2 + k_3} \right)$$

$$k_D = k_1 \left( \frac{k_3}{k_{-1} + k_2 + k_3} \right).$$

Note that since  $k_2$  is proportional to  $[M]$ ,  $k_S$  and  $k_D$  are dependent on the nature and concentration of the third body, M, as well as being temperature dependent. As for the combination and dissociation reactions, these expressions for  $k_S$  and  $k_D$  have to be extended by suitable broadening factors,  $F$ , in order to account for the multistep nature of Process (2) and the energy dependences of (1), (-1), and (3). These broadening factors differ, however, from those for combination and dissociation reactions. For simplicity, in most cases they are ignored in this evaluation so that at high pressures

$$k_D = k_1 k_3 / k_2$$

which is inversely proportional to  $[M]$ .  $k_D$  may also be expressed by

$$k_D \approx k_D^0 k_S / k_S^0,$$

where  $k_D^0$  and  $k_S^0$  are the respective limiting low pressure rate constants for the formation of C+D or A+B at the considered  $[M]$ . When it is established that complex formation is involved, this equation is used to characterize the increasing suppression of C+D formation with increasing  $[M]$ .

## 2.6. Assignment of Errors

The reliability of a preferred expression for  $k$  is expressed in terms of an estimated  $\Delta \log k$  at the extremes of the temperature range covered by the recommended expression. Thus a quoted  $\Delta \log k = \pm X$  is equivalent to the statement that the range of values of  $k$  encompassed by these error limits may be found by multiplication and division of  $k$  by a factor  $G$ , where  $X = \log G$ .

No attempt has been made to assign explicit error limits to the temperature coefficient of  $k$ . The error limits in  $\Delta \log k$  assigned at the extremes of the temperature range indicate how the quality of the data varies with temperature without attempting to define the form which this variation takes. In the opinion of the evaluators the available data rarely merit a more elaborate assignment of errors over a wide temperature range.

The assignment of error limits in  $k$  is a subjective assessment by the evaluators. Modern techniques are capable in favorable circumstances of measuring rate coefficients with the precision represented by a standard deviation as small as 10%. However, data obtained in different laboratories on the same reaction and often by the same technique are rarely concordant to the extent that might be expected from the precision of the measurements: mean values may differ by many standard deviations. This is indicative of systematic errors, which are difficult to detect and which cannot be incorporated simply into quoted error limits.

## 2.7. Thermodynamic Data

In the two previous publications in this series<sup>1,2</sup> it was decided that, for internal consistency, the thermodynamic data would be taken from a single publication, that prepared for the Sandia Chemkin Program,<sup>13</sup> even though it was rec-

ognized that there were considerable uncertainties in many of the values quoted. In Supplement II a more extensive survey of the available thermodynamic data has been made and the values used have been drawn from a number of sources.

The standard enthalpy of formation and entropy at 298 K of all of the reactant and product species is given in a Table preceding the section containing the data sheets. Wherever possible the values are based on experimental data but, where they are lacking, resort has been made to estimations based on a number of semi-empirical schemes relating thermodynamic properties to molecular structure. Such estimated values must be treated with caution; substantial uncertainty limits need to be assigned but no attempt has been made to estimate them. "Brief Comments" accompany the entries in the Table indicating the origins of the values and references to their sources are given. Values of the heat capacities of the species are not given but the comments and references also indicate the sources used. Throughout the selection of the data every attempt has been made to ensure that the final set is internally consistent.

On each data sheet the standard enthalpy and entropy changes at 298 K and the equilibrium constant as a function of temperature are given for each reaction channel. The equilibrium constant is expressed in terms of the constants A, B, and n using the form  $K_c(T) = AT^n \exp(B/T)$ . The quality of the thermodynamic data rarely justify the use of an expression for  $K_c(T)$  involving more than three constants and the functional form chosen mirrors that used to express the rate constants. To derive the expression for  $K_c(T)$  values of the heat capacities, expressed as NASA polynomials, were used to calculate values of  $\Delta H^\circ$ ,  $\Delta S^\circ$  and hence  $K_c$  at a number of temperatures in the range 300–5000 K; in a few cases it was necessary to accept a lower upper limit owing to lack of data. The expression for  $K_c(T)$  was then fitted to these values by a least squares procedure.

Because  $K_c$  is very sensitive to the values of the thermodynamic quantities, particularly  $\Delta H^\circ$ , uncertainties in the thermodynamic data may introduce substantial uncertainties in any rate coefficient calculated from the equilibrium constant and the rate coefficient for the reaction in one direction.

Wherever kinetic data are available for the rate coefficients for the reaction in both forward and reverse directions, an attempt has been made to reconcile them with the thermodynamic data quoted.

## 2.8. Acknowledgments

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## 2.9. References

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### 3. Thermodynamic Data

#### 3.1. Guide to the Table

The standard enthalpy of formation and entropy at 298 K of all of the reactant and product species used in this eval-

uation is given in the Table which follows (Sec. 3.2). The data set was originally compiled in 1998 taking data from recent reviews and evaluations of thermodynamic data (for example, Refs. 1–11) or recent published experimental data. Where no experimental data are available we have taken values determined from *ab initio* calculations, (e.g., Ref. 12) and in other instances properties have been estimated by applying methods based on group additivity<sup>13,14</sup> or hydrogen bond increments.<sup>15</sup> Such estimated values must be treated with caution; substantial uncertainty limits need to be assigned. Brief comments accompany the entries in the Table indicating the origins of the values and references to their sources are given (Sec. 3.3). Data on heat capacities of the species, over a range of temperatures, were also compiled. Values of the heat capacities of the species are not given but the comments and references indicate the sources used (Sec. 3.3). The data were expressed as a function of temperature in polynomial form (NASA polynomials) and used to calculate values of  $K_c$  as described in Sec. 2.7. Throughout the selection of the data every attempt has been made to ensure that the final set is internally consistent.

In some reactions, where a number of very similar isomeric products may be formed, only thermodynamic data for one of the channels is quoted. There are also a few reaction channels for which we have not attempted to estimate the thermodynamic data.

#### 3.2. Table of Thermodynamic Properties

Standard Enthalpy of Formation and Entropy, at 298 K, of Reactants and Products

Species	Name	$\Delta_f H^\circ_{298}$ /kJ mol <sup>-1</sup>	$S^\circ_{298}$ /J K <sup>-1</sup> mol <sup>-1</sup>	Comments
<i>O Compounds</i>				
O( <sup>3</sup> P)	Atomic oxygen (ground state)	249.16	161.04	(1)
O( <sup>1</sup> D)	Atomic oxygen (first electronic excited state)	438.92	156.69	(2)
O <sub>2</sub>	Diatomeric oxygen	0.00	205.12	(3)
<i>H Compounds</i>				
H	Atomic hydrogen	217.97	114.59	(4)
H <sub>2</sub>	Diatomeric hydrogen	0.00	130.57	(5)
OH(X <sup>2</sup> Π)	Hydroxyl radical (ground state)	37.17	183.71	(6)
OH(A <sup>2</sup> Σ <sup>+</sup> )	Hydroxyl radical (first electronic excited state)	424.70	184.70	(7)
HO <sub>2</sub>	Hydroperoxy radical	14.60	229.07	(8)
H <sub>2</sub> O	Water	-241.82	188.80	(9)
H <sub>2</sub> O <sub>2</sub>	Hydrogen peroxide	-136.31	234.49	(10)
<i>N Compounds</i>				
N( <sup>4</sup> S)	Atomic nitrogen (ground state)	472.68	153.17	(11)
N( <sup>2</sup> D)	Atomic nitrogen (first electronic excited state)	702.76	160.79	(12)
N <sub>2</sub>	Diatomeric nitrogen	0.00	191.49	(13)
NO	Nitric oxide	90.29	210.63	(14)
NO <sub>2</sub>	Nitrogen dioxide	33.09	239.89	(15)
NO <sub>3</sub>	Nitrate radical	73.70	252.53	(16)

## Standard Enthalpy of Formation and Entropy, at 298 K, of Reactants and Products—Continued

Species	Name	$\Delta_f H^\circ_{298}$ /kJ mol <sup>-1</sup>	$S^\circ_{298}$ /J K <sup>-1</sup> mol <sup>-1</sup>	Comments
N <sub>2</sub> O	Dinitrogen monoxide	82.05	219.86	(17)
NH	Imidogen radical	356.49	181.13	(18)
NH <sub>2</sub>	Amidogen radical	189.50	194.58	(19)
NH <sub>3</sub>	Ammonia	-45.92	192.60	(20)
NNH	NNH	245.05	224.36	(21)
HNO	Nitroxyl radical	107.10	249.52	(22)
HONO	Nitrous acid	-79.50	254.03	(23)
H <sub>2</sub> NO	Amineoxyl radical	66.10	233.98	(24)
NH <sub>2</sub> O <sub>2</sub>	Amineperoxy radical	161.92	263.98	(25)
NH <sub>2</sub> OH	Hydroxylamine	-50.00	236.18	(26)
NH(OH) <sub>2</sub>	Di hydroxylamine	-103.35	260.93	(27)
NH <sub>2</sub> OOH	Hydroperoxylamine	11.68	263.04	(28)
HN <sub>2</sub> O	adduct	235.70	263.50	(29)
NH <sub>2</sub> NO	Nitrosyl amide	95.69	242.96	(30)
<i>CHON Compounds</i>				
C	Monatomic carbon	716.71	157.99	(31)
C <sub>2</sub> (x <sup>1</sup> $\Sigma_g^+$ )	Diatomeric carbon (ground state)	837.84	191.18	(32)
C <sub>2</sub> (x <sup>3</sup> $\Pi_u$ )	Diatomeric carbon (first electronic excited state)	845.14	207.91	(33)
C <sub>3</sub>	Triatomic carbon	820.06	237.07	(34)
CO	Carbon monoxide	-110.54	197.52	(35)
CO <sub>2</sub>	Carbon dioxide	-393.53	213.71	(36)
CCO	Ketenylidene radical	383.10	232.95	(37)
CN	Cyano radical	435.40	202.53	(38)
CNN	Diazocarbene	571.12	231.61	(39)
NCN	NCN radical	473.00	226.20	(40)
NCO	Cyanato radical	127.00	232.11	(41)
CNO	Fulminyl radical	407.01	238.49	(42)
HCN	Hydrogen cyanide	135.15	201.73	(43)
HNCO	Isocyanic acid	-116.00	238.71	(44)
HO-CN	Cyanic acid	-9.00	247.85	(45)
HCNO	Fulminic acid	173.00	225.06	(46)
<i>CHO Compounds</i>				
CH	Methylidyne	596.40	182.91	(47)
CH <sub>2</sub> (X <sup>3</sup> $\Sigma_g^-$ )	Triplet methylene radical	390.39	194.87	(48)
CH <sub>2</sub> (a <sup>1</sup> A <sub>1</sub> )	Singlet methylene radical	428.30	188.69	(49)
CH <sub>3</sub>	Methyl radical	146.40	193.93	(50)
CH <sub>4</sub>	Methane	-74.90	186.03	(51)
CHO	Formyl radical	43.10	224.30	(52)
CHO <sup>+</sup>	Formyl cation	833.00	203.29	(53)
HOCO	Carboxyl radical	-217.00	251.70	(54)
HC(O)O	HC(O)O radical	-150.62	239.74	(55)
HC(O)OO	Formylperoxy radical	-37.66	298.58	(56)
HCHO	Formaldehyde	-108.58	218.73	(57)
HCOH	Hydroxymethylene radical	206.18	240.17	(58)
CH <sub>2</sub> OH	Hydroxymethyl radical	-17.80	243.88	(59)
CH <sub>3</sub> O	Methoxyl radical	17.20	229.35	(60)
CH <sub>2</sub> OOH	Hydroperoxymethyl radical	45.59	276.14	(61)
CH <sub>3</sub> OO	Methylperoxy radical	20.10	269.76	(62)
CH <sub>3</sub> OH	Methanol	-201.50	239.77	(63)
CH <sub>3</sub> OOH	Hydroperoxymethane	-138.10	272.06	(64)
CHN <sub>2</sub>	Dative adduct	494.92	249.79	(65)

## Standard Enthalpy of Formation and Entropy, at 298 K, of Reactants and Products—Continued

Species	Name	$\Delta_f H^\circ_{298}$ /kJ mol <sup>-1</sup>	$S^\circ_{298}$ /J K <sup>-1</sup> mol <sup>-1</sup>	Comments
CH <sub>2</sub> N	Methanimine radical	240.20	224.22	(66)
H <sub>2</sub> C=NO	Methyleneiminoxyl radical	173.41	249.87	(67)
CH <sub>3</sub> NO	Nitroso methane	69.90	257.29	(68)
<i>C<sub>2</sub>HO Compounds</i>				
C <sub>2</sub> H	Ethynyl radical	566.10	213.27	(69)
C <sub>2</sub> H <sub>2</sub>	Ethyne	228.20	200.88	(70)
C <sub>2</sub> H <sub>3</sub>	Vinyl radical	299.72	233.92	(71)
C <sub>2</sub> H <sub>4</sub>	Ethene	52.46	219.14	(72)
C <sub>2</sub> H <sub>5</sub>	Ethyl radical	120.90	247.08	(73)
C <sub>2</sub> H <sub>6</sub>	Ethane	-83.86	228.94	(74)
HCCO	Ketyl radical	175.30	245.25	(75)
OOCH=C=O	Ketoperoxyl radical	-83.29	155.22	(76)
CH <sub>2</sub> CO	Ketene	-47.50	241.86	(77)
HCCOH	Ethynol	93.17	249.10	(78)
(CHO) <sub>2</sub>	Glyoxal (trans)	-211.99	59.54	(79)
CH <sub>3</sub> CO	Acyl radical	-10.01	267.41	(80)
CH <sub>2</sub> OH	Formylmethyl radical	10.50	267.88	(81)
CH=CH(OH)	2-hydroxyvinyl radical	113.00	262.37	(82)
CH <sub>2</sub> =CHO	Vinoxyl radical	86.72	272.50	(83)
CH <sub>2</sub> =CHOO	Vinylperoxyl radical	16.60	138.67	(84)
CH <sub>3</sub> C(O)OO	Peroxyacyl radical	-175.05	319.59	(85)
OOCH <sub>2</sub> CHO	Formylmethylperoxyl radical	-53.16	322.29	(86)
CH <sub>3</sub> CHO	Ethanal	-166.19	263.91	(87)
[-CH <sub>2</sub> CH <sub>2</sub> O-]	Oxirane	-52.64	242.83	(88)
C <sub>2</sub> H <sub>5</sub> O	Ethoxyl radical	-15.22	274.41	(89)
CH <sub>3</sub> CHOH	1-hydroxyethyl radical	-51.59	280.83	(90)
CH <sub>2</sub> CH <sub>2</sub> OH	2-hydroxyethyl radical	-36.01	275.00	(91)
CH <sub>3</sub> OCH <sub>2</sub>	Methoxymethyl radical	-0.10	281.89	(92)
CH <sub>2</sub> CH <sub>2</sub> OOH	2-hydroperoxyethyl radical	32.98	333.91	(93)
CH <sub>3</sub> CHOOH	1-hydroperoxyethyl radical	1.69	319.16	(94)
C <sub>2</sub> H <sub>5</sub> OO	Ethylperoxyl radical	-27.40	313.73	(95)
C <sub>2</sub> H <sub>5</sub> OH	Ethanol	-234.95	280.54	(96)
CH <sub>3</sub> OCH <sub>3</sub>	Dimethyl ether	-184.05	267.33	(97)
C <sub>2</sub> H <sub>5</sub> OOH	Ethylhydroperoxide	-172.07	318.87	(98)
HOCH <sub>2</sub> CH <sub>2</sub> OH	1,2-ethandiol	-392.23	303.77	(99)
CH <sub>3</sub> OOC <sub>3</sub>	Dimethylperoxide	-125.70	312.26	(100)
<i>C<sub>3</sub>HO Compounds</i>				
C <sub>3</sub> H <sub>2</sub>	Cyclopropylidene biradical (singlet)	476.98	236.20	(101)
H <sub>2</sub> CCC	Propadienylidene radical	651.03	254.55	(102)
HCCCH	Prop-2-ynylidene radical (triplet)	755.25	260.78	(103)
CH <sub>2</sub> CCH	Propargyl radical	341.00	253.25	(104)
CH <sub>3</sub> CCH	Propyne	184.90	248.25	(105)
CH <sub>2</sub> CCH <sub>2</sub>	Allene	190.50	243.39	(106)
CH <sub>2</sub> CHCH <sub>2</sub>	a-C <sub>3</sub> H <sub>5</sub> radical	170.70	259.47	(107)
CH <sub>3</sub> CHCH	s-C <sub>3</sub> H <sub>5</sub> radical	262.73	271.16	(108)
C <sub>3</sub> H <sub>6</sub>	Propene	20.00	266.49	(109)
[-C <sub>3</sub> H <sub>6</sub> -]	Cyclopropane	53.50	237.40	(110)
n-C <sub>3</sub> H <sub>7</sub>	n-propyl radical	100.48	289.41	(111)
iso-C <sub>3</sub> H <sub>7</sub>	Isopropyl radical	90.00	289.29	(112)
C <sub>3</sub> H <sub>8</sub>	Propane	-104.70	270.13	(113)
HCCCO	Propynonyl radical	372.01	266.48	(114)
CH <sub>2</sub> CHCO	Vinylcarbonyl radical	72.4		(115)

## Standard Enthalpy of Formation and Entropy, at 298 K, of Reactants and Products—Continued

Species	Name	$\Delta_f H^\circ_{298}$ /kJ mol <sup>-1</sup>	$S^\circ_{298}$ /J K <sup>-1</sup> mol <sup>-1</sup>	Comments
CH <sub>2</sub> =CHCHO	Propenal	-75.00	281.94	(116)
CH <sub>2</sub> CHCH <sub>2</sub> O	2-propen-1-oxyl radical	93.90	305.89	(117)
C <sub>2</sub> H <sub>5</sub> C(O)	Propionyl radical	-32.31	309.24	(118)
C <sub>2</sub> H <sub>5</sub> CHO	Propanal	-185.60	304.45	(119)
CH <sub>2</sub> =CHCH <sub>2</sub> OH	2-propen-1-ol	-124.50	312.02	(120)
<i>C<sub>4</sub>HO Compounds</i>				
HCCCCH	1,3-Butadiyne	467.38	250.11	(121)
HC≡C-CH=CH	<i>n</i> -vinylacetylene radical	531.81	284.67	(122)
CH≡C-CH=CH <sub>2</sub>	Vinylacetylene	284.50	278.87	(123)
CH <sub>2</sub> =CHCHCH	1,3-butadien-1-yl radical	360.24	289.21	(124)
CH <sub>2</sub> =CHC=CH <sub>2</sub>	1,3-butadien-2-yl radical	309.60	286.95	(125)
CH <sub>2</sub> =CHCH=CH <sub>2</sub>	1,3-butadiene	110.00	278.24	(126)
C <sub>2</sub> H <sub>5</sub> -CH=CH	1-butenyl radical	247.40	313.57	(127)
CH <sub>2</sub> CH <sub>2</sub> CHCH <sub>2</sub>	3-butenyl radical	214.64	316.39	(128)
Z-CH <sub>3</sub> C=CHCH <sub>3</sub>	<i>cis</i> -2-buten-2-yl	230.99	319.77	(129)
E-CH <sub>3</sub> C=CHCH <sub>3</sub>	<i>trans</i> -2-buten-2-yl	226.69	303.36	(130)
Z-CH <sub>2</sub> CH=CHCH <sub>3</sub>	<i>cis</i> -2-butenyl	143.96	299.08	(131)
E-CH <sub>2</sub> CH=CHCH <sub>3</sub>	<i>trans</i> -2-butenyl	139.65	288.45	(132)
C <sub>2</sub> H <sub>5</sub> -CH=CH <sub>2</sub>	1-Butene	0.10	307.75	(133)
Z-2-C <sub>4</sub> H <sub>8</sub>	<i>cis</i> -2-butene	-7.10	300.69	(134)
E-2-C <sub>4</sub> H <sub>8</sub>	<i>trans</i> -2-butene	-11.40	295.82	(135)
(CH <sub>3</sub> ) <sub>2</sub> C=CH <sub>2</sub>	Isobutene	-16.90	296.61	(136)
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	1-butyl radical	80.49	331.63	(137)
(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub>	Isobutyl radical	72.71	319.45	(138)
(CH <sub>3</sub> ) <sub>3</sub> C	<i>t</i> -butyl radical	51.29	317.11	(139)
<i>n</i> -C <sub>4</sub> H <sub>10</sub>	Butane	-125.79	309.67	(140)
<i>iso</i> -C <sub>4</sub> H <sub>10</sub>	Isobutane	-134.65	295.29	(141)
(CH <sub>3</sub> ) <sub>2</sub> CHCO	Isobutyryl radical	-59.52	334.41	(142)
(CH <sub>3</sub> ) <sub>2</sub> CCHO	2-formyl-2-propyl radical	-59.15	354.21	(143)
CH <sub>2</sub> CH(CH <sub>3</sub> )CHO	2-formyl-1-propyl radical	-10.68	347.33	(144)
(CH <sub>3</sub> ) <sub>2</sub> CHCHO	2-methylpropanal	-215.70	332.32	(145)
<i>C<sub>5</sub>HO Compounds</i>				
[ <i>-C<sub>5</sub>H<sub>5</sub>-</i> ]	Cyclo-1,3-pentadien-5-yl radical	261.50	266.80	(146)
[ <i>-C<sub>5</sub>H<sub>6</sub>-</i> ]	Cyclopentadiene	134.28	274.10	(147)
[ <i>-CH=CH-(CH<sub>2</sub>)<sub>3</sub>-</i> ]	Cyclopentene	34.00	291.21	(148)
(CH <sub>3</sub> ) <sub>2</sub> CHCHCH	3-methyl-1-butenyl	219.79	339.16	(149)
C <sub>3</sub> H <sub>7</sub> CH=CH <sub>2</sub>	1-Pentene	-21.29	345.71	(150)
(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub>	2-methyl-4-butyl radical	50.19	358.47	(151)
<i>neo</i> -C <sub>5</sub> H <sub>12</sub>	2,2-dimethyl propane	-168.00	304.73	(152)
<i>t</i> -C <sub>4</sub> H <sub>9</sub> CO	2,2-dimethyl propionyl radical	-87.70		(153)
CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> CHO	2-methyl-2-formyl propyl radical	-38.90		(154)
<i>t</i> -C <sub>4</sub> H <sub>9</sub> CHO	2,2-dimethyl propanal	-243.92		(155)
<i>C<sub>6</sub>HO Compounds</i>				
CHCCHCHCCH	Hexa-3-en-1,5-diyne	512.63	321.22	(156)
<i>o</i> -[ <i>-C<sub>6</sub>H<sub>4</sub>-</i> ]	<i>ortho</i> -benzyne	441.50	291.04	(157)
HC≡-C-CH=CH-CH-CH=CH	Hexa-1,3-dien-5-ynyl radical	591.77	339.12	(158)
[ <i>-C<sub>6</sub>H<sub>5</sub>-</i> ]	Phenyl radical	338.00	288.28	(159)
[ <i>-C<sub>6</sub>H<sub>6</sub>-</i> ]	Benzene	82.60	269.01	(160)
[ <i>-C<sub>6</sub>H<sub>6</sub>-</i> ]-H (adduct)	2,4-cyclohexadienyl radical	208.78	301.25	(161)
CH <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub> CHCH <sub>2</sub>	1,5-hexadiene	84.42	379.70	(162)
(CH <sub>3</sub> ) <sub>3</sub> CCHCH	3,3-dimethyl but-1-enyl	186.99	347.39	(163)

## Standard Enthalpy of Formation and Entropy, at 298 K, of Reactants and Products—Continued

Species	Name	$\Delta_f H^\circ_{298}$ /kJ mol <sup>-1</sup>	$S^\circ_{298}$ /J K <sup>-1</sup> mol <sup>-1</sup>	Comments
(CH <sub>3</sub> ) <sub>3</sub> CCH <sub>2</sub> CH <sub>2</sub>	3,3-dimethyl butyl radical	19.48	371.99	(164)
(CH <sub>3</sub> ) <sub>2</sub> CHCH(CH <sub>3</sub> ) <sub>2</sub>	2,3-dimethyl butane	-178.10	365.83	(165)
[ -C <sub>5</sub> H <sub>4</sub> ]=CO	2,4-cyclopentadienylidene methanone	136.89	353.82	(166)
[ -C <sub>6</sub> H <sub>4</sub> ]-1,2-(O) <sub>2</sub>	<i>ortho</i> quinone	-104.60	336.34	(167)
[ -C <sub>6</sub> H <sub>4</sub> ]-1,4-(O) <sub>2</sub>	<i>para</i> quinone	-122.90	333.14	(168)
[ -C <sub>6</sub> H <sub>5</sub> ]-O	Phenoxy radical	47.70	313.25	(169)
[ -C <sub>6</sub> H <sub>4</sub> ]-2-OH	2-hydroxyphenyl radical	160.80	324.93	(170)
[ -C <sub>6</sub> H <sub>5</sub> ]-OO	Phenylperoxy radical	160.66	349.36	(171)
[ -C <sub>6</sub> H <sub>5</sub> ]-OH	Phenol	-96.39	314.79	(172)
[ -C <sub>6</sub> H <sub>6</sub> ]=O	1-oxo-2,4-cyclohexadiene	-17.59	324.66	(173)
[ -C <sub>6</sub> H <sub>6</sub> ]-OH (adduct)	1-hydroxy-2,4-cyclohexadien-5-yl radical	44.09	341.73	(174)
[ -C <sub>6</sub> H <sub>5</sub> ]-1,2-(OH) <sub>2</sub> (adduct)	1,2-dihydroxy-3,5-cyclohexadienyl-radical	-151.78	370.71	(175)
<i>C<sub>7</sub>HO Compounds</i>				
CH <sub>2</sub> =C=CHCH	3,5,6-heptatrienyl-1-yne	485.05	357.81	(176)
=CHC≡CH				
[ -C <sub>5</sub> H <sub>5</sub> ]-CCH	Cyclopentadienylethyne	367.77	313.34	(177)
[ -C <sub>6</sub> H <sub>5</sub> ]-CH <sub>2</sub>	Benzyl radical	207.94	319.01	(178)
[ -C <sub>6</sub> H <sub>4</sub> ]-2-CH <sub>3</sub>	2-methylphenyl radical	305.84	328.13	(179)
[ -C <sub>6</sub> H <sub>5</sub> ]-CH <sub>3</sub>	Toluene	50.50	320.11	(180)
[ -C <sub>6</sub> H <sub>6</sub> ]-1-(CH <sub>3</sub> ) (adduct)	1-methyl-2,4-cyclohexadienyl radical	170.83	334.73	(181)
CH <sub>2</sub> =CHCH <sub>2</sub> CH(CH <sub>3</sub> )CHCH <sub>3</sub>	4-methyl-1-hexen-5-yl radical	129.60	433.26	(182)
[ -C <sub>6</sub> H <sub>4</sub> ]-2-CHO	2-formylphenyl radical	218.71	345.76	(183)
[ -C <sub>6</sub> H <sub>5</sub> ]-CO	Benzoyl radical	119.00	339.61	(184)
[ -C <sub>6</sub> H <sub>5</sub> ]-CHO	Benzaldehyde	-36.72	335.86	(185)
[ -C <sub>6</sub> H <sub>4</sub> ]-1-OH;-2-CH <sub>3</sub>	<i>ortho</i> -cresol	-128.63	352.54	(186)
[ -C <sub>6</sub> H <sub>4</sub> ]-1-OH;-4-CH <sub>3</sub>	<i>para</i> -cresol	-125.32	350.70	(187)
[ -C <sub>6</sub> H <sub>5</sub> ]-OCH <sub>3</sub>	Methoxybenzene	-67.90	351.15	(188)
[ -C <sub>6</sub> H <sub>5</sub> ]-1-(CH <sub>3</sub> );-2-(OH) (adduct)	2-hydroxy-1-methyl-3,5-cyclohexadienyl radical	5.96	375.23	(189)
<i>C<sub>8</sub>HO Compounds</i>				
[ -C <sub>6</sub> H <sub>5</sub> ]-CCH	Phenylethyne	318.00	321.70	(190)
[ -C <sub>6</sub> H <sub>5</sub> ]-C <sub>2</sub> H <sub>2</sub>	2-phenylvinyl radical	395.30	350.76	(191)
[ -C <sub>6</sub> H <sub>5</sub> ]-CHCH <sub>2</sub>	Phenylethene	148.00	345.01	(192)
[ -C <sub>6</sub> H <sub>4</sub> ]-2-C <sub>2</sub> H <sub>5</sub>	2-ethylphenyl radical	285.39	396.37	(193)
[ -C <sub>6</sub> H <sub>5</sub> ]-CH <sub>2</sub> CH <sub>2</sub>	2-phenylethyl radical	235.03	374.54	(194)
[ -C <sub>6</sub> H <sub>5</sub> ]-CHCH <sub>3</sub>	1-phenylethyl radical	171.43	338.41	(195)
[ -C <sub>6</sub> H <sub>4</sub> ]-1-(CH <sub>2</sub> );-4-(CH <sub>3</sub> )	4-methylbenzyl radical	175.90	341.28	(196)
[ -C <sub>6</sub> H <sub>3</sub> ]-1,4-(CH <sub>3</sub> ) <sub>2</sub>	2,5-dimethylphenyl radical	273.64	479.36	(197)
[ -C <sub>6</sub> H <sub>4</sub> ]-1,4-(CH <sub>3</sub> ) <sub>2</sub>	<i>para</i> -xylene	18.10	352.03	(198)
[ -C <sub>6</sub> H <sub>5</sub> ]-C <sub>2</sub> H <sub>5</sub>	Ethylbenzene	30.00	359.55	(199)
[ -C <sub>6</sub> H <sub>5</sub> ]-1,4-(CH <sub>3</sub> ) <sub>2</sub> (adduct)	2-H-1,4-dimethyl-3,5-cyclohexadien-1-yl radical	137.75	370.34	(200)
[ -C <sub>6</sub> H <sub>5</sub> ]-1-(C <sub>2</sub> H <sub>5</sub> )(H) (adduct)	1-ethyl-2,4-cyclohexadienyl radical	149.90	374.05	(201)
(CH <sub>3</sub> ) <sub>3</sub> CC(CH <sub>3</sub> ) <sub>3</sub>	2,2,3,3-tetramethylbutane	-230.16	394.62	(202)
[ -C <sub>6</sub> H <sub>3</sub> ]-1-OH;-2,5-(CH <sub>3</sub> ) <sub>2</sub>	2,5-dimethylphenol	-158.65	394.80	(203)
[ -C <sub>6</sub> H <sub>4</sub> ]-OCH <sub>3</sub> ; -4-CH <sub>3</sub>	4-methylmethoxybenzene	-103.92	394.09	(204)
[ -C <sub>6</sub> H <sub>5</sub> ]-1-(C <sub>2</sub> H <sub>5</sub> );-2-(OH) (adduct)	2-hydroxy-1-ethyl-3,5-cyclohexadienyl radical	-14.96	414.55	(205)
[ -C <sub>6</sub> H <sub>4</sub> ]-1,4-(CH <sub>3</sub> ) <sub>2</sub> ; -2-(OH) (adduct)	2-hydroxy-1,4-dimethyl-3,5 cyclohexadienyl radical	-27.09	405.08	(206)

### Comments

- (1) Sandia Chemkin database,<sup>1</sup> fit to JANAF data.<sup>2</sup>
- (2) Calculated from data in JANAF tables.<sup>2</sup>
- (3) Burcat and McBride,<sup>3</sup> fit to TSIV data.<sup>4</sup>
- (4) Sandia Chemkin database,<sup>1</sup> fit to JANAF data.<sup>2</sup>
- (5) Sandia Chemkin database,<sup>1</sup> fit to JANAF data.<sup>2</sup>
- (6) Burcat and McBride,<sup>3</sup> fit to TSIV data.<sup>4</sup>  $\Delta_fH^\circ_{298}$  based on Ruscic *et al.*<sup>5</sup> and Joens.<sup>6</sup>
- (7) Calculated from data in JANAF tables.<sup>2</sup>
- (8)  $S^\circ_{298}$  and  $C_p^\circ$  polynomial coefficients from Burcat and McBride,<sup>3</sup> based on data of Jacox.<sup>7</sup>  $\Delta_fH^\circ_{298}$  from Kerr and Stocker.<sup>8</sup>
- (9) Burcat and McBride,<sup>3</sup> based on CODATA recommended values.<sup>9</sup>
- (10) Burcat and McBride,<sup>3</sup> fit to TSIV data.<sup>4</sup>
- (11)  $S^\circ_{298}$  and  $C_p^\circ$  polynomial coefficients from Sandia Chemkin database<sup>1</sup> (fit to JANAF data<sup>2</sup>),  $\Delta_fH^\circ_{298}$  from CODATA recommended values.<sup>9</sup>
- (12) Calculated from data in JANAF tables.<sup>2</sup>
- (13) Sandia Chemkin database,<sup>1</sup> fit to JANAF data.<sup>2</sup>
- (14) Sandia Chemkin database,<sup>1</sup> fit to JANAF data.<sup>2</sup>
- (15) Sandia Chemkin database,<sup>1</sup> fit to JANAF data.<sup>2</sup>
- (16)  $S^\circ_{298}$  and  $C_p^\circ$  polynomial coefficients from Burcat and McBride<sup>3</sup> (fit to JANAF data<sup>2</sup>),  $\Delta_fH^\circ_{298}$  from Kerr and Stocker.<sup>8</sup>
- (17) Sandia Chemkin database,<sup>1</sup> fit to JANAF data.<sup>2</sup>
- (18) Sandia Chemkin database,<sup>1</sup> fit to JANAF data.<sup>2</sup>
- (19)  $S^\circ_{298}$  and  $C_p^\circ$  polynomial coefficients from Sandia Chemkin database<sup>1</sup> (fit to JANAF data<sup>2</sup>),  $\Delta_fH^\circ_{298}$  from Sutherland and Michael.<sup>10</sup>
- (20) Sandia Chemkin database,<sup>1</sup> fit to JANAF data.<sup>2</sup>
- (21) Sandia Chemkin database,<sup>1</sup> fit to BAC-MP4 data, Melius<sup>11</sup> (compound reference R3G).
- (22)  $S^\circ_{298}$  and  $C_p^\circ$  polynomial coefficients from Sandia Chemkin database<sup>1</sup> (fit to JANAF data<sup>2</sup>),  $\Delta_fH^\circ_{298}$  from Anderson.<sup>12</sup>
- (23)  $S^\circ_{298}$  and  $C_p^\circ$  polynomial coefficients from Burcat and McBride<sup>3</sup> (fit to TSIV data<sup>4</sup>),  $\Delta_fH^\circ_{298}$  from Lide.<sup>13</sup>
- (24) Polynomial coefficients calculated from BAC-MP4 data, Melius<sup>11</sup> (compound reference; R5G).
- (25) Polynomial coefficients calculated from BAC-MP4 data, Melius<sup>11</sup> (compound reference; RK52).
- (26) Burcat<sup>14</sup> based on TSIV data.<sup>4</sup>
- (27) Polynomial coefficients calculated from BAC-MP4 data, Melius<sup>11</sup> (compound reference; D88F).
- (28)  $\Delta_fH^\circ_0$  calculated with  $D^\circ_{298}$  (H—OO) from Kerr and Stocker<sup>8</sup> and  $\Delta_fH^\circ_{298}(\text{NH}_2\text{OOH})$  from Sumathi and Peyerimhoff.<sup>15</sup>
- (29) Polynomial coefficients calculated from data of Diau and Lin.<sup>16</sup>
- (30)  $S^\circ_{298}$  and  $C_p^\circ$  polynomial coefficients calculated using frequencies of Diau and Smith,<sup>17</sup>  $\Delta_fH^\circ_{298}$  calculated relative to  $\Delta_fH^\circ_{298}(\text{NH}_2 + \text{NO})$ , Diau and Smith.<sup>17</sup>
- (31) Sandia Chemkin database,<sup>1</sup> fit to JANAF data.<sup>2</sup>
- (32) Calculated from data in JANAF tables.<sup>2</sup>
- (33) Calculated from data in JANAF tables.<sup>2</sup>
- (34) Sandia Chemkin database,<sup>1</sup> fit to JANAF data.<sup>2</sup>
- (35) Sandia Chemkin database,<sup>1</sup> fit to JANAF data.<sup>2</sup>
- (36) Sandia Chemkin database,<sup>1</sup> fit to JANAF data.<sup>2</sup>
- (37)  $S^\circ_{298}$  and  $C_p^\circ$  polynomial coefficients from Sandia Chemkin database,<sup>1</sup> fit to JANAF data.<sup>2</sup>  $\Delta_fH^\circ_{298}$  Zengin *et al.*<sup>18</sup> and Mordaunt *et al.*<sup>19</sup>
- (38)  $S^\circ_{298}$  and  $C_p^\circ$  polynomial coefficients from Sandia Chemkin database,<sup>1</sup> fit to JANAF data.<sup>2</sup>  $\Delta_fH^\circ_{298}$  Huang *et al.*<sup>20</sup>
- (39)  $S^\circ_{298}$  and  $C_p^\circ$  polynomial coefficients from Sandia Chemkin database,<sup>1</sup> fit to JANAF data.<sup>2</sup>  $\Delta_fH^\circ_{298}$  Clifford *et al.*<sup>21</sup>
- (40) Fit to JANAF data.<sup>2</sup>
- (41)  $S^\circ_{298}$  and  $C_p^\circ$  polynomial coefficients from Sandia Chemkin database,<sup>1</sup> fit to JANAF data.<sup>2</sup>  $\Delta_fH^\circ_{298}$  Cyr *et al.*,<sup>22</sup> Brown *et al.*,<sup>23</sup> and Zyrianov *et al.*<sup>24</sup> Enthalpy of formation compatible with HNCO data.
- (42)  $S^\circ_{298}$  and  $C_p^\circ$  calculated with frequencies of Koch and Frenking,<sup>25</sup>  $\Delta_fH^\circ_{298}$  calculated relative to  $\Delta_fH^\circ_{298}(\text{NCO})$ , Koch and Frenking.<sup>25</sup>
- (43) Sandia Chemkin database,<sup>1</sup> fit to JANAF data.<sup>2</sup>
- (44)  $S^\circ_{298}$  and  $C_p^\circ$  polynomial coefficients from Sandia Chemkin database,<sup>1</sup> fit to BAC-MP4 data, Melius.<sup>11</sup> (Compound reference RJ5)  $\Delta_fH^\circ_{298}$  Zhang *et al.*,<sup>26</sup> Brown *et al.*,<sup>23</sup> and Zyrianov *et al.*,<sup>24</sup> based on  $\Delta_fH^\circ_{298}(\text{NCO}) = 127 \text{ kJ mol}^{-1}$  determined by Cyr *et al.*<sup>22</sup>
- (45)  $S^\circ_{298}$  and  $C_p^\circ$  polynomial coefficients from Sandia Chemkin database,<sup>1</sup> fit to BAC-MP4 data, Melius.<sup>11</sup> (Compound reference RJ6)  $\Delta_fH^\circ_{298}$  relative to  $\Delta_fH^\circ_{298}$  (HNCO) calculated by East and Allen.<sup>27</sup>
- (46)  $S^\circ_{298}$  and  $C_p^\circ$  polynomial coefficients from Sandia Chemkin database,<sup>1</sup> fit to BAC-MP4 data, Melius.<sup>11</sup> (Compound reference C17B)  $\Delta_fH^\circ_{298}$  relative to  $\Delta_fH^\circ_{298}$  (HNCO) calculated by East and Allen.<sup>27</sup>
- (47)  $S^\circ_{298}$  and  $C_p^\circ$  polynomial coefficients from Sandia Chemkin database,<sup>1</sup> fit to JANAF data.<sup>2</sup>  $\Delta_fH^\circ_{298}$  from Kerr and Stocker.<sup>8</sup>
- (48) Burcat and McBride,<sup>3</sup> fit to TSIV data.<sup>4</sup>  $\Delta_fH^\circ_{298}$  agrees with Kerr and Stocker.<sup>8</sup>
- (49)  $S^\circ_{298}$  and  $C_p^\circ$  polynomial coefficients from Sandia Chemkin database,<sup>1</sup> fit to BAC-MP4 data, Melius.<sup>11</sup> (Compound reference R5S)  $\Delta_fH^\circ_{298}$  from Kerr and Stocker.<sup>8</sup>
- (50)  $S^\circ_{298}$  and  $C_p^\circ$  polynomial coefficients from Burcat and McBride,<sup>3</sup> fit to Pamidimukkala *et al.*<sup>28</sup>  $\Delta_fH^\circ_{298}$  from Kerr and Stocker.<sup>8</sup>
- (51) Sandia Chemkin database,<sup>1</sup> fit to JANAF data.<sup>2</sup>
- (52)  $S^\circ_{298}$  and  $C_p^\circ$  polynomial coefficients from Burcat and McBride,<sup>3</sup> based on data of Jacox<sup>7</sup> and Gurvich.<sup>4</sup>  $\Delta_fH^\circ_{298}$  average of values of Chuang *et al.*<sup>29</sup> and Becerra *et al.*<sup>30</sup>
- (53) Sandia Chemkin database,<sup>1</sup> fit to JANAF data.<sup>2</sup>
- (54)  $S^\circ_{298}$  and  $C_p^\circ$  polynomial coefficients from Burcat and McBride,<sup>3</sup> fit to TSIV data.<sup>4</sup>  $\Delta_fH^\circ_{298}$  from Fulle *et al.*<sup>31</sup>
- (55) From Burcat,<sup>14</sup> based on Benson.<sup>33</sup>
- (56) Estimated from properties of parent molecule,

- HC(O)OOH (formic acid), applying H-bond increment method. Increment for peroxy radicals from Lay *et al.*<sup>32</sup> Thermodynamic properties of HC(O)OOH estimated by group additivity.<sup>33,34</sup>
- (57) Burcat and McBride,<sup>3</sup> fit to TSIV data.<sup>4</sup>
  - (58) Polynomial coefficients calculated from BAC-MP4 data, Melius<sup>11</sup> (compound reference; N88L).
  - (59)  $S^o_{298}$  and  $C_p^o$  polynomial coefficients from Burcat and McBride,<sup>3</sup> based on data of Jacox<sup>7</sup> and Burcat and Kudchadker,<sup>35</sup>  $\Delta_fH^o_{298}$  from Johnson and Hudgens.<sup>36</sup>
  - (60)  $S^o_{298}$  and  $C_p^o$  polynomial coefficients from Burcat and McBride,<sup>3</sup> based on data of Jacox.<sup>7</sup>  $\Delta_fH^o_{298}$  from Kerr and Stocker.<sup>8</sup>
  - (61) Estimated from properties of parent molecule, CH<sub>3</sub>OOH, by applying the H-bond increment method. H-bond increment estimated based on the differences between CH<sub>3</sub>OH and CH<sub>2</sub>OH.
  - (62) Group additivity estimate,<sup>33</sup> group coefficients from Stocker and Pilling,<sup>37</sup> based on data of Knyazev and Slagle.<sup>38</sup>  $\Delta_fH^o_{298}$  from Blansky *et al.*<sup>40</sup>
  - (63)  $S^o_{298}$  and  $C_p^o$  polynomial coefficients from Burcat and McBride,<sup>3</sup> based on data of Chen *et al.*<sup>39</sup>  $\Delta_fH^o_{298}$  from Pedley.<sup>41</sup>
  - (64) (64)  $S^o_{298}$  and  $C_p^o$  polynomial coefficients from Burcat and McBride,<sup>3</sup> fit to BAC-MP4 data, Melius<sup>11</sup> (compound reference RH21).  $\Delta_fH^o_{298}$  based on data of Benassi *et al.*<sup>42</sup> and Tyblewski *et al.*<sup>43</sup>
  - (65)  $S^o_{298}$  and  $C_p^o$  polynomial coefficients calculated with frequencies of Martin and Taylor,<sup>44</sup>  $\Delta_fH^o_{298}$  from Fulle and Hippler.<sup>45</sup>
  - (66) Sandia Chemkin database,<sup>1</sup> fit to BAC-MP4 data, Melius<sup>11</sup> (compound reference N36A).
  - (67) Burcat and McBride,<sup>3</sup> fit to BAC-MP4 data, Melius<sup>11</sup> (compound reference C42).
  - (68)  $S^o_{298}$  and  $C_p^o$  calculated from data of Dognon *et al.*<sup>46</sup>  $\Delta_fH^o_{298}$  from Pedley.<sup>41</sup>
  - (69)  $S^o_{298}$  and  $C_p^o$  polynomial coefficients from Burcat and McBride,<sup>3</sup> based on data of Jacox.<sup>7</sup>  $\Delta_fH^o_{298}$  from Kerr and Stocker.<sup>8</sup>
  - (70)  $S^o_{298}$  and  $C_p^o$  polynomial coefficients from Sandia Chemkin database,<sup>1</sup> fit to JANAF data.<sup>2</sup>  $\Delta_fH^o_{298}$  Pedley.<sup>41</sup>
  - (71) Burcat and McBride,<sup>3</sup> based on data of Karni *et al.*<sup>47</sup>  $\Delta_fH^o_{298}$  from Ervin *et al.*<sup>48</sup>
  - (72) Sandia Chemkin database,<sup>1</sup> fit to JANAF data.<sup>2</sup>
  - (73)  $S^o_{298}$  and  $C_p^o$  polynomial coefficients from Burcat and McBride,<sup>3</sup> based on data of Chen *et al.*<sup>49</sup>  $\Delta_fH^o_{298}$  from Kerr and Stocker.<sup>8</sup>
  - (74) Burcat and McBride,<sup>3</sup> based on data of Chao *et al.*<sup>50</sup>  $\Delta_fH^o_{298}$  compatible with Pedley.<sup>41</sup>
  - (75)  $S^o_{298}$  and  $C_p^o$  polynomial coefficients from Burcat and McBride,<sup>3</sup> based on data of Endo and Hirota.<sup>51</sup>  $\Delta_fH^o_{298}$  from Kerr and Stocker.<sup>8</sup>
  - (76) Estimated from properties of parent molecule, HOOCH=C=O, by applying H-bond increment method. Increment for peroxy radicals from Lay *et al.*<sup>32</sup> Thermodynamic properties of HC(O)OOH estimated by group additivity.<sup>33</sup> Group values for C<sub>D</sub>—O group from ketene, assume properties for O—C<sub>D</sub>/O same as for O—C<sub>D</sub>/C where C<sub>D</sub> represents a double bonded carbon atom and O—C<sub>D</sub>/O represents an oxygen atom bonded to a sp<sup>2</sup> carbon atom and another oxygen atom.
  - (77)  $S^o_{298}$  and  $C_p^o$  polynomial coefficients from Burcat and McBride,<sup>3</sup> based on data of Moore and Pimental.<sup>52</sup>  $\Delta_fH^o_{298}$  from Pedley.<sup>41</sup>
  - (78) Burcat and McBride,<sup>3</sup> based on data of Jacox.<sup>53</sup>  $\Delta_fH^o_{298}$  from BAC-MP4 calculations, Melius<sup>11</sup> (compound reference A7).
  - (79) Burcat<sup>14</sup> based on Scuseria and Schaefer.<sup>54</sup>  $\Delta_fH^o_{298}$  from Pedley.<sup>41</sup>
  - (80) Burcat and McBride,<sup>3</sup> based on data of Nimlos *et al.*<sup>55</sup>  $\Delta_fH^o_{298}$  from Niiranen *et al.*,<sup>56</sup> agrees with Kerr and Stocker.<sup>8</sup>
  - (81)  $S^o_{298}$  and  $C_p^o$  polynomial coefficients from Burcat and McBride,<sup>3</sup> based on data of Burcat *et al.*<sup>57</sup>  $\Delta_fH^o_{298}$  from Kerr and Stocker.<sup>8</sup>
  - (82)  $S^o_{298}$  and  $C_p^o$  calculated from data of Sosa and Schlegel,<sup>58</sup> reported frequencies scaled by 0.85.  $\Delta_fH^o_{298}$  from Fulle *et al.*<sup>59</sup>
  - (83) Fit to the data of Osborn *et al.*<sup>60</sup>
  - (84) Estimate from properties of parent molecule, CH<sub>2</sub>=CHOOH, by applying H-bond increment method. Increment for peroxy radicals from Lay *et al.*<sup>32</sup> Thermodynamic properties of CH<sub>2</sub>=CHOOH estimated by group additivity<sup>33</sup> assuming group values for O—C<sub>D</sub>/O same as for O—C<sub>D</sub>/C, where C<sub>D</sub> represents a double bonded carbon atom and O—C/O represents an oxygen atom bonded to a carbon atom and another oxygen atom.
  - (85)  $S^o_{298}$  and  $C_p^o$  calculated from spectral data of Bridier *et al.*<sup>61</sup> and Bruckman and Willner.<sup>62</sup>  $\Delta_fH^o_{298}$  from Lightfoot *et al.*,<sup>63</sup> as estimated by Bridier *et al.*<sup>61</sup> based on  $\Delta_fH^o_{298}$ (CH<sub>3</sub>C(O)OOH) which was estimated by group additivity<sup>33</sup> and calculated (MNDO) difference in  $D^o_{298}$  (ROO—H) between CH<sub>3</sub>OOH, HOOH, and CH<sub>3</sub>C(O)OOH. Difference added to average of experimental  $D^o_{298}$  (CH<sub>3</sub>OO—H and HOO—H) values.
  - (86) Polynomial coefficients calculated from BAC-MP4 data, Melius<sup>11</sup> (compound reference; D85U).
  - (87)  $S^o_{298}$  and  $C_p^o$  polynomial coefficients from Burcat and McBride,<sup>3</sup> based on data of Chao *et al.*<sup>64</sup>  $\Delta_fH^o_{298}$  compatible with Pedley.<sup>41</sup>
  - (88)  $S^o_{298}$  and  $C_p^o$  polynomial coefficients from Burcat and McBride,<sup>3</sup> based on data of Shimanouchi.<sup>65</sup>  $\Delta_fH^o_{298}$  from JANAF tables.<sup>2</sup>
  - (89)  $S^o_{298}$  and  $C_p^o$  polynomial coefficients from Burcat and McBride,<sup>3</sup> based on data of Burcat *et al.*<sup>57</sup>  $\Delta_fH^o_{298}$  estimated from parent molecule, ethanol, applying H-bond increment method. Increment for alkoxy radicals from Lay *et al.*<sup>32</sup>
  - (90)  $S^o_{298}$  and  $C_p^o$  polynomial coefficients from Burcat and McBride,<sup>3</sup> based on data of Burcat *et al.*<sup>57</sup>  $\Delta_fH^o_{298}$  from study of I+CH<sub>3</sub>CH<sub>2</sub>OH→HI+CH<sub>3</sub>CHOH, Al-

- fassi and Golden.<sup>66</sup> Reported  $\Delta_fH^\circ_{298}$  revised assuming activation energy for the reverse reaction of  $-8 \text{ kJ mol}^{-1}$ , Berkowitz *et al.*<sup>67</sup>
- (91)  $S^\circ_{298}$  and  $C_p^\circ$  polynomial coefficients from Burcat and McBride,<sup>3</sup> based on data of Burcat *et al.*<sup>57</sup>  $\Delta_fH^\circ_{298}$  based on studies of Diau and Lee,<sup>68</sup> Ruscic and Berkowitz,<sup>69</sup> and Fulle *et al.*<sup>59</sup>
- (92)  $S^\circ_{298}$  and  $C_p^\circ$  polynomial coefficients from Burcat and McBride,<sup>3</sup> based on data of Burcat *et al.*<sup>57</sup>  $\Delta_fH^\circ_{298}$  from study of  $\text{I} + \text{CH}_3\text{OCH}_3 \rightarrow \text{HI} + \text{CH}_3\text{OCH}_2$ , Cruickshank and Benson.<sup>70</sup> Reported  $\Delta_fH^\circ_{298}$  revised assuming activation energy for the reverse reaction is  $-8 \text{ kJ mol}^{-1}$ , Berkowitz *et al.*<sup>67</sup>
- (93) Estimated from properties of parent molecule, ethylhydroperoxide, applying H-bond increment method. Increment for primary C-H from Lay *et al.*<sup>71</sup>
- (94) Estimated from properties of parent molecule, ethylhydroperoxide, applying H-bond increment method. Entropy and heat capacity increments based on difference between  $\text{C}_2\text{H}_5\text{OH}$  and  $\text{CH}_3\text{CHOH}$ .<sup>3</sup>  $\Delta_fH^\circ_{298}$  increment based on the difference between  $\Delta_fH^\circ_{298}(\text{CH}_3\text{OH})$ , and  $\Delta_fH^\circ_{298}(\text{CH}_2\text{OH})$  and scaled for difference between primary and secondary  $D^\circ_{298}$  (C-H) in  $\text{C}_3\text{H}_8$ .<sup>8</sup>
- (95) Group additivity estimate,<sup>33</sup> group coefficients from Stocker and Pilling,<sup>37</sup> based on data of Knyazev and Slagle.<sup>38</sup>  $\Delta_fH^\circ_{298}$  compatible with the value of Blanksby *et al.*<sup>40</sup>
- (96) Burcat and McBride,<sup>3</sup> based on data of Chao *et al.*<sup>64</sup>  $\Delta_fH^\circ_{298}$  compatible with Pedley.<sup>41</sup>
- (97) Burcat and McBride,<sup>3</sup> based on data of Chao *et al.*<sup>64</sup>  $\Delta_fH^\circ_{298}$  compatible with Pedley.<sup>41</sup>
- (98) Group additivity estimate,<sup>33</sup> group coefficients from Lay *et al.*<sup>72</sup>
- (99)  $S^\circ_{298}$  and  $C_p^\circ$  polynomial coefficients based on data of Chao *et al.*<sup>64</sup>  $\Delta_fH^\circ_{298}$  from Pedley.<sup>41</sup>
- (100)  $S^\circ_{298}$  and  $C_p^\circ$  polynomial coefficients estimated by group additivity.<sup>33,34</sup>  $\Delta_fH^\circ_{298}$  from Pedley.<sup>41</sup>
- (101) Burcat<sup>14</sup> based on Vereeken *et al.*<sup>73</sup>  $\Delta_fH^\circ_{298}$  from Kiefer *et al.*<sup>74</sup>
- (102) Burcat<sup>14</sup> based on Melius.<sup>11</sup>  $\Delta_fH^\circ_{298}$  from Kiefer *et al.*<sup>74</sup>
- (103) Burcat<sup>14</sup> based on Vereeken *et al.*<sup>73</sup>  $\Delta_fH^\circ_{298}$  from Melius.<sup>11</sup>
- (104)  $S^\circ_{298}$  and  $C_p^\circ$  polynomial coefficients from Burcat and McBride,<sup>3</sup> based on data of Tsang.<sup>75</sup>  $\Delta_fH^\circ_{298}$  from Kerr and Stocker.<sup>8</sup>
- (105)  $S^\circ_{298}$  and  $C_p^\circ$  polynomial coefficients from Burcat and McBride,<sup>3</sup> based on data of Shimanouchi.<sup>65</sup>  $\Delta_fH^\circ_{298}$  from Pedley.<sup>41</sup>
- (106)  $S^\circ_{298}$  and  $C_p^\circ$  polynomial coefficients from Burcat and McBride,<sup>3</sup> based on data of Shimanouchi.<sup>65</sup>  $\Delta_fH^\circ_{298}$  from Pedley.<sup>41</sup>
- (107)  $S^\circ_{298}$  and  $C_p^\circ$  polynomial coefficients calculated from data of Tsang.<sup>76</sup>  $\Delta_fH^\circ_{298}$  from Kerr and Stocker.<sup>8</sup>
- (108)  $S^\circ_{298}$  and  $C_p^\circ$  polynomial coefficients from Burcat and McBride,<sup>3</sup> estimated by group additivity.<sup>33,77</sup>  $\Delta_fH^\circ_{298}$  from Wu and Kern.<sup>78</sup>
- (109)  $S^\circ_{298}$  and  $C_p^\circ$  polynomial coefficients from Burcat and McBride,<sup>3</sup> based on data of Chao and Zwolinski.<sup>79</sup>  $\Delta_fH^\circ_{298}$  from Pedley.<sup>41</sup>
- (110)  $S^\circ_{298}$  and  $C_p^\circ$  polynomial coefficients from Burcat and McBride,<sup>3</sup> based on data of Shimanouchi.<sup>65</sup>  $\Delta_fH^\circ_{298}$  from Pedley.<sup>41</sup>
- (111)  $S^\circ_{298}$  and  $C_p^\circ$  polynomial coefficients calculated from data of Tsang.<sup>76</sup>  $\Delta_fH^\circ_{298}$  from Tsang.<sup>80</sup>
- (112)  $S^\circ_{298}$  and  $C_p^\circ$  polynomial coefficients calculated from data of Tsang.<sup>76</sup>  $\Delta_fH^\circ_{298}$  from Kerr and Stocker.<sup>8</sup>
- (113)  $S^\circ_{298}$  and  $C_p^\circ$  polynomial coefficients from Burcat and McBride,<sup>3</sup> based on data of Chao *et al.*<sup>50</sup>  $\Delta_fH^\circ_{298}$  from Pedley.<sup>41</sup>
- (114)  $\Delta_fH^\circ_{298}$ ,  $S^\circ_{298}$ , and  $C_p^\circ$  from *ab initio* study of Tomasi and Scuseria.<sup>81</sup>
- (115)  $\Delta_fH^\circ_{298}$  Kerr and Stocker.<sup>8</sup>
- (116)  $S^\circ_{298}$  and  $C_p^\circ$  polynomial coefficients estimated by group additivity.<sup>33,34</sup>  $\Delta_fH^\circ_{298}$  from Frenkel *et al.*<sup>82</sup>
- (117) Estimated from properties of parent molecule,  $\text{CH}_2=\text{CHCH}_2\text{OH}$ , by applying H-bond increment method. Increment for alkoxy radicals from Lay *et al.*<sup>32</sup> Thermodynamic properties of  $\text{CH}_2=\text{CHCH}_2\text{OH}$  estimated by group additivity.<sup>33,34</sup>
- (118)  $S^\circ_{298}$  and  $C_p^\circ$  polynomial coefficients estimated by group additivity.<sup>33,34</sup>  $\Delta_fH^\circ_{298}$  from Watkins and Thompson,<sup>83</sup> value adjusted to  $\Delta H^\circ_{f298}(\text{C}_2\text{H}_5) = 120.9 \text{ kJ mol}^{-1}$ .
- (119)  $S^\circ_{298}$  and  $C_p^\circ$  polynomial coefficients from Burcat and McBride,<sup>3</sup> based on data of Chao *et al.*<sup>64</sup>  $\Delta_fH^\circ_{298}$  from Pedley.<sup>41</sup>
- (120)  $S^\circ_{298}$  and  $C_p^\circ$  polynomial coefficients estimated by group additivity.<sup>33,34</sup>  $\Delta_fH^\circ_{298}$  from Pedley.<sup>41</sup>
- (121) Sandia Chemkin database.<sup>1</sup>  $S^\circ$  compatible with Stull *et al.*<sup>84</sup> (Note, values given in Burcat and McBride<sup>3</sup> have been estimated by group additivity<sup>33</sup> employing the group coefficients of Stein *et al.*<sup>85</sup> The estimated  $\Delta_fH^\circ_{298}$  does not agree as well with the experimental data of Wu and Kern.<sup>78</sup>)
- (122)  $\Delta_fH^\circ_{298}$ ,  $S^\circ_{298}$ , and  $C_p^\circ$  polynomial coefficients estimated from properties of parent molecule,  $\text{CH}\equiv\text{C}-\text{CH}=\text{CH}_2$ , by applying H-bond increment method.<sup>71</sup>
- (123)  $S^\circ_{298}$  and  $C_p^\circ$  polynomial coefficients from Burcat and McBride,<sup>3</sup> based on the data of Torneng *et al.*<sup>86</sup>  $\Delta_fH^\circ_{298}$  estimated by group additivity,<sup>33,77,87</sup> value agrees with results of BAC-MP4 calculations, Melius.<sup>11</sup>
- (124) Fit to BAC-MP4 data, Melius.<sup>11</sup> Compound reference A66W
- (125) Estimate from properties of parent molecule,  $\text{CH}_2=\text{CHCH}=\text{CH}_2$ , by applying H-bond increment method. Increment for  $\text{C}=\text{CC}=\text{C}$  from Lay *et al.*<sup>71</sup>
- (126)  $S^\circ_{298}$  and  $C_p^\circ$  polynomial coefficients from Burcat and McBride,<sup>3</sup> estimated by group additivity.<sup>33</sup>  $\Delta_fH^\circ_{298}$  from Pedley.<sup>41</sup>
- (127) Estimate from properties of parent molecule,

- 1-butene, by applying H-bond increment method. Increment for vinyl radicals from Lay *et al.*<sup>71</sup>
- (128) Fit to BAC-MP4 data, Melius.<sup>11</sup> Compound reference P670.
- (129) Estimate from properties of parent molecule, Z-2-butene, by applying H-bond increment method. Increment for secondary vinyl radicals from Lay *et al.*<sup>71</sup>
- (130) Estimate from properties of parent molecule, E-2-butene, by applying H-bond increment method. Increment for secondary vinyl radicals from Lay *et al.*<sup>71</sup>
- (131) Estimate from properties of parent molecule, Z-2-butene, by applying H-bond increment method. Increment for primary allyl radicals from Lay *et al.*<sup>71</sup>
- (132) Estimate from properties of parent molecule, E-2-butene, by applying H-bond increment method. Increment for primary allyl radicals from Lay *et al.*<sup>71</sup>
- (133)  $S^o_{298}$  and  $C_p^o$  polynomial coefficients from Burcat and McBride,<sup>3</sup> based on the data of Chao and Hall.<sup>88</sup>  $\Delta_fH^o_{298}$  from Pedley.<sup>41</sup>
- (134)  $S^o_{298}$  and  $C_p^o$  polynomial coefficients from Burcat and McBride,<sup>3</sup> based on the data of Chao and Hall.<sup>88</sup>  $\Delta_fH^o_{298}$  from Pedley.<sup>41</sup>
- (135)  $S^o_{298}$  and  $C_p^o$  polynomial coefficients from Burcat and McBride,<sup>3</sup> based on the data of Chao and Hall.<sup>88</sup>  $\Delta_fH^o_{298}$  from Pedley.<sup>41</sup>
- (136)  $S^o_{298}$  and  $C_p^o$  polynomial coefficients from Burcat and McBride,<sup>3</sup> based on the data of Chao and Hall.<sup>88</sup>  $\Delta_fH^o_{298}$  from Pedley.<sup>41</sup>
- (137) Estimated by group additivity.<sup>33</sup> Group coefficients from Stocker and Pilling.<sup>37</sup>
- (138) Estimated by group additivity.<sup>33</sup> Group coefficients from Stocker and Pilling.<sup>37</sup>
- (139) Estimated by group additivity.<sup>33</sup> Group coefficients from Stocker and Pilling.<sup>37</sup>
- (140) Burcat and McBride,<sup>3</sup> based on the data of Chen *et al.*<sup>89</sup>  $\Delta_fH^o_{298}$  agrees with Pedley.<sup>41</sup>
- (141) Burcat and McBride,<sup>3</sup> based on the data of Chen *et al.*<sup>89</sup>  $\Delta_fH^o_{298}$  agrees with Pedley.<sup>41</sup>
- (142)  $S^o_{298}$  and  $C_p^o$  polynomial coefficients estimated by group additivity.<sup>33,34</sup>  $\Delta_fH^o_{298}$  based on enthalpy of formation of parent molecule,  $(\text{CH}_3)_2\text{CHCHO}$ , and  $D^o_{298}(\text{H}-\text{C}(=\text{O})\text{R}) = 373.8 \text{ kJ mol}^{-1}$ .<sup>8</sup>
- (143) Estimated from properties of parent molecule,  $(\text{CH}_3)_2\text{CHCHO}$ , by applying H-bond increment method. Increment for tertiary C—H from Lay *et al.*<sup>71</sup>  $\Delta_fH^o_{298}$  increment adjusted for difference between  $D^o_{298}(\text{H}-\text{CH}_2\text{CH}_3) = 423.0$  and  $D^o_{298}(\text{H}-\text{CH}_2\text{CHO}) = 373.8 \text{ kJ mol}^{-1}$ .<sup>8</sup>
- (144) Estimated from properties of parent molecule,  $(\text{CH}_3)_2\text{CHCHO}$ , by applying H-bond increment method. Increment for primary C—H from Lay *et al.*<sup>71</sup>
- (145)  $S^o_{298}$  and  $C_p^o$  polynomial coefficients estimated by group additivity.<sup>33,34</sup>  $\Delta_fH^o_{298}$  from Pedley.<sup>41</sup>
- (146)  $S^o_{298}$ ,  $C_p^o$ , and  $\Delta_fH^o_{298}$  from Roy *et al.*<sup>90</sup>
- (147)  $S^o_{298}$  and  $C_p^o$  polynomial coefficients from Burcat and McBride,<sup>3</sup> based on the data of Dorofeeva *et al.*<sup>91</sup>  $\Delta_fH^o_{298}$  from Pedley.<sup>41</sup>
- (148)  $S^o_{298}$  and  $C_p^o$  polynomial coefficients from Burcat and McBride,<sup>3</sup> based on the data of Dorofeeva *et al.*<sup>91</sup>  $\Delta_fH^o_{298}$  from Pedley.<sup>41</sup>
- (149) Estimated from properties of parent molecule,  $(\text{CH}_3)_2\text{CHCH}=\text{CH}_2$ , by applying H-bond increment method.<sup>71</sup> Increment for vinyl C—H from Lay *et al.*<sup>71</sup>  $(\text{CH}_3)_2\text{CHCH}=\text{CH}_2$  polynomial coefficients from Burcat and McBride,<sup>3</sup> based on data of Stull *et al.*<sup>84</sup>
- (150) Polynomial coefficients from Burcat and McBride,<sup>3</sup> based on Frenkel *et al.*<sup>82</sup>  $\Delta_fH^o_{298}$  compatible with Pedley,<sup>41</sup>  $S^o_{298}$  and  $C_p^o$  with Stull *et al.*<sup>84</sup>
- (151) Estimated by group additivity. Group coefficients from Stocker and Pilling.<sup>37</sup>
- (152) Polynomial coefficients from Burcat and McBride,<sup>3</sup> based on Frenkel *et al.*<sup>82</sup>  $\Delta_fH^o_{298}$  from Pedley.<sup>41</sup>  $S^o_{298}$  and  $C_p^o$  compatible with Stull *et al.*<sup>84</sup>
- (153)  $\Delta_fH^o_{298}$  from  $\Delta_fH^o_{298}((\text{CH}_3)_3\text{CCHO})$  with  $D^o_{298}(\text{H}-\text{C}(=\text{O})\text{R}) = 373.8 \text{ kJ mol}^{-1}$ .<sup>8</sup>
- (154)  $\Delta_fH^o_{298}$  from  $\Delta_fH^o_{298}((\text{CH}_3)_3\text{CCHO})$  with  $D^o_{298}(\text{H}-\text{CH}_2\text{R}) = 423.0 \text{ kJ mol}^{-1}$ .<sup>8,71</sup>
- (155)  $\Delta_fH^o_{298}$  from Liebman.<sup>92</sup>
- (156) Estimated by group additivity.<sup>33,34</sup>
- (157)  $S^o_{298}$  and  $C_p^o$  polynomial coefficients from Burcat and McBride,<sup>3</sup> based on the data of Bauer and Duff.<sup>93</sup>  $\Delta_fH^o_{298}$  from Wentholt *et al.*<sup>94</sup> and Guo and Grabowski.<sup>95</sup>
- (158)  $S^o_{298}$  and  $C_p^o$  polynomial coefficients from Burcat and McBride,<sup>3</sup> based on the data of Dewar *et al.*<sup>96</sup>  $\Delta_fH^o_{298}$  calculated with  $D^o_{298}(\text{H}-\text{CH}=\text{CH}_2) = 465.3 \text{ kJ mol}^{-1}$ ,<sup>8</sup> and  $\Delta_fH^o_{298}(\text{HCCCHCHCHCH}_2)$  estimated by group additivity.<sup>33,34</sup>
- (159)  $S^o_{298}$  and  $C_p^o$  polynomial coefficients from Burcat and McBride,<sup>3</sup> based on the data of Burcat *et al.*<sup>97</sup>  $\Delta_fH^o_{298}$  from Heckmann *et al.*<sup>98</sup>
- (160)  $S^o_{298}$  and  $C_p^o$  polynomial coefficients from Burcat and McBride,<sup>3</sup> based on the data of Shimanouchi.<sup>65</sup>  $\Delta_fH^o_{298}$  from Pedley.<sup>41</sup>
- (161)  $\Delta_fH^o_{298}$ ,  $S^o_{298}$ , and  $C_p^o$  fitted to the data of Wang and Frenklach.<sup>87</sup>
- (162) Estimated by group additivity.<sup>33,34</sup>  $\Delta_fH^o_{298}$  agrees with Pedley.<sup>41</sup>
- (163) Estimated from properties of parent molecule,  $(\text{CH}_3)_3\text{CCH}=\text{CH}_2$ , applying H-bond increment method. Increment for vinyl C—H from Lay *et al.*<sup>8,71</sup> Thermodynamic properties of  $(\text{CH}_3)_3\text{CCH}=\text{CH}_2$  estimated by group additivity.<sup>33,34</sup>
- (164) Estimated by group additivity.<sup>33,34</sup> Group coefficients from Stocker and Pilling.<sup>37</sup>
- (165)  $S^o_{298}$  and  $C_p^o$  polynomial coefficients from Burcat and McBride,<sup>3</sup> based on the data of Frenkel *et al.*<sup>82</sup>  $\Delta_fH^o_{298}$  from Pedley.<sup>41</sup>
- (166) Estimated by group additivity. Group values for  $\text{C}_\text{D}=\text{O}$  group from ketene, and ring correction from  $\Delta H_f^o$  (fullvene, 298 K), Burcat and McBride,<sup>3</sup>

- based BAC-MP4 calculations, Melius.<sup>11</sup> (compound reference A70D) C<sub>D</sub>—O represents the =C=O group.
- (167)  $\Delta_f H^\circ_{298}$  estimated value, Liebman.<sup>92</sup>
- (168)  $\Delta_f H^\circ_{298}$  from Pedley.<sup>41</sup>
- (169)  $S^\circ_{298}$  and  $C_p^\circ$  polynomial coefficients from Sandia Chemkin database,<sup>1</sup> fit to BAC-MP4 data, Melius.<sup>11</sup> (compound reference D85P).  $\Delta_f H^\circ_{298}$  from Kerr and Stocker.<sup>8</sup>
- (170) Estimated by group additivity.<sup>33,34</sup>  $\Delta_f H^\circ_{298}(C_B/\cdot)$  coefficient from  $D^\circ_{298}(C_6H_5-H)=473.1\text{ kJ mol}^{-1}$  C<sub>B</sub>/· represents the phenyl radical center.<sup>98</sup> Thermodynamic properties of other isomers similarly estimated. ( $\Delta_f H^\circ_{298}([-C_6H_4-]-3-OH)$   
 $=\Delta_f H^\circ_{298}([-C_6H_4-]-4-OH)=160.8\text{ kJ mol}^{-1}$ ;  
 $S^\circ_{298}([-C_6H_4-]-3-OH)=324.93$  and  
 $S^\circ_{298}([-C_6H_4-]-4-OH)=319.17\text{ J K}^{-1}\text{ mol}^{-1}$ .
- (171) Fit to BAC-MP4 data Melius.<sup>11</sup> (Compound reference Q12C).
- (172) Burcat and McBride,<sup>3</sup> based on the data of Burcat *et al.*<sup>97</sup>  $\Delta_f H^\circ_{298}$  compatible with Pedley,<sup>41</sup>  $S^\circ_{298}$  and  $C_p^\circ$  agree with Stull *et al.*<sup>84</sup>
- (173) Fit to BAC-MP4 data Melius,<sup>11</sup> (Compound reference P11A).
- (174) Estimated from properties of parent molecule, 1-hydroxy-2,4-cyclohexadiene, applying H-bond increment method. Increment for 1,3-cyclohexadiene C—H, Lay *et al.*,<sup>32</sup> Wang and Frenklach,<sup>87</sup> and Tsang.<sup>99</sup> Thermodynamic properties of 1-hydroxy-2,4-cyclohexadiene estimated by group additivity.<sup>33,34</sup>
- (175) Estimated from properties of parent molecule, 1,2-dihydroxy-3,5-cyclohexadiene, applying H-bond increment method. Increment for 1,3-cyclohexadiene C—H, Lay *et al.*,<sup>32</sup> Wang and Frenklach,<sup>87</sup> and Tsang.<sup>101</sup> Thermodynamic properties of 1,2-dihydroxy-3,5-cyclohexadiene estimated by group additivity.<sup>33,34</sup> Thermodynamic properties of other isomers similarly estimated:  $[-C_6H_5-]-2,3-(OH)_2$  ( $\Delta_f H^\circ_{298}=-121.53\text{ kJ mol}^{-1}$ ;  
 $S^\circ_{298}=384.77\text{ J K}^{-1}\text{ mol}^{-1}$ ) estimated from properties of 1,2-dihydroxy-2,4-cyclohexadiene,  $[-C_6H_5-]-2,6-(OH)_2$  ( $\Delta_f H^\circ_{298}=-121.53\text{ kJ mol}^{-1}$ ;  
 $S^\circ_{298}=384.77\text{ J K}^{-1}\text{ mol}^{-1}$ ) estimated from 1,5-dihydroxy-2,4-cyclohexadiene,  $[-C_6H_5-]-2,4-(OH)_2$  ( $\Delta_f H^\circ_{298}=-121.53\text{ kJ mol}^{-1}$ ;  
 $S^\circ_{298}=384.77\text{ J K}^{-1}\text{ mol}^{-1}$ ) estimated from properties of 1,3-dihydroxy-2,4-cyclohexadiene,  $[-C_6H_5-]-2,5-(OH)_2$  ( $\Delta_f H^\circ_{298}=-113.95\text{ kJ mol}^{-1}$ ;  
 $S^\circ_{298}=385.66\text{ J K}^{-1}\text{ mol}^{-1}$ ) estimated from properties of 1,4-dihydroxy-2,4-cyclohexadiene. Thermodynamic properties of parent molecules estimated by group additivity.<sup>33,34</sup>
- (176) Estimated by group additivity.<sup>33,34</sup>
- (177) Estimated by group additivity.<sup>33,34</sup>
- (178)  $S^\circ_{298}$  and  $C_p^\circ$  calculated from spectroscopic data of Ellison *et al.*<sup>100</sup> (scaled by 0.9).  $\Delta_f H^\circ_{298}$  from Ellison *et al.*<sup>100</sup>
- (179) Estimated by group additivity.<sup>30,31</sup>  $\Delta_f H^\circ_{298}(C_B/\cdot)$  coefficient from  $D^\circ_{298}(C_6H_5-H)=473.1\text{ kJ mol}^{-1}$ .<sup>100</sup> C<sub>B</sub>/· represents the phenyl radical center. Thermodynamic properties of other isomers similarly estimated. ( $\Delta_f H^\circ_{298}([-C_6H_4-]-3-CH_3)$   
 $=\Delta_f H^\circ_{298}([-C_6H_4-]-4-CH_3)=305.84\text{ kJ mol}^{-1}$ ;  
 $S^\circ_{298}([-C_6H_4-]-3-CH_3)=328.13$  and  
 $S^\circ_{298}([-C_6H_4-]-4-CH_3)=323.13\text{ J K}^{-1}\text{ mol}^{-1}$ .
- (180)  $S^\circ_{298}$  and  $C_p^\circ$  polynomial coefficients from Burcat and McBride,<sup>3</sup> based on the data of Hitchcock and Laposi.<sup>101</sup>  $\Delta_f H^\circ_{298}$  from Pedley.<sup>41</sup>
- (181) Estimated from properties of parent molecule, 5-methyl-1,3-cyclohexadiene, applying H-bond increment method. Increment for 1,3-cyclohexadiene C—H, Lay *et al.*,<sup>31</sup> Wang and Frenklach,<sup>87</sup> and Tsang.<sup>99</sup> Thermodynamic properties of 5-methyl-1,3-cyclohexadiene estimated by group additivity.<sup>30,31</sup> Thermodynamic properties of other isomers similarly estimated:  $[-C_6H_5-]-6-(CH_3)(H)$  ( $\Delta_f H^\circ_{298}=180.82\text{ kJ mol}^{-1}$ ;  
 $S^\circ_{298}=334.73\text{ J K}^{-1}\text{ mol}^{-1}$ ) estimated from properties of 5-methyl-1,3-cyclohexadiene,  $[-C_6H_5-]-5-(CH_3)(H)$  ( $\Delta_f H^\circ_{298}=174.42\text{ kJ mol}^{-1}$ ;  
 $S^\circ_{298}=338.19\text{ J K}^{-1}\text{ mol}^{-1}$ ) estimated from properties of 4-methyl-1,3-cyclohexadiene,  $[-C_6H_5-]-2-(CH_3)(H)$  ( $\Delta_f H^\circ_{298}=174.42\text{ kJ mol}^{-1}$ ;  
 $S^\circ_{298}=338.19\text{ J K}^{-1}\text{ mol}^{-1}$ ) estimated from properties of 4-methyl-1,3-cyclohexadiene,  $[-C_6H_5-]-4-(CH_3)(H)$  ( $\Delta_f H^\circ_{298}=175.88\text{ kJ mol}^{-1}$ ;  
 $S^\circ_{298}=336.89\text{ J K}^{-1}\text{ mol}^{-1}$ ) estimated from properties of 3-methyl-1,3-cyclohexadiene,  $[-C_6H_5-]-3-(CH_3)(H)$  ( $\Delta_f H^\circ_{298}=175.88\text{ kJ mol}^{-1}$ ;  
 $S^\circ_{298}=331.13\text{ J K}^{-1}\text{ mol}^{-1}$ ) estimated from properties of 3-methyl-1,3-cyclohexadiene. Thermodynamic properties of parent molecules estimated by group additivity.<sup>33,34</sup>
- (182) Estimated by group additivity.<sup>33,34</sup>
- (183) Estimated by group additivity.<sup>33,34</sup>  $\Delta_f H^\circ_{298}(C_B/\cdot)$  coefficient from  $D^\circ_{298}(C_6H_5-H)=473.1\text{ kJ mol}^{-1}$ .<sup>92</sup> C<sub>B</sub>/· represents the phenyl radical center. Group coefficients for the group CO—C<sub>B</sub>/H (representing a carbonyl group bonded to an H atom and phenyl-carbon atom) calculated from the thermodynamic properties of benzaldehyde. Thermodynamic properties of other isomers similarly estimated. ( $\Delta_f H^\circ_{298}([-C_6H_4-]-3-CHO)$   
 $=\Delta_f H^\circ_{298}([-C_6H_4-]-4-CHO)=218.71\text{ kJ mol}^{-1}$ ;  
 $S^\circ_{298}([-C_6H_4-]-3-CHO)=345.76$  and  
 $S^\circ_{298}([-C_6H_4-]-4-CHO)=339.99\text{ J K}^{-1}\text{ mol}^{-1}$ .
- (184)  $S^\circ_{298}$  and  $C_p^\circ$  calculated from spectral data of Solly and Benson.<sup>102</sup>  $\Delta_f H^\circ_{298}$  determined from  $\Delta_f H^\circ_{298}([-C_6H_5-]-CHO)$  with  $D^\circ_{298}(H-C(=O)R)=373.8\text{ kJ mol}^{-1}$ ,<sup>8</sup> in good agreement with the results of a study of reaction I+ $[-C_6H_5-]-CHO \rightarrow [-C_6H_5-]-CO+HI$ ,<sup>102</sup> if activation energy of reverse reaction is assumed to be  $-8\text{ kJ mol}^{-1}$ ,<sup>65</sup> and the results determined from a photofragmentation study of acetophenone by Zhao *et al.*<sup>103</sup>

- (185)  $S^{\circ}_{298}$  and  $C_p^{\circ}$  polynomial coefficients calculated from the spectral data of Ambrose *et al.*<sup>104</sup>  $\Delta_fH^{\circ}_{298}$  from Pedley.<sup>41</sup>
- (186)  $S^{\circ}_{298}$  and  $C_p^{\circ}$  polynomial coefficients calculated from the spectral data of Kudchadker *et al.*<sup>105</sup>  $\Delta_fH^{\circ}_{298}$  from Pedley.<sup>41</sup>
- (187)  $S^{\circ}_{298}$  and  $C_p^{\circ}$  polynomial coefficients calculated from the spectral data of Kudchadker *et al.*<sup>105</sup>  $\Delta_fH^{\circ}_{298}$  from Pedley<sup>41</sup>
- (188) Estimated by group additivity.<sup>33,34</sup>
- (189) Estimated from properties of parent molecule, 5-hydroxy-6-methyl-1,3-cyclohexadiene, applying H-bond increment method. Increment for 1,3-cyclohexadiene C—H, Lay *et al.*,<sup>32</sup> Wang and Frenklach,<sup>87</sup> and Tsang.<sup>99</sup> Thermodynamic properties of 5-hydroxy-6-methyl-1,3-cyclohexadiene estimated by group additivity.<sup>33,34</sup> Thermodynamic properties of other isomers similarly estimated:  $[-C_6H_5-]-2-(CH_3)-2-(OH)$  ( $\Delta_fH^{\circ}_{298} = 0.35 \text{ kJ mol}^{-1}$ ,  $S^{\circ}_{298} = 371.99 \text{ J K}^{-1} \text{ mol}^{-1}$ ) estimated from properties of 5-hydroxy-5-methyl-1,3-cyclohexadiene. Thermodynamic properties of 5-hydroxy-5-methyl-1,3-cyclohexadiene estimated by group additivity,<sup>29,30</sup> assuming the group coefficients for the group C—C<sub>2</sub>/C<sub>D</sub>/O (representing a carbon atom bonded to two other *sp*<sup>3</sup> carbon atoms, an *sp*<sup>2</sup> carbon atom and an oxygen atom) are the same as for the group C—C<sub>3</sub>/O (representing a carbon atom bonded to three other *sp*<sup>3</sup> carbon atoms and an oxygen atom),  $[-C_6H_5-]-3-(CH_3)-2-(OH)$  ( $\Delta_fH^{\circ}_{298} = 9.56 \text{ kJ mol}^{-1}$ ,  $S^{\circ}_{298} = 372.88 \text{ J K}^{-1} \text{ mol}^{-1}$ ), estimated from properties of 5-hydroxy-4-methyl-1,3-cyclohexadiene,  $[-C_6H_5-]-6-(CH_3)-2-(OH)$  ( $\Delta_fH^{\circ}_{298} = 9.56 \text{ kJ mol}^{-1}$ ,  $S^{\circ}_{298} = 372.88 \text{ J K}^{-1} \text{ mol}^{-1}$ ), estimated from properties of 5-hydroxy-4-methyl-1,3-cyclohexadiene,  $[-C_6H_5-]-4-(CH_3)-2-(OH)$  ( $\Delta_fH^{\circ}_{298} = 9.56 \text{ kJ mol}^{-1}$ ,  $S^{\circ}_{298} = 378.64 \text{ J K}^{-1} \text{ mol}^{-1}$ ), estimated from properties of 5-hydroxy-3-methyl-1,3-cyclohexadiene,  $[-C_6H_5-]-5-(CH_3)-2-(OH)$  ( $\Delta_fH^{\circ}_{298} = 11.02 \text{ kJ mol}^{-1}$ ,  $S^{\circ}_{298} = 371.58 \text{ J K}^{-1} \text{ mol}^{-1}$ ), estimated from properties of 5-hydroxy-3-methyl-1,3-cyclohexadiene. Thermodynamic properties of parent molecules estimated by group additivity.<sup>33,34</sup>
- (190)  $C_p^{\circ}$  polynomial coefficients from Burcat and McBride,<sup>3</sup>  $S^{\circ}_{298}$  from Stull *et al.*<sup>84</sup>  $\Delta_fH^{\circ}_{298}$  based on  $\Delta_fH^{\circ}_{298}([-C_6H_5-] + C_2H_2 \rightarrow [-C_6H_5-] - CCH + H)$  calculated by Yu *et al.*<sup>106</sup>
- (191) Estimated from properties of parent molecule, phenylethene, applying H-bond increment method. Increment for vinyl C—H from Lay *et al.*<sup>8,71</sup>
- (192)  $S^{\circ}_{298}$  and  $C_p^{\circ}$  polynomial coefficients from Burcat and McBride,<sup>3</sup> based on data of Stull *et al.*<sup>84</sup>  $\Delta_fH^{\circ}_{298}$  from Pedley.<sup>41</sup>
- (193) Estimated by group additivity.<sup>33,34</sup>  $\Delta_fH^{\circ}_{298}(C_B/\cdot)$  coefficient from  $D^{\circ}_{298}(C_6H_5-H) = 473.1 \text{ kJ mol}^{-1}$ .<sup>98</sup>
- (194) Estimated from properties of parent molecule, ethylbenzene, applying H-bond increment method. Increment for primary C—H from Lay *et al.*<sup>8,71</sup>
- (195) Estimated from properties of parent molecule, ethylbenzene, applying H-bond increment method. Increment for secondary benzyl C—H from Lay *et al.*<sup>71</sup>
- (196) Estimated from properties of parent molecule, *p*-xylene, applying H-bond increment method. Increment for primary benzyl C—H from Lay *et al.*<sup>71</sup> and  $D^{\circ}_{298}(H-CH_2C_6H_5)$  from Ellison *et al.*<sup>100</sup>
- (197) Estimated by group additivity.<sup>30,31</sup>  $\Delta_fH^{\circ}_{298}(C_B/\cdot)$  coefficient from  $D^{\circ}_{298}(C_6H_5-H) = 473.1 \text{ kJ mol}^{-1}$ .<sup>93</sup>  $C_B/\cdot$  represents the phenyl radical center.
- (198)  $S^{\circ}_{298}$  and  $C_p^{\circ}$  polynomial coefficients from Burcat and McBride,<sup>3</sup> based on the data of Draeger and Scott.<sup>107</sup>  $\Delta_fH^{\circ}_{298}$  from Pedley.<sup>41</sup>
- (199)  $S^{\circ}_{298}$  and  $C_p^{\circ}$  polynomial coefficients from Burcat and McBride,<sup>3</sup> estimated by group additivity.<sup>33</sup>  $S^{\circ}_{298}$  and  $C_p^{\circ}$  agree with Stull *et al.*,<sup>84</sup> and  $\Delta_fH^{\circ}_{298}$  with Pedley.<sup>41</sup>
- (200) Estimated from properties of parent molecule, 2,5-dimethyl-1,3-cyclohexadiene, applying H-bond increment method. Increment for 1,3-cyclohexadiene C—H, Lay *et al.*,<sup>32</sup> Wang and Frenklach,<sup>87</sup> and Tsang.<sup>99</sup> Thermodynamic properties of 2,5-dimethyl-1,3-cyclohexadiene estimated by group additivity.<sup>33,34</sup>
- (201) Estimated from properties of parent molecule, 5-ethyl-1,3-cyclohexadiene, applying H-bond increment method. Increment for 1,3-cyclohexadiene C—H, Lay *et al.*,<sup>32</sup> Wang and Frenklach,<sup>87</sup> and Tsang.<sup>99</sup> Thermodynamic properties of 5-ethyl-1,3-cyclohexadiene estimated by group additivity.<sup>33,34</sup> Thermodynamic properties of other isomers similarly estimated:  $[-C_6H_5-]-6-(C_2H_5)(H)$  ( $\Delta_fH^{\circ}_{298} = 159.90 \text{ kJ mol}^{-1}$ ,  $S^{\circ}_{298} = 374.05 \text{ J K}^{-1} \text{ mol}^{-1}$ ) estimated from properties of 5-ethyl-1,3-cyclohexadiene,  $[-C_6H_5-]-5-(C_2H_5)(H)$  ( $\Delta_fH^{\circ}_{298} = 154.50 \text{ kJ mol}^{-1}$ ,  $S^{\circ}_{298} = 379.18 \text{ J K}^{-1} \text{ mol}^{-1}$ ), estimated from properties of 4-ethyl-1,3-cyclohexadiene,  $[-C_6H_5-]-2-(C_2H_5)(H)$  ( $\Delta_fH^{\circ}_{298} = 154.50 \text{ kJ mol}^{-1}$ ,  $S^{\circ}_{298} = 379.18 \text{ J K}^{-1} \text{ mol}^{-1}$ ), estimated from properties of 4-ethyl-1,3-cyclohexadiene,  $[-C_6H_5-]-4-(C_2H_5)(H)$  ( $\Delta_fH^{\circ}_{298} = 155.97 \text{ kJ mol}^{-1}$ ,  $S^{\circ}_{298} = 377.89 \text{ J K}^{-1} \text{ mol}^{-1}$ ), estimated from properties of 3-ethyl-1,3-cyclohexadiene,  $[-C_6H_5-]-3-(C_2H_5)(H)$  ( $\Delta_fH^{\circ}_{298} = 155.97 \text{ kJ mol}^{-1}$ ,  $S^{\circ}_{298} = 383.65 \text{ J K}^{-1} \text{ mol}^{-1}$ ), estimated from properties of 3-ethyl-1,3-cyclohexadiene. Thermodynamic properties of parent molecules estimated by group additivity.<sup>33,34</sup>
- (202) Estimated by group additivity.<sup>33,34</sup>

- (203) Estimated by group additivity.<sup>33,34</sup>
- (204) Estimated by group additivity.<sup>33,34</sup>
- (205) Estimated from properties of parent molecule, 5-hydroxy-6-ethyl-1,3-cyclohexadiene, applying H-bond increment method. Increment for 1,3-cyclohexadiene C—H, Lay *et al.*,<sup>32</sup> Wang and Frenklach,<sup>87</sup> and Tsang.<sup>99</sup> Thermodynamic properties of 5-hydroxy-6-ethyl-1,3-cyclohexadiene estimated by group additivity.<sup>33,34</sup> Thermodynamic properties of other isomers similarly estimated: [-C<sub>6</sub>H<sub>5</sub>-]-2-(C<sub>2</sub>H<sub>5</sub>);-2-(OH) ( $\Delta_f H^\circ_{298}$  = -20.57 kJ mol<sup>-1</sup>,  $S^\circ_{298}$  = 411.31 J K<sup>-1</sup> mol<sup>-1</sup>) estimated from properties of 5-hydroxy-5-ethyl-1,3-cyclohexadiene, [-C<sub>6</sub>H<sub>5</sub>]-3-(C<sub>2</sub>H<sub>5</sub>);-2-(OH) ( $\Delta_f H^\circ_{298}$  = -10.36 kJ mol<sup>-1</sup>,  $S^\circ_{298}$  = 419.63 J K<sup>-1</sup> mol<sup>-1</sup>) estimated from properties of 5-hydroxy-4-ethyl-1,3-cyclohexadiene, [-C<sub>6</sub>H<sub>5</sub>]-6-(C<sub>2</sub>H<sub>5</sub>);-2-(OH) ( $\Delta_f H^\circ_{298}$  = -10.36 kJ mol<sup>-1</sup>,  $S^\circ_{298}$  = 419.63 J K<sup>-1</sup> mol<sup>-1</sup>) estimated from properties of 5-hydroxy-4-ethyl-1,3-cyclohexadiene, [-C<sub>6</sub>H<sub>5</sub>]-4-(C<sub>2</sub>H<sub>5</sub>);-2-(OH) ( $\Delta_f H^\circ_{298}$  = -11.31 kJ mol<sup>-1</sup>,  $S^\circ_{298}$  = 421.84 J K<sup>-1</sup> mol<sup>-1</sup>) estimated from properties of 5-hydroxy-3-ethyl-1,3-cyclohexadiene, [-C<sub>6</sub>H<sub>5</sub>]-5-(C<sub>2</sub>H<sub>5</sub>);-2-(OH) ( $\Delta_f H^\circ_{298}$  = -8.89 kJ mol<sup>-1</sup>,  $S^\circ_{298}$  = 412.58 J K<sup>-1</sup> mol<sup>-1</sup>) estimated from properties of 5-hydroxy-3-ethyl-1,3-cyclohexadiene. Thermodynamic properties of parent molecules estimated by group additivity.<sup>33,34</sup>
- (206) Estimated from properties of parent molecule, 5-hydroxy-3,6-dimethyl-1,3-cyclohexadiene, applying H-bond increment method. Increment for 1,3-cyclohexadiene C—H, Lay *et al.*,<sup>32</sup> Wang and Frenklach,<sup>87</sup> and Tsang.<sup>99</sup> Thermodynamic properties of 5-hydroxy-3,6-dimethyl-1,3-cyclohexadiene estimated by group additivity.<sup>33,34</sup> Thermodynamic properties of other isomers similarly estimated: [-C<sub>6</sub>H<sub>4</sub>]-2,5-(CH<sub>3</sub>)<sub>2</sub>; -2-(OH) ( $\Delta_f H^\circ_{298}$  = -32.70 kJ mol<sup>-1</sup>,  $S^\circ_{298}$  = 396.08 J K<sup>-1</sup> mol<sup>-1</sup>) estimated from properties of 5-hydroxy-2,5-dimethyl-1,3-cyclohexadiene, [-C<sub>6</sub>H<sub>4</sub>]-3,6-(CH<sub>3</sub>)<sub>2</sub>; -2-(OH) ( $\Delta_f H^\circ_{298}$  = -37.19 kJ mol<sup>-1</sup>,  $S^\circ_{298}$  = 393.89 J K<sup>-1</sup> mol<sup>-1</sup>) estimated from properties of 5-hydroxy-1,4-dimethyl-1,3-cyclohexadiene. Thermodynamic properties of parent molecules estimated by group additivity.<sup>33,34</sup>

### 3.3. References

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## 4. Index of Reactions and Summary Table

### 4.1. Guide to the Summary Table

### 4.2. Summary of Preferred Rate Data

TABLE 4.1. Bimolecular reactions

Reaction	$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Error limits ( $\Delta \log k$ )
<i>O Atom Reactions</i>			
$\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$	$[6.34 \cdot 10^{-12} \exp(-4000/T) + 1.46 \cdot 10^{-9} \exp(-9650/T)]$	298–3300	$\pm 0.2$ over the range 298–3300 K.
$\text{O} + \text{OH} \rightarrow \text{O}_2 + \text{H}$	$2.0 \cdot 10^{-10} T^{-0.352} \exp(113/T)$	250–3000	$\pm 0.2$
$\text{O} + \text{HO}_2 \rightarrow \text{OH} + \text{O}_2$	$2.7 \cdot 10^{-11} \exp(224/T)$	220–1000	$\pm 0.1$ at 220 K, rising to $\pm 0.5$ at 1000 K.
$\text{O} + \text{H}_2\text{O}_2 \rightarrow \text{OH} + \text{HO}_2$ $\rightarrow \text{O}_2 + \text{H}_2\text{O}$	$1.4 \cdot 10^{-12} \exp(-2000/T)$	283–500	$\pm 0.3$
$\text{O} + \text{N}_2 \rightarrow \text{NO} + \text{N}$	$3.0 \cdot 10^{-10} \exp(-38400/T)$	1700–4000	$\pm 0.15$
$\text{O} + \text{NO} \rightarrow \text{O}_2 + \text{N}$	$1.14 \cdot 10^{-15} T^{1.13} \exp(-19200/T)$	1500–5000	$\pm 0.3$
$\text{O} + \text{NO}(\text{+M}) \rightarrow \text{NO}_2(\text{+M})$	See Table 4.2		
$\text{O} + \text{N}_2\text{O} \rightarrow \text{NO} + \text{NO}$	$1.5 \cdot 10^{-10} \exp(-13930/T)$	1000–4000	$\pm 0.2$ at 2000 K, rising to $\pm 0.3$ at 4000 K and $\pm 0.4$ at 1000 K.
$\rightarrow \text{O}_2 + \text{N}_2$	$6.1 \cdot 10^{-12} \exp(-8020/T)$	1000–2500	$\pm 0.2$ at 2000 K, rising to $\pm 0.5$ at 2500 K and 1000 K.
$\text{O} + \text{NH} \rightarrow \text{NO} + \text{H}$ $\rightarrow \text{OH} + \text{N}$	$(k_1 + k_2) = 1.8 \cdot 10^{-10} \exp(-300/T)$ $k_2 \leqslant 1.7 \cdot 10^{-13}$	295–3500 298	$\pm 0.5$
$\text{O} + \text{NH}_3 \rightarrow \text{OH} + \text{NH}_2$	$2.7 \cdot 10^{-17} T^{1.85} \exp(-3250/T)$	300–2000	$\pm 0.2$ at 300 K, rising to $\pm 0.3$ at 2000 K.
$\text{O} + \text{CN} \rightarrow \text{CO} + \text{N}({}^4\text{S})$ $\rightarrow \text{CO} + \text{N}({}^2\text{D})$	$5 \cdot 10^{-11} \exp(-200/T)$	295–4500	$\pm 0.5$
$\text{O} + \text{NCO} \rightarrow \text{NO} + \text{CO}$ $\rightarrow \text{O}_2 + \text{CN}$	$7.2 \cdot 10^{-11}$ $1.2 \cdot 10^{-8} T^{-0.783} \exp(-7390/T)$	1450–3100 290–4500	$\pm 0.3$ $\pm 0.5$
$\text{O} + \text{HCN} \rightarrow \text{CO} + \text{NH}$ $\rightarrow \text{NCO} + \text{H}$ $\rightarrow \text{OH} + \text{CN}$	$2.3 \cdot 10^{-18} T^{2.1} \exp(-3075/T)$	450–2500	$\pm 0.2$ at 450 K, rising to $\pm 0.3$ at 2500 K.
$\text{O} + \text{HNCO} \rightarrow \text{OH} + \text{NCO}$ $\rightarrow \text{CO}_2 + \text{NH}$ $\rightarrow \text{CO} + \text{HNO}$	$3.7 \cdot 10^{-18} T^{2.11} \exp(-5750/T)$ $1.6 \cdot 10^{-14} T^{1.41} \exp(-4290/T)$ No recommendation; see data sheet.	500–3000 500–3000	$\pm 0.3$ $\pm 0.3$

TABLE 4.1. Bimolecular reactions—Continued

Reaction	$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Error limits ( $\Delta \log k$ )
$\text{O} + \text{CH} \rightarrow \text{CO} + \text{H}$	$6.6 \cdot 10^{-11}$	295–2000	$\pm 0.5$
$\rightarrow \text{OH} + \text{C}$	No recommendation; see data sheet.		
$\rightarrow \text{HCO}^+ + \text{e}$	$4.2 \cdot 10^{-13} \exp(-850/T)$	295–2500	$\pm 0.5$
$\text{O} + {}^3\text{CH}_2 \rightarrow \text{CO} + 2\text{H}$	$k = 3.4 \cdot 10^{-10} \exp(-270/T)$	290–2500	$\pm 0.2$ at 290 K, rising to $\pm 0.3$ at 3000 K.
$\rightarrow \text{CO} + \text{H}_2$	$k_1/k = 0.6$	290–2500	$\Delta(k_1/k) = \pm 0.3$
$\text{O} + \text{CH}_3 \rightarrow \text{HCHO} + \text{H}$	$k = 1.4 \cdot 10^{-10}$	294–2500	$\pm 0.1$
$\rightarrow \text{HCO} + \text{H}_2$	$k_1/k = 0.8$ ; $k_3/k = 0.2$	298	$\Delta(k_1/k) = \Delta(k_3/k) = \pm 0.1$
$\rightarrow \text{CO} + \text{H}_2 + \text{H}$			
$\rightarrow \text{OH} + \text{CH}_2$			
$\text{O} + \text{CH}_4 \rightarrow \text{OH} + \text{CH}_3$	$7.3 \cdot 10^{-19} T^{2.5} \exp(-3310/T)$	400–2500	$\pm 0.3$ over the range 600–2500 K, rising to $\pm 0.5$ at 400 K.
$\text{O} + \text{HCO} \rightarrow \text{OH} + \text{CO}$	$5 \cdot 10^{-11}$	300–2500	$\pm 0.3$
$\rightarrow \text{CO}_2 + \text{H}$	$5 \cdot 10^{-11}$	300–2500	$\pm 0.3$
$\text{O} + \text{HCHO} \rightarrow \text{OH} + \text{HCO}$	$6.9 \cdot 10^{-13} T^{0.57} \exp(-1390/T)$	250–2200	$\pm 0.1$ at 250 K, rising to $\pm 0.3$ at 2200 K.
$\text{O} + \text{CH}_3\text{O} \rightarrow \text{O}_2 + \text{CH}_3$	$k = 2.5 \cdot 10^{-11}$	298–1000	$\pm 0.3$ at 298 K, rising to $\pm 0.7$ at 1000 K.
$\rightarrow \text{OH} + \text{HCHO}$	$k_2/k = 0.25$	298	$\Delta(k_2/k) = {}^{+0.2}_{-0.1}$ at 298 K.
$\text{O} + \text{CH}_3\text{OH} \rightarrow \text{OH} + \text{CH}_2\text{OH}$	$4.1 \cdot 10^{-11} \exp(-2670/T)$	350–1000	$\pm 0.2$
$\rightarrow \text{OH} + \text{CH}_3\text{O}$			
$\text{O} + \text{CH}_3\text{OOH} \rightarrow \text{OH} + \text{CH}_3\text{O}_2$	$4.1 \cdot 10^{-11} \exp(-2460/T)$	297–1000	$\pm 0.3$ at 297 K, rising to $\pm 0.5$ at 1000 K.
$\rightarrow \text{OH} + \text{CH}_2\text{OOH}$			
$\text{O} + \text{C}_2\text{H} \rightarrow \text{Products}$	$9.9 \cdot 10^{-11}$	290–2500	$\pm 0.5$
$\text{O} + \text{C}_2\text{H}_2 \rightarrow \text{CO} + {}^3\text{CH}_2$	$k = 1.95 \cdot 10^{-15} T^{1.40} \exp(-1110/T)$	200–2500	$\pm 0.2$ over the range 200–2000 K, rising to $\pm 0.3$ at 2500 K.
$\rightarrow \text{CHCO} + \text{H}$	$k_2/k = 0.8$	250–2500	$\Delta(k_2/k) = \pm 0.1$
$\text{O} + \text{C}_2\text{H}_3 \rightarrow \text{OH} + \text{C}_2\text{H}_2$	$5.0 \cdot 10^{-11}$	250–2000	$\pm 0.5$
$\rightarrow \text{CO} + \text{CH}_3$			
$\rightarrow \text{HCO} + \text{CH}_2$			
$\text{O} + \text{C}_2\text{H}_4 \rightarrow \text{CH}_2\text{CHO} + \text{H}$	$2.25 \cdot 10^{-17} T^{1.88} \exp(-92/T)$	220–2000	$\pm 0.1$ over the range 300–1000 K, rising to $\pm 0.3$ at 220 K and 2000 K.
$\rightarrow \text{HCO} + \text{CH}_3$	$k_1/k = 0.35$	298 K and $P < 1 \text{ bar}$	$\Delta(k_1/k) = \pm 0.05$ at 298 K
$\rightarrow \text{HCHO} + \text{CH}_2$	$k_2/k = 0.6$		$\Delta(k_2/k) = \pm 0.1$ at 298 K
$\rightarrow \text{CH}_2\text{CO} + \text{H}_2$	$k_4/k = 0.05$		$\Delta(k_4/k) = \pm 0.1$ at 298 K
$\text{O} + \text{C}_2\text{H}_5 \rightarrow \text{CH}_3\text{CHO} + \text{H}$	$k = 2.2 \cdot 10^{-10}$	298–1000	$\pm 0.3$ at 298 K, rising to $\pm 0.5$ at 1000 K.
$\rightarrow \text{HCHO} + \text{CH}_3$	$k_1/k = 0.4$	298–450	$\Delta(k_1/k) = \pm 0.05$
$\rightarrow \text{OH} + \text{C}_2\text{H}_4$	$k_2/k = 0.3$	298–450	$\Delta(k_2/k) = \pm 0.1$
$\rightarrow \text{CO} + \text{CH}_4 + \text{H}$	$k_3/k = 0.2$	298–450	$\Delta(k_3/k) = \pm 0.1$
$\rightarrow \text{CO} + \text{CH}_3 + \text{H}_2$			
$\text{O} + \text{C}_2\text{H}_6 \rightarrow \text{OH} + \text{C}_2\text{H}_5$	$3.0 \cdot 10^{-19} T^{2.8} \exp(-2920/T)$	500–1400	$\pm 0.15$ over the range 500–1100 K, rising to $\pm 0.3$ at 1400 K.
$\text{O} + \text{HCCO} \rightarrow 2\text{CO} + \text{H}$	$k = 1.6 \cdot 10^{-10}$	280–2500	$\pm 0.2$
$\rightarrow \text{CO}_2 + \text{CH}(X^2\Pi)$	$(k_2 + k_3) = 4.9 \cdot 10^{-11} \exp(-560/T)$	280–1000	$\pm 0.3$
$\rightarrow \text{CO}_2 + \text{CH}(a^4\Sigma^-)$			

TABLE 4.1. Bimolecular reactions—Continued

Reaction	$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Error limits ( $\Delta \log k$ )
O + CH <sub>2</sub> CO → HCHO + CO → HCO + H + CO → 2HCO → CO <sub>2</sub> + <sup>3</sup> CH <sub>2</sub>	$k = 3.0 \cdot 10^{-12} \exp(-680/T)$ $k_1/k = 0.2$ $(k_2+k_3)/k = 0.2$ $k_4/k = 0.6$	296–1000 298 298 298	± 0.3 at 296 K, rising to ± 1.0 at 1000 K. $\Delta(k_1/k) = \pm 0.1$ $\Delta[(k_2+k_3)/k] = \pm 0.1$ $\Delta(k_4/k) = \pm 0.2$
O + CH <sub>3</sub> CO → OH + CH <sub>2</sub> CO → CO <sub>2</sub> + CH <sub>3</sub>	$k = 3.5 \cdot 10^{-10}$ $k_1/k = 0.25$ $k_2/k = 0.75$ $9.7 \cdot 10^{-12} \exp(-910/T)$	295–1000 298 298 298–1500	± 0.3 $\Delta(k_1/k) = \pm 0.2$ $\Delta(k_2/k) = \pm 0.2$ ± 0.1 at 298 K, rising to ± 0.5 at 1500 K.
O + CH <sub>3</sub> CHO → OH + CH <sub>3</sub> CO → OH + CH <sub>2</sub> CHO	$5.4 \cdot 10^{-12} \exp(-1320/T)$ $1 \cdot 10^{-18} T^{2.5} \exp(-930/T)$	220–450 298–1000	± 0.2 ± 0.2
O + C <sub>2</sub> H <sub>5</sub> OH → OH + CH <sub>3</sub> CHOH → OH + CH <sub>2</sub> CH <sub>2</sub> OH → OH + CH <sub>3</sub> CH <sub>2</sub> O	$1.10 \cdot 10^{-10} \exp(-2090/T)$	298–1000	± 0.5 at 298 K, rising to ± 0.7 at 1000 K.
O + C <sub>2</sub> H <sub>5</sub> OOH → OH + C <sub>2</sub> H <sub>4</sub> OOH → OH + C <sub>2</sub> H <sub>5</sub> O <sub>2</sub>	$3.0 \cdot 10^{-10}$ $< 3 \cdot 10^{-11}$	300–1000 300–1000	± 0.2 over the range 300–600 K, rising to ± 0.4 over the range 600–1000 K.
O + [-C <sub>6</sub> H <sub>5</sub> -] → CO + [-C <sub>5</sub> H <sub>5</sub> -] → [-C <sub>5</sub> H <sub>4</sub> -]-CO + H	$1.7 \cdot 10^{-10}$	1050–1500	± 0.3
O + [-C <sub>6</sub> H <sub>6</sub> -](+M) → [-C <sub>6</sub> H <sub>5</sub> -]-OH(+M) → [-C <sub>6</sub> H <sub>5</sub> -]-O + H(+M)	See Table 4.2		
O + [-C <sub>6</sub> H <sub>6</sub> -] → OH + [-C <sub>6</sub> H <sub>5</sub> -]	No recommendation; see data sheet.		
O + [-C <sub>6</sub> H <sub>5</sub> -]-O → [-C <sub>6</sub> H <sub>4</sub> -]-1,2-(O) <sub>2</sub> +H → [-C <sub>6</sub> H <sub>4</sub> -]-1,4-(O) <sub>2</sub> +H → CO <sub>2</sub> + [-C <sub>5</sub> H <sub>5</sub> -]	$2.8 \cdot 10^{-10}$	295–1500	± 0.3
O + [-C <sub>6</sub> H <sub>5</sub> -]-OH → Products	$2.82 \cdot 10^{-11} \exp(-1540/T)$	298–870	± 0.3
O + [-C <sub>6</sub> H <sub>5</sub> -]-CH <sub>2</sub> → HCO + [-C <sub>6</sub> H <sub>6</sub> -] → [-C <sub>6</sub> H <sub>5</sub> -]-CHO + H → HCHO + [-C <sub>6</sub> H <sub>5</sub> -]	$(k_1+k_2) = 5.5 \cdot 10^{-10}$	298	± 0.3
O + [-C <sub>6</sub> H <sub>5</sub> -]-CH <sub>3</sub> (+M) → [-C <sub>6</sub> H <sub>4</sub> -]-1-OH; -2-CH <sub>3</sub> (+M) → [-C <sub>6</sub> H <sub>4</sub> -]-1-OH; -4-CH <sub>3</sub> (+M) → [-C <sub>6</sub> H <sub>5</sub> -]-OCH <sub>3</sub> (+M)	$5.3 \cdot 10^{-15} T^{1.21} \exp(-1260/T)$	298–2800	± 0.1 at 298 K, rising to ± 0.3 at 2800 K.
O + [-C <sub>6</sub> H <sub>5</sub> -]-CH <sub>3</sub> → OH + [-C <sub>6</sub> H <sub>5</sub> -]-CH <sub>2</sub> → OH + [-C <sub>6</sub> H <sub>4</sub> -]-CH <sub>3</sub>			
O + [-C <sub>6</sub> H <sub>5</sub> -]-CHO → OH + [-C <sub>6</sub> H <sub>5</sub> -]-CO → OH + [-C <sub>6</sub> H <sub>4</sub> -]-CHO	$k_1 = 1.1 \cdot 10^{-11} \exp(-910/T)$ See data sheet for information on other channels.	298–1500	± 0.3 at 298 K, rising to ± 0.7 at 1500 K.
O + [-C <sub>6</sub> H <sub>5</sub> -]-CHO(+M) → [-C <sub>6</sub> H <sub>4</sub> -]-CO(O)(O)(+M)			
O + [-C <sub>6</sub> H <sub>4</sub> -]-1,4-(CH <sub>3</sub> ) <sub>2</sub> (+M) → [-C <sub>6</sub> H <sub>3</sub> -]-1-OH; -2,5-(CH <sub>3</sub> ) <sub>2</sub> (+M) → [-C <sub>6</sub> H <sub>4</sub> -]-1-OCH <sub>3</sub> ; -4-CH <sub>3</sub> (+M)	$5.1 \cdot 10^{-11} \exp(-1630/T)$	298–1000	± 0.3
O + [-C <sub>6</sub> H <sub>3</sub> -]-1,4-(CH <sub>3</sub> ) <sub>2</sub> → OH + [-C <sub>6</sub> H <sub>4</sub> -]-1-CH <sub>2</sub> ; -4-CH <sub>3</sub>			
O + [-C <sub>6</sub> H <sub>5</sub> -]-C <sub>2</sub> H <sub>5</sub> → OH + [-C <sub>6</sub> H <sub>5</sub> -]-CHCH <sub>3</sub>	$3.7 \cdot 10^{-11} \exp(-1910/T)$	298–900	± 0.2
<i>O<sub>2</sub> Reactions</i>			

TABLE 4.1. Bimolecular reactions—Continued

Reaction	$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Error limits ( $\Delta \log k$ )
$\text{O}_2 + \text{CH}_4 \rightarrow \text{HO}_2 + \text{CH}_3$	$8.1 \cdot 10^{-19} T^{2.5} \exp(-26370/T)$	500–2000	$\pm 0.5$ over the range 500–1000 K, rising to $\pm 0.7$ at 2000 K.
$\text{O}_2 + \text{HCHO} \rightarrow \text{HO}_2 + \text{HCO}$	$4.05 \cdot 10^{-19} T^{2.5} \exp(-18350/T)$	600–2500	$\pm 0.3$ at 600 K, rising to $\pm 0.5$ at 2500 K.
$\text{O}_2 + \text{C}_2\text{H}_6 \rightarrow \text{HO}_2 + \text{C}_2\text{H}_5$	$1.21 \cdot 10^{-18} T^{2.5} \exp(-24740/T)$	500–2000	$\pm 0.5$ over the range 500–1100 K, rising to $\pm 1.0$ at 2000 K.
$\text{O}_2 + \text{CH}_3\text{CHO} \rightarrow \text{HO}_2 + \text{CH}_3\text{CO}$	$2.0 \cdot 10^{-19} T^{2.5} \exp(-18900/T)$	600–1500	$\pm 0.4$ over the range 600–1000 K, rising to $\pm 0.7$ at 1500 K.
$\text{O}_2 + \text{CH}_3\text{OCH}_3 \rightarrow \text{HO}_2 + \text{CH}_2\text{OCH}_3$	$1.21 \cdot 10^{-18} T^{2.5} \exp(-22240/T)$	500–2000	$\pm 0.5$ over the range 500–1000 K, rising to $\pm 0.7$ at 2000 K.
$\text{O}_2 + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{HO}_2 + \text{CH}_3\text{CHOH}$ $\rightarrow \text{HO}_2 + \text{CH}_2\text{CH}_2\text{OH}$ $\rightarrow \text{HO}_2 + \text{CH}_3\text{CH}_2\text{O}$	$4.0 \cdot 10^{-19} T^{2.5} \exp(-22170/T)$ $6.0 \cdot 10^{-19} T^{2.5} \exp(-24030/T)$ $2.0 \cdot 10^{-19} T^{2.5} \exp(-26530/T)$	500–2000 500–2000 500–2000	$\pm 0.5$ over the range 500–1000 K, rising to $\pm 1.0$ at 2000 K. $\pm 1.0$ over the range 500–1000 K.
$\text{O}_2 + \text{C}_3\text{H}_6 \rightarrow \text{HO}_2 + \text{C}_3\text{H}_5$	$1.8 \cdot 10^{-20} T^{2.5} \exp(-17980/T)$	600–1500	$\pm 0.3$ over the range 600–800 K, rising to $\pm 0.5$ at 1000 K, and falling to $\pm 0.3$ at 1500 K.
$\text{O}_2 + [-\text{C}_6\text{H}_5^-] \cdot \text{CH}_3 \rightarrow \text{HO}_2 + [-\text{C}_6\text{H}_5^-] \cdot \text{CH}_2$	$1.9 \cdot 10^{-17} T^{2.5} \exp(-22620/T)$	500–2000	$\pm 0.4$ over the range 500–1400 K, rising to $\pm 0.6$ at 2000 K.
<i>H Atom Reactions</i>			
$\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$	$3.43 \cdot 10^{-10} T^{-0.097} \exp(-7560/T)$	800–3500	$\pm 0.1$ at 800 K, rising to $\pm 0.2$ at 3500 K.
$\text{H} + \text{O}_2 (+\text{M}) \rightarrow \text{HO}_2 (+\text{M})$	See Table 4.2		
$\text{H} + \text{H} (+\text{M}) \rightarrow \text{H}_2 (+\text{M})$	See Table 4.2		
$\text{H}_2 (+\text{M}) \rightarrow \text{H} + \text{H} (+\text{M})$	See Table 4.3		
$\text{H} + \text{OH} (+\text{M}) \rightarrow \text{H}_2\text{O} (+\text{M})$	See Table 4.2		
$\text{H}_2\text{O} (+\text{M}) \rightarrow \text{H} + \text{OH} (+\text{M})$	See Table 4.3		
$\text{H} + \text{HO}_2 \rightarrow \text{H}_2 + \text{O}_2$ $\rightarrow 2\text{OH}$ $\rightarrow \text{H}_2\text{O} + \text{O}$	$1.75 \cdot 10^{-10} \exp(-1030/T)$ $7.4 \cdot 10^{-10} \exp(-700/T)$ $2.4 \cdot 10^{-12}$	250–1000 250–1000 298	$\pm 0.3$ $\pm 0.15$ $\pm 0.5$
$\text{H} + \text{H}_2\text{O} \rightarrow \text{OH} + \text{H}_2$	$7.5 \cdot 10^{-16} T^{1.6} \exp(-9030/T)$	800–2500	$\pm 0.2$
$\text{H} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2 + \text{HO}_2$ $\rightarrow \text{OH} + \text{H}_2\text{O}$	$2.8 \cdot 10^{-12} \exp(-1890/T)$ $1.7 \cdot 10^{-11} \exp(-1800/T)$	280–1000 300–1000	$\pm 0.5$ $\pm 0.3$
$\text{H} + \text{NO} \rightarrow \text{OH} + \text{N}$	$3.6 \cdot 10^{-10} \exp(-24910/T)$	1500–4500	$\pm 0.3$
$\text{H} + \text{NO} (+\text{M}) \rightarrow \text{HNO} (+\text{M})$	See Table 4.2		
$\text{HNO} (+\text{M}) \rightarrow \text{H} + \text{NO} (+\text{M})$	See Table 4.3		
$\text{H} + \text{NO}_2 \rightarrow \text{OH} + \text{NO}$	$4.2 \cdot 10^{-10} \exp(-340/T)$	230–800	$\pm 0.1$ at 230 K, rising to $\pm 0.3$ at 800 K.
$\text{H} + \text{N}_2\text{O} (+\text{M}) \rightarrow \text{HN}_2\text{O} (+\text{M})$ $\text{H} + \text{N}_2\text{O} \rightarrow \text{OH} + \text{N}_2$ $\rightarrow \text{NH} + \text{NO}$	$[5.5 \cdot 10^{-14} \exp(-2560/T) + 1.3 \cdot 10^{-9} \exp(-9750/T)]$ Branching ratios—see data sheet.	350–2500	$\pm 0.3$
$\text{H} + \text{NH} \rightarrow \text{H}_2 + \text{N}$	$5 \cdot 10^{-11}$	1500–2500	$\pm 0.3$
$\text{H} + \text{NH}_2 (+\text{M}) \rightarrow \text{NH}_3 (+\text{M})$	See Table 4.2	1100–3000	$\pm 0.2$
$\text{H} + \text{NH}_2 \rightarrow \text{H}_2 + \text{NH}$	$8.8 \cdot 10^{-11} \exp(-2515/T)$		
$\text{NH}_3 (+\text{M}) \rightarrow \text{NH} + \text{H}_2 (+\text{M})$ $\rightarrow \text{NH}_2\text{H} (+\text{M})$	See Table 4.3		
$\text{H} + \text{CO} (+\text{M}) \rightarrow \text{HCO} (+\text{M})$	See Table 4.2		
$\text{HCO} (+\text{M}) \rightarrow \text{H} + \text{CO} (+\text{M})$	See Table 4.3		
$\text{H} + \text{CO}_2 \rightarrow \text{OH} + \text{CO}$	$4.6 \cdot 10^{-10} \exp(-13915/T)$	1000–3000	$\pm 0.2$

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TABLE 4.1. Bimolecular reactions—Continued

Reaction	$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Error limits ( $\Delta \log k$ )
$\text{H} + \text{NCO} \rightarrow \text{NH} + \text{CO}$ $\quad \rightarrow \text{HCN} + \text{O}$	$1.2 \cdot 10^{-10} \exp(-500/T)$ $4.4 \cdot 10^{-14} T^{1.02} \exp(-8630/T)$	295–1500 500–2500	$\pm 0.3$ at 295 K, rising to $\pm 0.5$ at 1500 K. $\pm 0.7$
$\text{H} + \text{HNCO} \rightarrow \text{NH}_2 + \text{CO}$ $\quad \rightarrow \text{H}_2 + \text{NCO}$	$5.96 \cdot 10^{-20} T^{2.49} \exp(-1180/T)$ $1.49 \cdot 10^{-16} T^{1.66} \exp(-7000/T)$	500–3300 500–3300	$\pm 1.0$ at 500 K, falling to $\pm 0.4$ over the range 2000–3300 K.
$\text{H} + \text{CH} \rightarrow \text{H}_2 + \text{C}$	$2.0 \cdot 10^{-10}$	1500–2500	$\pm 0.6$
$\text{H} + {}^3\text{CH}_2 \rightarrow \text{H}_2 + \text{CH}$	$2.0 \cdot 10^{-10}$	298–3000	$\pm 0.3$ at 298 K, rising to $\pm 1.0$ at 3000 K.
$\text{H} + \text{CH}_3 \rightarrow \text{H}_2 + {}^1\text{CH}_2$	$2.1 \cdot 10^{-8} T^{-0.56} \exp(-8000/T)$	300–2500	$\pm 0.15$ over the range 300–1000 K $\pm 0.3$ over the range 1000–1700 K $\pm 0.2$ over the range 1700–2500 K
$\text{H} + \text{CH}_3(+\text{M}) \rightarrow \text{CH}_4(+\text{M})$	See Table 4.2		
$\text{CH}_4(+\text{M}) \rightarrow \text{H} + \text{CH}_3(+\text{M})$	See Table 4.3		
$\text{H} + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3$	$1.02 \cdot 10^{-18} T^{2.50} \exp(-4825/T)$	350–2500	$\pm 0.2$ at 1000 K, rising to $\pm 0.4$ at 350 K and 2500 K.
$\text{H} + \text{HCO} \rightarrow \text{H}_2 + \text{CO}$	$1.5 \cdot 10^{-10}$	298–2500	$\pm 0.3$
$\text{H} + \text{HCHO} \rightarrow \text{H}_2 + \text{HCO}$	$3.34 \cdot 10^{-23} T^{-3.81} \exp(-202/T)$	290–2500	$\pm 0.1$ at 290 K, rising to $\pm 0.5$ at 2500 K.
$\text{H} + \text{CH}_3\text{O} \rightarrow \text{H}_2 + \text{HCHO}$ $\quad \rightarrow \text{OH} + \text{CH}_3$	$k = 9.0 \cdot 10^{-11} \exp(-300/T)$ $k_1/k = 0.7; k_2/k = 0.3.$	298–1000 298	$\pm 0.1$ at 298 K, rising to $\pm 0.3$ at 1000 K. $\Delta(k_1/k) = +0.15\text{--}0.20; \Delta(k_2/k) = \pm 0.2$ at 298 K.
$\text{H} + \text{CH}_2\text{OH} \rightarrow \text{HCHO} + \text{H}_2$ $\quad \rightarrow \text{CHOH} + \text{H}_2$ $\quad \rightarrow \text{CH}_3 + \text{OH}$	$k = 5.8 \cdot 10^{-11}$ $(k_1 + k_2)/k = 0.7$	298 298	$\pm 0.3$ $\Delta[(k_1 + k_2)/k] = \pm 0.1$
$\text{H} + \text{CH}_2\text{OH}(+\text{M}) \rightarrow \text{CH}_3\text{OH}(+\text{M})$	See Table 4.2		
$\text{H} + \text{CH}_3\text{OH} \rightarrow \text{H}_2 + \text{CH}_2\text{OH}$ $\quad \rightarrow \text{H}_2 + \text{CH}_3\text{O}$	$5.7 \cdot 10^{-15} T^{1.24} \exp(-2260/T)$	295–2500	$\pm 0.3$ at 295 K, rising to $\pm 0.6$ at 2500 K.
$\text{H} + \text{C}_2\text{H}_2 \rightarrow \text{H}_2 + \text{C}_2\text{H}$	$1.67 \cdot 10^{-14} T^{1.64} \exp(-15250/T)$	300–3000	$\pm 0.2$ at 300 K, rising to $\pm 0.7$ at 3000 K.
$\text{H} + \text{C}_2\text{H}_2(+\text{M}) \rightarrow \text{C}_2\text{H}_3(+\text{M})$	See Table 4.2		
$\text{C}_2\text{H}_3(+\text{M}) \rightarrow \text{C}_2\text{H}_2 + \text{H}(+\text{M})$	See Table 4.3		
$\text{H} + \text{C}_2\text{H}_3 \rightarrow \text{H}_2 + \text{C}_2\text{H}_2$	$7 \cdot 10^{-11}$	300	$\pm 0.3$
$\text{H} + \text{C}_2\text{H}_3(+\text{M}) \rightarrow \text{C}_2\text{H}_4(+\text{M})$	See Table 4.2		
$\text{C}_2\text{H}_4(+\text{M}) \rightarrow \text{C}_2\text{H}_2 + \text{H}_2(+\text{M})$ $\quad \rightarrow \text{C}_2\text{H}_3 + \text{H}(+\text{M})$	See Table 4.3		
$\text{H} + \text{C}_2\text{H}_4 \rightarrow \text{H}_2 + \text{C}_2\text{H}_3$	$3.9 \cdot 10^{-22} T^{3.62} \exp(-5670/T)$	400–2000	$\pm 0.4$
$\text{H} + \text{C}_2\text{H}_4(+\text{M}) \rightarrow \text{C}_2\text{H}_5(+\text{M})$	See Table 4.2		
$\text{C}_2\text{H}_5(+\text{M}) \rightarrow \text{H} + \text{C}_2\text{H}_4(+\text{M})$	See Table 4.3		
$\text{H} + \text{C}_2\text{H}_5 \rightarrow \text{H}_2 + \text{C}_2\text{H}_4$	$7.0 \cdot 10^{-11}$	298–2000	$\pm 0.3$ at 298 K, rising to $\pm 0.8$ at 2000 K.
$\text{H} + \text{C}_2\text{H}_5(+\text{M}) \rightarrow \text{C}_2\text{H}_6(+\text{M})$	No recommendation—see data sheet		
$\text{H} + \text{C}_2\text{H}_6 \rightarrow \text{H}_2 + \text{C}_2\text{H}_5$	$1.63 \cdot 10^{-10} \exp(-4640/T)$	298–1500	$\pm 0.4$ at 298 K, falling to $\pm 0.3$ at 1500 K.
$\text{H} + \text{HCCO} \rightarrow {}^3\text{CH}_2 + \text{CO}$ $\quad \rightarrow {}^1\text{CH}_2 + \text{CO}$	$(k_1 + k_2) = 2.2 \cdot 10^{-10}$ $k_1/(k_1 + k_2) = 0.08; k_2/(k_1 + k_2) = 0.92$	280–2000 298	$\pm 0.2$ $\Delta(k_1/k) = {}^{+0.2}_{-0.08}; \Delta(k_2/k) = {}^{+0.08}_{-0.2}$ at 298 K.
$\text{H} + \text{HCCO}(+\text{M}) \rightarrow \text{HCCOH}(+\text{M})$	No recommendation—see data sheet		
$\text{H} + \text{CH}_2\text{CO} \rightarrow \text{CH}_3 + \text{CO}$	$5.4 \cdot 10^{-14} T^{0.85} \exp(-1430/T)$	298–2000	$\pm 0.3$ at 298 K, rising to $\pm 0.5$ at 2000 K.

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TABLE 4.1. Bimolecular reactions—Continued

Reaction	$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Error limits ( $\Delta \log k$ )
$\begin{array}{l} \text{H} + \text{CH}_3\text{CHO} \rightarrow \text{H}_2 + \text{CH}_3\text{CO} \\ \quad \rightarrow \text{H}_2 + \text{CH}_2\text{CHO} \\ \quad \rightarrow \text{C}_2\text{H}_5 + \text{O} \end{array}$	$6.8 \cdot 10^{-15} T^{1.16} \exp(-1210/7)$	298–2000	$\pm 0.1$ at 298 K, rising to $\pm 0.4$ at 2000 K.
$\begin{array}{l} \text{H} + \text{CH}_3\text{OCH}_3 \rightarrow \text{H}_2 + \text{CH}_3\text{OCH}_2 \\ \quad \rightarrow \text{H}_2 + \text{CH}_2\text{CH}_2\text{OH} \\ \quad \rightarrow \text{H}_2 + \text{CH}_3\text{CH}_2\text{O} \end{array}$	$5.3 \cdot 10^{-17} T^{1.9} \exp(-1860/T) \text{ K}$	270–2000	$\pm 0.3$ at 270 K, rising to $\pm 0.5$ at 2000 K.
$\begin{array}{l} \text{H} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{H}_2 + \text{CH}_3\text{CHOH} \\ \quad \rightarrow \text{H}_2 + \text{CH}_2\text{CH}_2\text{OH} \\ \quad \rightarrow \text{H}_2 + \text{CH}_3\text{CH}_2\text{O} \end{array}$	$7.0 \cdot 10^{-12} \exp(-2110/T)$	295–700	$\pm 0.3$
$\begin{array}{l} \text{H} + \text{C}_3\text{H}_5(+\text{M}) \rightarrow \text{C}_3\text{H}_6(+\text{M}) \\ \quad \rightarrow \text{H}_2 + \text{C}_2\text{H}_3 + \text{CH}_3 \\ \quad \rightarrow \text{H}_2 + \text{C}_2\text{H}_4 \end{array}$	$(k_1^\infty + k_2) = 2.8 \cdot 10^{-10}$ $3 \cdot 10^{-11}$	300–1000 300–1000	$\pm 0.2$ at 300 K, rising to $\pm 0.5$ at 1000 K. $\pm 0.5$
$\text{H} + [-\text{C}_6\text{H}_5^-](+\text{M}) \rightarrow [-\text{C}_6\text{H}_6^-](+\text{M})$	See Table 4.2		
$[-\text{C}_6\text{H}_6^-](+\text{M}) \rightarrow \text{C}_4\text{H}_4 + \text{H}_2$	See Table 4.3		
$\rightarrow [-\text{C}_6\text{H}_5^-] + \text{H}(+\text{M})$			
$\text{H} + [-\text{C}_6\text{H}_6^-] \rightarrow \text{H}_2 + [-\text{C}_6\text{H}_5^-]$	$2.16 \cdot 10^{-7} T^{-0.70} \exp(-10070/T)$	500–2200	$\pm 0.15$
$\text{H} + [-\text{C}_6\text{H}_6^-](+\text{M}) \rightarrow [-\text{C}_6\text{H}_7^-](+\text{M})$	See Table 4.2		
$\text{H} + [-\text{C}_6\text{H}_5^-]\text{-O}(+\text{M}) \rightarrow [-\text{C}_6\text{H}_5^-]\text{-OH}(+\text{M})$	$k = 2 \cdot 10^{-10}$	295–1000	$\pm 0.4$
$\rightarrow [-\text{C}_6\text{H}_5^-] = \text{O}(+\text{M})$	Branching ratios—see data sheet		
$\text{H} + [-\text{C}_6\text{H}_5^-]\text{-O} \rightarrow [-\text{C}_5\text{H}_6^-] + \text{CO}$			
$\text{H} + [-\text{C}_6\text{H}_5^-]\text{-OH} \rightarrow \text{H}_2 + [-\text{C}_6\text{H}_5^-]\text{-O}$	$1.9 \cdot 10^{-10} \exp(-6240/T)$	1000–1500	$\pm 0.2$
$\rightarrow \text{OH} + [-\text{C}_6\text{H}_6^-]$	$3.7 \cdot 10^{-11} \exp(-3990/T)$	1000–1500	$\pm 0.2$
$k_1/k = 0.892 - 540/T; k_2/k = (1 - k_1/k)$		1000–1500	$\Delta(k_1/k) = \Delta(k_2/k) = \pm 0.2$
$\text{H} + [-\text{C}_6\text{H}_5^-]\text{-CH}_2(+\text{M}) \rightarrow [-\text{C}_6\text{H}_5^-]\text{-CH}_3(+\text{M})$	See Table 4.2		
$[-\text{C}_6\text{H}_5^-]\text{-CH}_3(+\text{M}) \rightarrow \text{H} + [-\text{C}_6\text{H}_5^-]\text{-CH}_2(+\text{M})$	See Table 4.3		
$\rightarrow \text{CH}_3 + [-\text{C}_6\text{H}_5^-](+\text{M})$			
$\text{H} + [-\text{C}_6\text{H}_5^-]\text{-CH}_3(+\text{M}) \rightarrow [-\text{C}_6\text{H}_6^-]\text{-CH}_3(+\text{M})$	See Table 4.2		
$\text{H} + [-\text{C}_6\text{H}_5^-]\text{-CH}_3 \rightarrow \text{H}_2 + [-\text{C}_6\text{H}_5^-]\text{-CH}_2$	$6.6 \cdot 10^{-22} T^{3.44} \exp(-1570/T)$	600–2500	$\pm 0.3$
$\rightarrow [-\text{C}_6\text{H}_6^-] + \text{CH}_3$	$9.6 \cdot 10^{-11} \exp(-4070/T)$	770–1100	$\pm 0.3$
$\rightarrow \text{H}_2 + [-\text{C}_6\text{H}_4^-]\text{-CH}_3$	No recommendation—see data sheet		
$\text{H} + [-\text{C}_6\text{H}_4^-]\text{-1,4-(CH}_3)_2(+\text{M}) \rightarrow [-\text{C}_6\text{H}_5^-]\text{-1,4-(CH}_3)_2(+\text{M})$	See Table 4.2		
$\text{H} + [-\text{C}_6\text{H}_4^-]\text{-1,4-(CH}_3)_2 \rightarrow \text{H}_2 + [-\text{C}_6\text{H}_4^-]\text{-1,(CH}_2)\text{-4-(CH}_3)$	$6.6 \cdot 10^{-10} \exp(-4210/T)$	1200–1800	$\pm 0.5$
$\rightarrow \text{H}_2 + [-\text{C}_6\text{H}_3^-]\text{-1,4-(CH}_3)_2$	No recommendation—see data sheet		
$\text{H} + [-\text{C}_6\text{H}_5^-]\text{-C}_2\text{H}_5(+\text{M}) \rightarrow [-\text{C}_6\text{H}_5^-]\text{-C}_2\text{H}_5(+\text{M})$	See Table 4.2		
$\text{H} + [-\text{C}_6\text{H}_5^-]\text{-C}_2\text{H}_5 \rightarrow \text{H}_2 + [-\text{C}_6\text{H}_5^-]\text{-CHCH}_3$	$4.4 \cdot 10^{-22} T^{3.44} \exp(-505/T)$	600–1200	$\pm 0.3$ over the range 600–800 K, rising to $\pm 0.5$ at 1200 K.
$\rightarrow \text{C}_6\text{H}_6 + \text{C}_2\text{H}_5$	$9.6 \cdot 10^{-11} \exp(-4070/T)$	700–1100	$\pm 0.3$ over the range 700–900 K, rising to $\pm 0.5$ at 1100 K.
$\rightarrow \text{H}_2 + [-\text{C}_6\text{H}_5^-]\text{-CH}_2\text{CH}_2$	$3.9 \cdot 10^{-22} T^{1.90} \exp(-3340/T)$	500–2000	$\pm 0.3$ over the range 500–1000 K, rising to $\pm 0.5$ at 2000 K.
$\rightarrow \text{H}_2 + [-\text{C}_6\text{H}_4^-]\text{-C}_2\text{H}_5$	$1.3 \cdot 10^{-17} \exp(-4880/T)$	600–1200	$\pm 0.3$ over the range 600–800 K, rising to $\pm 0.5$ at 1200 K.
<b><i>H<sub>2</sub> Reactions</i></b>			
$\text{H}_2(+\text{M}) \rightarrow 2\text{H}(+\text{M})$	See Table 4.3		
<b><i>OH Radical Reactions</i></b>			
$\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$	$3.6 \cdot 10^{-16} T^{1.52} \exp(-1740/T)$	250–2500	$\pm 0.1$ at 250 K, rising to $\pm 0.3$ at 2500 K.

TABLE 4.1. Bimolecular reactions—Continued

Reaction	$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Error limits ( $\Delta \log k$ )
$\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}$	$5.56 \cdot 10^{-20} T^{2.42} \exp(970/T)$	250–2400	$\pm 0.15$
$\text{OH} + \text{OH} (+\text{M}) \rightarrow \text{H}_2\text{O}_2 (+\text{M})$	See Table 4.2		
$\text{H}_2\text{O}_2 (+\text{M}) \rightarrow \text{OH} + \text{OH} (+\text{M})$	See Table 4.3		
$\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$	$4.8 \cdot 10^{-11} \exp(250/T)$	250–400	$\pm 0.2$
	$1.54 \cdot 10^{-8} \exp(-8810/T)$	1300–2000	$\pm 0.5$
$\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2$	$[2.72 \cdot 10^{-6} \exp(-14800/T) + 3.2 \cdot 10^{-12} \exp(-215/T)]$	240–1700	$\pm 0.2$ over the range 240–800 K and $\pm 0.5$ over the range 800–1700 K.
$\text{OH} + \text{NH} \rightarrow \text{NO} + \text{H}_2$	$k = 8.0 \cdot 10^{-11}$	300–2000	$\pm 0.5$ at 300 K, rising to $\pm 1.0$ at 2000 K.
$\rightarrow \text{H}_2\text{O} + \text{N}$	Branching ratios—see data sheet		
$\rightarrow \text{H} + \text{HNO}$			
$\text{OH} + \text{NH}_2 (+\text{M}) \rightarrow \text{NH}_2\text{OH} (+\text{M})$	See Table 4.2		
$\text{OH} + \text{NH}_2 \rightarrow \text{H}_2\text{O} + \text{NH}$	No recommendation—see data sheet		
$\rightarrow \text{O} + \text{NH}_3$	$4.2 \cdot 10^{-20} T^{2.3} \exp(140/T)$	300–200	$\pm 0.3$ at 300 K, rising to $\pm 0.5$ at 2000 K.
$\text{OH} + \text{CO} (+\text{M}) \rightarrow \text{HOCO} (+\text{M})$	See Table 4.2		
$\text{OH} + \text{CO} \rightarrow \text{H} + \text{CO}_2$			
$\text{OH} + \text{CN} \rightarrow \text{H} + \text{NCO}$	$6.7 \cdot 10^{-11}$	1250–3000	$\pm 0.2$
$\rightarrow \text{O} + \text{HCN}$	$1 \cdot 10^{-11} \exp(-1000/T)$	1250–3000	$\pm 0.6$
$\text{OH} + \text{HCN} \rightarrow \text{HNCO} + \text{H}$	No recommendation—see data sheet		
$\rightarrow \text{H}_2\text{O} + \text{CN}$	$k_2 = 6.5 \cdot 10^{-18} T^{1.83} \exp(-5180/T)$	500–2500	$\pm 0.2$ over the range 1000–2500 K, rising to $\pm 0.5$ at 500 K; $\Delta(k_2/k) = \pm 0.2$
$\rightarrow \text{HOCN} + \text{H}$	$k_2/k > 0.5$ for $T > 1500$ K		
$\text{OH} + \text{HCN} (+\text{M}) \rightarrow \text{H}(\text{OH})\text{CN} (+\text{M})$	No recommendation—see data sheet		
$\text{OH} + \text{HNCO} \rightarrow \text{H}_2\text{O} + \text{NCO}$	No recommendation—see data sheet		
$\rightarrow \text{CO}_2 + \text{NH}_2$	$6.03 \cdot 10^{-17} T^{1.5} \exp(-1809/T)$	600–2300	$\pm 0.15$
	Branching ratios—see data sheet		
$\text{OH} + \text{CH}_3 (+\text{M}) \rightarrow \text{CH}_3\text{OH} (+\text{M})$	See Table 4.2		
$\text{OH} + \text{CH}_3 \rightarrow \text{CH}_2 + \text{H}_2\text{O}$	See Table 4.2		
$\rightarrow \text{H} + \text{CH}_2\text{OH}$	$1.2 \cdot 10^{-12} \exp(-2760/T)$	298–2000	$\pm 1.0$
$\rightarrow \text{H} + \text{CH}_3\text{O}$	$2.0 \cdot 10^{-14} \exp(-6990/T)$	298–2000	$\pm 1.0$
$\rightarrow \text{HCHO} + \text{H}_2$	$5.3 \cdot 10^{-15} \exp(-2530/T)$	298–2000	$\pm 1.0$
$\rightarrow \text{HCOH} + \text{H}_2$	See Table 4.2 for pressure dependent expression		
$\text{CH}_3\text{OH} (+\text{M}) \rightarrow \text{OH} + \text{CH}_3 (+\text{M})$	See Table 4.3		
$\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \text{CH}_3$	$2.27 \cdot 10^{-18} T^{2.18} \exp(-1350/T)$	250–2400	$\pm 0.1$ over the range 250–350 K, rising to $\pm 0.2$ at 800 K and $\pm 0.3$ at 2400 K.
$\rightarrow \text{H}_2\text{O} + \text{CH}_3$			
$\text{OH} + \text{HCO} \rightarrow \text{H}_2\text{O} + \text{CO}$	$1.8 \cdot 10^{-10}$	296–2500	$\pm 0.3$
$\text{OH} + \text{HCHO} \rightarrow \text{H}_2\text{O} + \text{HCO}$	$2.31 \cdot 10^{-11} \exp(-304/T)$	300–1500	$\pm 0.1$ at 300 K, rising to $\pm 0.3$ at 1500 K
$\text{OH} + \text{CH}_3\text{OH} \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{OH}$	$k = 1.03 \cdot 10^{-17} T^{1.92} \exp(144/T)$	240–2000	$\pm 0.1$ at 300 K, rising to $\pm 0.2$ at 240 K and $\pm 0.3$ at 2000 K.
$\rightarrow \text{H}_2\text{O} + \text{CH}_3\text{O}$	$k_2/k = 0.15$	300	$\Delta(k_2/k) = \pm 0.1$
$\text{OH} + \text{CH}_3\text{OOH} \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{OOH}$	$1.2 \cdot 10^{-12} \exp(130/T)$	250–1000	$\pm 0.2$ at 250 K, rising to $\pm 0.4$ at 1000 K
$\rightarrow \text{H}_2\text{O} + \text{CH}_3\text{O}_2$	$1.8 \cdot 10^{-12} \exp(220/T)$	250–1000	$\pm 0.1$ at 250 K, rising to $\pm 0.3$ at 1000 K
$\text{OH} + \text{C}_2\text{H}_2 \rightarrow \text{CH}_2\text{CO} + \text{H}$	$(k_1 + k_2 + k_3) = 1.3 \cdot 10^{-10} \exp(-6800/T)$	1000–2000	$\pm 0.5$ at 1000 K, rising to $\pm 1.0$ at 2000 K
$\rightarrow \text{HOCCH} + \text{H}$			
$\rightarrow \text{H}_2\text{O} + \text{C}_2\text{H}$			

TABLE 4.1. Bimolecular reactions—Continued

Reaction	$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Error limits ( $\Delta \log k$ )
$\text{OH} + \text{C}_2\text{H}_2(+\text{M}) \rightarrow \text{C}_2\text{H}_2\text{OH}(\text{+M})$	No recommendation—see data sheet		
$\text{OH} + \text{C}_2\text{H}_4 \rightarrow \text{H}_2\text{O} + \text{C}_2\text{H}_3$	No recommendation—see data sheet		
$\begin{aligned} &\rightarrow \text{HCHO} + \text{CH}_3 \\ &\rightarrow \text{CH}_2\text{CHOH} + \text{H} \\ &\rightarrow \text{CH}_3\text{CHO} + \text{H} \end{aligned}$	$(k_2 + k_3 + k_4) = 3.4 \cdot 10^{-11} \exp(-2990/T)$	650–1500	$\pm 0.5$
$\text{OH} + \text{C}_2\text{H}_4(+\text{M}) \rightarrow \text{CH}_2\text{CH}_2\text{OH}(\text{+M})$	No recommendation—see data sheet		
$\text{OH} + \text{C}_2\text{H}_6 \rightarrow \text{H}_2\text{O} + \text{C}_2\text{H}_5$	$1.52 \cdot 10^{-17} T^{2.0} \exp(-500/T)$	200–2000	$\pm 0.08$ at 298 K, rising to $\pm 0.15$ at 200 K and to $\pm 0.2$ at 2000 K.
$\begin{aligned} \text{OH} + \text{CH}_2\text{CO} &\rightarrow \text{CH}_3 + \text{CO}_2 \\ &\rightarrow \text{CH}_2\text{OH} + \text{CO} \\ &\rightarrow \text{HCO} + \text{H}_2\text{CO} \\ &\rightarrow \text{H}_2\text{O} + \text{HCCO} \end{aligned}$	$k = 2.8 \cdot 10^{-12} \exp(510/T)$ $k_2/k = 0.6; k_3/k < 0.02; k_4/k < 0.01$	296–1000 298	$\pm 0.2$ at 296 K, rising to $\pm 0.6$ at 1000 K. $\Delta(k_2/k) = \pm 0.2$
$\begin{aligned} \text{OH} + \text{CH}_3\text{CHO} &\rightarrow \text{H}_2\text{O} + \text{CH}_3\text{CO} \\ &\rightarrow \text{H}_2\text{O} + \text{CH}_2\text{CHO} \end{aligned}$	$4.8 \cdot 10^{-16} T^{1.35} \exp(792/T)$ $k_1/k = 0.93$	280–1000 298	$\pm 0.1$ at 280 K, rising to $\pm 0.2$ at 1000 K. $\Delta(k_1/k) = \pm 0.18$
$\text{OH} + \text{CH}_3\text{OCH}_3 \rightarrow \text{H}_2\text{O} + \text{CH}_3\text{OCH}_2$	$8.2 \cdot 10^{-17} T^{1.73} \exp(-176/T)$	250–1200	$\pm 0.1$ over the range 250–500 K, rising to $\pm 0.3$ at 1200 K.
$\begin{aligned} \text{OH} + \text{CH}_3\text{CH}_2\text{OH} &\rightarrow \text{H}_2\text{O} + \text{CH}_3\text{CHOH} \\ &\rightarrow \text{H}_2\text{O} + \text{CH}_2\text{CH}_2\text{OH} \\ &\rightarrow \text{H}_2\text{O} + \text{C}_2\text{H}_5\text{O} \end{aligned}$	$k = 3.0 \cdot 10^{-17} T^{1.78} \exp(425/T)$ $k_2/k = 0.15$	290–1250 600	$\pm 0.1$ at 290 K, rising to $\pm 0.2$ at 1250 K. $\Delta(k_2/k) = \pm 0.10$ at 600 K
$\begin{aligned} \text{OH} + \text{C}_2\text{H}_5\text{OOH} &\rightarrow \text{H}_2\text{O} + \text{C}_2\text{H}_5\text{O}_2 \\ &\rightarrow \text{H}_2\text{O} + \text{CH}_3\text{CHOH} \\ &\rightarrow \text{H}_2\text{O} + \text{CH}_2\text{CH}_2\text{OH} \end{aligned}$	$3.0 \cdot 10^{-12} \exp(190/T)$ (estimate) $k_1/k = k_2/k = k_3/k = 0.33$	250–1000 250–1000	$\pm 0.3$ at 250 K, rising to $\pm 0.7$ at 1000 K. $\Delta(k_1/k) = \Delta(k_2/k) = \Delta(k_3/k) = \pm 0.15$
$\text{OH} + \text{C}_3\text{H}_5 \rightarrow \text{H}_2\text{O} + \text{C}_3\text{H}_4$	$k_1 = 1.0 \cdot 10^{-11}$	300–1000	$\pm 0.5$
$\begin{aligned} &\rightarrow \text{CH}_2\text{CHCHO} + 2\text{H} \\ \text{OH} + \text{C}_3\text{H}_5(+\text{M}) &\rightarrow \text{CH}_2\text{CHCH}_2\text{OH}(\text{+M}) \end{aligned}$	$(k_2 + k_3^\infty) = 2.5 \cdot 10^{-11}$	300–1000	$\pm 0.3$
$\text{OH} + [-\text{C}_6\text{H}_5^-] \rightarrow \text{H}_2\text{O} + [-\text{C}_6\text{H}_5^-]$	$2.80 \cdot 10^{-11} \exp(-2302/T)$	298–1500	$\pm 0.3$ at 298 K, falling to $\pm 0.1$ over the range 500–1500 K.
$\begin{aligned} \text{OH} + [-\text{C}_6\text{H}_5^-](+\text{M}) &\rightarrow [-\text{C}_6\text{H}_5^-]\text{-OH}(\text{+M}) \\ \text{OH} + [-\text{C}_6\text{H}_5^-]\text{-OH} &\rightarrow \text{H}_2\text{O} + [-\text{C}_6\text{H}_5^-]\text{-O} \\ &\rightarrow \text{H}_2\text{O} + [-\text{C}_6\text{H}_4^-]\text{-OH} \end{aligned}$	$2.2 \cdot 10^{-11} \exp(-5330/T)$ No recommendation—see data sheet $(k_1 + k_2) = 1.6 \cdot 10^{-11} \exp(-443/T)$	1000–1150	$\pm 0.3$
$\text{OH} + [-\text{C}_6\text{H}_5^-]\text{-OH}(\text{+M}) \rightarrow [-\text{C}_6\text{H}_5^-]\text{-}(\text{OH})_2(\text{+M})$	See Table 4.2		
$\begin{aligned} \text{OH} + [-\text{C}_6\text{H}_5^-]\text{-CH}_3 &\rightarrow \text{H}_2\text{O} + [-\text{C}_6\text{H}_5^-]\text{-CH}_2 \\ &\rightarrow \text{H}_2\text{O} + [-\text{C}_6\text{H}_4^-]\text{-CH}_3 \end{aligned}$	$8.6 \cdot 10^{-15} T \exp(-440/T)$	400–1200	$\pm 0.5$
$\text{OH} + [-\text{C}_6\text{H}_5^-]\text{-CH}_3(\text{+M}) \rightarrow [-\text{C}_6\text{H}_5^-]\text{-}(\text{CH}_3)(\text{OH})(\text{+M})$	$1.3 \cdot 10^{-11}$	298–1500	$\pm 0.1$ at 298 K, rising to $\pm 0.5$ at 1500 K.
$\text{OH} + [-\text{C}_6\text{H}_5^-]\text{-CHO} \rightarrow \text{H}_2\text{O} + [-\text{C}_6\text{H}_5^-]\text{-CO}$	$6.4 \cdot 10^{-11} \exp(-1440/T)$	500–960	$\pm 0.1$
$\begin{aligned} \text{OH} + [-\text{C}_6\text{H}_4^-]\text{-}1,4-(\text{CH}_3)_2 &\rightarrow \text{H}_2\text{O} + [-\text{C}_6\text{H}_4^-]\text{-}1,4-(\text{CH}_3)(\text{CH}_2) \\ \text{OH} + [-\text{C}_6\text{H}_4^-]\text{-}1,4-(\text{CH}_3)_2(\text{+M}) &\rightarrow [-\text{C}_6\text{H}_4^-]\text{-}1-(\text{OH})\text{-}2,5-(\text{CH}_3)_2(\text{+M}) \end{aligned}$	See Table 4.2		
$\begin{aligned} \text{OH} + [-\text{C}_6\text{H}_5^-]\text{-C}_2\text{H}_5 &\rightarrow \text{H}_2\text{O} + [-\text{C}_6\text{H}_5^-]\text{-CHCH}_3 \\ &\rightarrow \text{H}_2\text{O} + [-\text{C}_6\text{H}_5^-]\text{-CH}_2\text{CH}_2 \\ &\rightarrow \text{H}_2\text{O} + [-\text{C}_6\text{H}_4^-]\text{-C}_2\text{H}_5 \end{aligned}$	No recommendation—see data sheet		
$\text{OH} + [-\text{C}_6\text{H}_5^-]\text{-C}_2\text{H}_5(\text{+M}) \rightarrow [-\text{C}_6\text{H}_5^-]\text{-}2-(\text{C}_2\text{H}_5)\text{-}2-(\text{OH})(\text{+M})$	See Table 4.2		
$\text{HO}_2$ Radical Reactions			

TABLE 4.1. Bimolecular reactions—Continued

Reaction	$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Error limits ( $\Delta \log k$ )
$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	$[7.0 \cdot 10^{-10} \exp(-6030/T) + 2.2 \cdot 10^{-13} \exp(820/T)]$	550–1250	$\pm 0.15$ over the range 550–800 K, rising to $\pm 0.4$ at 1250 K
$\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2$	$3.4 \cdot 10^{-12} \exp(250/T)$	200–2000	$\pm 0.15$
$\text{HO}_2 + \text{NH}_2 \rightarrow \text{H}_2\text{O} + \text{HNO}$	$2.6 \cdot 10^{-11}$	300–400	$\pm 0.3$
$\begin{aligned} \rightarrow \text{O}_2 + \text{NH}_3 \\ \rightarrow \text{OH} + \text{NH}_2\text{O} \end{aligned}$	Branching ratios—see data sheet		
$\text{HO}_2 + \text{CH}_3 \rightarrow \text{OH} + \text{CH}_3\text{O}$	$3 \cdot 10^{-11}$	600–1200	$\pm 1.0$
$\begin{aligned} \rightarrow \text{O}_2 + \text{CH}_4 \\ \rightarrow \text{HCHO} + \text{H}_2\text{O} \end{aligned}$	No recommendation—see data sheet		
$\text{HO}_2 + \text{CH}_4 \rightarrow \text{H}_2\text{O}_2 + \text{CH}_3$	$7.8 \cdot 10^{-20} T^{2.5} \exp(-10570/T)$	600–200	$\pm 0.15$ over the range 600–800 K, rising to $\pm 0.3$ at 1000 K and to $\pm 0.7$ at 2000 K.
$\text{HO}_2 + \text{HCHO} \rightarrow \text{H}_2\text{O}_2 + \text{HCO}$	$6.8 \cdot 10^{-20} T^{2.5} \exp(-5140/T)$	600–2000	$\pm 0.2$ at 600 K, rising to $\pm 0.4$ at 2000 K.
$\text{HO}_2 + \text{HCHO} (+\text{M}) \rightarrow \text{HOCH}_2\text{OO} (+\text{M})$	See data sheet		
$\text{HO}_2 + \text{CH}_2\text{OH} \rightarrow \text{Products}$	$3 \cdot 10^{-11}$	298	$\pm 0.5$
$\text{HO}_2 + \text{CH}_3\text{O}_2 \rightarrow \text{CH}_3\text{OOH} + \text{O}_2$	$k = 4.2 \cdot 10^{-13} \exp(750/T)$	225–700	$\pm 0.1$ at 225 K, rising to $\pm 0.3$ at 700 K.
$\begin{aligned} \rightarrow \text{HCHO} + \text{H}_2\text{O} + \text{O}_2 \end{aligned}$	$k_2/k = 0.1$	298	$\Delta(k_2/k) = \pm 0.05$
$\text{HO}_2 + \text{C}_2\text{H}_4 \rightarrow \text{OH} + [-\text{C}_2\text{H}_4\text{O}-]$	$6.3 \cdot 10^{-12} \exp(-8990/T)$	600–900	$\pm 0.15$ over the range 600–750 K, rising to $\pm 0.25$ at 900 K.
$\begin{aligned} \rightarrow \text{C}_2\text{H}_5 + \text{O}_2 \\ \rightarrow \text{HO}_2 + \text{C}_2\text{H}_5 \end{aligned}$	$1.0 \cdot 10^{-13} T^{0.07} \exp(-6580/T)$	700–1500	$\pm 0.2$ at 700 K, rising to $\pm 0.4$ at 1500 K.
$\text{HO}_2 + \text{C}_2\text{H}_6 \rightarrow \text{H}_2\text{O}_2 + \text{C}_2\text{H}_5$	$1.83 \cdot 10^{-19} T^{2.5} \exp(-8480/T)$	500–2000	$\pm 0.15$ over the range 500–800 K, rising to $\pm 0.3$ at 1000 K and to $\pm 0.7$ at 2000 K.
$\text{HO}_2 + \text{CH}_3\text{CHO} \rightarrow \text{H}_2\text{O}_2 + \text{CH}_3\text{CO}$	$6.8 \cdot 10^{-20} T^{2.5} \exp(-5135/T)$	600–1500	$\pm 0.4$ over the range 600–1000 K, rising to $\pm 0.7$ at 1500 K.
$\text{HO}_2 + \text{C}_3\text{H}_5 \rightarrow \text{C}_3\text{H}_6 + \text{O}_2$	$4.4 \cdot 10^{-12}$	300–1000	$\pm 0.3$ over the range 600–800 K, rising to $\pm 0.5$ at 1000 K.
$\begin{aligned} \rightarrow \text{CO}_2 + \text{products} \\ \text{HO}_2 + [-\text{C}_6\text{H}_5-] - \text{CH}_3 \rightarrow \text{H}_2\text{O}_2 + [-\text{C}_6\text{H}_5-] - \text{CH}_2 \end{aligned}$	$1.1 \cdot 10^{-11}$	500–900	$\pm 0.3$
$\begin{aligned} \rightarrow \text{H}_2\text{O}_2 + [-\text{C}_6\text{H}_4-] - 2 - \text{CH}_3 \\ \rightarrow \text{H}_2\text{O}_2 + [-\text{C}_6\text{H}_4-] - 3 - \text{CH}_3 \\ \rightarrow \text{H}_2\text{O}_2 + [-\text{C}_6\text{H}_4-] - 4 - \text{CH}_3 \end{aligned}$	$1.55 \cdot 10^{-19} T^{2.5} \exp(-7390/T)$	600–1500	$\pm 0.3$ over the range 600–800 K, rising to $\pm 0.7$ at 1500 K.
$\text{HO}_2 + [-\text{C}_6\text{H}_5-] - \text{C}_2\text{H}_5 \rightarrow \text{H}_2\text{O}_2 + [-\text{C}_6\text{H}_5-] - \text{CHCH}_3$	$k_2 = k_3 = 3.0 \cdot 10^{-20} T^{2.5} \exp(-13900/T)$	600–1200	$\pm 0.5$ over the range 600–800 K, rising to $\pm 1.0$ at 1200 K.
$\begin{aligned} \rightarrow \text{H}_2\text{O}_2 + [-\text{C}_6\text{H}_4-] - 2 - \text{CH}_2\text{CH}_2 \\ \rightarrow \text{H}_2\text{O}_2 + [-\text{C}_6\text{H}_4-] - 2 - \text{C}_2\text{H}_5 \\ \rightarrow \text{H}_2\text{O}_2 + [-\text{C}_6\text{H}_4-] - 3 - \text{C}_2\text{H}_5 \\ \rightarrow \text{H}_2\text{O}_2 + [-\text{C}_6\text{H}_4-] - 4 - \text{C}_2\text{H}_5 \end{aligned}$	$1.5 \cdot 10^{-20} T^{2.5} \exp(-13900/T)$	600–1500	$\pm 0.3$ over the range 600–800 K, rising to $\pm 0.7$ at 1500 K.
$\begin{aligned} \rightarrow \text{H}_2\text{O}_2 + [-\text{C}_6\text{H}_4-] - 2 - \text{CH}_2\text{CH}_2 \\ \rightarrow \text{H}_2\text{O}_2 + [-\text{C}_6\text{H}_4-] - 2 - \text{C}_2\text{H}_5 \\ \rightarrow \text{H}_2\text{O}_2 + [-\text{C}_6\text{H}_4-] - 3 - \text{C}_2\text{H}_5 \\ \rightarrow \text{H}_2\text{O}_2 + [-\text{C}_6\text{H}_4-] - 4 - \text{C}_2\text{H}_5 \end{aligned}$	$1.03 \cdot 10^{-19} T^{2.5} \exp(-6805T)$	600–1500	$\pm 0.3$ over the range 600–800 K, rising to $\pm 0.5$ at 1500 K.
$\begin{aligned} \rightarrow \text{H}_2\text{O}_2 + [-\text{C}_6\text{H}_4-] - 2 - \text{CH}_2\text{CH}_2 \\ \rightarrow \text{H}_2\text{O}_2 + [-\text{C}_6\text{H}_4-] - 2 - \text{C}_2\text{H}_5 \\ \rightarrow \text{H}_2\text{O}_2 + [-\text{C}_6\text{H}_4-] - 3 - \text{C}_2\text{H}_5 \\ \rightarrow \text{H}_2\text{O}_2 + [-\text{C}_6\text{H}_4-] - 4 - \text{C}_2\text{H}_5 \end{aligned}$	$5.9 \cdot 10^{-20} T^{2.5} \exp(-8480/T)$	600–1500	$\pm 0.3$ over the range 600–800 K, rising to $\pm 0.5$ at 1500 K.
$\begin{aligned} \rightarrow \text{H}_2\text{O}_2 + [-\text{C}_6\text{H}_4-] - 2 - \text{CH}_2\text{CH}_2 \\ \rightarrow \text{H}_2\text{O}_2 + [-\text{C}_6\text{H}_4-] - 2 - \text{C}_2\text{H}_5 \\ \rightarrow \text{H}_2\text{O}_2 + [-\text{C}_6\text{H}_4-] - 3 - \text{C}_2\text{H}_5 \\ \rightarrow \text{H}_2\text{O}_2 + [-\text{C}_6\text{H}_4-] - 4 - \text{C}_2\text{H}_5 \end{aligned}$	$k_3 = k_4 = 3.0 \cdot 10^{-20} T^{2.5} \exp(-13900/T)$	600–1500	$\pm 0.5$ over the range 600–800 K, rising to $\pm 1.0$ at 1500 K.
$\begin{aligned} \rightarrow \text{H}_2\text{O}_2 + [-\text{C}_6\text{H}_4-] - 2 - \text{CH}_2\text{CH}_2 \\ \rightarrow \text{H}_2\text{O}_2 + [-\text{C}_6\text{H}_4-] - 2 - \text{C}_2\text{H}_5 \\ \rightarrow \text{H}_2\text{O}_2 + [-\text{C}_6\text{H}_4-] - 3 - \text{C}_2\text{H}_5 \\ \rightarrow \text{H}_2\text{O}_2 + [-\text{C}_6\text{H}_4-] - 4 - \text{C}_2\text{H}_5 \end{aligned}$	$1.5 \cdot 10^{-20} T^{2.5} \exp(-13900/T)$	600–1500	$\Delta \log k_3 = \Delta \log k_4 = \Delta \log k_5 = \pm 0.5$ over the range 600–800 K, rising to $\pm 1$ at 1500 K.
<i>H<sub>2</sub>O Reactions</i>	See Table 4.3		
$\text{H}_2\text{O} (+\text{M}) \rightarrow \text{H} + \text{OH} (+\text{M})$	See Table 4.3		
<i>H<sub>2</sub>O<sub>2</sub> Reactions</i>	See Table 4.3		
$\text{H}_2\text{O}_2 (+\text{M}) \rightarrow 2\text{OH} (+\text{M})$			
<i>N Atom Reactions</i>			
$\text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O}$	$9.7 \cdot 10^{-15} T^{1.01} \exp(-3120/T)$	280–5000	$\pm 0.2$ over the range 280–1500 K, rising to $\pm 0.5$ at 5000 K.

TABLE 4.1. Bimolecular reactions—Continued

Reaction	$k/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$	T/K	Error limits ( $\Delta \log k$ )
$\text{N} + \text{OH} \rightarrow \text{NO} + \text{H}$	$1.8 \cdot 10^{-10} T^{-0.2}$	100–2500	$\pm 0.1$ at 300 K, rising to $\pm 0.3$ at 100 K and to $\pm 0.4$ at 2500 K.
$\rightarrow \text{NH} + \text{O}$	No recommendation— $k_2 \ll k_1$ —see data sheet		
$\text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O}$	$3.5 \cdot 10^{-11}$	210–3700	$\pm 0.3$
$\text{N} + \text{CN} \rightarrow \text{N}_2 + \text{C}$	$9.8 \cdot 10^{-10} T^{-0.4}$	300–3000	$\pm 0.3$ at 300 K, rising to $\pm 0.5$ at 3000 K.
$\text{N} + \text{CN}(\text{+M}) \rightarrow \text{NCN}(\text{+M})$			
$\text{N} + \text{NCO} \rightarrow \text{N}_2 + \text{CO}$	$2.3 \cdot 10^{-10} T^{-0.25}$	298–1700	$\pm 0.2$ at 298 K, rising to $\pm 0.5$ at 1700 K.
$\rightarrow \text{CN} + \text{NO}$	No recommendation— $k_2 \ll k_1$ —see data sheet		
<i>N<sub>2</sub>O Reactions</i>			
$\text{N}_2\text{O}(\text{+M}) \rightarrow \text{O} + \text{N}_2(\text{+M})$	See Table 4.3		
<i>NH Radical Reactions</i>			
$\text{NH} + \text{O}_2 \rightarrow \text{NO} + \text{OH}$	$1.5 \cdot 10^{-13} \exp(-770/T)$	250–3300	$\pm 0.4$
$\rightarrow \text{H} + \text{NO}_2$	No recommendation— $k_2 \ll (k_1 + k_3)$		
$\rightarrow \text{HNO} + \text{O}$	$4.0 \cdot 10^{-11} \exp(-6970/T)$	250–3300	$\pm 0.1$
$\text{NH} + \text{NO} \rightarrow \text{N}_2 + \text{OH}$	$k = (k_1 + k_2) + (k_3 + k_4)$	298–3300	$\pm 0.3$
$\rightarrow \text{N}_2\text{O} + \text{H}$	$(k_1 + k_2) = 5.7 \cdot 10^{-9} T^{-0.78} \exp(-40/T)$	298–3300	$\pm 0.3$ over the range 298–1200 K, rising to
$\rightarrow \text{N}_2 + \text{H} + \text{O}$	$(k_3 + k_4) = 7.4 \cdot 10^{-10} \exp(-10540/T)$	298–3300	$\pm 0.5$ over the range 2000–3300 K.
$\rightarrow \text{N}_2\text{H} + \text{O}$	$k_1/k = 0.2; k_2/k = 0.8$	298	$\Delta(k_1/k) = \Delta(k_2/k) = \pm 0.15$
<i>NH<sub>2</sub> Radical Reactions</i>			
$\text{NH}_2 + \text{O}_2 \rightarrow \text{NO} + \text{H}_2\text{O}$	$k = 3.65 \cdot 10^{-10} \exp(-12630/T)$	1400–2400	$\pm 0.4$
$\rightarrow \text{NO}_2 + \text{H}_2$	$k_1 = 2.9 \cdot 10^{-10} \exp(-12420/T)$	1400–2400	$\pm 0.5$
$\rightarrow \text{HONO} + \text{H}$	$k_4 = 1.66 \cdot 10^{-11} \exp(-13230/T)$	1400–2400	$\pm 0.5$
$\rightarrow \text{HNO} + \text{OH}$	$k_5 = 1.0 \cdot 10^{-10} \exp(-15030/T)$	1400–2400	$\pm 0.5$
$\rightarrow \text{NH}_2\text{O} + \text{O}$	$k_2, k_3, k_6 \ll k$		
$\text{NH}_2 + \text{O}_2(\text{+M}) \rightarrow \text{NH}_2\text{O}_2(\text{+M})$			
$\text{NH}_2 + \text{NO} \rightarrow \text{N}_2 + \text{H}_2\text{O}$	$k = 1.14 \cdot 10^{-8} T^{-1.203} \exp(106/T)$	200–2500	$\pm 0.1$
$\rightarrow \text{N}_2\text{O} + \text{H}_2$	$(k_3 + k_4) = 0.7 + 3.36 \cdot 10^{-4}(T - 2200)$	600–2200	$\Delta[(k_3 + k_4)/k] = \pm 0.05$
$\rightarrow \text{N}_2 + \text{OH} + \text{H}$	$k_1/k \leq 1 - (k_3 + k_4)/k$	600–2200	
$\rightarrow \text{N}_2\text{H} + \text{OH}$			
$\rightarrow \text{HNO} + \text{NH}$			
$\text{NH}_2 + \text{NO}(\text{+M}) \rightarrow \text{NH}_2\text{NO}(\text{+M})$			
$\text{NH}_2 + \text{NO}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$	$k = 1.38 \cdot 10^{-9} T^{-0.74}$	300–1600	$\pm 0.1$ at 298 K, rising to $\pm 0.4$ at 1600 K.
$\rightarrow \text{N}_2 + \text{H}_2\text{O}_2$	$k_1/k = 0.2$	300–1600	$\Delta(k_1/k) = \pm 0.05$
$\rightarrow \text{N}_2 + \text{OH} + \text{H}$			
$\rightarrow \text{H}_2\text{NO} + \text{NO}$			
$\rightarrow \text{HNO} + \text{HNO}$			
<i>NH<sub>3</sub> Reactions</i>			
$\text{NH}_3(\text{+M}) \rightarrow \text{NH} + \text{H}_2(\text{+M})$	See Table 4.3		
$\rightarrow \text{NH}_2 + \text{H}(\text{+M})$			
<i>HNO Radical Reactions</i>			
$\text{HNO}(\text{+M}) \rightarrow \text{H} + \text{NO}(\text{+M})$	See Table 4.3		
<i>C Atom Reactions</i>			
$\text{C} + \text{O}_2 \rightarrow \text{CO} + \text{O}({}^3\text{P})$	$1.1 \cdot 10^{-10} \exp(-320/T)$	298–4000	$\pm 0.15$ at 298 K rising to $\pm 0.5$ at 4000 K.
$\rightarrow \text{CO} + \text{O}({}^1\text{D})$			

TABLE 4.1. Bimolecular reactions—Continued

Reaction	$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Error limits ( $\Delta \log k$ )
$\text{C} + \text{N}_2 \rightarrow \text{CN} + \text{N}$	$8.69 \cdot 10^{-11} \exp(-22600/T)$	2000–5000	$\pm 0.15$
$\text{C} + \text{N}_2(+\text{M}) \rightarrow \text{CNN}(+\text{M})$	See Table 4.2		
$\text{C} + \text{NO} \rightarrow \text{CO} + \text{N}$ $\rightarrow \text{CN} + \text{O}$	$k = 8.0 \cdot 10^{-11}$ $k_1/k = 0.60; k_2/k = 0.40$	290–4050 1500–4050	$\pm 0.3$ $\Delta(k_1/k) = \Delta(k_2/k) = \pm 0.3$
$\text{C} + \text{H}_2\text{O} \rightarrow \text{Products}$	See data sheet (Table 6.1)		
$\text{C} + \text{CO}(+\text{M}) \rightarrow \text{C}_2\text{O}(+\text{M})$	See data sheet (Table 6.1)		
$\text{C} + \text{CO}_2 \rightarrow \text{Products}$	See data sheet (Table 6.1)		
$\text{C} + \text{N}_2\text{O} \rightarrow \text{Products}$	See data sheet (Table 6.1)		
$\text{C} + \text{CH}_4 \rightarrow \text{Products}$	See data sheet (Table 6.1)		
$\text{C} + \text{C}_2\text{H}_2 \rightarrow \text{Products}$	See data sheet (Table 6.1)		
$\text{C} + \text{C}_2\text{H}_4 \rightarrow \text{Products}$	See data sheet (Table 6.1)		
$\text{C} + \text{CH}_3\text{CCH} \rightarrow \text{Products}$	See data sheet (Table 6.1)		
$\text{C} + \text{CH}_2\text{CCH}_2 \rightarrow \text{Products}$	See data sheet (Table 6.1)		
$\text{C} + \text{C}_3\text{H}_6 \rightarrow \text{Products}$	See data sheet (Table 6.1)		
$\text{C} + [-\text{C}_6\text{H}_6] \rightarrow \text{Products}$	See data sheet (Table 6.1)		
$\text{C} + [-\text{C}_6\text{H}_5] - \text{CH}_3 \rightarrow \text{Products}$	See data sheet (Table 6.1)		
<i><sup>1</sup>C<sub>2</sub> Radical Reactions</i>			
${}^1\text{C}_2 + \text{O}_2 \rightarrow \text{Products}$	See data sheet (Table 6.2)		
${}^1\text{C}_2 + \text{H}_2 \rightarrow \text{Products}$	See data sheet (Table 6.2)		
${}^1\text{C}_2 + \text{H}_2\text{O} \rightarrow \text{Products}$	See data sheet (Table 6.2)		
${}^1\text{C}_2 + \text{N}_2 \rightarrow \text{Products}$	See data sheet (Table 6.2)		
${}^1\text{C}_2 + \text{NO} \rightarrow \text{Products}$	See data sheet (Table 6.2)		
${}^1\text{C}_2 + \text{CO}_2 \rightarrow \text{Products}$	See data sheet (Table 6.2)		
${}^1\text{C}_2 + \text{CH}_4 \rightarrow \text{Products}$	See data sheet (Table 6.2)		
${}^1\text{C}_2 + \text{C}_2\text{H}_2 \rightarrow \text{Products}$	See data sheet (Table 6.2)		
${}^1\text{C}_2 + \text{C}_2\text{H}_4 \rightarrow \text{Products}$	See data sheet (Table 6.2)		
${}^1\text{C}_2 + \text{C}_2\text{H}_6 \rightarrow \text{Products}$	See data sheet (Table 6.2)		
${}^1\text{C}_2 + \text{C}_3\text{H}_8 \rightarrow \text{Products}$	See data sheet (Table 6.2)		
${}^1\text{C}_2 + [-\text{C}_6\text{H}_6] \rightarrow \text{Products}$	See data sheet (Table 6.2)		
<i><sup>3</sup>C<sub>2</sub> Radical Reactions</i>			
${}^3\text{C}_2(+\text{M}) \rightarrow {}^1\text{C}_2(+\text{M})$	See data sheet (Table 6.2)		
${}^3\text{C}_2 + \text{O}_2 \rightarrow \text{Products}$	See data sheet (Table 6.2)		
${}^3\text{C}_2 + \text{H}_2 \rightarrow \text{Products}$	See data sheet (Table 6.2)		
${}^3\text{C}_2 + \text{H}_2\text{O} \rightarrow \text{Products}$	See data sheet (Table 6.2)		
${}^3\text{C}_2 + \text{N}_2 \rightarrow \text{Products}$	See data sheet (Table 6.2)		
${}^3\text{C}_2 + \text{NO} \rightarrow \text{Products}$	See data sheet (Table 6.2)		
${}^3\text{C}_2 + \text{CH}_4 \rightarrow \text{Products}$	See data sheet (Table 6.2)		
${}^3\text{C}_2 + \text{C}_2\text{H}_2 \rightarrow \text{Products}$	See data sheet (Table 6.2)		
${}^3\text{C}_2 + \text{C}_2\text{H}_4 \rightarrow \text{Products}$	See data sheet (Table 6.2)		
${}^3\text{C}_2 + \text{C}_2\text{H}_6 \rightarrow \text{Products}$	See data sheet (Table 6.2)		
${}^3\text{C}_2 + \text{C}_3\text{H}_8 \rightarrow \text{Products}$	See data sheet (Table 6.2)		
${}^3\text{C}_2 + n\text{-C}_4\text{H}_{10} \rightarrow \text{Products}$	See data sheet (Table 6.2)		
${}^3\text{C}_2 + [-\text{C}_6\text{H}_6] \rightarrow \text{Products}$	See data sheet (Table 6.2)		
<i><sup>1</sup>C<sub>2</sub>/<sup>3</sup>C<sub>2</sub> Radical Reactions</i>			
$\text{C}_2(+\text{M}) \rightarrow \text{C} + \text{C}(+\text{M})$	See data sheet (Table 6.2)		
$\text{C}_2 + \text{O}_2 \rightarrow \text{Products}$	See data sheet (Table 6.2)		
$\text{C}_2 + \text{H}_2 \rightarrow \text{C}_2\text{H} + \text{H}$	See data sheet (Table 6.2)		

TABLE 4.1. Bimolecular reactions—Continued

Reaction	$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Error limits ( $\Delta \log k$ )
$\text{C}_2 + \text{N}_2 \rightarrow 2\text{CN}$	See data sheet (Table 6.2)		
$\text{C}_2 + \text{C}_2 \rightarrow \text{C} + \text{C}_3$	See data sheet (Table 6.2)		
<i>CN Radical Reactions</i>			
$\text{CN} + \text{O}_2 \rightarrow \text{CO} + \text{NO}$	$k = 1.2 \cdot 10^{-11} \exp(210/T)$	200–4500	$\pm 0.1$ at 200 K, rising to $\pm 0.4$ at 4500 K.
$\rightarrow \text{NCO} + \text{O}$	$k_1/k = 0.25$	298	$\Delta(k_1/k) = \pm 0.05$
$\rightarrow \text{N} + \text{CO}_2$	$k_2/k = 1.0$	>1000	
$\text{CN} + \text{H}_2 \rightarrow \text{HCN} + \text{H}$	$1.8 \cdot 10^{-19} T^{2.60} \exp(-960/T)$	200–3500	$\pm 0.2$
$\text{CN} + \text{H}_2\text{O} \rightarrow \text{HCN} + \text{OH}$	$1.3 \cdot 10^{-11} \exp(-3750/T)$	500–3000	$\pm 0.3$ at 500 K, rising to $\pm 0.5$ at 3000 K.
$\rightarrow \text{HO} + \text{CN} + \text{H}$			
$\text{CN} + \text{NO}_2 \rightarrow \text{CO}_2 + \text{N}_2$	$k = 1.02 \cdot 10^{-9} T^{-0.752} \exp(-173/T)$	296–1600	$\pm 0.1$ at 296 K, rising to $\pm 0.2$ at 1600 K.
$\rightarrow \text{CO} + \text{N}_2\text{O}$	$k_1/k = 0.06; k_2/k = 0.08; k_3/k = 0.86$	298	$\Delta(k_1/k) = \pm 0.06; \Delta(k_2/k) = \pm 0.08; \Delta(k_3/k) = \pm 0.14$
$\rightarrow \text{NCO} + \text{NO}$			
$\text{CN} + \text{CH}_4 \rightarrow \text{HCN} + \text{CH}_3$	$[6.2 \cdot 10^{-12} \exp(-735/T) + 2.20 \cdot 10^{-10} \exp(-3100/T)]$	160–1500	$\pm 0.1$ at 300 K, rising to $\pm 0.15$ at 1500 K and at 160 K.
<i>NCO Radical Reactions</i>			
$\text{NCO}(\text{+M}) \rightarrow \text{N} + \text{CO}(\text{+M})$	See Table 4.3		
$\text{NCO} + \text{NO} \rightarrow \text{CO}_2 + \text{N}_2$	$k = 2.3 \cdot 10^{-6} T^{-1.73} \exp(-380/T)$	300–2700	$\pm 0.15$ at 300 K, rising to $\pm 0.3$ at 2700 K.
$\rightarrow \text{CO} + \text{N}_2\text{O}$	$k_1/k = 5.2 T^{-0.35} \exp(-61.3/T)$	300–2700	$\Delta(k_1/k) = \Delta(k_2/k) = \pm 0.1$ at 300 K, rising to $^{+0.3}_{-0.1}$ at 2700 K.
$\rightarrow \text{CO} + \text{N}_2 + \text{O}$	$k_2/k = 0.142 T^{0.20} \exp(-20.5T)$	300–2700	
	$k_3 \ll k_1$ and $k_2$	300–2700	
<i>CH Radical Reactions</i>			
$\text{CH} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}$	$k = 4 \cdot 10^{-11}$	290–380	$\pm 0.3$ at 290 K, rising to $\pm 0.5$ at 800 K.
$\rightarrow \text{CO} + \text{OH}$	$k = 1.4 \cdot 10^{-10}$	2200–3500	$\pm 0.3$ over the range 2200–3500 K.
$\rightarrow \text{HCO} + \text{O}$			
$\rightarrow \text{CO} + \text{H} + \text{O}$			
$\rightarrow \text{CO} + \text{OH}(A^2\Sigma)$	Branching ratios—see data sheet		
$\text{CH} + \text{H}_2 \rightarrow \text{CH}_2 + \text{H}$	$2.9 \cdot 10^{-10} \exp(-1670/T)$	200–1000	$\pm 0.3$
$\text{CH} + \text{H}_2(\text{+M}) \rightarrow \text{CH}_3(\text{+M})$	See Table 4.2		
$\text{CH}_3(\text{+M}) \rightarrow \text{CH} + \text{H}_2(\text{+M})$	See Table 4.3		
$\rightarrow \text{CH}_2 + \text{H}(\text{+M})$			
$\text{CH} + \text{H}_2\text{O} \rightarrow \text{Products}$	$7.6 \cdot 10^{-8} T^{-1.42}$	290–1000	$\pm 0.5$ at 290 K, rising to $\pm 1.0$ at 1000 K.
$\text{CH} + \text{N}_2 \rightarrow \text{HCN} + \text{N}$	$(k_1 + k_2) = 6.0 \cdot 10^{-12} \exp(-11060/T)$	1000–4000	$\pm 0.3$ over the range 2500–4000 K, rising to $\pm 0.7$ at 1000 K.
$\rightarrow \text{NCN} + \text{H}$			
$\text{CH} + \text{N}_2(\text{+M}) \rightarrow \text{CHN}_2(\text{+M})$	See Table 4.2		
$\text{CH} + \text{NO} \rightarrow \text{CO} + \text{NH}$	$k = 1.9 \cdot 10^{-10}$	200–4000	$\pm 0.15$ at 200 K, rising to $\pm 0.3$ at 4000 K.
$\rightarrow \text{NCO} + \text{H}$	$k_1/k = 0.08; k_2/k = 0.13; k_3/k = 0.69$	200–4000	$\Delta(k_1/k) = \Delta(k_2/k) = 0.05; \Delta(k_3/k) = \pm 0.15;$
$\rightarrow \text{HCN} + \text{O}$	$k_4/k = 0.01; k_5/k = 0.06; k_6/k = 0.03$	200–4000	$\Delta(k_4/k) = \pm 0.01; \Delta(k_5/k) = \pm 0.05; \Delta(k_6/k) = \pm 0.02$
$\rightarrow \text{CN} + \text{OH}$			
$\rightarrow \text{HCO} + \text{N}$			
$\rightarrow \text{CNO} + \text{H}$			
$\text{CH} + \text{CO} \rightarrow \text{C}_2\text{O} + \text{H}$	$3.1 \cdot 10^{-13}$	2500–3500	$\pm 0.3$
$\text{CH} + \text{CO}(\text{+M}) \rightarrow \text{HCCO}(\text{+M})$	See Table 4.2		
$\text{CH} + \text{CO}_2 \rightarrow \text{HCO} + \text{CO}$	$1.06 \cdot 10^{-16} T^{1.51} \exp(360/T)$	296–3500	$\pm 0.15$ at 296 K, rising to $\pm 0.3$ at 3500 K.
$\rightarrow 2\text{CO} + \text{H}$			

TABLE 4.1. Bimolecular reactions—Continued

Reaction	$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Error limits ( $\Delta \log k$ )
$\text{CH} + \text{CH}_4 \rightarrow \text{C}_2\text{H}_4 + \text{H}$	$2.2 \cdot 10^{-8} T^{-0.94} \exp(-29/T)$	160–750	$\pm 0.2$
$\quad \rightarrow \text{CH}_2 + \text{CH}_3$			
$\text{CH} + \text{HCHO} \rightarrow \text{Products}$	$1.6 \cdot 10^{-10} \exp(260/T)$	300–700	$\pm 1.0$
$\text{CH} + \text{C}_2\text{H}_2 \rightarrow \text{H}_2\text{CCC} + \text{H}$	$3.1 \cdot 10^{-10} \exp(61/T)$	200–700	$\pm 0.3$
$\quad \rightarrow c\text{-C}_3\text{H}_2 + \text{H}$			
$\quad \rightarrow \text{HCCC} + \text{H}_2$			
$\text{CH} + \text{C}_2\text{H}_4 \rightarrow \text{Products}$	$2.2 \cdot 10^{-10} \exp(173/T)$	200–700	$\pm 0.5$
$\text{CH} + \text{C}_2\text{H}_6 \rightarrow \text{Products}$	$1.8 \cdot 10^{-10} \exp(132/T)$	200–700	$\pm 0.5$
$\text{CH} + \text{CH}_3\text{CCH} \rightarrow \text{Products}$	No recommendation—see data sheet		
$\text{CH} + \text{C}_3\text{H}_8 \rightarrow \text{Products}$	$1.9 \cdot 10^{-10} \exp(240/T)$	298–700	$\pm 0.5$
$\text{CH} + n\text{-C}_4\text{H}_{10} \rightarrow \text{Products}$	$4.4 \cdot 10^{-10} \exp(28/T)$	250–700	$\pm 0.5$
$\text{CH} + i\text{-C}_4\text{H}_{10} \rightarrow \text{Products}$	$2.0 \cdot 10^{-10} \exp(240/T)$	298–700	$\pm 0.7$
$\text{CH} + neo\text{-C}_5\text{H}_{12} \rightarrow \text{Products}$	$1.6 \cdot 10^{-10} \exp(340/T)$	298–700	$\pm 0.7$
<i><sup>3</sup>CH<sub>2</sub> Radical Reactions</i>			
${}^3\text{CH}_2(+\text{M}) \rightarrow \text{C} + \text{H}_2(+\text{M})$	See Table 4.3		
$\quad \rightarrow \text{CH} + \text{H}(+\text{M})$			
$\quad \rightarrow {}^1\text{CH}_2(+\text{M})$			
${}^3\text{CH}_2 + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2$	$3.0 \cdot 10^{-12}$	250–1700	$\pm 0.34$ at 250 K, rising to $\pm 0.7$ at 1700 K.
$\quad \rightarrow \text{CO} + \text{H}_2\text{O}$			
$\quad \rightarrow \text{HOOC} + \text{H}$			
$\quad \rightarrow \text{CO}_2 + 2\text{H}$			
$\quad \rightarrow \text{HCO} + \text{OH}$			
$\quad \rightarrow \text{HC(O)O} + \text{H}$			
$\quad \rightarrow \text{CO} + \text{H}_2 + \text{O}$			
$\quad \rightarrow \text{HCHO} + \text{O}$			
$\quad \rightarrow \text{CO} + \text{OH} + \text{H}$			
${}^3\text{CH}_2 + \text{NO} \rightarrow \text{CO} + \text{NH}_2$	$5.6 \cdot 10^{-12} \exp(500/T)$	290–1000	$\pm 0.4$ at 290 K, rising to $\pm 0.7$ at 1000 K.
$\quad \rightarrow \text{HNCO} + \text{H}$			
$\quad \rightarrow \text{H}_2 + \text{NCO}$			
$\quad \rightarrow \text{HCN} + \text{OH}$			
$\quad \rightarrow \text{H}_2\text{O} + \text{CN}$			
$\quad \rightarrow \text{HO} + \text{CN}$			
$\quad \rightarrow \text{HCHO} + \text{N}$			
$\quad \rightarrow \text{HCNO} + \text{H}$			
$\quad \rightarrow \text{HCO} + \text{NH}$			
$\quad \rightarrow \text{H}_2 + \text{CNO}$			
$\quad \rightarrow \text{CH}_2\text{N} + \text{O}$			
${}^3\text{CH}_2 + \text{NO}(\text{+M}) \rightarrow \text{CH}_2\text{NO}(\text{+M})$			
${}^3\text{CH}_2 + {}^3\text{CH}_2 \rightarrow \text{C}_2\text{H}_2 + \text{H}_2$	$3.0 \cdot 10^{-9} \exp(-6000/T)$	1000–3000	$\pm 0.5$
$\quad \rightarrow \text{C}_2\text{H}_2 + 2\text{H}$			
$\quad \rightarrow \text{C}_2\text{H}_3 + \text{H}$			
${}^3\text{CH}_2 + \text{CH}_3 \rightarrow \text{H} + \text{C}_2\text{H}_4$	$1.2 \cdot 10^{-10}$	298–3000	$\pm 0.3$ at 298 K, rising to $\pm 0.7$ at 3000 K.

TABLE 4.1. Bimolecular reactions—Continued

Reaction	$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Error limits ( $\Delta \log k$ )
${}^3\text{CH}_2 + \text{C}_2\text{H}_2 \rightarrow \text{CH}_2\text{CCH} + \text{H}$ $\quad \rightarrow {}^1\text{CH}_2 + \text{C}_2\text{H}_2$	$k = 2.0 \cdot 10^{-11} \exp(-3330/T)$	296–2000	$\pm 0.3$ at 296 K, rising to $\pm 0.6$ at 2000 K.
${}^3\text{CH}_2 + \text{C}_2\text{H}_2 (+\text{M}) \rightarrow \text{CH}_2\text{CCH}_2 (+\text{M})$ $\quad \rightarrow \text{CH}_3\text{CCH} (+\text{M})$	$k_2 = 5.5 \cdot 10^{-9} \exp(-4570/T)$	296–1000	$\pm 0.6$
${}^3\text{CH}_2 + \text{C}_2\text{H}_4 \rightarrow \text{CH}_2\text{CHCH}_2 + \text{H}$ $\quad \rightarrow {}^1\text{CH}_2 + \text{C}_2\text{H}_4$	$k = 5.3 \cdot 10^{-12} \exp(-2660/T)$	296–1000	$\pm 0.3$
${}^3\text{CH}_2 + \text{C}_2\text{H}_4 (+\text{M}) \rightarrow \text{C}_3\text{H}_6 (+\text{M})$ $\quad \rightarrow c\text{-C}_3\text{H}_6 (+\text{M})$	$k_2 = 9.4 \cdot 10^{-12} \exp(-4290/T)$	296–1000	$\pm 0.5$
<i><sup>1</sup>CH<sub>2</sub> Radical Reactions</i>			
${}^1\text{CH}_2 (\text{+He}) \rightarrow {}^3\text{CH}_2 (\text{+He})$	$1.1 \cdot 10^{-11} \exp(-380/T)$	200–1000	$\pm 0.2$ over the range 200–300 K, increasing to $\pm 0.4$ at 1000 K.
${}^1\text{CH}_2 (\text{+Ar}) \rightarrow {}^3\text{CH}_2 (\text{+Ar})$	$3.0 \cdot 10^{-14} T^{0.93}$	200–1000	$\pm 0.2$
${}^1\text{CH}_2 (\text{+N}_2) \rightarrow {}^3\text{CH}_2 (\text{+N}_2)$	$2.0 \cdot 10^{-11} \exp(-237/T)$	200–1000	$\pm 0.2$ at 200 K, rising to $\pm 0.3$ at 1000 K.
${}^1\text{CH}_2 (\text{+H}_2) \rightarrow {}^3\text{CH}_2 (\text{+H}_2)$	$1.0 \cdot 10^{-11}$	200–1000	See data sheet
${}^1\text{CH}_2 (\text{+O}_2) \rightarrow {}^3\text{CH}_2 (\text{+O}_2)$	$5.2 \cdot 10^{-11}$	300–1000	See data sheet
${}^1\text{CH}_2 (\text{+H}_2\text{O}) \rightarrow {}^3\text{CH}_2 (\text{+H}_2\text{O})$	$2.5 \cdot 10^{-11} \exp(217/T)$	300–1000	See data sheet
${}^1\text{CH}_2 (\text{+CO}_2) \rightarrow {}^3\text{CH}_2 (\text{+CO}_2)$	$2.2 \cdot 10^{-11}$	300–1000	See data sheet
${}^1\text{CH}_2 (\text{+CH}_4) \rightarrow {}^3\text{CH}_2 (\text{+CH}_4)$	$3.1 \cdot 10^{-12} \exp(250/T)$	200–1000	See data sheet
${}^1\text{CH}_2 (\text{+C}_2\text{H}_2) \rightarrow {}^3\text{CH}_2 (\text{+C}_2\text{H}_2)$	$1.1 \cdot 10^{-8} T^{-0.9}$	200–1000	See data sheet
${}^1\text{CH}_2 (\text{+C}_2\text{H}_4) \rightarrow {}^3\text{CH}_2 (\text{+C}_2\text{H}_4)$	$1.9 \cdot 10^{-11} \exp(280/T)$	200–1000	See data sheet
${}^1\text{CH}_2 + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2$ $\quad \rightarrow \text{CO} + \text{H}_2\text{O}$ $\quad \rightarrow \text{HOOC} + \text{H}$ $\quad \rightarrow \text{CO}_2 + 2\text{H}$ $\quad \rightarrow \text{HCO} + \text{OH}$ $\quad \rightarrow \text{HC(O)O} + \text{H}$ $\quad \rightarrow \text{CO} + \text{H}_2 + \text{O}$ $\quad \rightarrow \text{HCHO} + \text{O}$ $\quad \rightarrow \text{CO} + \text{H} + \text{OH}$ $\quad \rightarrow {}^3\text{CH}_2 + \text{O}_2$	$k = k_{10} = 5.2 \cdot 10^{-11}$	300–1000	$\pm 0.3$ at 300 K, rising to $\pm 0.5$ at 1000 K.
${}^1\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_3 + \text{H}$ $\quad \rightarrow {}^3\text{CH}_2 + \text{H}_2$	$k = 1.0 \cdot 10^{-10}$ $k_2/k = 0.1$	298–2100 200–1000	$\pm 0.1$ at 300 K, rising to $\pm 0.3$ at 200 K and at 2100 K. $\Delta(k_2/k) = {}^{+0.3}_{-0.1}$ at 300 K, rising to ${}^{+0.5}_{-0.1}$ at 200 K and 1000 K.

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TABLE 4.1. Bimolecular reactions—Continued

Reaction	$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Error limits ( $\Delta \log k$ )
${}^1\text{CH}_2 + \text{NO} \rightarrow \text{CO} + \text{NH}_2$	$k = 1.6 \cdot 10^{-10}$	293–1000	$\pm 0.2$ at 293 K, rising to $\pm 0.3$ at 1000 K.
$\rightarrow \text{HNCO} + \text{H}$			
$\rightarrow \text{H}_2 + \text{NCO}$			
$\rightarrow \text{HCN} + \text{OH}$			
$\rightarrow \text{H}_2\text{O} + \text{CN}$			
$\rightarrow \text{HO CN} + \text{H}$			
$\rightarrow \text{HCHO} + \text{N}$			
$\rightarrow \text{HCNO} + \text{H}$			
$\rightarrow \text{HCO} + \text{NH}$			
$\rightarrow \text{H}_2 + \text{CNO}$			
$\rightarrow \text{CH}_2\text{N} + \text{O}$			
$\rightarrow {}^3\text{CH}_2 + \text{NO}$			
${}^1\text{CH}_2 + \text{NO} (+\text{M}) \rightarrow \text{CH}_2\text{NO} (+\text{M})$			
${}^1\text{CH}_2 + \text{CH}_4 \rightarrow \text{CH}_3 + \text{CH}_3$	$k = 3.1 \cdot 10^{-11} \exp(250/T)$	200–1200	$\pm 0.1$ at 300 K, rising to $\pm 0.3$ at 200 K and 1200 K.
$\rightarrow \text{C}_2\text{H}_5 + \text{H}$	$(k_1 + k_2)/k = 0.9; k_3/k = 0.1$	200–1200	$\Delta(k_3/k) = {}^{+0.3}_{-0.1}$ at 300 K, rising to ${}^{+0.5}_{-0.1}$ at 200 K and 1200 K.
$\rightarrow {}^3\text{CH}_2 + \text{CH}_4$			
${}^1\text{CH}_2 + \text{C}_2\text{H}_2 \rightarrow \text{CH}_2\text{CCH} + \text{H}$	$k = 5.6 \cdot 10^{-8} T^{-0.9}$	200–1000	$\pm 0.2$ at 200 K, rising to $\pm 0.4$ at 1000 K.
$\rightarrow {}^3\text{CH}_2 + \text{C}_2\text{H}_2$	$k_1/k = 0.8; k_4/k = 0.2$	200–1000	$\Delta(k_2/k) = {}^{+0.3}_{-0.2}$ at 300 K, rising to ${}^{+0.6}_{-0.2}$ at 200 K and 1000 K.
${}^1\text{CH}_2 + \text{C}_2\text{H}_2 (+\text{M}) \rightarrow \text{CH}_2\text{CCH}_2 (+\text{M})$			
$\rightarrow \text{CH}_2\text{CCH} (+\text{M})$			
${}^1\text{CH}_2 + \text{C}_2\text{H}_4 \rightarrow \text{CH}_2\text{CHCH}_2 + \text{H}$	$k = 9.4 \cdot 10^{-11} \exp(280/T)$	210–1000	$\pm 0.1$ at 210 K, rising to $\pm 0.3$ at 1000 K.
$\rightarrow {}^3\text{CH}_2 + \text{C}_2\text{H}_4$	$k_2/k = 0.2$	210–1000	$\Delta(k_2/k) = \pm 0.2$ at 300 K, rising to ${}^{+0.5}_{-0.2}$ at 210 K and 1000 K.
${}^1\text{CH}_2 + \text{C}_2\text{H}_4 (+\text{M}) \rightarrow \text{C}_3\text{H}_6 (+\text{M})$			
$\rightarrow c\text{-C}_3\text{H}_6 (+\text{M})$			
<i>CH<sub>3</sub> Radical Reactions</i>			
$\text{CH}_3 (+\text{M}) \rightarrow \text{CH}_2 + \text{H} (+\text{M})$	See Table 4.3		
$\rightarrow \text{CH} + \text{H}_2 (+\text{M})$			
$\text{CH}_3 + \text{O}_2 \rightarrow \text{HCHO} + \text{OH}$	$\leq 1.1 \cdot 10^{-12} \exp(-7094/T)$	1000–2500	$\pm 0.3$ at 1000 K, falling to $\pm 0.15$ at 2500 K.
$\rightarrow \text{CH}_3\text{O} + \text{O}$	$3.5 \cdot 10^{-11} \exp(-16340/T)$	1000–2500	$\pm 0.3$ at 1000 K, falling to $\pm 0.15$ at 2500 K.
$\text{CH}_3 + \text{O}_2 (+\text{M}) \rightarrow \text{CH}_3\text{O}_2 (+\text{M})$	See Table 4.2		
$\text{CH}_3 + \text{H}_2 \rightarrow \text{CH}_4 + \text{H}$	$1.8 \cdot 10^{-21} T^{2.88} \exp(-4060/T)$	370–2000	$\pm 0.15$
$\text{CH}_3 + \text{NO} \rightarrow \text{HCN} + \text{H}_2\text{O}$	$(k_1 + k_2) = 1 \cdot 10^{-12} \exp(-7550/T)$	1100–1300	$\pm 0.2$
$\rightarrow \text{CH}_2\text{N} + \text{OH}$	Branching ratios—see data sheet		
$\text{CH}_3 + \text{NO} (+\text{M}) \rightarrow \text{CH}_3\text{NO} (+\text{M})$	See Table 4.2		
$\text{CH}_3 + \text{CO} (+\text{M}) \rightarrow \text{CH}_3\text{CO} (+\text{M})$	See Table 4.2		
$\text{CH}_3\text{CO} (+\text{M}) \rightarrow \text{CH}_3 + \text{CO} (+\text{M})$	See Table 4.3		
$\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_5 + \text{H}$	$(k_1) = 9.0 \cdot 10^{-11} \exp(-8080/T)$	1200–2500	$\pm 0.3$
$\rightarrow \text{C}_2\text{H}_4 + \text{H}_2$	$k_2 \ll k_1$	1200–2500	
$\text{CH}_3 + \text{CH}_3 (+\text{M}) \rightarrow \text{C}_2\text{H}_6 (+\text{M})$	See Table 4.2		
$\text{C}_2\text{H}_6 (+\text{M}) \rightarrow \text{CH}_3 + \text{CH}_3 (+\text{M})$	See Table 4.3		
$\text{CH}_3 + \text{HCHO} \rightarrow \text{CH}_4 + \text{HCO}$	$5.3 \cdot 10^{-23} T^{3.36} \exp(-2170/T)$	300–2000	$\pm 0.2$
$\text{CH}_3 + \text{CH}_3\text{OH} \rightarrow \text{CH}_4 + \text{CH}_2\text{OH}$	$k = 5.0 \cdot 10^{-23} T^{3.45} \exp(-4020/T)$	300–2000	$\pm 0.2$ at 300 K, rising to $\pm 1.0$ at 2000 K.
$\rightarrow \text{CH}_4 + \text{CH}_3\text{O}$	$k_1/k = 0.33; k_2/k = 0.67$	300–525	$\Delta(k_1/k_2) = \pm 0.2; \Delta(k_2/k) = \pm 0.2$
$\text{CH}_3 + \text{CH}_3\text{OCH}_3 \rightarrow \text{CH}_4 + \text{CH}_3\text{OCH}_2$	$1.0 \cdot 10^{-20} T^{2.68} \exp(-4190/T)$	300–1600	$\pm 0.2$ at 300 K, rising to $\pm 0.4$ at 1600 K.

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TABLE 4.1. Bimolecular reactions—Continued

Reaction	$k/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$	T/K	Error limits ( $\Delta \log k$ )
$\text{CH}_3 + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_4 + \text{CH}_3\text{CHOH}$ [ $\rightarrow \text{CH}_4 + \text{CH}_2\text{CH}_2\text{OH}$ $\rightarrow \text{CH}_4 + \text{CH}_3\text{CH}_2\text{O}$ ]	$k = 9.9 \cdot 10^{-13} \exp(-4880/T)$ $k_1 = 7.8 \cdot 10^{-13} \exp(-4880/T)$ $k_2 = 6.0 \cdot 10^{-14} \exp(-4800/T)$ $k_3 = 1.5 \cdot 10^{-13} \exp(-4730/T)$	400–700	$\pm 0.2$ at 400 K, rising to $\pm 0.3$ at 700 K. $\pm 0.2$ at 400 K, rising to $\pm 0.3$ at 700 K. $\pm 0.3$ at 400 K, rising to $\pm 0.5$ at 700 K. $\pm 0.2$ at 400 K, rising to $\pm 0.3$ at 700 K.
$\text{CH}_3 + \text{C}_2\text{H}_2 \rightarrow \text{CH}_4 + \text{C}_2\text{H}$ [ $\rightarrow \text{CH}_3\text{CCH} + \text{H}$ ]	No recommendation—see data sheet		
$\text{CH}_3 + \text{C}_2\text{H}_2(+\text{M}) \rightarrow \text{CH}_3\text{CHCH}(+\text{M})$	See Table 4.2	650–2800	$\pm 0.5$
$\text{CH}_3 + \text{C}_2\text{H}_4 \rightarrow \text{CH}_4 + \text{C}_2\text{H}_3$	$1.0 \cdot 10^{-16} T^{1.56} \exp(-8370/T)$	650–2800	$\pm 0.5$
$\text{CH}_3 + \text{C}_2\text{H}_4(+\text{M}) \rightarrow n\text{-C}_3\text{H}_7(+\text{M})$	See Table 4.2		
$\text{CH}_3 + \text{C}_2\text{H}_5 \rightarrow \text{CH}_4 + \text{C}_2\text{H}_4$	$1.5 \cdot 10^{-12}$	300–2000	$\pm 0.4$ at 300 K, rising to $\pm 0.7$ at 2000 K.
$\text{CH}_3 + \text{C}_2\text{H}_5(+\text{M}) \rightarrow \text{C}_3\text{H}_8(+\text{M})$	See Table 4.2		
$\text{C}_3\text{H}_8(+\text{M}) \rightarrow \text{CH}_3 + \text{C}_2\text{H}_5(+\text{M})$	See Table 4.3		
$\text{CH}_3 + \text{C}_2\text{H}_6 \rightarrow \text{CH}_4 + \text{C}_2\text{H}_5$	$[9.3 \cdot 10^{-14} \exp(-4740/T) + 1.4 \cdot 10^{-9} \exp(-11200/T)]$	350–1500	$\pm 0.1$ at 350 K, rising to $\pm 0.2$ at 1500 K.
$\text{CH}_3 + \text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CH}_3\text{CO}$ [ $\rightarrow \text{CH}_4 + \text{CH}_2\text{CHO}$ ]	$5.8 \cdot 10^{-32} T^{6.21} \exp(-820/T)$ Branching ratios—see data sheet	298–1250	$\pm 0.1$ at 298 K, rising to $\pm 0.3$ at 1250 K.
$\text{CH}_3 + \text{C}_3\text{H}_5 \rightarrow \text{CH}_4 + \text{CH}_2\text{CCH}_2$	$6.0 \cdot 10^{-13}$	500–800	$\pm 0.2$
$\text{CH}_3 + \text{C}_3\text{H}_5(+\text{M}) \rightarrow \text{C}_2\text{H}_5\text{CHCH}_2(+\text{M})$	See Table 4.2		
<i>CH<sub>4</sub> Reactions</i>			
$\text{CH}_4(+\text{M}) \rightarrow \text{CH}_3 + \text{H}(+\text{M})$	See Table 4.3		
<i>CHO Radical Reactions</i>			
$\text{HCO}(+\text{M}) \rightarrow \text{H} + \text{CO}(+\text{M})$	See Table 4.3		
$\text{HCO} + \text{O}_2 \rightarrow \text{CO} + \text{HO}_2$ [ $\rightarrow \text{CO}_2 + \text{OH}$ ]	$4.5 \cdot 10^{-14} T^{0.68} \exp(236/T)$	200–2500	$\pm 0.15$ at 200 K, rising to $\pm 0.5$ at 2500 K.
$\text{HCO} + \text{O}_2(+\text{M}) \rightarrow \text{HCO}_3(+\text{M})$			
$\text{HCO} + \text{HCO} \rightarrow \text{HCHO} + \text{CO}$ [ $\rightarrow \text{H}_2 + 2\text{CO}$ ]	$k = 5.0 \cdot 10^{-11}$ Branching ratios—see data sheet	230–1000	$\pm 0.2$ at 230 K, rising to $\pm 0.3$ at 1000 K.
<i>HCHO Reactions</i>			
$\text{HCHO}(+\text{M}) \rightarrow \text{H} + \text{HCO}(+\text{M})$ [ $\rightarrow \text{H}_2 + \text{CO}(+\text{M})$ ]	See Table 4.3		
<i>CH<sub>2</sub>OH Radical Reactions</i>			
$\text{CH}_2\text{OH}(+\text{M}) \rightarrow \text{CH}_3\text{O}(+\text{M})$ [ $\rightarrow \text{HCHO} + \text{H}(+\text{M})$ ]	See Table 4.3		
$\text{CH}_2\text{OH} + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2$	$[4.8 \cdot 10^{-8} T^{-1.5} + 1.2 \cdot 10^{-10} \exp(-1880/T)]$	298–1200	$\pm 0.1$ at 298 K, rising to $\pm 0.3$ at 1200 K.
$\text{CH}_2\text{OH} + \text{O}_2(+\text{M}) \rightarrow \text{O}_2\text{CH}_2\text{OH}(+\text{M})$			
$\text{CH}_2\text{OH} + \text{CH}_2\text{OH} \rightarrow \text{Products}$	$1.5 \cdot 10^{-11}$	298	$\pm 0.5$
<i>CH<sub>3</sub>O Radical Reactions</i>			
$\text{CH}_3\text{O}(+\text{M}) \rightarrow \text{HCHO} + \text{H}(+\text{M})$	See Table 4.3		
$\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2$	$3.6 \cdot 10^{-14} \exp(-880/T)$	298–1000	$\pm 0.1$ at 298 K, rising to $\pm 0.3$ at 1000 K.
<i>CH<sub>3</sub>O<sub>2</sub> Radical Reactions</i>			
$\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2 \rightarrow \text{CH}_3\text{O} + \text{CH}_3\text{O} + \text{O}_2$ [ $\rightarrow \text{CH}_3\text{OH} + \text{HCHO} + \text{O}_2$ $\rightarrow \text{CH}_3\text{OOCH}_3 + \text{O}_2$ ]	$9.5 \cdot 10^{-14} \exp(390/T)$ $k_1/k_2 = 26.2 \exp(-1130/T)$ $k_3/k = 0$	250–700 250–700 250–700	$\pm 0.1$ at 250 K, rising to $\pm 0.3$ at 700 K. $\Delta(k_1/k_2) = \pm 0.1$ at 250 K, rising to $\pm 0.3$ at 700 K.
$\text{CH}_3\text{O}_2 + \text{C}_3\text{H}_5 \rightarrow \text{CH}_3\text{O} + \text{CH}_2\text{CHCH}_2\text{O}$	$2.0 \cdot 10^{-11}$	500–1200	$\pm 0.5$
<i>CH<sub>3</sub>OH Reactions</i>			

TABLE 4.1. Bimolecular reactions—Continued

Reaction	$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Error limits ( $\Delta \log k$ )
$\text{CH}_3\text{OH}(\text{+M}) \rightarrow \text{CH}_3 + \text{OH}(\text{+M})$ [ $\rightarrow {}^1\text{CH}_2 + \text{H}_2\text{O}(\text{+M})$ $\rightarrow \text{CH}_2\text{OH} + \text{H}(\text{+M})$ ]	See Table 4.3		
<i>CH<sub>3</sub>OOH Reactions</i>			
$\text{CH}_3\text{OOH}(\text{+M}) \rightarrow \text{CH}_3\text{O} + \text{OH}(\text{+M})$	See Table 4.3		
<i>C<sub>2</sub>H Radical Reactions</i>			
$\text{C}_2\text{H} + \text{O}_2 \rightarrow \text{HCO} + \text{CO}$ [ $\rightarrow 2\text{CO} + \text{H}$ $\rightarrow \text{CO}_2 + \text{CH}$ $\rightarrow \text{C}_2\text{O} + \text{OH}$ $\rightarrow \text{HCCO} + \text{O}$ ]	$2.7 \cdot 10^{-10} T^{-0.35}$ Branching ratios; see data sheet	200–1500	$\pm 0.2$ at 200 K, rising to $\pm 0.3$ at 1500 K.
$\text{C}_2\text{H} + \text{H}_2 \rightarrow \text{C}_2\text{H}_2 + \text{H}$	$3.5 \cdot 10^{-18} T^{2.32} \exp(-444/T)$	180–3000	$\pm 0.15$ at 300 K, rising to $\pm 0.2$ at 180 K and $\pm 0.5$ at 3000 K.
$\text{C}_2\text{H} + \text{H}_2\text{O} \rightarrow \text{Products}$	No recommendation—see data sheet		
$\text{C}_2\text{H} + \text{NO} \rightarrow \text{Products}$	$1.0 \cdot 10^{-10} \exp(-287/T)$	295–450	$\pm 0.2$
$\text{C}_2\text{H} + \text{CO}(\text{+M}) \rightarrow \text{HCCCO}(\text{+M})$	No recommendation—see data sheet		
$\text{C}_2\text{H} + \text{CH}_4 \rightarrow \text{C}_2\text{H}_2 + \text{CH}_3$	$3.6 \cdot 10^{-14} T^{0.94} \exp(-328/T)$	150–780	$\pm 0.2$
$\text{C}_2\text{H} + \text{C}_2\text{H}_2 \rightarrow \text{C}_4\text{H}_2 + \text{H}$	$1.3 \cdot 10^{-10}$	200–2700	$\pm 0.1$ over the range 200–1000 K, rising to $\pm 0.5$ at 2700 K.
$\text{C}_2\text{H} + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_2 + \text{C}_2\text{H}_5$	$6.75 \cdot 10^{-12} T^{0.28} \exp(62/T)$	150–780	$\pm 0.2$
<i>C<sub>2</sub>H<sub>3</sub> Radical Reactions</i>			
$\text{C}_2\text{H}_3(\text{+M}) \rightarrow \text{C}_2\text{H}_2 + \text{H}(\text{+M})$	See Table 4.3		
$\text{C}_2\text{H}_3 + \text{O}_2 \rightarrow \text{C}_2\text{H}_2 + \text{HO}_2$ $\rightarrow \text{HCHO} + \text{HCO}$ [ $\rightarrow \text{C}_2\text{H}_3\text{O} + \text{O}$ ]	No recommendation—see data sheet $k_2 = 6.4 \cdot 10^{-12} \exp(120/T)$ No recommendation—see data sheet	290–900	$\pm 0.1$ at 290 K, rising to $\pm 0.3$ at 900 K.
$\text{C}_2\text{H}_3 + \text{O}_2(\text{+M}) \rightarrow \text{C}_2\text{H}_3\text{O}_2(\text{+M})$			
$\text{C}_2\text{H}_3 + \text{C}_2\text{H}_2 \rightarrow \text{C}_4\text{H}_4 + \text{H}$ [ $\text{C}_2\text{H}_3 + \text{C}_2\text{H}_2(\text{+M}) \rightarrow n\text{-C}_4\text{H}_5(\text{+M})$ ]	$k = 2.3 \cdot 10^{-12} \exp(-2764/T)$ Branching ratios—see data sheet	300–1000	$\pm 0.6$ at 300 K, falling to $\pm 0.2$ at 1000 K.
$\text{C}_2\text{H}_3 + \text{C}_2\text{H}_3 \rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_2$ [ $\text{C}_2\text{H}_3 + \text{C}_2\text{H}_3(\text{+M}) \rightarrow \text{CH}_2\text{CHCHCH}_2(\text{+M})$ ]	$k = 1.4 \cdot 10^{-10}$ Branching ratios—see data sheet	298	$\pm 0.2$
$\text{C}_2\text{H}_3 + \text{C}_2\text{H}_4 \rightarrow \text{C}_4\text{H}_6 + \text{H}$	$1.3 \cdot 10^{-13}$	1100	$\pm 1$
<i>C<sub>2</sub>H<sub>4</sub> Reactions</i>			
$\text{C}_2\text{H}_4(\text{+M}) \rightarrow \text{C}_2\text{H}_2 + \text{H}_2(\text{+M})$ [ $\rightarrow \text{C}_2\text{H}_3 + \text{H}(\text{+M})$ ]	See Table 4.3		
<i>C<sub>2</sub>H<sub>5</sub> Radical Reactions</i>			
$\text{C}_2\text{H}_5(\text{+M}) \rightarrow \text{C}_2\text{H}_4 + \text{H}(\text{+M})$	See Table 4.3		
$\text{C}_2\text{H}_5 + \text{O}_2 \rightarrow \text{C}_2\text{H}_4 + \text{HO}_2$	$1.0 \cdot 10^{-13}$	700–1500	$\pm 0.2$ at 700 K, rising to $\pm 0.4$ at 1500 K.
$\text{C}_2\text{H}_5 + \text{O}_2(\text{+M}) \rightarrow \text{C}_2\text{H}_5\text{O}_2(\text{+M})$	See data sheet for information on modeling the pressure dependence		
$\text{C}_2\text{H}_5 + \text{H}_2 \rightarrow \text{C}_2\text{H}_6 + \text{H}$	$5.1 \cdot 10^{-24} T^{3.6} \exp(-4250/T)$	700–1200	$\pm 0.2$ at 700 K, rising to $\pm 0.6$ at 1200 K.
$\text{C}_2\text{H}_5 + \text{C}_2\text{H}_2(\text{+M}) \rightarrow \text{C}_2\text{H}_5\text{CHCH}(\text{+M})$	See Table 4.2		
$\text{C}_2\text{H}_5 + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_6 + \text{C}_2\text{H}_3$	$8.1 \cdot 10^{-31} T^{5.82} \exp(-6000/T)$	600–900	$\pm 0.5$
$\text{C}_2\text{H}_5 + \text{C}_2\text{H}_4(\text{+M}) \rightarrow n\text{-C}_4\text{H}_9(\text{+M})$	See Table 4.2		
$\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_6 + \text{C}_2\text{H}_4$	$2.3 \cdot 10^{-12}$	295–1200	$\pm 0.3$
$\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5(\text{+M}) \rightarrow n\text{-C}_4\text{H}_{10}(\text{+M})$	See Table 4.2		

TABLE 4.1. Bimolecular reactions—Continued

Reaction	$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Error limits ( $\Delta \log k$ )
$\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5\text{CHO} \rightarrow \text{C}_2\text{H}_6 + \text{C}_2\text{H}_5\text{CO}$	$2.9 \cdot 10^{-13} \exp(-3660/T)$	300–700	$\pm 0.3$
$\text{C}_2\text{H}_5 + \text{C}_3\text{H}_5 \rightarrow \text{C}_2\text{H}_6 + \text{CH}_2\text{CCH}_2$	$1.6 \cdot 10^{-12} \exp(66/T)$	500–1200	$\pm 0.3$
$\quad \rightarrow \text{C}_2\text{H}_4 + \text{C}_3\text{H}_6$	$4.3 \cdot 10^{-12} \exp(66/T)$	500–1200	$\pm 0.4$
$\text{C}_2\text{H}_5 + \text{C}_3\text{H}_5 (+\text{M}) \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CHCH}_2 (+\text{M})$	See Table 4.2		
<i>C<sub>2</sub>H<sub>6</sub> Reactions</i>			
$\text{C}_2\text{H}_6 (+\text{M}) \rightarrow 2\text{CH}_3 (+\text{M})$	See Table 4.3		
<i>CHCO Radical Reactions</i>			
$\text{HCCO} + \text{O}_2 \rightarrow \text{HCO} + \text{CO}_2$	$2.7 \cdot 10^{-12} \exp(-430/T)$ for M=He, and $P \leq 40$ mbar	290–550	$\pm 0.7$
$\quad \rightarrow \text{H} + \text{CO} + \text{CO}_2$			
$\quad \rightarrow \text{HCOO} + \text{CO}$			
$\quad \rightarrow \text{OH} + 2\text{CO}$			
$\quad \rightarrow \text{HCO} + \text{CO} + \text{O}$			
$\quad \rightarrow \text{C}_2\text{O} + \text{HO}_2$			
$\text{HCCO} + \text{O}_2 (+\text{M}) \rightarrow \text{O}_2\text{CHCO} (+\text{M})$			
$\text{HCCO} + \text{NO} \rightarrow \text{HCNO} + \text{NO}$	$1.0 \cdot 10^{-10} \exp(-350/T)$	300–2000	$\pm 0.2$ at 300 K, rising to $\pm 0.4$ at 2000 K.
$\quad \rightarrow \text{HCN} + \text{CO}_2$	$k_1/k = 0.8; k_2/k = 0.2$	300–2000	$\Delta(k_1/k) = \Delta(k_2/k) = \pm 0.1$
<i>CH<sub>2</sub>CHO Radical Reactions</i>			
$\text{CH}_2\text{CHO} + \text{O}_2 \rightarrow \text{CH}_2\text{CO} + \text{HO}_2$	No recommendation for $k$ (see data sheet)		
$\quad \rightarrow \text{HCHO} + \text{CO} + \text{OH}$	$k_2/k = 0.2$ (at low pressures)	298	$\pm 0.2$
$\quad \rightarrow (\text{CHO})_2 + \text{OH}$			
$\text{CH}_2\text{CHO} + \text{O}_2 (+\text{M}) \rightarrow \text{O}_2\text{CH}_2\text{CHO} (+\text{M})$	See Table 4.2		
<i>CH<sub>3</sub>CO Radical Reactions</i>			
$\text{CH}_3\text{CO} (+\text{M}) \rightarrow \text{CH}_3 + \text{CO} (+\text{M})$	See Table 4.3		
$\text{CH}_3\text{CO} + \text{O}_2 \rightarrow \text{CH}_2\text{C}(\text{O})\text{O} + \text{OH}$	$k = 3.2 \cdot 10^{-12}$ at $P = 1$ bar	220–500	$\pm 0.2$ at 220 K, rising to $\pm 0.3$ at 500 K.
$\text{CH}_3\text{CO} + \text{O}_2 (+\text{M}) \rightarrow \text{CH}_3\text{CO}_3 (+\text{M})$	Branching ratios—see data sheet		
<i>CH<sub>3</sub>CHO Reactions</i>			
$\text{CH}_3\text{CHO} (+\text{M}) \rightarrow \text{CH}_3 + \text{CHO} (+\text{M})$	See Table 4.3		
<i>CH<sub>2</sub>CH<sub>2</sub>OH Radical Reactions</i>			
$\text{CH}_2\text{CH}_2\text{OH} (+\text{M}) \rightarrow \text{C}_2\text{H}_4 + \text{OH} (+\text{M})$	See Table 4.3		
$\text{CH}_2\text{CH}_2\text{OH} + \text{O}_2 \rightarrow \text{Products}$	$3 \cdot 10^{-12}$	298	$\pm 0.3$
<i>CH<sub>3</sub>CHOH Radical Reactions</i>			
$\text{CH}_3\text{CHOH} (+\text{M}) \rightarrow \text{Products}$	See Table 4.3		
$\text{CH}_3\text{CHOH} + \text{O}_2 \rightarrow \text{HO}_2 + \text{CH}_3\text{CHO}$	$[1.8 \cdot 10^{-11} T^{-1.2} + 8.0 \cdot 10^{-10} \exp(-2525/T)]$	300–1000	$\pm 0.3$ at 300 K, rising to $\pm 0.5$ at 1000 K.
$\text{CH}_3\text{CHOH} + \text{O}_2 (+\text{M}) \rightarrow \text{CH}_3\text{CH}(\text{O}_2)\text{OH} (+\text{M})$			
<i>C<sub>2</sub>H<sub>5</sub>O Radical Reactions</i>			
$\text{C}_2\text{H}_5\text{O} (+\text{M}) \rightarrow \text{HCHO} + \text{CH}_3 (+\text{M})$	See Table 4.3		
$\quad \rightarrow \text{CH}_3\text{CHO} + \text{H} (+\text{M})$			
$\text{C}_2\text{H}_5\text{O} + \text{O}_2 \rightarrow \text{CH}_3\text{CHO} + \text{HO}_2$	$3.8 \cdot 10^{-14} \exp(-440/T)$	290–1000	$\pm 0.2$ at 290 K, rising to $\pm 0.5$ at 1000 K.
<i>CH<sub>3</sub>OCH<sub>3</sub> Reactions</i>			
$\text{CH}_3\text{OCH}_3 (+\text{M}) \rightarrow \text{CH}_3\text{O} + \text{CH}_3 (+\text{M})$	See Table 4.3		
<i>C<sub>2</sub>H<sub>5</sub>OH Reactions</i>			
$\text{C}_2\text{H}_5\text{OH} (+\text{M}) \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O} (+\text{M})$	See Table 4.3		
$\quad \rightarrow \text{CH}_2\text{OH} + \text{CH}_3 (+\text{M})$			
$\quad \rightarrow \text{C}_2\text{H}_5 + \text{OH} (+\text{M})$			
<i>C<sub>2</sub>H<sub>5</sub>OOH Radical Reactions</i>			

TABLE 4.1. Bimolecular reactions—Continued

Reaction	$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Error limits ( $\Delta \log k$ )
$\text{C}_2\text{H}_5\text{OOH} + \text{M} \rightarrow \text{C}_2\text{H}_5\text{O} + \text{OH} + \text{M}$	See Table 4.3		
<i>C<sub>3</sub>H<sub>3</sub> Radical Reactions</i>			
$\text{C}_3\text{H}_3 + \text{C}_3\text{H}_3 \rightarrow \text{Products}$	$6.5 \cdot 10^{-11}$	298–1000	$\pm 0.5$
<i>C<sub>3</sub>H<sub>5</sub> Radical Reactions</i>			
$\text{C}_3\text{H}_5 + \text{M} \rightarrow \text{CH}_2\text{CCH}_2 + \text{H} + \text{M}$	See Table 4.3		
$\text{C}_3\text{H}_5 + \text{O}_2 \rightarrow \text{CH}_2\text{CCH}_2 + \text{HO}_2$	$1.71 \cdot 10^{-12} \exp(-11400/T)$	600–1200	$\pm 0.3$ at 600 K, rising to $\pm 0.5$ at 1200 K.
$\rightarrow \text{CO} + \text{products}$	$7.6 \cdot 10^{-12} \exp(-9450/T)$	600–1200	$\pm 0.3$
$\text{C}_3\text{H}_5 + \text{H}_2 \rightarrow \text{C}_3\text{H}_6 + \text{H}$	$1.8 \cdot 10^{-19} T^{2.4} \exp(-9550/T)$	300–1100	$\pm 0.7$ at 300 K, falling to $\pm 0.3$ at 1100 K.
$\text{C}_3\text{H}_5 + \text{CH}_4 \rightarrow \text{C}_3\text{H}_6 + \text{CH}_3$	$6.6 \cdot 10^{-23} T^{3.4} \exp(-11670/T)$	300–1200	$\pm 0.4$
$\text{C}_3\text{H}_5 + \text{HCHO} \rightarrow \text{C}_3\text{H}_6 + \text{CHO}$	$1.2 \cdot 10^{-16} T^{1.8} \exp(-9155/T)$	300–1000	$\pm 0.4$
$\text{C}_3\text{H}_5 + \text{C}_2\text{H}_4 \rightarrow \text{C}_3\text{H}_6 + \text{C}_2\text{H}_3$	$6.6 \cdot 10^{-23} T^{3.4} \exp(-13120/T)$	600–1200	$\pm 0.5$
$\rightarrow c\text{-C}_5\text{H}_8 + \text{H}$	$1.0 \cdot 10^{-13} \exp(-9620/T)$	600–1200	$\pm 0.7$
$\text{C}_3\text{H}_5 + \text{C}_2\text{H}_6 \rightarrow \text{C}_3\text{H}_6 + \text{C}_2\text{H}_5$	$3.9 \cdot 10^{-22} T^{3.3} \exp(-9990/T)$	300–1200	$\pm 0.4$
$\text{C}_3\text{H}_5 + \text{C}_3\text{H}_5 + \text{M} \rightarrow \text{CH}_2\text{CHCH}_2\text{CH}_2\text{CHCH}_2 + \text{M}$	See Table 4.2		
$\text{C}_3\text{H}_5 + \text{C}_3\text{H}_5 \rightarrow \text{C}_3\text{H}_6 + \text{CH}_2\text{CCH}_2$	$1.0 \cdot 10^{-13}$	300–1000	$\pm 0.7$
$\text{C}_3\text{H}_5 + \text{C}_3\text{H}_8 \rightarrow \text{C}_3\text{H}_6 + \text{CH}_3\text{CH}_2\text{CH}_2$	$3.9 \cdot 10^{-22} T^{3.3} \exp(-9990/T)$	300–1200	$\pm 0.4$ over the range 600–1000 K, rising to
$\rightarrow \text{C}_3\text{H}_6 + \text{CH}_3\text{CHCH}_3$	$1.3 \cdot 10^{-22} T^{3.3} \exp(-8660/T)$	300–1200	$\pm 0.7$ at other temperatures.
$\text{C}_3\text{H}_5 + 2\text{-C}_4\text{H}_8 \rightarrow \text{C}_3\text{H}_6 + \text{CH}_2\text{CHCHCH}_3$	$3.6 \cdot 10^{-11} \exp(-8180/T)$	600–1000	$\pm 1.0$
$\rightarrow \text{C}_3\text{H}_6 + \text{CH}_3\text{CCHCH}_3$	$3.3 \cdot 10^{-23} T^{3.4} \exp(-12160/T)$	600–1000	$\pm 0.5$
$\text{C}_3\text{H}_5 + 2\text{-C}_4\text{H}_8 + \text{M} \rightarrow \text{CH}_2\text{CHCH}_2\text{CH}(\text{CH}_3)\text{CHCH}_3 + \text{M}$	See Table 4.2		
$\text{C}_3\text{H}_5 + i\text{-C}_4\text{H}_{10} \rightarrow \text{C}_3\text{H}_6 + (\text{CH}_3)_2\text{CHCH}_2$	$5.9 \cdot 10^{-22} T^{3.3} \exp(-9990/T)$	300–1200	$\pm 0.4$ over the range 600–1000 K, rising to
$\rightarrow \text{C}_3\text{H}_6 + (\text{CH}_3)_3\text{C}$	$7 \cdot 10^{-23} T^{3.3} \exp(-7800/T)$	300–1200	$\pm 0.7$ at other temperatures.
$\text{C}_3\text{H}_5 + [-\text{C}_6\text{H}_5\text{-}] - \text{CH}_3 \rightarrow \text{C}_3\text{H}_6 + [-\text{C}_6\text{H}_5\text{-}] - \text{CH}_2$	$1.8 \cdot 10^{-11} \exp(-8660/T)$	600–1000	$\pm 1.0$
<i>i-C<sub>3</sub>H<sub>7</sub> Radical Reactions</i>			
$i\text{-C}_3\text{H}_7 + \text{M} \rightarrow \text{C}_3\text{H}_6 + \text{H} + \text{M}$	See Table 4.3		
$i\text{-C}_3\text{H}_7 + \text{O}_2 \rightarrow \text{C}_3\text{H}_6 + \text{HO}_2$	$3.3 \cdot 10^{-14} \exp(1290/T)$	600–800	$\pm 0.5$
$i\text{-C}_3\text{H}_7 + \text{H}_2 \rightarrow \text{C}_3\text{H}_8 + \text{H}$	$1.3 \cdot 10^{-23} T^{3.28} \exp(-4360/T)$	300–1200	$\pm 0.5$
$i\text{-C}_3\text{H}_7 + \text{C}_2\text{H}_2 + \text{M} \rightarrow (\text{CH}_3)_2\text{CHCHCH} + \text{M}$	See Table 4.2		
$i\text{-C}_3\text{H}_7 + \text{C}_2\text{H}_4 + \text{M} \rightarrow (\text{CH}_3)_2\text{CHCH}_2\text{CH}_2 + \text{M}$	See Table 4.2		
$i\text{-C}_3\text{H}_7 + i\text{-C}_3\text{H}_7 + \text{M} \rightarrow (\text{CH}_3)_2\text{CHCH}(\text{CH}_3)_2 + \text{M}$	See Table 4.2		
$i\text{-C}_3\text{H}_7 + i\text{-C}_3\text{H}_7 \rightarrow \text{C}_3\text{H}_8 + \text{C}_3\text{H}_6$	$4.2 \cdot 10^{-12}$	300–1000	$\pm 0.1$ at 300 K, rising to $\pm 0.5$ at 1000 K.
$i\text{-C}_3\text{H}_7 + i\text{-C}_3\text{H}_7\text{CHO} \rightarrow \text{C}_3\text{H}_8 + (\text{CH}_3)_2\text{CHCO}$	$6.6 \cdot 10^{-14} \exp(-3170/T)$	300–650	$\pm 0.5$
$\rightarrow \text{C}_3\text{H}_8 + (\text{CH}_3)_2\text{CCHO}$	$5.3 \cdot 10^{-14} \exp(-4780/T)$	500–650	$\pm 0.5$
<i>C<sub>3</sub>H<sub>8</sub> Reactions</i>			
$\text{C}_3\text{H}_8 + \text{M} \rightarrow \text{CH}_3 + \text{C}_2\text{H}_5 + \text{M}$	See Table 4.3		
<i>t-C<sub>4</sub>H<sub>9</sub> Radical Reactions</i>			
$t\text{-C}_4\text{H}_9 + \text{M} \rightarrow i\text{-C}_4\text{H}_8 + \text{H} + \text{M}$	See Table 4.3		
$t\text{-C}_4\text{H}_9 + \text{O}_2 \rightarrow i\text{-C}_4\text{H}_8 + \text{HO}_2$	$1.0 \cdot 10^{-13} \exp(1590/T)$	298–800	$\pm 0.5$
$t\text{-C}_4\text{H}_9 + \text{H}_2 \rightarrow i\text{-C}_4\text{H}_{10} + \text{H}$	$3.1 \cdot 10^{-26} T^{4.24} \exp(-4510/T)$	300–1200	$\pm 0.5$
$t\text{-C}_4\text{H}_9 + \text{C}_2\text{H}_2 + \text{M} \rightarrow (\text{CH}_3)_3\text{CCHCH} + \text{M}$	See Table 4.2		
$t\text{-C}_4\text{H}_9 + \text{C}_2\text{H}_4 + \text{M} \rightarrow (\text{CH}_3)_3\text{CCH}_2\text{CH}_2 + \text{M}$	See Table 4.2		
$t\text{-C}_4\text{H}_9 + t\text{-C}_4\text{H}_9 + \text{M} \rightarrow (\text{CH}_3)_3\text{CC(CH}_3)_3 + \text{M}$	See Table 4.2		
$t\text{-C}_4\text{H}_9 + t\text{-C}_4\text{H}_9 \rightarrow i\text{-C}_4\text{H}_{10} + i\text{-C}_4\text{H}_8$	$1.2 \cdot 10^{-7} T^{-1.73}$	300–1000	$\pm 0.15$ at 300 K, rising to $\pm 0.5$ at 1000 K.

TABLE 4.1. Bimolecular reactions—Continued

Reaction	$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Error limits ( $\Delta \log k$ )
$t\text{-C}_4\text{H}_9 + t\text{-C}_4\text{H}_9\text{CHO} \rightarrow i\text{-C}_4\text{H}_{10} + t\text{-C}_4\text{H}_9\text{CO}$ $\quad \rightarrow i\text{-C}_4\text{H}_{10} + \text{CH}_2\text{C}(\text{CH}_3)_2\text{CHO}$	$1.0 \cdot 10^{-14} \exp(-3200/T)$ $3.9 \cdot 10^{-14} \exp(-5540/T)$	300–700 500–700	$\pm 0.5$ $\pm 0.5$
$[-\text{C}_5\text{H}_5^-]$ Radical Reactions			
$[-\text{C}_5\text{H}_5^-](+\text{M}) \rightarrow \text{Products}$	See Table 4.3		
$[-\text{C}_5\text{H}_6^-]$ Reactions			
$[-\text{C}_5\text{H}_6^-](+\text{M}) \rightarrow [-\text{C}_5\text{H}_5^-] + \text{H} (+\text{M})$	See Table 4.3		
$[-\text{C}_6\text{H}_5^-]$ Radical Reactions			
$[-\text{C}_6\text{H}_5^-](+\text{M}) \rightarrow \text{CHC}(\text{CH}_4)_4 (+\text{M})$ $\quad \rightarrow [-\text{C}_6\text{H}_4^-] + \text{H} (+\text{M})$ $\quad \rightarrow \text{CHCCCHCHCCH} + \text{H} (+\text{M})$ $\quad \rightarrow \text{C}_4\text{H}_3 + \text{C}_2\text{H}_2 (+\text{M})$ $\quad \rightarrow \text{C}_2\text{H}_3 + \text{C}_4\text{H}_2 (+\text{M})$	See Table 4.3		
$[-\text{C}_6\text{H}_5^-] + \text{O}_2 \rightarrow [-\text{C}_6\text{H}_5^-]\text{-O} + \text{O}$ $\quad \rightarrow [-\text{C}_6\text{H}_4^-]\text{-1,2-(O)}_2 + \text{H}$ $\quad \rightarrow [-\text{C}_6\text{H}_4^-]\text{-1,4-(O)}_2 + \text{H}$	$1.7 \cdot 10^{-11} \exp(-1802/T)$ $(k_2 + k_3) = 7.5 \cdot 10^{-12} \exp(-1814/T)$	1050–1500 1100–1400	$\pm 0.2$ $\pm 0.3$
$[-\text{C}_6\text{H}_5^-] + \text{O}_2(+\text{M}) \rightarrow [-\text{C}_6\text{H}_5^-]\text{-O}_2(+\text{M})$	See Table 4.2		
$[-\text{C}_6\text{H}_5^-] + \text{C}_2\text{H}_2 \rightarrow [-\text{C}_6\text{H}_5^-]\text{-C}_2\text{H} + \text{H}$ $[-\text{C}_6\text{H}_5^-] + \text{C}_2\text{H}_2 (+\text{M}) \rightarrow [-\text{C}_6\text{H}_5^-]\text{-C}_2\text{H}_2 (+\text{M})$	$k = 4.0 \cdot 10^{-18} T^{1.77} \exp(-1152/T)$ $k_1 = 6.6 \cdot 10^{-11} \exp(-5080/T)$	297–550 900–1500	$\pm 0.3$ $\pm 0.3$
$[-\text{C}_6\text{H}_6^-]$ Reactions			
$[-\text{C}_6\text{H}_6^-](+\text{M}) \rightarrow \text{C}_4\text{H}_4 + \text{C}_2\text{H}_2 (+\text{M})$ $\quad \rightarrow [-\text{C}_6\text{H}_5^-] + \text{H} (+\text{M})$	See Table 4.3		
$[-\text{C}_6\text{H}_5^-]\text{-O}$ Radical Reactions			
$[-\text{C}_6\text{H}_5^-]\text{-O} (+\text{M}) \rightarrow [-\text{C}_5\text{H}_5^-] + \text{CO} (+\text{M})$	See Table 4.3		
$[-\text{C}_6\text{H}_5^-]\text{-CH}_2$ Radical Reactions			
$[\text{C}_6\text{H}_5^-]\text{-CH}_2 (+\text{M}) \rightarrow [-\text{C}_5\text{H}_5^-] + \text{C}_2\text{H}_2 (+\text{M})$ $\quad \rightarrow [-\text{C}_5\text{H}_5^-]\text{-C}\equiv\text{CH} + \text{H} (+\text{M})$ $\quad \rightarrow \text{linear C}_7\text{H}_6 + \text{H} (+\text{M})$	See Table 4.3		
$[-\text{C}_6\text{H}_5^-]\text{-CH}_3$ Reactions			
$[\text{C}_6\text{H}_5^-]\text{-CH}_3 (+\text{M}) \rightarrow [-\text{C}_6\text{H}_5^-]\text{-CH}_2 + \text{H} (+\text{M})$ $\quad \rightarrow [-\text{C}_6\text{H}_4^-]\text{-CH}_3 + \text{H} (+\text{M})$	See Table 4.3		
$[-\text{C}_6\text{H}_5^-]\text{-1,4-(CH}_3)_2$ Reactions			
$[-\text{C}_6\text{H}_4^-]\text{-1,4-(CH}_3)_2 (+\text{M}) \rightarrow [-\text{C}_6\text{H}_4^-]\text{-1-(CH}_2)\text{-4-(CH}_3) + \text{H} (+\text{M})$ $\quad \rightarrow [-\text{C}_6\text{H}_4^-]\text{-4-CH}_3 + \text{CH}_3 (+\text{M})$	See Table 4.3		
$[-\text{C}_6\text{H}_5^-]\text{-C}_2\text{H}_5$ Reactions			
$[-\text{C}_6\text{H}_5^-]\text{-C}_2\text{H}_5 (+\text{M}) \rightarrow [-\text{C}_6\text{H}_6^-] + \text{C}_2\text{H}_4 (+\text{M})$ $\quad \rightarrow [-\text{C}_6\text{H}_5^-]\text{-C}_2\text{H}_3 + \text{H}_2 (+\text{M})$ $\quad \rightarrow [-\text{C}_6\text{H}_5^-]\text{-CH}_2 + \text{CH}_3 (+\text{M})$ $\quad \rightarrow [-\text{C}_6\text{H}_5^-]\text{-CHCH}_3 + \text{H} (+\text{M})$ $\quad \rightarrow [-\text{C}_6\text{H}_5^-]\text{-CH}_2\text{CH}_2 + \text{H} (+\text{M})$ $\quad \rightarrow [-\text{C}_6\text{H}_5^-] + \text{C}_2\text{H}_5 (+\text{M})$	See Table 4.2		

TABLE 4.2. Combination reactions

Reaction	$k_0/\text{cm}^6 \text{molecule}^{-2} \text{s}^{-1}$	$k_\infty/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$	$F_c$	$k/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} = \frac{k_0 k_\infty [\text{M}]}{k_0 [\text{M}] + k_\infty} F$	T/K	Error limits ( $\Delta \log k$ )
O + NO(+ M) → NO <sub>2</sub> (+ M)	$k_0(\text{N}_2) = 9.2 \cdot 10^{-28} T^{-1.6}$				200–2200	± 0.3
	$k_0(\text{Ar}) = 6.3 \cdot 10^{-28} T^{-1.6}$				200–2200	± 0.3
	$k_\infty = 4.9 \cdot 10^{-10} T^{-0.4}$				200–2200	± 0.3
	$F_c(\text{N}_2) = 0.8$				200–2200	$\Delta F_c = \pm 0.2$
	$F_c(\text{Ar}) = 0.8$				200–2200	$\Delta F_c = \pm 0.2$
	$3.7 \cdot 10^{-11} \exp(-2280/T)$				298–1400	± 0.3
O + [-C <sub>6</sub> H <sub>6</sub> -](+ M) → [-C <sub>6</sub> H <sub>5</sub> -]-OH(+ M) → [-C <sub>6</sub> H <sub>5</sub> -]-O+H(+ M)						
H + O <sub>2</sub> (+ M) → HO <sub>2</sub> (+ M)	$k_0(\text{Ar}) = 1.9 \cdot 10^{-29} T^{-1.2}$				298–2000	± 0.1 at 298 K, rising to ± 0.2 at 2000 K.
	$k_0(\text{N}_2) = 7.3 \cdot 10^{-29} T^{-1.3}$				298–2000	± 0.1 at 298 K, rising to ± 0.2 at 2000 K.
	$k_0(\text{H}_2\text{O}) = 1.0 \cdot 10^{-28} T^{-1.0}$				298–2000	± 0.1 at 298 K, rising to ± 0.3 at 2000 K.
	$k_\infty = [0.32T^{0.56} + 2.9 \cdot 10^4 T^{-1.7}] \cdot 10^{-11}$				298–1500	± 0.5
	$F_c(\text{Ar}) = 0.51$				298–1500	$\Delta F_c = \pm 0.1$
	$F_c(\text{N}_2) = 0.57$				298–1500	$\Delta F_c = \pm 0.1$
	$F_c(\text{Ar}) = 0.81$				298–1500	$\Delta F_c = \pm 0.1$
H + H(+ M) → H <sub>2</sub> (+ M)	$k_0(\text{H}_2) = 2.8 \cdot 10^{-31} T^{-0.6}$				200–5000	± 0.5
	$k_0(\text{Ar}) = 1.8 \cdot 10^{-30} T^{-1.0}$				200–2500	± 0.5
	$k_0(\text{Ar}) = 2.3 \cdot 10^{-26} T^{-2.0}$				300–3000	± 0.3
	$k_0(\text{N}_2) = 6.1 \cdot 10^{-26} T^{-2.0}$				300–3000	± 0.5
	$k_0(\text{H}_2\text{O}) = 3.9 \cdot 10^{-25} T^{-2.0}$				300–3000	± 0.5
	$k_0(\text{H}_2) = 4.23 \cdot 10^{-30} T^{-0.77}$				230–750	± 0.3
H + NO(+ M) → HNO(+ M)	$k_0(\text{Ar}) = 7.6 \cdot 10^{-35} T^{0.387} \exp(7840/T)$				2000–3000	± 0.4
H + NH <sub>2</sub> (+ M) → NH <sub>3</sub> (+ M)	$k_\infty = 7.6 \cdot 10^{-10} \exp(-850/T)$				2000–3000	± 0.5
	$F_c(\text{Ar}) = 0.58 \exp(-T/4581) + 0.42 \exp(-T/102)$				2000–3000	$\Delta F_c = 0.1$
H + CO(+ M) → HCO(+ M)	$k_0(\text{Ar}) = 2.0 \cdot 10^{-35} T^{0.2}$				300–800	± 0.3
	$k_0(\text{He}) = 1.5 \cdot 10^{-36} T^{0.6}$				300–800	± 0.3
H + CH <sub>3</sub> (+ M) → CH <sub>4</sub> (+ M)	$k_0(\text{He}) = 1.8 \cdot 10^{-24} T^{-1.8}$				300–1000	± 0.3
	$k_0(\text{Ar}) = 1.7 \cdot 10^{-24} T^{-1.8}$				300–1000	± 0.5
	$k_0(\text{C}_2\text{H}_6) = 8.6 \cdot 10^{-24} T^{-1.8}$				300–1000	± 0.5
	$k_\infty = 3.5 \cdot 10^{-10}$				300–2000	± 0.3
	$F_c(\text{He}, \text{Ar}) = 0.63 \exp(-T/3315) + 0.37 \exp(-T/61)$				300–2000	$\Delta F_c = \pm 0.1$
H + C <sub>2</sub> H <sub>2</sub> (+ M) → C <sub>2</sub> H <sub>3</sub> (+ M)	$F_c(\text{C}_2\text{H}_6) = 0.71 \exp(-T/3079) + 0.29 \exp(-T/54)$				300–2000	$\Delta F_c = \pm 0.1$
	$k_0(\text{He}) = 1.6 \cdot 10^{-20} T^{-3.47} \exp(-475/T)$				200–2000	± 0.3
	$k_0(\text{N}_2) = 1.0 \cdot 10^{-20} T^{-3.38} \exp(-426/T)$				200–2000	± 0.3
	$k_\infty = 9.2 \cdot 10^{-16} T^{1.64} \exp(-1055/T)$				200–2000	± 0.3
	$F_c(\text{He}) = 7.94 \cdot 10^{-4} T^{0.78}$				200–2000	$\Delta F_c = \pm 0.1$
	$F_c(\text{N}_2) = 7.37 \cdot 10^{-4} T^{0.80}$				200–2000	$\Delta F_c = \pm 0.1$
H + C <sub>2</sub> H <sub>3</sub> (+ M) → C <sub>2</sub> H <sub>4</sub> (+ M)	$k_0(\text{He}) = 3.5 \cdot 10^{-27}$				300	± 0.3
	$k_\infty = 1.6 \cdot 10^{-10}$				300	± 0.3
	$F_c(\text{He}) = 0.5$				300	$\Delta F_c = \pm 0.1$
H + C <sub>2</sub> H <sub>4</sub> (+ M) → C <sub>2</sub> H <sub>5</sub> (+ M)	$k_0(\text{He}) = 1.3 \cdot 10^{-29} \exp(-380/T)$				300–800	± 0.3
	$k_0(\text{N}_2) = 1.3 \cdot 10^{-29} \exp(-380/T)$				300–800	± 0.3
	$k_\infty = 6.6 \cdot 10^{-15} T^{1.28} \exp(-650/T)$				200–1100	± 0.3
	$F_c(\text{He}, \text{N}_2) = 0.24 \exp(-T/40) + 0.76 \exp(-T/1025)$				300–800	$\Delta F_c = \pm 0.1$

TABLE 4.2. Combination reactions—Continued

Reaction	$k_0 / \text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$	$k_\infty / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$F_c$	$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} = \frac{k_0 k_\infty [\text{M}]}{k_0 [\text{M}] + k_\infty} F$	T/K	Error limits ( $\Delta \log k$ )
$\text{H} + \text{C}_3\text{H}_5(+\text{M}) \rightarrow \text{C}_3\text{H}_6(+\text{M})$	See Table 4.1					
$\text{H} + [-\text{C}_6\text{H}_5^-](+\text{M}) \rightarrow [-\text{C}_6\text{H}_5^-](+\text{M})$	$1.3 \cdot 10^{-10}$				300–1700	$\pm 0.5$
$\text{H} + [-\text{C}_6\text{H}_6^-](+\text{M}) \rightarrow [-\text{C}_6\text{H}_7^-](+\text{M})$	$6.7 \cdot 10^{-11} \exp(-2170/T)$				298–500	$\pm 0.15$
$\text{H} + [-\text{C}_6\text{H}_5^-]\text{-O}(+\text{M}) \rightarrow [-\text{C}_6\text{H}_5^-]\text{-OH}(+\text{M})$ $\rightarrow [-\text{C}_6\text{H}_6^-]=\text{O}(+\text{M})$	See Table 4.1					
$\text{H} + [-\text{C}_6\text{H}_5^-]\text{-CH}_2(+\text{M}) \rightarrow [-\text{C}_6\text{H}_5^-]\text{-CH}_3(+\text{M})$	$4.3 \cdot 10^{-10}$				300–1650	$\pm 0.3$
$\text{H} + [-\text{C}_6\text{H}_5^-]\text{-CH}_3(+\text{M}) \rightarrow [-\text{C}_6\text{H}_6^-]\text{-CH}_3(+\text{M})$	$1.8 \cdot 10^{-13}$				298–350	$\pm 0.2$
$\text{H} + [-\text{C}_6\text{H}_4^-]\text{-1,4-(CH}_3)_2(+\text{M}) \rightarrow [-\text{C}_6\text{H}_5^-]\text{-1,4-(CH}_3)_2(+\text{M})$	$3.8 \cdot 10^{-13}$				298	$\pm 0.4$
$\text{H} + [-\text{C}_6\text{H}_5^-]\text{-C}_2\text{H}_5(+\text{M}) \rightarrow [-\text{C}_6\text{H}_6^-]\text{-C}_2\text{H}_5(+\text{M})$	$2.9 \cdot 10^{-13}$				298	$\pm 0.3$
$\text{OH} + \text{OH}(+\text{M}) \rightarrow \text{H}_2\text{O}_2(+\text{M})$	$k_0(\text{N}_2) = 6.6 \cdot 10^{-29} T^{-0.8}$ $k_0(\text{H}_2\text{O}) = 4.0 \cdot 10^{-30}$ $k_\infty = 2.6 \cdot 10^{-11}$ $F_c(\text{N}_2, \text{H}_2\text{O}) = 0.5$ $3.1 \cdot 10^{-11} T^{0.2}$				200–400	$\pm 0.2$
$\text{OH} + \text{NH}_2(+\text{M}) \rightarrow \text{NH}_2\text{OH}(+\text{M})$	$k_0(\text{N}_2) = [1.67 \cdot 10^{-11} \exp(-8050/T) + 1.50 \cdot 10^{-12} \exp(-2300/T)]$ $+ 1.68 \cdot 10^{-13} \exp(-30/T)]$				200–500 ( $P = 1 \text{ bar}$ )	$\pm 1$
$\text{OH} + \text{CO}(+\text{M}) \rightarrow \text{HOOC}(+\text{M})$	$k_\infty = [2.04 \cdot 10^{-9} \exp(-7520/T) + 1.83 \cdot 10^{-11} \exp(-1850/T) + 1.33 \cdot 10^{-12} \exp(-120/T)]$				80–3000	$\pm 0.1$
$\text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H}$	$k(P) = k_0[1 + 3.2(P/\text{bar})\exp(-T/161)]$ for $\text{M} = \text{N}_2$ $k_1^\circ(\text{He}) = 1.06 \cdot 10^{-10} T^{-6.21} \exp(-671/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ $k_1^\infty = 7.2 \cdot 10^{-9} T^{-0.79} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ $F_{c,1}(\text{He}) = 0.75 \exp(-T/7210) + 0.25 \exp(-T/1434)$ $k_2^\circ(\text{He}) = 1.8 \cdot 10^{-8} T^{-0.91} \exp(-275/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ $k_2^\infty = 6.4 \cdot 10^{-8} T^{5.8} \exp(485/T) \text{ s}^{-1}$ $F_{c,2}(\text{He}) = 0.664 \exp(-T/3569) + 0.336 \exp(-T/108)$ $+ \exp(-3240/T)$ $k_6^\circ(\text{He}) = 3.8 \cdot 10^{-14} T^{-0.12} \exp(209/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ $k_6^\infty = 1.14 \cdot 10^{-17} T^{8.0} \exp(1240/T) \text{ s}^{-1}$ $F_{c,6}(\text{He}) = 0.295 \exp(-T/3704) + 0.705 \exp(-T/312)$ $+ \exp(-1238/T)$				80–800	$\pm 0.1$
Note for the above reaction:	(i) The numbering of the rate constants corresponds to that on the data sheet and in Table 4.1. (ii) The pressure dependent <i>bimolecular</i> rate constants for channels (2) and (6) are given by $k = \{k_0 k_\infty / (k_\infty + k_0[\text{M}])\}F$ , where $F$ is the usual broadening factor.					
$\text{OH} + [-\text{C}_6\text{H}_5^-]\text{-OH}(+\text{M}) \rightarrow [-\text{C}_6\text{H}_5^-]\text{-}(\text{OH})_2(+\text{M})$	$1.3 \cdot 10^{-12} \exp(914/T)$				300–375	$\pm 0.4$
$\text{OH} + [-\text{C}_6\text{H}_4^-]\text{-1,4-(CH}_3)_2(+\text{M})$ $\rightarrow [-\text{C}_6\text{H}_4^-]\text{-2,5-(CH}_3)_2\text{-1-(OH)(+M)}$	$1.4 \cdot 10^{-11}$				298–320	$\pm 0.1$
$\text{OH} + [-\text{C}_6\text{H}_5^-]\text{-}(\text{C}_2\text{H}_5)(+\text{M}) \rightarrow [-\text{C}_6\text{H}_5^-]\text{-}(\text{C}_2\text{H}_5)(\text{OH})(+\text{M})$	$7.1 \cdot 10^{-12}$ [Ar] $3.1 \cdot 10^{-33}$				298 ( $P \leq 1 \text{ bar}$ )	$\pm 0.1$
$\text{C} + \text{N}_2(+\text{M}) \rightarrow \text{CNN}(+\text{M})$	$k_0(\text{Ar}) = 4.7 \cdot 10^{-26} T^{-1.6}$				298	$\pm 0.5$
$\text{CH} + \text{H}_2(+\text{M}) \rightarrow \text{CH}_3(+\text{M})$	$k_\infty = 8.5 \cdot 10^{-11} T^{0.15}$				200–1000	$\pm 0.3$
$\text{CH} + \text{N}_2(+\text{M}) \rightarrow \text{CHN}_2(+\text{M})$	$F_c(\text{Ar}) = 0.48 + 0.25 \exp(-T/300)$ $k_0(\text{Ar}, \text{N}_2) = 4.4 \cdot 10^{-26} T^{-2.2}$ $k_\infty = 9.6 \cdot 10^{-11} T^{-0.15}$ $F_c(\text{Ar}, \text{N}_2) = \exp(-T/660) + \exp(-1080/T)$				200–1000 500–1000 200–1000 200–500	$\pm 0.1$ $\pm 0.2$ $\pm 0.3$ $\pm 0.1$

TABLE 4.2. Combination reactions—Continued

Reaction	$k_0 / \text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$	$k_\infty / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$F_c$	$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} = \frac{k_0 k_\infty [\text{M}]}{k_0 [\text{M}] + k_\infty} F$	T/K	Error limits ( $\Delta \log k$ )
$\text{CH} + \text{CO} (+\text{M}) \rightarrow \text{HCCO} (+\text{M})$	$k_0(\text{Ar}) = 6.3 \cdot 10^{-24} T^{-2.5}$ $k_\infty = 1.7 \cdot 10^{-9} T^{-0.4}$ $F_c(\text{Ar}) = 0.6$				200–1000 200–1000 200–1000	$\pm 0.3$ $\pm 0.3$ $\pm 0.1$
$\text{CH}_3 + \text{O}_2 (+\text{M}) \rightarrow \text{CH}_3\text{O}_2 (+\text{M})$	$k_0(\text{Ar}) = 1.5 \cdot 10^{-22} T^{-3.3}$ $k_0(\text{N}_2) = 1.6 \cdot 10^{-22-3.3}$ $k_\infty = 1.3 \cdot 10^{-15} T^{1.2}$ $F_c(\text{Ar}, \text{N}_2) = 0.466 - 1.30 \cdot 10^{-4} T$ $k_0(\text{Ar}) = 2.9 \cdot 10^{-32} \exp(1430/T)$ $k_\infty = 2.05 \cdot 10^{-11} \exp(-60/T)$ $F_c(\text{Ar}) = 0.46$			300–800 300–800 300–800 300–800 250–550 250–550 298	$\Delta \log k = \pm 0.3$ over the range $P/\text{mbar} = (0.5–2000)$ . $\pm 0.3$ $\pm 0.1$ $\pm 0.3$ $\pm 0.3$ $\pm 0.2$	
$\text{CH}_3 + \text{NO} (+\text{M}) \rightarrow \text{CH}_3\text{NO} (+\text{M})$	$k_0(\text{He}) = 1.6 \cdot 10^{-37} T^{1.05} \exp(-1300/T)$ $k_0(\text{N}_2) = 5.9 \cdot 10^{-36}$ $k_\infty = 3.1 \cdot 10^{-16} T^{1.05} \exp(-2850/T)$ $F_c(\text{He}) = 0.5$ $F_c(\text{N}_2) = 0.6$			400–500 300–350 300–500 400–500 300–350	$\pm 0.2$ $\pm 0.5$ $\pm 0.5$ $\Delta F_c = \pm 0.1$ $\Delta F_c = \pm 0.1$	
$\text{CH}_3 + \text{CO} (+\text{M}) \rightarrow \text{CH}_3\text{CO} (+\text{M})$	$k_0(\text{Ar}) = 3.5 \cdot 10^{-7} T^{-7} \exp(-1390/T)$ $k_\infty = 6.0 \cdot 10^{-11}$ $F_c(\text{Ar}) = 0.38 \exp(-T/73) + 0.62 \exp(-T/1180)$ $1.0 \cdot 10^{-12} \exp(-3900/T)$ (at $P = 1$ bar) $3.5 \cdot 10^{-13} \exp(-3700/T)$			300–2000 300–2000 300–2000 300–600 300–600	$\pm 0.3$ $\pm 0.3$ $\pm 0.1$ $\pm 0.5$ $\pm 0.3$	
$\text{CH}_3 + \text{CH}_3 (+\text{M}) \rightarrow \text{C}_2\text{H}_6 (+\text{M})$	$k_\infty = 6.1 \cdot 10^{-11}$ $k_\infty = 1.55 \cdot 10^{-9} T^{-0.54} \exp(-117/T)$ $5.6 \cdot 10^{-14} \exp(-3520/T)$ $1.8 \cdot 10^{-13} \exp(-3670/T)$			300–800 300–600 300–600 300–2000	$\pm 0.2$ at 300 K, rising to $\pm 0.5$ at 1200 K. $\pm 0.5$ $\pm 0.5$	
$\text{C}_2\text{H}_5 + \text{C}_2\text{H}_2 (+\text{M}) \rightarrow \text{C}_2\text{H}_5\text{CHCH}_2 (+\text{M})$	$k_\infty = 1.9 \cdot 10^{-11}$			295–1200	$\pm 0.3$	
$\text{C}_2\text{H}_5 + \text{C}_2\text{H}_4 (+\text{M}) \rightarrow n\text{-C}_4\text{H}_9 (+\text{M})$	$k_\infty = 3.3 \cdot 10^{-10} \exp(66/T)$			500–1200	$\pm 0.4$	
$\text{C}_2\text{H}_5 + \text{C}_3\text{H}_5 (+\text{M}) \rightarrow n\text{-C}_4\text{H}_{10} (+\text{M})$	$k_0(\text{N}_2) = 1.6 \cdot 10^{-30}$			298	$\pm 0.3$	
$\text{C}_2\text{H}_5 + \text{C}_3\text{H}_5 (+\text{M}) \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CHCH}_2 (+\text{M})$	$k_\infty = 1.9 \cdot 10^{-13}$			298	$\pm 0.3$	
$\text{CH}_2\text{CHO} + \text{O}_2 (+\text{M}) \rightarrow \text{O}_2\text{CH}_2\text{CHO} (+\text{M})$	$F_c(\text{N}_2) = 0.5$			298	$\Delta F_c = \pm 0.1$	
$\text{CH}_3\text{CO} + \text{O}_2 (+\text{M}) \rightarrow \text{CH}_3\text{CO}_3 (+\text{M})$	See Table 4.1					
$\text{C}_3\text{H}_5 + \text{C}_3\text{H}_5 (+\text{M}) \rightarrow \text{CH}_2\text{CHCH}_2\text{CH}_2\text{CHCH}_2 (+\text{M})$	$k_\infty = 2.3 \cdot 10^{-11}$			300–1000	$\pm 0.2$	
$\text{C}_3\text{H}_5 + 2\text{-C}_4\text{H}_8 (+\text{M}) \rightarrow \text{CH}_2\text{CHCH}_2\text{CH}(\text{CH}_3)\text{CHCH}_3 (+\text{M})$	$k_\infty = 1.0 \cdot 10^{-13} \exp(-9620/T)$			600–1200	$\pm 0.7$	
$i\text{-C}_3\text{H}_7 + \text{C}_2\text{H}_2 (+\text{M}) \rightarrow (\text{CH}_3)_2\text{CHCHCH} (+\text{M})$	$5.3 \cdot 10^{-14} \exp(-3470/T)$			300–600	$\pm 0.5$	
$i\text{-C}_3\text{H}_7 + \text{C}_2\text{H}_4 (+\text{M}) \rightarrow (\text{CH}_3)_2\text{CHCH}_2\text{CH}_2 (+\text{M})$	$7.5 \cdot 10^{-14} \exp(-3470/T)$			300–600	$\pm 0.5$	
$i\text{-C}_3\text{H}_7 + i\text{-C}_3\text{H}_7 (+\text{M}) \rightarrow (\text{CH}_3)_2\text{CHCH}(\text{CH}_3)_2 (+\text{M})$	$k_\infty = 6.8 \cdot 10^{-12}$			300–1000	$\pm 0.1$ at 300 K, rising to $\pm 0.3$ at 1000 K.	
$t\text{-C}_4\text{H}_9 + \text{C}_2\text{H}_2 (+\text{M}) \rightarrow (\text{CH}_3)_3\text{CCHCH} (+\text{M})$	$1.2 \cdot 10^{-13} \exp(-4320/T)$			300–600	$\pm 0.5$	
$t\text{-C}_4\text{H}_9 + \text{C}_2\text{H}_4 (+\text{M}) \rightarrow (\text{CH}_3)_3\text{CCH}_2\text{CH}_2 (+\text{M})$	$3.3 \cdot 10^{-14} \exp(-4020/T)$			300–650	$\pm 0.5$	
$t\text{-C}_4\text{H}_9 + t\text{-C}_4\text{H}_9 (+\text{M}) \rightarrow (\text{CH}_3)_3\text{CC}(\text{CH}_3)_3 (+\text{M})$	$k_\infty = 5.2 \cdot 10^{-8} T^{-1.73}$			300–1000	$\pm 0.15$ at 300 K rising to $\pm 0.3$ at 1000 K.	
$[-\text{C}_6\text{H}_5^-] + \text{O}_2 (+\text{M}) \rightarrow [-\text{C}_6\text{H}_5^-]\text{-O}_2 (+\text{M})$	$1.0 \cdot 10^{-11} \exp(161/T)$			297–500	$\pm 0.2$	
$[-\text{C}_6\text{H}_5^-] + \text{C}_2\text{H}_2 (+\text{M}) \rightarrow [-\text{C}_6\text{H}_5^-]\text{-C}_2\text{H}_2 (+\text{M})$	See Table 4.1					

TABLE 4.3. Decomposition reactions

Reaction	$k_\infty / \text{s}^{-1}$ $k_0 / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$F_c$	$k / \text{s}^{-1} = \frac{k_0 k_\infty [\text{M}]}{k_0 [\text{M}] + k_\infty} F$	T/K	Error limits ( $\Delta \log k$ )
$\text{H}_2(+\text{M}) \rightarrow \text{H} + \text{H}(+\text{M})$	$k_0(\text{Ar}) = 3.7 \cdot 10^{-10} \exp(-48350/T)$ $k_0(\text{H}_2) = 1.5 \cdot 10^{-9} \exp(-48350/T)$			2500–8000	$\pm 0.3$
$\text{H}_2\text{O}(+\text{M}) \rightarrow \text{H} + \text{OH}(+\text{M})$	$k_0(\text{N}_2) = 8 \cdot 10^{-9} \exp(-52920/T)$			2500–8000	$\pm 0.5$
$\text{H}_2\text{O}_2(+\text{M}) \rightarrow 2\text{OH}(+\text{M})$	$k_0(\text{Ar}) = 3.8 \cdot 10^{-8} \exp(-21960/T)$ $k_0(\text{N}_2) = 2.0 \cdot 10^{-7} \exp(-22900/T)$ $k_\infty = 3.0 \cdot 10^{14} \exp(-24400/T)$			2000–6000 1000–1500 700–1500 1000–1500	$\pm 0.5$ $\pm 0.2$ $\pm 0.5$ $\pm 0.2$
$\text{N}_2\text{O}(+\text{M}) \rightarrow \text{O} + \text{N}_2(+\text{M})$	$F_c(\text{Ar}) = 0.5$ $k_0(\text{Ar}) = 1.0 \cdot 10^{-9} \exp(-28910/T)$ $k_\infty = 9.9 \cdot 10^{10} \exp(-29140/T)$ $F_c(\text{Ar}) = 1.167 - 1.25 \cdot 10^{-4} T$			700–1500 1000–3000 1000–3000 1000–3000	$\Delta F_c = \pm 0.1$ $\pm 0.3$ $\pm 0.5$ $\Delta F_c = \pm 0.1$
$\text{NH}_3(+\text{M}) \rightarrow \text{NH} + \text{H}_2(+\text{M})$ $\rightarrow \text{NH}_2 + \text{H}(+\text{M})$	$k_0(\text{Ar}) = 3.1 \cdot 10^{-8} \exp(-46860/T)$ $k_\infty = 2.8 \cdot 10^{17} T^{-0.39} \exp(-55525/T)$ $F_c(\text{Ar}) = 0.58 \exp(-T/4581) + 0.42 \exp(-T/102)$			2000–3000 2000–3000 2000–3000	$\pm 0.3$ $\pm 0.5$ $\Delta F_c = \pm 0.1$
$\text{HNO}(+\text{M}) \rightarrow \text{H} + \text{NO}(+\text{M})$	$k_0(\text{H}_2) = 3.8 \cdot 10^{-7} T^{-0.262} \exp(-23180/T)$			230–750	$\pm 0.4$
$\text{NCO}(+\text{M}) \rightarrow \text{CO} + \text{N}(+\text{M})$	$k_0(\text{Ar}) = 3.7 \cdot 10^{-10} \exp(-27200/T)$			2000–3100	$\pm 0.2$
${}^3\text{C}_2(+\text{M}) \rightarrow {}^1\text{C}_2(+\text{M})$	See data sheets (M=O <sub>2</sub> , Kr, Xe)				
$({}^1\text{C}_2 / {}^3\text{C}_2)(+\text{M}) \rightarrow \text{C} + \text{C}(+\text{M})$	See data sheets				
${}^3\text{CH}_2(+\text{M}) \rightarrow \text{C} + \text{H}_2(+\text{M})$ $\rightarrow \text{CH} + \text{H}(+\text{M})$ $\rightarrow {}^1\text{CH}_2(+\text{M})$	$k_1 = 5.0 \cdot 10^{-10} \exp(-32600/T)$ $k_2 = 1.56 \cdot 10^{-8} \exp(-44880/T)$ $k_3 = K k_{-3}$ (see <sup>1</sup> CH <sub>2</sub> +M data sheet for values of $k_{-3}$ )			1700–4000 1700–4000	$\pm 0.7$ at 1700 K, falling to $\pm 0.4$ at 4000 K. $\pm 0.7$ at 1700 K, falling to $\pm 0.4$ at 4000 K.
$\text{CH}_3(+\text{M}) \rightarrow \text{CH}_2 + \text{H}(+\text{M})$ $\rightarrow \text{CH} + \text{H}_2(+\text{M})$	$1.7 \cdot 10^{-8} \exp(-45600/T)$ $1.1 \cdot 10^{-8} \exp(-42800/T)$			1500–3500 1500–3500	$\pm 0.5$ $\pm 0.5$
$\text{CH}_4(+\text{M}) \rightarrow \text{CH}_3 + \text{H}(+\text{M})$	$k_0(\text{Ar}) = 7.5 \cdot 10^{-7} \exp(-45700/T)$ $k_0(\text{Ar}) = 7.8 \cdot 10^{23} T^{-8.2} \exp(-59200/T)$ $k_0(\text{CH}_4) = 1.4 \cdot 10^{-6} \exp(-45700/T)$ $k_\infty = 2.4 \cdot 10^{16} \exp(-52800/T)$ $F_c(\text{Ar}) = \exp(-T/1350) + \exp(-7834/T)$ $F_c(\text{CH}_4) = 0.31 \exp(-T/91) + 0.69 \exp(-T/2207)$			1000–1700 1700–5000 1000–2000 1000–3000 1000–5000 1000–5000	$\pm 0.3$ $\pm 0.3$ $\pm 0.3$ $\pm 0.3$ $\Delta F_c = \pm 0.1$ $\Delta F_c = \pm 0.1$
$\text{HCO}(+\text{M}) \rightarrow \text{H} + \text{CO}(+\text{M})$	$k_0(\text{Ar}) = 6.6 \cdot 10^{-11} \exp(-7820/T)$			500–2500	$\pm 0.3$
$\text{HCHO}(+\text{M}) \rightarrow \text{HCO} + \text{H}(+\text{M})$ $\rightarrow \text{CO} + \text{H}_2(+\text{M})$	$[\text{Ar}] 8.09 \cdot 10^{-9} \exp(-38050/T)$ $[\text{Ar}] 4.7 \cdot 10^{-9} \exp(-32100/T)$			1700–3000 1700–3000	$\pm 0.3$ $\pm 0.4$
$\text{CH}_2\text{OH}(+\text{M}) \rightarrow \text{CH}_3\text{O}(+\text{M})$ $\rightarrow \text{HCHO} + \text{H}(+\text{M})$	$k_0(\text{N}_2) = 1 \cdot 10^{10} T^{-5.39} \exp(-18217/T)$ $k_\infty = 2.8 \cdot 10^{14} T^{-0.73} \exp(-16515/T)$ $F_c(\text{N}_2) = 0.04 \exp(-T/67.6) + 0.96 \exp(-T/1855) + \exp(-7543/T)$			300–2500 300–2500 300–2500	$\pm 0.5$ $\pm 0.5$ $\Delta F_c = \pm 0.5$
$\text{CH}_3\text{O}(+\text{M}) \rightarrow \text{HCHO} + \text{H}(+\text{M})$	$k_0(\text{N}_2) = 31 T^{-3.0} \exp(-12230/T)$ $k_\infty = 6.8 \cdot 10^{13} \exp(-13170/T)$ $F_c(\text{N}_2) = 0.97 - T/1950$			500–1000 500–1000 500–1000	$\pm 0.3$ $\pm 0.5$ $\Delta F_c = \pm 0.1$
$\text{CH}_3\text{OH}(+\text{M}) \rightarrow \text{CH}_3 + \text{OH}(+\text{M})$ $\rightarrow {}^1\text{CH}_2 + \text{H}_2\text{O}(+\text{M})$ $\rightarrow \text{CH}_2\text{OH} + \text{H}(+\text{M})$	$k_0(\text{Ar}) = 1.1 \cdot 10^{-7} \exp(-33080/T)$ $k_\infty = 2.5 \cdot 10^{19} T^{-0.94} \exp(-47030/T)$ $F_c(\text{Ar}) = 0.18 \exp(-T/200) + 0.82 \exp(-T/1438)$			1000–2000 1000–2000 1000–2000	$\pm 0.3$ $\pm 0.5$ $\Delta F_c = \pm 0.1$
$\text{CH}_3\text{OOH}(+\text{M}) \rightarrow \text{CH}_3\text{O} + \text{OH}(+\text{M})$	$6 \cdot 10^{14} \exp(-21300/T)$ ( $P = 1$ bar)			500–800	$\pm 0.2$ at 500 K, rising to $\pm 0.5$ at 800 K.

EVALUATED KINETIC DATA FOR COMBUSTION MODELING

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TABLE 4.3. Decomposition reactions—Continued

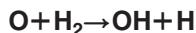
Reaction	$k_\infty / \text{s}^{-1}$ $k_0 / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ $F_c$ $k/\text{s}^{-1} = \frac{k_0 k_\infty [\text{M}]}{k_0 [\text{M}] + k_\infty} F$	T/K	Error limits ( $\Delta \log k$ )
$\text{C}_2\text{H}_3(+\text{M}) \rightarrow \text{C}_2\text{H}_2 + \text{H}(+\text{M})$	$k_0(\text{He}) = 6.6 \cdot 10^3 T^{-3.5} \exp(-18070/T)$ $k_0(\text{N}_2) = 4.3 \cdot 10^3 T^{-3.4} \exp(-18020/T)$ $k_\infty = 3.9 \cdot 10^8 T^{1.62} \exp(-18650/T)$ $F_c(\text{He}) = 7.94 \cdot 10^{-4} T^{0.78}$ $F_c(\text{N}_2) = 7.37 \cdot 10^{-4} T^{0.80}$	200–2000 200–2000 200–2000 200–2000 200–2000	$\pm 0.3$ $\pm 0.3$ $\pm 0.3$ $\Delta F_c = \pm 0.1$ $\Delta F_c = \pm 0.1$
$\text{C}_2\text{H}_4(+\text{M}) \rightarrow \text{C}_2\text{H}_2 + \text{H}_2(+\text{M})$ $\rightarrow \text{C}_2\text{H}_3 + \text{H}(+\text{M})$	$k_0(\text{Ar}) = 3.4 \cdot 10^{-7} T \exp(-39390/T)$ $k_0(\text{Ar}) = 4.3 \cdot 10^{-7} \exp(-48600/T)$	1500–3200 1500–3200	$\pm 0.3$ $\pm 0.5$
$\text{C}_2\text{H}_5(+\text{M}) \rightarrow \text{C}_2\text{H}_4 + \text{H}(+\text{M})$	$k_0(\text{C}_2\text{H}_6) = 1.7 \cdot 10^{-6} \exp(-16800/T)$ $k_\infty = 8.2 \cdot 10^{13} \exp(-20070/T)$ $F_c(\text{C}_2\text{H}_6) = 0.25 \exp(-T/97) + 0.75 \exp(-T/1379)$	700–900 700–1100 700–1100	$\pm 0.3$ $\pm 0.3$ $\Delta F_c = \pm 0.1$
$\text{C}_2\text{H}_6(+\text{M}) \rightarrow 2\text{CH}_3(+\text{M})$	$k_0(\text{Ar}) = 2.6 \cdot 10^{25} T^{-8.37} \exp(-47290/T)$ $k_0(\text{N}_2) = 2.6 \cdot 10^{25} T^{-8.37} \exp(-47290/T)$ $k_0(\text{C}_2\text{H}_6) = 4.5 \cdot 10^{-2} \exp(-41930/T)$ $k_\infty = 4.5 \cdot 10^{21} T^{-1.37} \exp(-45900/T)$ $F_c(\text{Ar}, \text{N}_2) = 0.38 \exp(-T/73) + 0.62 \exp(-T/1180)$ $F_c(\text{C}_2\text{H}_6) = 0.54 \exp(-T/1250)$	300–2000 300–2000 800–1000 300–2000 300–2000 800–1000	$\pm 0.5$ $\pm 0.5$ $\pm 0.5$ $\pm 0.3$ $\Delta F_c = \pm 0.1$ $\Delta F_c = \pm 0.1$
$\text{CH}_3\text{CO}(+\text{M}) \rightarrow \text{CH}_3 + \text{CO}(+\text{M})$	$k_0(\text{He}) = 1.0 \cdot 10^{-8} \exp(-7080/T)$ $k_0(\text{Ar}) = 7.0 \cdot 10^{-18}$ $k_\infty = 2.0 \cdot 10^{13} \exp(-8630/T)$ $F_c(\text{He}) = 0.5$ $k_\infty = 2.1 \cdot 10^{16} \exp(-41135/T)$ $2 \cdot 10^{14} \exp(-10170/T) (P = 900 \text{ mbar})$	400–500 353 300–500 400–500 750–1700 300–600	$\pm 0.2$ $\pm 0.4$ $\pm 0.5$ $\pm 0.2$ $\Delta F_c = \pm 0.1$ $\pm 1.0$
$\text{CH}_3\text{CHO}(+\text{M}) \rightarrow \text{CH}_3 + \text{CO}(+\text{M})$	$k_\infty = 2.6 \cdot 10^{15} \exp(-39080/T)$	700–1700	$\pm 0.5$
$\text{C}_2\text{H}_5\text{O}(+\text{M}) \rightarrow \text{HCHO} + \text{CH}_3(+\text{M})$ $\rightarrow \text{CH}_3\text{CHO} + \text{H}(+\text{M})$	$6.2 \cdot 10^{11} \exp(-11900/T) \text{ s}^{-1}$	500–800	$\pm 0.3$
$\text{CH}_3\text{OCH}_3(+\text{M}) \rightarrow \text{CH}_3\text{O} + \text{CH}_3(+\text{M})$	$k_\infty = 2.6 \cdot 10^{15} \exp(-39080/T)$	700–1700	$\pm 0.5$
$\text{CH}_2\text{CH}_2\text{OH}(+\text{M}) \rightarrow \text{C}_2\text{H}_4 + \text{OH}(+\text{M})$	$6.2 \cdot 10^{11} \exp(-11900/T) \text{ s}^{-1}$	500–800	$\pm 0.3$
$\text{CH}_3\text{CHOH}(+\text{M}) \rightarrow \text{Products}$	No recommendation; see data sheet		
$\text{C}_2\text{H}_5\text{OH}(+\text{M}) \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O}(+\text{M})$ $\rightarrow \text{CH}_2\text{OH} + \text{CH}_3(+\text{M})$ $\rightarrow \text{C}_2\text{H}_5 + \text{OH}(+\text{M})$	No recommendation; see data sheet		
$\text{C}_2\text{H}_5\text{OOH}(+\text{M}) \rightarrow \text{C}_2\text{H}_5\text{O} + \text{OH}(+\text{M})$	$k_\infty = 4 \cdot 10^{15} \exp(-21600/T) \text{ (estimate)}$	400–800	$\pm 0.3$
$\text{C}_3\text{H}_5(+\text{M}) \rightarrow \text{CH}_2\text{CCH}_2(+\text{M})$	$k_\infty = 1.5 \cdot 10^{11} T^{0.84} \exp(-30050/T)$	800–1500	$\pm 0.3$
$i\text{-C}_3\text{H}_7(+\text{M}) \rightarrow \text{C}_3\text{H}_6 + \text{H}(+\text{M})$	$k_0(\text{He}) = 3.56 \cdot 10^{-7} \exp(-14200/T)$ $k_\infty = 8.76 \cdot 10^7 T^{1.76} \exp(-17870/T)$ $F_c(\text{He}) = 0.35$	750–830 170–1000 750–830	$\pm 0.3$ $\pm 0.3$ $\Delta F_c = \pm 0.1$
$\text{C}_3\text{H}_8(+\text{M}) \rightarrow \text{CH}_3 + \text{C}_2\text{H}_5(+\text{M})$	$k_0(\text{Ar}) = 1.3 \cdot 10^{-5} \exp(-32700/T)$ $k_\infty = 4.0 \cdot 10^{23} T^{-1.87} \exp(-45394/T)$ $F_c(\text{Ar}) = 0.24 \exp(-T/1946) + 0.76 \exp(-T/38)$	700–2000 700–2000 700–2000	$\pm 0.5$ $\pm 0.3$ $\Delta F_c = \pm 0.2$
$t\text{-C}_4\text{H}_9(+\text{M}) \rightarrow i\text{-C}_4\text{H}_8 + \text{H}(+\text{M})$	$k_\infty = 8.3 \cdot 10^{13} \exp(-19200/T)$	300–800	$\pm 0.5$
$[-\text{C}_5\text{H}_5^-](+\text{M}) \rightarrow \text{Products}$	$5.0 \cdot 10^{13} \exp(-16760/T)$	1000–1600	$\pm 0.5$
$[-\text{C}_5\text{H}_6^-](+\text{M}) \rightarrow [-\text{C}_5\text{H}_5^-] + \text{H}(+\text{M})$	$4.0 \cdot 10^{14} \exp(-38760/T)$	1250–1600	$\pm 0.3$

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TABLE 4.3. Decomposition reactions—Continued

Reaction	$k_\infty / \text{s}^{-1}$ $k_0 / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ $F_c$ $k/\text{s}^{-1} = \frac{k_0 k_\infty [\text{M}]}{k_0 [\text{M}] + k_\infty} F$	T/K	Error limits ( $\Delta \log k$ )
$[-\text{C}_6\text{H}_5^-](+\text{M}) \rightarrow \text{CHC(CH)}_4(+\text{M})$ [ $\rightarrow \text{H}[-\text{C}_6\text{H}_4^-](+\text{M})$ $\rightarrow \text{H}[\text{CHCCHCHCCH}(+\text{M})$ $\rightarrow \text{C}_4\text{H}_3 + \text{C}_2\text{H}_2(+\text{M})$ $\rightarrow \text{C}_2\text{H}_3 + \text{C}_4\text{H}_2(+\text{M})$ ]	$k_2 = 4.0 \cdot 10^{13} \exp(-36700/T)$ See data sheet for information on other channels	1450–1900	$\pm 0.4$
$[-\text{C}_6\text{H}_6^-](+\text{M}) \rightarrow \text{C}_4\text{H}_4 + \text{C}_2\text{H}_2(+\text{M})$ [ $\rightarrow [-\text{C}_6\text{H}_5^-] + \text{H}(+\text{M})$ ]	$9.0 \cdot 10^{15} \exp(-54060/T) \text{ s}^{-1}$	1200–2500	$\pm 0.4$ at 1200 K, falling to $\pm 0.3$ at 2000 K
$[-\text{C}_6\text{H}_5^-]\text{-O}(\text{+M}) \rightarrow [-\text{C}_5\text{H}_5^-] + \text{CO}(\text{+M})$	$7.4 \cdot 10^{11} \exp(-22070/T) \text{ s}^{-1}$	1000–1600	$\pm 0.2$
$[\text{C}_6\text{H}_5^-]\text{-CH}_2(\text{+M}) \rightarrow [-\text{C}_5\text{H}_5^-] + \text{C}_2\text{H}_2(\text{+M})$ $\rightarrow [-\text{C}_5\text{H}_5^-]\text{-C}\equiv\text{CH} + \text{H}(\text{+M})$ $\rightarrow \text{linear C}_7\text{H}_6 + \text{H}(\text{+M})$	No recommendation; see data sheet $(k_2 + k_3) = 3.4 \cdot 10^{15} \exp(-42900/T) \text{ s}^{-1}$	1200–1750	$\pm 0.3$
$[\text{C}_6\text{H}_5^-]\text{-CH}_3(\text{+M}) \rightarrow [-\text{C}_6\text{H}_5^-]\text{-CH}_2 + \text{H}(\text{+M})$ $\rightarrow [-\text{C}_6\text{H}_5^-] + \text{CH}_3(\text{+M})$	$3.1 \cdot 10^{15} \exp(-44890/T) \text{ s}^{-1}$ $1.2 \cdot 10^{14} \exp(-41972/T) \text{ s}^{-1}$	920–2200 1000–2100	$\pm 0.3$ at 920 K, rising to $\pm 0.5$ at 2200 K $\pm 0.7$ at 1000 K, falling to $\pm 0.5$ at 2100 K
$[-\text{C}_6\text{H}_4^-]\text{-1,4-(CH}_3)_2(\text{+M}) \rightarrow [-\text{C}_6\text{H}_4^-]\text{-1-(CH}_2)\text{-4-(CH}_3) + \text{H}(\text{+M})$ [ $\rightarrow [-\text{C}_6\text{H}_4^-]\text{-4-CH}_3 + \text{CH}_3(\text{+M})$ ]	$k_\infty = 5 \cdot 10^{15} \exp(-42700/T)$ $k_1/k = 0.85; k_2/k = 0.15$	1000–1800 1500	$\pm 0.3$ $\Delta(k_1/k) = \Delta(k_2/k) = \pm 0.1$
$[-\text{C}_6\text{H}_5^-]\text{-C}_2\text{H}_5(\text{+M}) \rightarrow [-\text{C}_6\text{H}_6^-] + \text{C}_2\text{H}_4(\text{+M})$ $\rightarrow [-\text{C}_6\text{H}_5^-]\text{-C}_2\text{H}_3 + \text{H}_2(\text{+M})$ $\rightarrow [-\text{C}_6\text{H}_5^-]\text{-CH}_2 + \text{CH}_3(\text{+M})$ $\rightarrow [-\text{C}_6\text{H}_5^-]\text{-CHCH}_3 + \text{H}(\text{+M})$ $\rightarrow [-\text{C}_6\text{H}_5^-]\text{-CH}_2\text{CH}_2 + \text{H}(\text{+M})$ $\rightarrow [-\text{C}_6\text{H}_5^-] + \text{C}_2\text{H}_5(\text{+M})$	$k_3 = 7.1 \cdot 10^{15} \exp(-37800/T) \text{ s}^{-1}$	770–1800	$\pm 0.1$ at 770 K, rising to $\pm 0.4$ at 1800 K

## 5. Data Sheets



### *Thermodynamic Data*

$$\begin{aligned}\Delta H^\circ_{298} &= 5.90 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298} &= 6.69 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 1.87 \times T^{0.023} \exp(-694/T) \\ &(300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

### Rate Coefficient Data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$3.1 \cdot 10^{-10} \exp(-6976/T)$	1700–2500	Frank and Just, 1985 <sup>1</sup>	(a)
$5.25 \cdot 10^{-12} \exp(-3985/T)$	297–471	Presser and Gordon, 1985 <sup>2</sup>	(b)
$3.80 \cdot 10^{-10} \exp(-6920/T)$	1850–2500	Roth and Just, 1985 <sup>3</sup>	(c)
$7.3 \cdot 10^{-21} T^{2.93} \exp(-2980/T)$	350–1420	Marshall and Fontijn, 1987 <sup>4</sup>	(d)
$6.18 \cdot 10^{-18} T^{2.17} \exp(-4080/T)$	1713–3532	Natarajan and Roth, 1987 <sup>5</sup>	(e)
$7.19 \cdot 10^{-11} \exp(-5249/T)$	504–923	Sutherland <i>et al.</i> , 1986 <sup>6</sup>	(f)
$3.10 \cdot 10^{-10} \exp(-6853/T)$	880–2495		(g)
$1.05 \cdot 10^{-17}$	298	Zhu, Arepalli, and Gordon, 1989 <sup>7</sup>	(h)
$1.31 \cdot 10^{-9} \exp(-9381/T)$	1790–2250	Shin, Fujii, and Gardiner, 1989 <sup>8</sup>	(i)
$1.35 \cdot 10^{-9} \exp(-9540/T)$	2120–2750	Davidson and Hanson, 1990 <sup>9</sup>	(j)
$6.14 \cdot 10^{-10} \exp(-7818/T)$	1600–2250	Yang, Shin, and Gardiner, 1993 <sup>10</sup>	(k)
$3.12 \cdot 10^{-10} \exp(-6897/T)$	1424–2427	Ryu, Hwang, and Rabinowitz, 1995 <sup>11</sup>	(l)
$1.54 \cdot 10^{-9} \exp(-9740/T)$	2690–3360	Javoy <i>et al.</i> , 2000 <sup>12</sup>	(m)
<i>Reviews and Evaluations</i>			
$1.80 \cdot 10^{-20} T^{2.80} \exp(-2980/T)$	298–2500	Cohen and Westberg, 1983 <sup>13</sup>	(n)
$8.50 \cdot 10^{-20} T^{2.67} \exp(-3165/T)$	300–2500	CEC, 1992; 1994 <sup>14</sup>	(o)

### Comments

- (a) Shock tube study of  $\text{H}_2/\text{N}_2\text{O}/\text{Ar}$  mixtures. [O] monitored by ARAS.  $k$  derived by fitting [O] profiles to a mechanism of 11 reactions.
- (b) Flash photolysis of  $\text{H}_2/\text{O}_2/\text{Ar}$  mixtures. [O] monitored by time-resolved resonance fluorescence under pseudo-first-order conditions of O-atom removal. Total pressures, 0.13–0.79 bar.
- (c) Shock tube study using reflected shocks in  $\text{CH}_4/\text{O}_2/\text{Ar}$  mixtures. [O] and [H] monitored by ARAS.  $k$  derived from numerical simulations using a 27-reaction mechanism. The expression of Pamidimukkala and Skinner, 1982<sup>15</sup> found to be suitable for fitting [O] and [H] profiles. Nominal total pressure, 1.8 bar.
- (d) Flash photolysis of  $\text{H}_2/\text{CO}_2/\text{Ar}$  mixtures in high-temperature photochemical reaction cell. [O] monitored by time-resolved resonance fluorescence under pseudo-first-order conditions of O-atom decay. Total pressures, 0.05–2.0 bar.
- (e) Shock tube study using reflected shocks in  $\text{H}_2/\text{N}_2\text{O}/\text{Ar}$  mixtures. [O] and [H] monitored by ARAS  $k$  derived by numerical simulations of [O] and [H] profiles using a 13-reaction mechanism. Total pressure, 1.4–2.0 bar.
- (f) Flash photolysis of  $\text{H}_2/\text{NO}/\text{Ar}$  mixtures in a heated reaction cell. [O] monitored by time-resolved reso-

nance fluorescence under pseudo-first order conditions of O-atom decay. Total pressure, 0.066–0.13 bar.

- (g) Shock tube study using reflected shocks in  $\text{NO}/\text{H}_2/\text{Ar}$  mixtures and O-atom production by flash photolysis of NO. [O] monitored by ARAS detection under pseudo first order conditions of O-atom decay. Total pressure, 0.3–1.0 bar.
- (h) Pulsed excimer laser photolysis of  $\text{H}_2/\text{O}_2/\text{Ar}$  mixtures. [O] monitored by time-resolved resonance fluorescence under pseudo first order conditions of O-atom decay. Total pressure, 0.39 bar.
- (i) Shock tube study using reflected shocks in lean  $\text{H}_2/\text{O}_2/\text{Ar}$  mixtures. Relative [OH] monitored by cw laser absorption.  $k$  derived by numerical simulations using a 9-reaction mechanism. Total pressure, 1.5–3.0 bar.
- (j) Shock tube study using reflected shocks in  $\text{H}_2/\text{NO}/\text{N}_2\text{O}/\text{Ar}$  mixtures with O atoms produced by excimer laser photolysis of the NO or pyrolysis of  $\text{N}_2\text{O}$ . [O] monitored by time resolved ARAS under pseudo-first-order conditions of O-atom decay. Nominal total pressure, 0.5 bar.
- (k) Shock tube study using reflected shock in  $\text{H}_2/\text{O}_2/\text{Ar}$  and  $\text{H}_2/\text{NO}/\text{Ar}$  mixtures. Relative [OH] monitored by

cw laser absorption.  $k$  derived by numerical simulations using a detailed reaction mechanisms. Total pressure, 1.2–2.2 bar.

- (l) Shock tube study using reflected shock in lean H<sub>2</sub>/O<sub>2</sub>/Ar mixtures. Relative [OH] monitored by cw laser absorption.  $k$  derived by numerical simulations using a 20-reaction mechanism. Total pressure, 1.8–2.1 bar.
- (m) Shock tube study using reflected shocks in N<sub>2</sub>O/H<sub>2</sub>/Ar mixtures at total pressures of ~250 kPa. [O] was monitored by time resolved ARAS at 130.5 nm. Values of  $k$  were derived by fitting the O-atom profiles using a detailed reaction mechanism. Checks were carried out to confirm the sensitivity of [O] to  $k$  under the conditions used.
- (n) See Comments on Preferred Values.
- (o) Adopted recommendation of Sutherland *et al.*, 1988.<sup>6</sup>

### Preferred Values

$$k = [6.34 \cdot 10^{-12} \exp(-4000/T) + 1.46 \cdot 10^{-9} \exp(-9650/T)] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the range } 298\text{--}3300 \text{ K.}$$

### Reliability

$\Delta \log k = \pm 0.2$  over the range 298–3300 K.

### Comments on Preferred Values

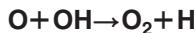
There have been numerous measurements of the rate constant of this reaction and a number of excellent reviews. Baulch *et al.*,<sup>16</sup> and later Cohen and Westberg,<sup>13</sup> evaluated the older data and the recommendations of the latter were adopted in the review of Tsang and Hampson.<sup>17</sup> Cohen and Westberg<sup>13</sup> concluded that the reliable low temperature studies were those of Clyne and Thrush,<sup>18</sup> Hoyermann, Wagner, and Wolfrum,<sup>19</sup> Westenberg and de Haas,<sup>20</sup> Balakhnin *et al.*,<sup>21</sup> Dubinsky and McKenney,<sup>22</sup> Campbell and Thrush,<sup>23</sup> Light and Matsumoto,<sup>24</sup> and Campbell and Handy.<sup>25</sup> At higher temperatures their recommendations were based on the data of Pamidimukkala and Skinner,<sup>15</sup> Frank and Just,<sup>26</sup> and the reanalyzed results of Gutman *et al.*,<sup>27</sup> Schott,<sup>28,32</sup> Jachimowski and Houghton,<sup>29</sup> Getzinger *et al.*,<sup>30</sup> and Brabbs *et al.*<sup>31</sup> Since the review of Cohen and Westberg<sup>13</sup> there have been a number of studies in excellent agreement which have served to define  $k$  much more precisely over a wide temperature range. Only these more recent studies are cited in the table.

In our previous evaluations,<sup>14</sup> for our preferred expression for  $k$  we adopted an expression derived by Sutherland *et al.*<sup>6</sup>

which extrapolates well to higher temperatures being in excellent agreement with the data of Natarajan and Roth<sup>5</sup> and of Javoy *et al.*<sup>12</sup> and also with the expression derived by Natarajan and Roth<sup>5</sup> to cover this high temperature range (1713–3532 K). However, in our present evaluation an alternative expression is used which slightly improves the fit to the lower temperature data.

### References

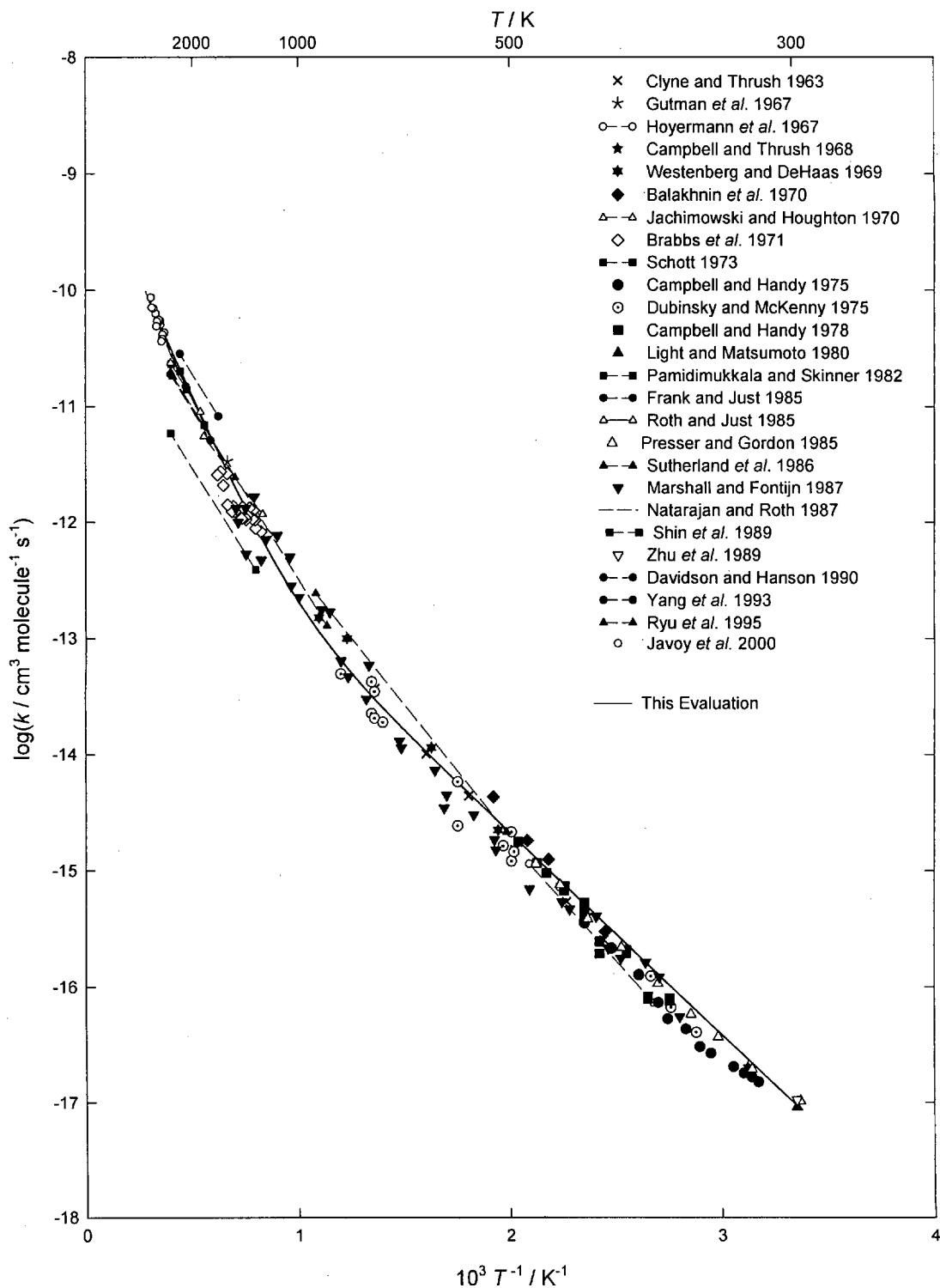
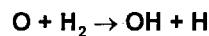
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### Thermodynamic Data

$$\begin{aligned}\Delta H_{298}^{\circ} &= -68.29 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= -25.04 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 3.48 \cdot 10^{-3} T^{0.367} \exp(+8390/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.



## Rate Coefficient Data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$2.0 \cdot 10^{-11} \exp(112/T)$	221–499	Lewis and Watson, 1980 <sup>1</sup>	(a)
$3.8 \cdot 10^{-11}$	298	Howard and Smith, 1980 <sup>2</sup>	(b)
$6.7 \cdot 10^{-10} T^{-0.5}$	250–515	Howard and Smith, 1981 <sup>3</sup>	(b)
$3.1 \cdot 10^{-11}$	300	Brune, Schwab, and Anderson, 1983 <sup>4</sup>	(c)
$3.5 \cdot 10^{-11}$	299	Keyser, 1983 <sup>5</sup>	(d)
$4.2 \cdot 10^{-11}$	294	Smith and Stewart, 1994 <sup>6</sup>	(e)
$4.5 \cdot 10^{-11}$	227		
$5.2 \cdot 10^{-11}$	190		
$6.1 \cdot 10^{-11}$	158		
<i>Reviews and Evaluations</i>			
$5.42 \cdot 10^{-13} T^{0.375} \exp(1112/T)$	1000–5300	Michael, 1992 <sup>7</sup>	(f)
$2.0 \cdot 10^{-11} \exp(112/T)$	220–500	CEC, 1992; 1994 <sup>8</sup>	(g)
$2.4 \cdot 10^{-11}$	1000–2000		
$2.2 \cdot 10^{-11} \exp(120/T)$	220–500	NASA, 1997 <sup>9</sup>	(h)
$2.3 \cdot 10^{-11} \exp(110/T)$	220–500	IUPAC, 1997 <sup>10</sup>	(i)

## Comments

- (a) Discharge flow system with O generated by a discharge in O<sub>2</sub> and OH by the H+NO<sub>2</sub> reaction. [OH] monitored by resonance fluorescence.
- (b) Discharge flow system with O generated by the N+NO reaction and OH by flash photolysis of H<sub>2</sub>O. [OH] monitored by resonance fluorescence.
- (c) Discharge flow study with O atoms in excess over OH. [OH] monitored by LMR and rf, [O] by rf and absorption, and [H] by resonance fluorescence.
- (d) Discharge flow system with HO and HO<sub>2</sub> generated by the reaction of H with NO<sub>2</sub> and O<sub>2</sub>, respectively. A steady state concentration of HO and HI<sub>2</sub> was established in the presence of excess O by the reaction sequence O+HO<sub>2</sub>→HO+O<sub>2</sub>, O+OH→H+O<sub>2</sub>, H+O<sub>2</sub>+M→HO<sub>2</sub>+M. [HO] monitored by rf and [HO<sub>2</sub>] by titration with NO and detection of OH. The measured [HO]/[HO<sub>2</sub>] gives  $k/k(O+HO_2)$ . Value of  $k$  calculated using  $k(O+HO_2)=5.7 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (this evaluation).
- (e) Fast flow system in which OH radicals were created by pulsed laser photolysis at 266 nm of HNO<sub>3</sub> in the presence of a much higher concentration of O atoms previously produced upstream of the HNO<sub>3</sub> injection point by the N+NO reaction. [OH] was monitored by LIF, pumping at ~282.5 nm and observing at ~310 nm. The time delay between the pulse generating OH and the LIF probe pulse was varied. Results were also obtained at 103 K, 50 K, and 10 K but with large uncertainties.
- (f) Calculated from thermodynamic data and  $k(H+O_2)$ .
- (g) Expression of Lewis and Watson<sup>1</sup> adopted for low temperature range and high temperature expression derived from thermodynamic data and  $k(H+O_2)$ .
- (h) Based on the data of Westenberg *et al.*,<sup>11</sup> Lewis and Watson,<sup>1</sup> and Howard and Smith.<sup>3</sup>

(i) Based on the data of Lewis and Watson<sup>1</sup> and Howard and Smith.<sup>3</sup>

## Preferred Values

$$k = 2.00 \cdot 10^{-10} T^{-0.352} \exp(113/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the range 250–3000 K.

## Reliability

$$\Delta \log k = \pm 0.2 \text{ over the range 250–3000 K.}$$

## Comments on Preferred Values

The only direct studies on this reaction have been carried out at low temperatures where there is excellent agreement among the more recent of them.<sup>1–6</sup> There are also a number of older studies<sup>11–18</sup> where the agreement is less good but which generally support the more recent work. The data in this regime have been reviewed by the NASA<sup>9</sup> and IUPAC<sup>11</sup> Panels whose findings are accepted.

Although there have been no direct measurements of  $k$  above 515 K the reverse reaction has been extensively investigated at temperatures in the range 800–3400 K. The preferred expression for  $k$  has been derived, therefore, by a fit to the data obtained by combining the expression for  $k(H+O_2)$  from the present evaluation with the thermodynamic data at temperatures above 800 K together with the directly obtained experimental data at temperatures below 500 K. The reaction has been the subject of a number of theoretical studies; see Miller,<sup>19–21</sup> Troe,<sup>22</sup> Harding *et al.*,<sup>23</sup> and Troe and Ushakov.<sup>24</sup>

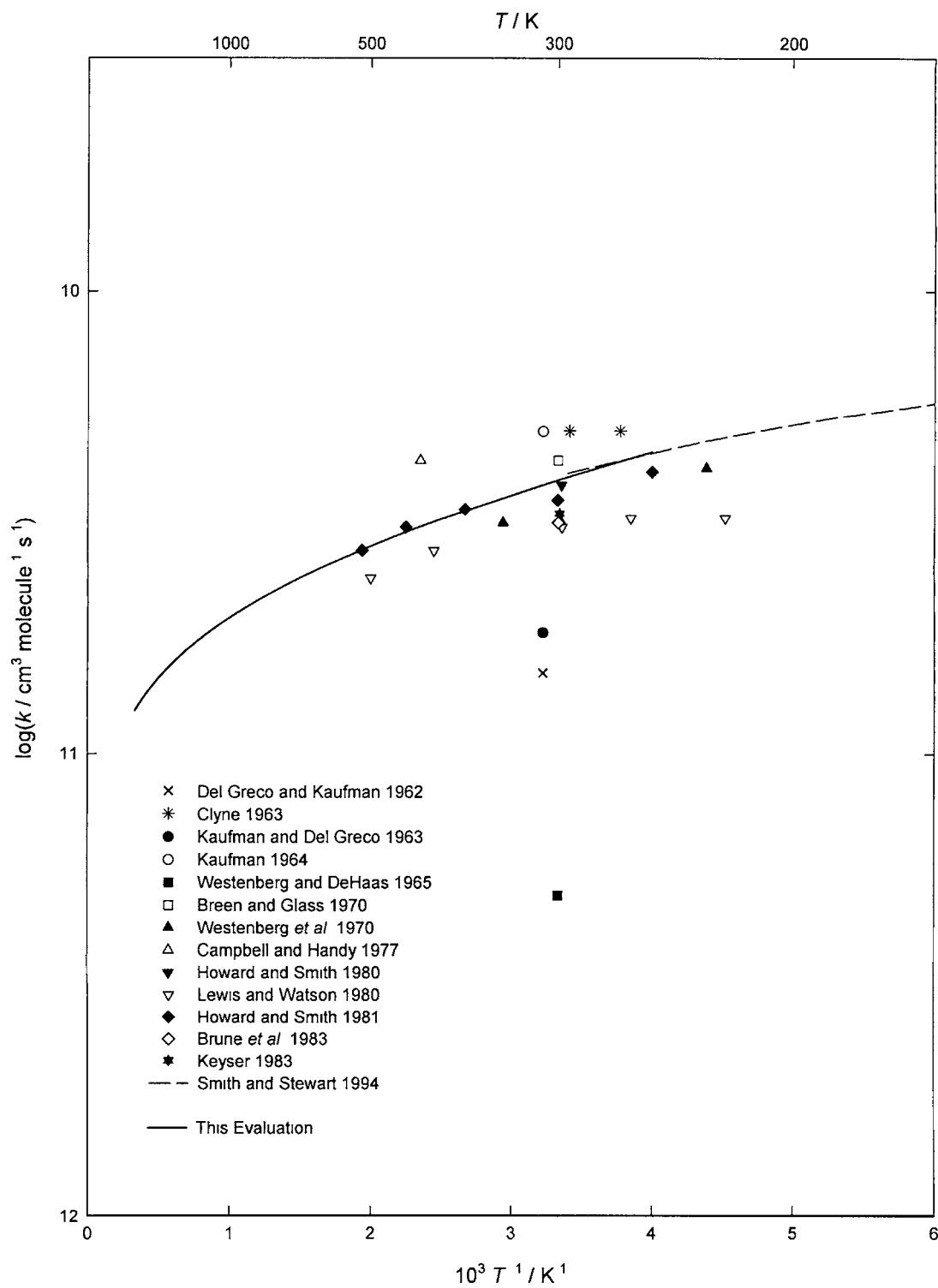
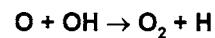
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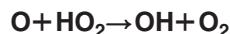
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*Thermodynamic Data*

$$\begin{aligned}\Delta H_{298}^{\circ} &= -223.4 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= -1.28 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 11.1 T^{-0.342} \exp(+26700/T) \\ &\quad (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$5.4 \cdot 10^{-11}$	296	Sridharan, Qiu, and Kaufman, 1982 <sup>1</sup>	(a)
$3.1 \cdot 10^{-11} \exp(200/T)$	230–370	Keyser, 1982 <sup>2</sup>	(b)
$6.2 \cdot 10^{-11}$	298	Ravishankara, Wine, and Nicovich, 1983 <sup>3</sup>	(c)
$5.2 \cdot 10^{-11}$	300	Brune, Schwab, and Anderson, 1983 <sup>4</sup>	(d)
$2.9 \cdot 10^{-11} \exp(228/T)$	266–391	Nicovich and Wine, 1987 <sup>5</sup>	(e)
<i>Reviews and Evaluations</i>			
$2.8 \cdot 10^{-11} \exp(200/T)$	300–1000	Tsang and Hampson, 1986 <sup>6</sup>	(f)
$5.4 \cdot 10^{-11}$	300–1000	CEC, 1992; 1994 <sup>7</sup>	(g)
$3.0 \cdot 10^{-11} \exp(200/T)$	220–400	NASA, 1997 <sup>8</sup>	(h)
$2.7 \cdot 10^{-11} \exp(224/T)$	220–400	IUPAC, 1997 <sup>9</sup>	(i)

**Comments**

- (a) Discharge flow study; HO<sub>2</sub> generated by the F+H<sub>2</sub>O<sub>2</sub> reaction. [H] and [O] monitored by VUV resonance fluorescence, [OH] by LIF, and [HO<sub>2</sub>] by quantitative conversion to OH with an excess of NO.
- (b) Discharge flow study; HO<sub>2</sub> generated by the F+H<sub>2</sub>O<sub>2</sub> reaction. [H], [O], and [OH] monitored by resonance fluorescence and [HO<sub>2</sub>] by quantitative conversion to OH with an excess of NO.
- (c) Pulsed laser photolysis of H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>/N<sub>2</sub> (or Ar) mixtures at 248 nm. [H<sub>2</sub>O<sub>2</sub>] determined by absorption spectroscopy. [O] monitored by time-resolved resonance fluorescence.  $k$  found to be independent of pressure in the range 13–660 mbar.
- (d) Discharge flow study performed with both HO<sub>2</sub> and with O atoms in excess. [OH] monitored by laser magnetic resonance and by absorption, [H] by resonance fluorescence, and [HO<sub>2</sub>] by laser magnetic resonance and by quantitative conversion to OH by an excess of NO.
- (e) Pulsed laser photolysis of H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>/N<sub>2</sub> mixtures. [O] monitored by time-resolved resonance fluorescence. Total pressure, 105 mbar.
- (f) Accepts the evaluation by the CODATA Panel.<sup>10</sup>
- (g) Based on the data of Sridharan *et al.*<sup>1</sup>
- (h) Based on the data in Refs. 1–5.
- (i) Takes the mean value at 298 K from Refs. 1–5 and combines it with the mean value of  $E/R$  from Refs. 2 and 5.

**Preferred Values**

$k = 2.7 \cdot 10^{-11} \exp(224/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 220–1000 K.

*Reliability*

$\Delta \log k = \pm 0.1$  at 220 K, rising to  $\pm 0.5$  at 1000 K.

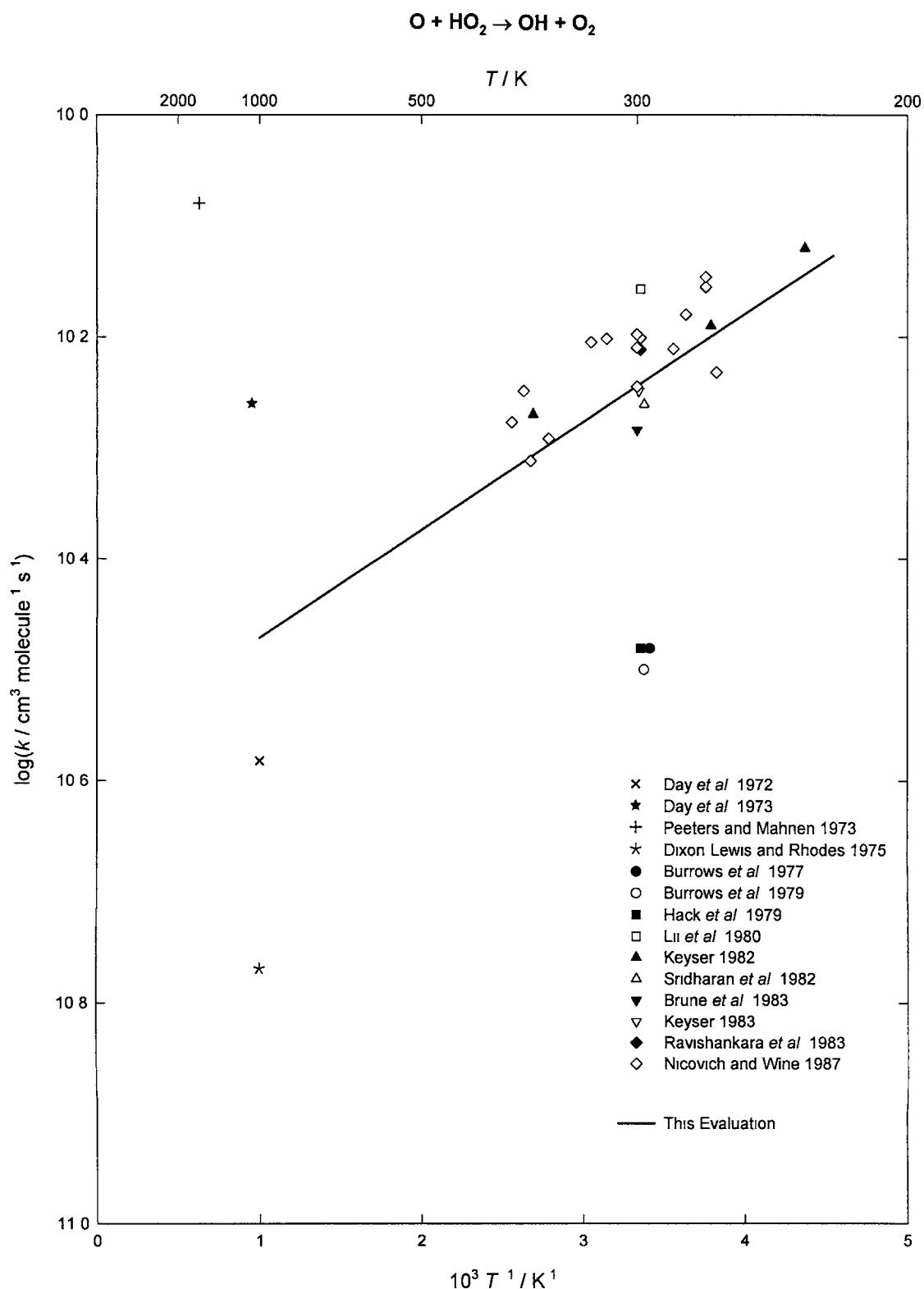
*Comments on Preferred Values*

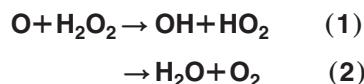
The only reliable data on this reaction have been obtained at low temperatures. All of the low temperature data<sup>1–5,11–16</sup> have been thoroughly evaluated by the NASA and IUPAC Panels. Based on the studies cited in the table, on which we base our preferred expression for  $k$ , they recommend very similar expressions. The only available data at high temperatures have been obtained from flame modelling<sup>17</sup> or are estimates.<sup>18</sup> However, the low temperature data indicate that the temperature coefficient of  $k$  is small. We therefore recommend use of the low temperature Arrhenius expression up to 1000 K with substantial error limits at high temperatures.

A theoretical treatment of the reaction<sup>19</sup> suggests that at low temperatures it will proceed by an addition mechanism giving rise to the negative temperature dependence of  $k$ , as observed experimentally, but at higher temperatures direct abstraction of H may become competitive, and be dominant above 1000 K, which would lead to a positive temperature dependence of  $k$  at high temperatures. The error limits suggested at 1000 K takes into account a possible contribution from abstraction.

**References**

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- <sup>8</sup> NASA Evaluation No. 12, 1997 (see references in Introduction).
- <sup>9</sup> IUPAC, Supplement VI, 1997 (see references in Introduction).
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*Thermodynamic Data*

$$\begin{aligned}\Delta H^\circ_{298}(1) &= -59.9 \text{ kJ mole}^{-1} \\ \Delta S^\circ_{298}(1) &= 17.26 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 2.45 \cdot 10^2 T^{-0.486} \exp(+7000/T) \\ &(300 \leq T/\text{K} \leq 5000)\end{aligned}$$

$$\begin{aligned}\Delta H^\circ_{298}(2) &= -254.7 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(2) &= -1.61 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 61.9 T^{-0.640} \exp(+42470/T) \\ &(200 \leq T/\text{K} \leq 6000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data ( $k = k_1 + k_2$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$2.8 \cdot 10^{-12} \exp(-2125/T)$	283–368	Davis, Wong, and Schiff, 1974 <sup>1</sup>	(a)
$1.1 \cdot 10^{-12} \exp(-2000/T)$	298–386	Wine <i>et al.</i> , 1983 <sup>2</sup>	(b)
<i>Reviews and Evaluations</i>			
$1.1 \cdot 10^{-12} \exp(-2000/T)$	300–500	CEC, 1992; 1994 <sup>3</sup>	(c)
$1.4 \cdot 10^{-12} \exp(-2000/T)$	280–390	NASA, 1997; <sup>4</sup> IUPAC, 1997 <sup>5</sup>	(c)

**Comments**

- (a) O atoms generated by pulsed laser photolysis of O<sub>3</sub> at 600 nm. [O] monitored by resonance fluorescence.
- (b) O atoms generated by pulsed laser photolysis of O<sub>3</sub> at 532 nm. [O] monitored by resonance fluorescence.
- (c) Based on the data of Davis *et al.*<sup>1</sup> and Wine *et al.*<sup>2</sup>

**Preferred Values**

$k = 1.4 \cdot 10^{-12} \exp(-2000/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 283–500 K.

**Reliability**

$\Delta \log k = \pm 0.3$  over the range 283–500 K.

**Comments on Preferred Values**

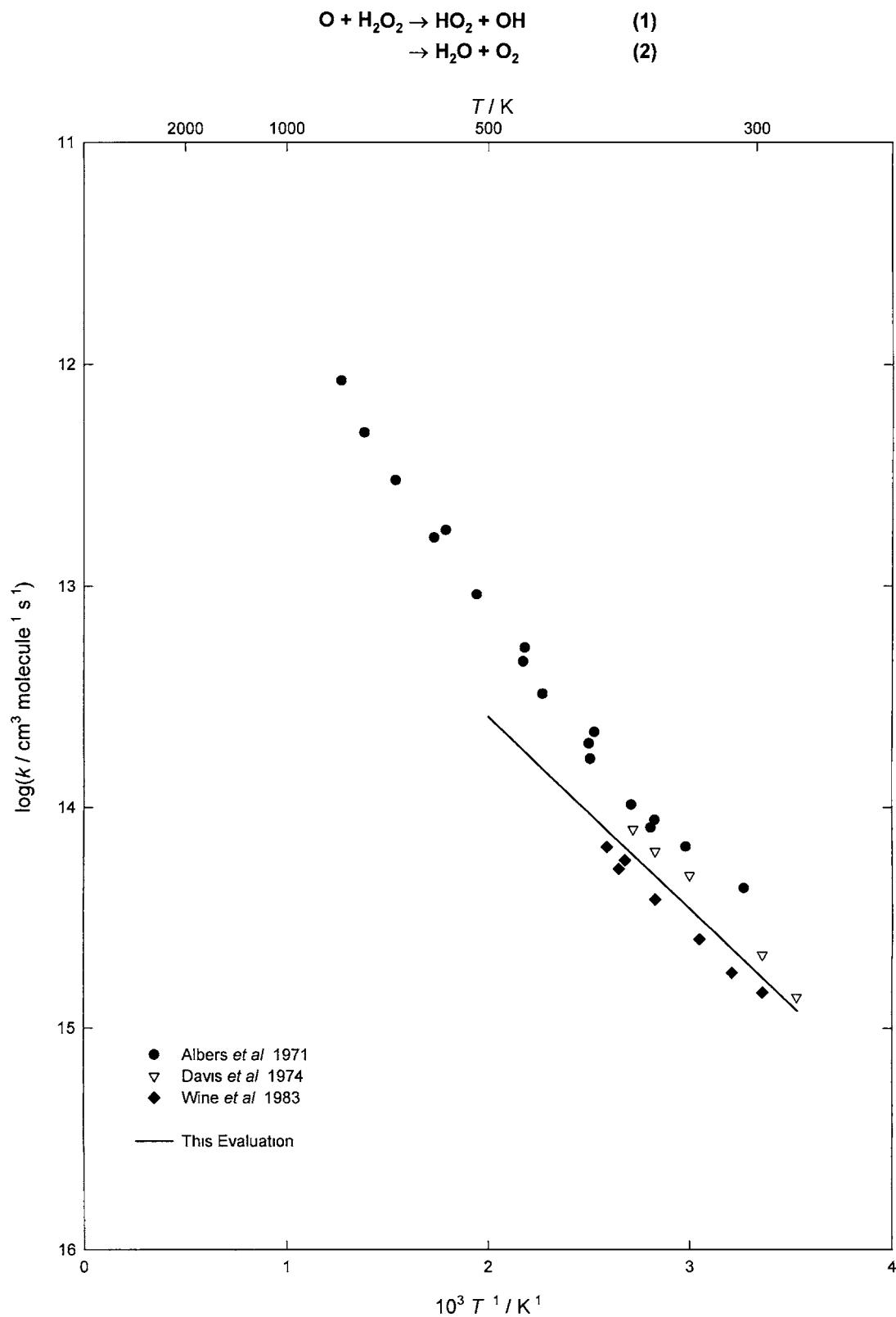
The studies of Davis *et al.*<sup>1</sup> and Wine *et al.*<sup>2</sup> are in excellent agreement on the temperature coefficient of  $k$ , but differ by approximately a factor of 2 in the absolute values of  $k$  obtained throughout the temperature range of their studies. The preferred expression accepts the temperature dependence from the study of Wine *et al.*<sup>2</sup> and combines it with a pre-exponential factor which reproduces the mean value of  $k$

at 298 K obtained from the two studies.<sup>1,2</sup> Roscoe<sup>6</sup> has discussed the early work on this reaction<sup>1,7,8</sup> and, on the basis of his experimental and modeling results, comes to the conclusion that, apart from the study of Davis *et al.*,<sup>1</sup> pre-1982 studies are unreliable due to the effects of secondary chemistry in all of the systems used.

Information on the branching ratios from experiment is indirect and approximate. Albers *et al.*<sup>7</sup> concluded from their measurements on the reaction stoichiometry that  $k_1/k \sim 0.5$ , whereas Roscoe<sup>6</sup> decided that the data from his discharge flow work was best explained by assuming a value of unity for  $k_1/k$ . In the study of Wine *et al.*,<sup>2</sup> their results could be modeled with values  $k_1/k$  in the range 0.4–0.8 and all that could be concluded with certainty was that  $k_1/k > 0.2$ .

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- <sup>3</sup> CEC, 1992; Supplement I, 1994 (see references in Introduction).
- <sup>4</sup> NASA Evaluation No 12, 1997 (see references in Introduction).
- <sup>5</sup> IUPAC, Supplement VI, 1997 (see references in Introduction).
- <sup>6</sup> J. M. Roscoe, *Int. J. Chem. Kinet.* **14**, 471 (1982).
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**O+N<sub>2</sub>→NO+N**

## Thermodynamic Data

$$\begin{aligned}\Delta H_{298}^{\circ} &= 313.8 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= 11.2 \text{ J mol}^{-1} \text{ K}^{-1} \\ K_c &= 1.93 T^{0.093} \exp(-37700/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

<i>k/cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup></i>	<i>T/K</i>	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$3.06 \cdot 10^{-10} \exp(-38370/T)$	2380–3850	Monat, Hanson, and Kruger, 1979 <sup>1</sup>	(a)
$3.0 \cdot 10^{-10} \exp(-38300/T)$	2400–4100	Thielen and Roth, 1984 <sup>2</sup>	(b)
<i>Reviews and Evaluations</i>			
$3.0 \cdot 10^{-10} \exp(-38370/T)$	2000–4000	Hanson and Salimian, 1984 <sup>3</sup>	(c)
$3 \cdot 10^{-10} \exp(-38300/T)$	1400–4000	CEC, 1994 <sup>4</sup>	(d)

**Comments**

- (a) Shock tube study. O atoms generated by pyrolysis of N<sub>2</sub>O in N<sub>2</sub>/O<sub>2</sub>/Kr mixtures optimized to maximize the sensitivity of the results to *k*. [NO] was monitored behind the incident shock wave by infrared (IR) emission at 5.3 μm and absorption of CO laser radiation at 5.17 μm. The [NO] profile was fitted using a 9-step reaction mechanism to derive *k*. Uncertainty estimated to be ±35% over the temperature range.
- (b) Shock tube study. O atoms generated by pyrolysis of N<sub>2</sub>O in N<sub>2</sub>/O<sub>2</sub>/Ar mixtures. [O] and [N] monitored by time resolved ARAS behind reflected shock wave to give values of *k* directly. Uncertainty in *k* estimated to be ±40%.
- (c) Accepts the expression obtained by Monat *et al.*<sup>1</sup>
- (d) Based on the data of Monat *et al.*<sup>1</sup> and Thielen and Roth.<sup>2</sup>

**Preferred Values**

$k = 3.0 \cdot 10^{-10} \exp(-38400/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 1700–4000 K.

**Reliability**

$\Delta \log k = \pm 0.15$  over the range 1700–4000 K.

**Comments on Preferred Values**

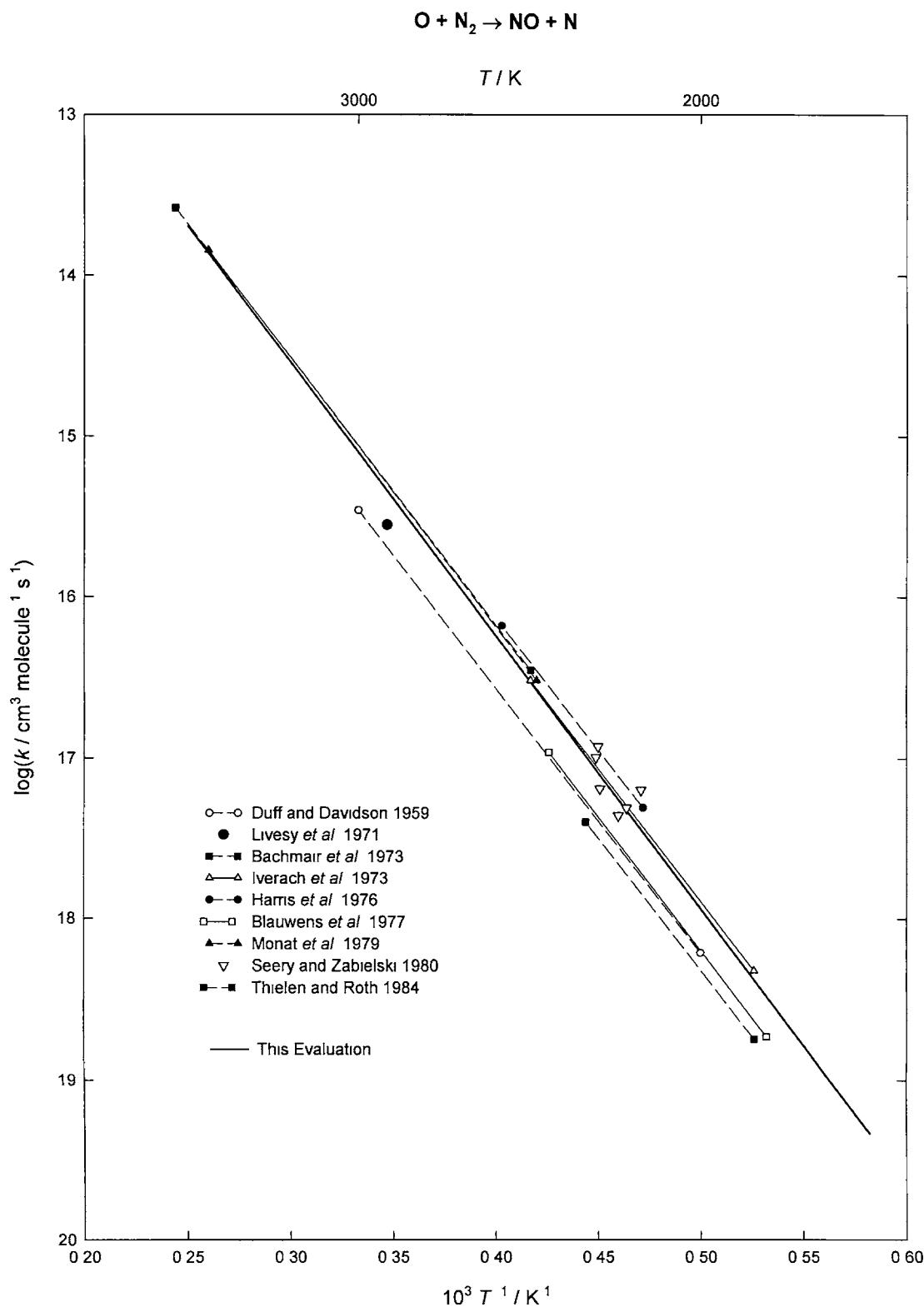
There have been a number of measurements of the rate constant of this reaction<sup>1,2,5–11</sup> which are in excellent agree-

ment on the value of *E/R*, but give absolute values of *k* which scatter over a range of approximately 4. The preferred values are based on the studies of Monat *et al.*<sup>1</sup> and Thielen and Roth<sup>2</sup> which are considered to be the most direct. The preferred expression for *k* is unchanged from our previous evaluation<sup>4</sup> and is virtually identical with that suggested by Hanson and Salimian.<sup>3</sup>

Measurements of the rate constant for the reverse reaction (see this evaluation) are in excellent agreement with these recommendations and the thermodynamic data.

**References**

- <sup>1</sup>J. P. Monat, R. K. Hanson, and C. H. Kruger, Proceedings 17th Symposium (Int.) Combustion, 1979, p. 543.
- <sup>2</sup>K. Thielen and P. Roth, Proceedings 20th Symposium (Int.) Combustion, 1984, p. 685.
- <sup>3</sup>R. K. Hanson and S. Salimian, in *Combustion Chemistry*, edited by W. C. Gardiner (Springer, New York, 1984).
- <sup>4</sup>CEC, 1994 (see references in Introduction).
- <sup>5</sup>R. E. Duff and N. Davidson, J. Chem. Phys. **31**, 1018 (1959).
- <sup>6</sup>J. B. Livesey, A. L. Roberts, and A. Williams, Combust. Sci. Technol. **4**, 9 (1971).
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- <sup>9</sup>R. J. Harris, M. Nasralia, and A. Williams, Combust. Sci. Technol. **14**, 85 (1976).
- <sup>10</sup>J. Blauwens, B. Smets, and J. Peeters, Proceedings 16th Symposium (Int.) Combustion, 1977, p. 1055.
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#### Thermodynamic Data

$$\begin{aligned}\Delta H_{298}^{\circ} &= 133.2 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= -13.37 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 8.13 \cdot 10^{-2} T^{0.117} \exp(-15950/T) \\ &\quad (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$k = 6.03 \cdot 10^{-12} \exp(-19900/T)$	1575–1655	Kaufman and Decker, 1959 <sup>1</sup>	(a)
$k = 6.0 \cdot 10^{-13}$	5000	Wray and Teare, 1962 <sup>2</sup>	(b)
$k = 1.48 \cdot 10^{-14}$	3000	Clark <i>et al.</i> , 1969 <sup>3</sup>	(c)
$k = 3.89 \cdot 10^{-15} T \exp(-19450/T)$	2500–4100	Hanson <i>et al.</i> , 1974 <sup>4</sup>	(d)
$k = 2.89 \cdot 10^{-15} T \exp(-19450/T)$	1750–2100	McCullough, 1977 <sup>5</sup>	(e)
<i>Reviews and Evaluations</i>			
$k = 6.3 \cdot 10^{-15} T \exp(-20850/T)$	1500–5000	Hanson and Salimian, 1984 <sup>6</sup>	(f)
$k = 3 \cdot 10^{-15} T \exp(-19500/T)$	200–2500	Tsang and Herron, 1991 <sup>7</sup>	(g)
$k = 1.14 \cdot 10^{-15} T^{1.13} \exp(-19200/T)$	1000–5000	CEC, 1994 <sup>8</sup>	(h)

#### Comments

- (a) Heated static reactor study using O<sub>2</sub>/NO mixtures in molar ratios in the range 0–40. Unreacted [NO] monitored by UV absorption spectrometry. Equilibrium of O atoms with O<sub>2</sub> was assumed.
- (b) Shock tube study on NO/O<sub>2</sub>/Ar mixtures. [NO] monitored behind the incident shock wave by absorption at 127 nm. The [NO] profile was fitted to a detailed kinetic mechanism but only data acquired in NO/O<sub>2</sub>/Ar = 0.5%/0.25%/99.25% mixtures near 5000 K were sufficiently insensitive to other rate constants to derive values of  $k$ .
- (c) N<sub>2</sub>O decomposition studied using reflected shock waves and mass spectrometric detection of NO, O<sub>2</sub>, and O.  $k$  was derived from the small changes in the measured NO concentration.
- (d) Shock tube study of N<sub>2</sub>O/Ar or N<sub>2</sub>O/Kr mixtures with [NO] monitored by absorption at 5.3  $\mu\text{m}$ . Values of  $k$  were derived by fitting the [NO] profile using a detailed kinetic model.
- (e) Flow tube study of NO/Ar mixtures. [NO] monitored as a function of flow rate by chemiluminescence. Values of  $k$  were derived by detailed modeling of the kinetics and flow.
- (f) Based on the data from Refs. 1–5.
- (g) Accepts the evaluation of Hanson and Salimian.<sup>6</sup>
- (h) Accepts the analysis of Hanson and Salimian<sup>6</sup> and derives a similar expression.

#### Preferred Values

$k = 1.14 \cdot 10^{-15} T^{1.13} \exp(-19200/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 1500–5000 K.

#### Reliability

$\Delta \log k = \pm 0.3$  over the range 1500–5000 K.

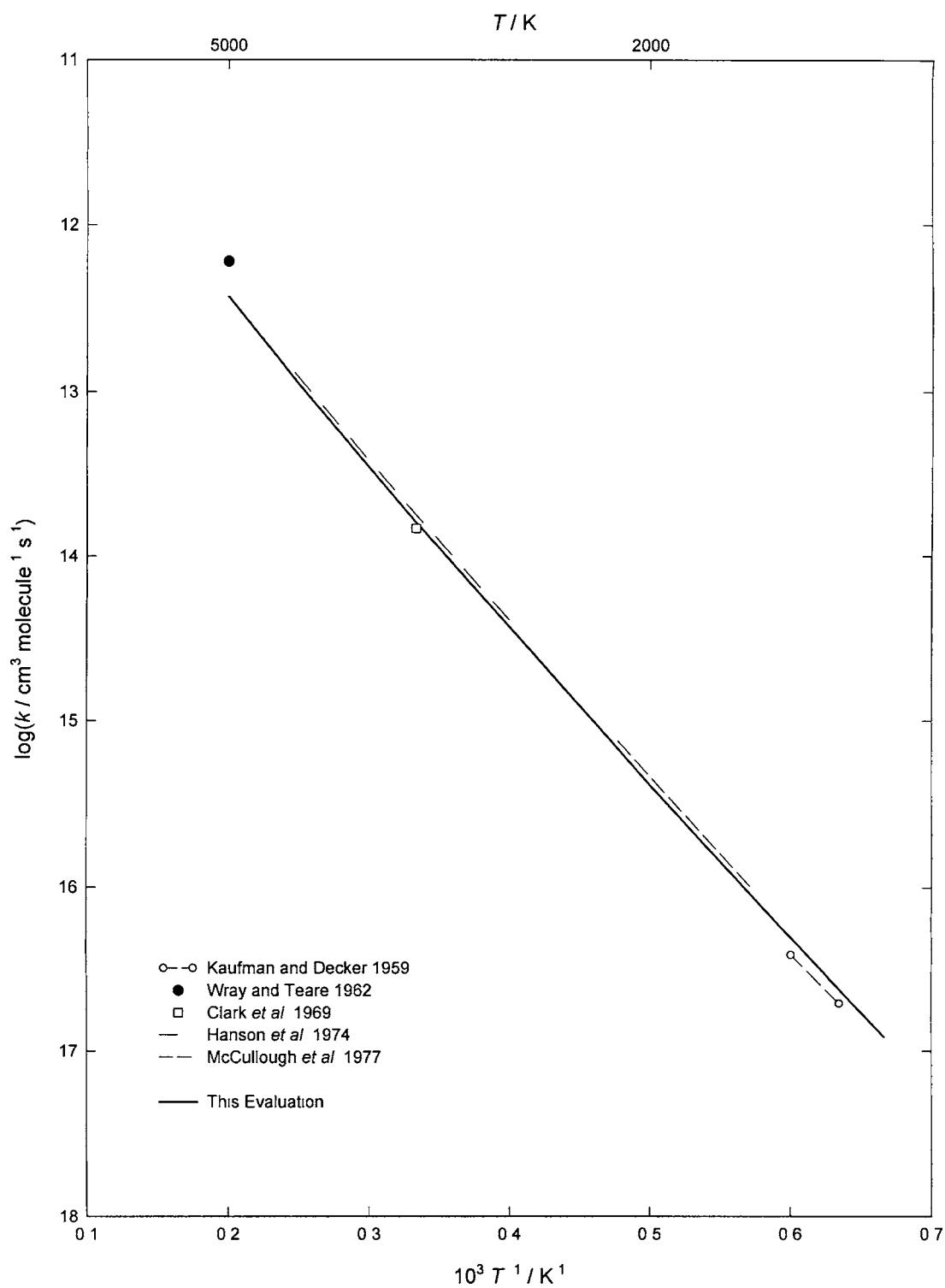
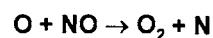
#### Comments on Preferred Values

There have been no new studies of this reaction since our previous evaluation<sup>8</sup> and our Preferred Values are unchanged. The kinetics of the reaction can only be studied conveniently at high temperatures and all of the available data have been obtained at temperatures above 1500 K. These studies, all of which are cited in the Table, are in good agreement. The data have been reviewed previously by Hanson and Salimian,<sup>6</sup> Tsang and Herron,<sup>7</sup> and by Cohen<sup>9</sup> all of whom derive expressions for  $k$  very similar to that suggested here. There has also been a theoretical treatment of the reaction<sup>10</sup> in which the potential energy surface and kinetic properties have been analyzed and  $k$  estimated from the kinetics of the reverse reaction.

At low temperatures the reaction proceeds by the addition channel, O+NO(+M)→NO<sub>2</sub>(+M), the data for which are evaluated in the data sheet which follows the present one.

#### References

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**O+NO(+M)→NO<sub>2</sub>(+M)***Thermodynamic Data*

$$\Delta H_{298}^{\circ} = -306.4 \text{ kJ mol}^{-1}$$

$$\Delta S_{298}^{\circ} = -131.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c = 1.28 \cdot 10^{-28} T^{0.622} \exp(+36930/T) \text{ cm}^3 \text{ molecule}^{-1}$$

$$(300 \leq T/\text{K} \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	[M]/molecule cm <sup>-3</sup>	Reference	Comments
<i>Rate Coefficient Measurements</i>				
<i>Low Pressure Range</i>				
$[\text{Ar}] 2.1 \cdot 10^{-33} (T/2000)^{-1.8}$	1450–2200	$(9.0\text{--}1506) \cdot 10^{18}$	Troe, 1969 <sup>1</sup>	(a)
$[\text{Ar}] 6.0 \cdot 10^{-32}$	296	$3.3 \cdot 10^{17}$	Slinger, Wood, and Black, 1973 <sup>2</sup>	(b)
$[\text{Ar}] 1.3 \cdot 10^{-31}$	241			
$[\text{N}_2\text{O}] 2.6 \cdot 10^{-32} \exp(-450/T)$	300–392	$(1.3\text{--}2.2) \cdot 10^{18}$	Atkinson and Pitts, 1974 <sup>3</sup>	(c)
$[\text{N}_2] 7.4 \cdot 10^{-32}$	295		Hippler, Schippert, and Troe, 1975 <sup>4</sup>	(d)
$[\text{Ar}] 8.3 \cdot 10^{-32}$				
$[\text{N}_2\text{O}] 1.7 \cdot 10^{-32} \exp(+620/T)$	298–473	$(6.1\text{--}23) \cdot 10^{17}$	Singleton <i>et al.</i> , 1975 <sup>5</sup>	(e)
$[\text{N}_2] 5.0 \cdot 10^{-33} \exp(+900/T)$	285–425	$(6.8\text{--}10) \cdot 10^{15}$	Campbell and Handy, 1976 <sup>6</sup>	(f)
$[\text{N}_2] 1.55 \cdot 10^{-32} \exp(+1160/T)$	217–500	$(4.5\text{--}23) \cdot 10^{17}$	Whytock, Michael, and Payne, 1976 <sup>7</sup>	(g)
$[\text{He}] 1.08 \cdot 10^{-32} \exp(+520/T)$	217–250	$(1.2\text{--}77) \cdot 10^{17}$	Michael, Payne, and Whytock, 1976 <sup>8</sup>	(h)
$[\text{Ne}] 9.33 \cdot 10^{-33} \exp(+515/T)$				
$[\text{Ar}] 9.01 \cdot 10^{-33} \exp(+590/T)$				
$[\text{Ar}] 6.4 \cdot 10^{-32}$	300			
$[\text{Kr}] 9.52 \cdot 10^{-32} \exp(+570/T)$				
$[\text{Ar}] 1.46 \cdot 10^{-32} \exp(+473/T)$	298–439	$(5.7\text{--}8.4) \cdot 10^{17}$	Atkinson, Perry, and Pitts, 1977 <sup>9</sup>	(i)
$[\text{Ar}] 7.04 \cdot 10^{-32}$	298			
$[\text{Ar}] 2.6 \cdot 10^{-33} (T/2000)^{-1.8}$	1600–2200	$(4.2\text{--}30) \cdot 10^{18}$	Endo, Glänzer, and Troe, 1979 <sup>10</sup>	(j)
$[\text{Ar}] 4.2 \cdot 10^{-33} (T/2000)^{-1.8}$	1600–1900			
$[\text{Ar}] 1.27 \cdot 10^{-32} \exp(+508/T)$	240–360		Anderson and Stephens, 1979 <sup>11</sup>	(k)
$[\text{N}_2] 7.7 \cdot 10^{-32}$	298	$(9.7\text{--}32) \cdot 10^{18}$	Sugawara, Ishikawa, and Sato, 1980 <sup>12</sup>	(l)
$[\text{N}_2] 8.8 \cdot 10^{-32} (T/300)^{-1.44}$	200–370	$(1.8\text{--}35) \cdot 10^{17}$	Schieferstein, Kohse-Höinghaus, and Stuhl, 1983 <sup>13</sup>	(m)
$[\text{Ar}] 6.7 \cdot 10^{-32} (T/300)^{-1.41}$	300–1341	$(2.2\text{--}97) \cdot 10^{17}$	Yarwood <i>et al.</i> , 1991 <sup>14</sup>	(n)
<i>High Pressure Range</i>				
$\geq 4.0 \cdot 10^{-11}$	1500	$(9.0\text{--}1506) \cdot 10^{18}$ (Ar)	Troe, 1969 <sup>1</sup>	(a)
$3.0 \cdot 10^{-11}$	295		Hippler, Schippert, and Troe, 1975 <sup>4</sup>	(d)
$5 \cdot 10^{-11} (T/300)^{-0.4}$	200–300		Hippler <i>et al.</i> , 1999 <sup>15</sup>	(o)
<i>Reviews and Evaluations</i>				
$k_0[\text{Ar}] = [\text{Ar}] 3.0 \cdot 10^{-33} \exp(+940/T)$	220–500		Baulch <i>et al.</i> , 1973 <sup>16</sup>	(p)
$k_0[\text{N}_2] = [\text{N}_2] 9.6 \cdot 10^{-32}$	300			
$k_0[\text{air}] = [\text{air}] 9.0 \cdot 10^{-32} (T/300)^{-1.5}$	200–370		NASA, 1997 <sup>17</sup>	(q)
$k_0[\text{N}_2] = [\text{N}_2] 1.0 \cdot 10^{-31} (T/300)^{-1.6}$	200–300		IUPAC, 1997 <sup>18</sup>	(r)
$k_\infty = 3.0 \cdot 10^{-11} (T/300)^{0.3}$	200–1500			
$F_c(\text{N}_2) = \exp(-T/1850)$	200–300			

**Comments**

- (a) Shock wave study of the dissociation of NO<sub>2</sub>. [NO<sub>2</sub>] monitored by absorption at 400 or 562 nm. Recombination rate coefficients obtained via equilibrium constant.
- (b) O atoms generated by O<sub>2</sub> photolysis at 147 nm and detected by the chemiluminescence generated following the reaction O+NO.

- (c) O atoms generated by Hg sensitization of N<sub>2</sub>O. Analysis carried out by the modulation-phase shift technique monitoring the NO<sub>2</sub> afterglow emission at  $\lambda > 450$  nm.
- (d) Photolysis of NO<sub>2</sub> in presence of NO, [NO<sub>2</sub>] determined from absorption of photolyzing radiation.  $k/k(\text{O+NO}_2) = 9.3 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Relative efficiencies;

$\text{He:Ne:Ar:CO:N}_2:\text{CO}_2:\text{CH}_4:\text{C}_2\text{H}_6:\text{c-C}_3\text{H}_6:\text{C}_3\text{F}_8:\text{SF}_6 = 2.1:1.7:3.0:3.3:2.7:5.0:5.3:4.5:5.3:6.2:5.5$ , respectively.

- (e) Modulated Hg photosensitized decomposition of  $\text{N}_2\text{O}$  used to generate O atoms. Rate coefficients obtained by phase shift measurements of  $\text{NO}_2$  chemiluminescence monitored at 254 nm.
- (f) Measurements of air afterglow chemiluminescence in  $\text{N}_2$  carrier in a discharge flow stirred reactor.
- (g) Flash photolysis of NO at 142 nm with time resolved detection of O atoms by resonance fluorescence.
- (h) O atoms generated by flash photolysis of NO at 142 nm and detected by resonance fluorescence.
- (i) O atoms formed after flash photolysis of  $\text{O}_2$  and detected by the  $\text{O}+\text{NO}$  chemiluminescent reaction.
- (j) Thermal dissociation of  $\text{NO}_2$  studied behind reflected shock waves.  $[\text{NO}_2]$  decay followed by absorption at 405 nm. Theoretical analysis of weak collision effects for several bath gases. Recombination rate coefficients obtained via equilibrium constant.
- (k) O atoms formed by vacuum UV flash photolysis of NO and detected by  $\text{NO}_2$  chemiluminescence produced following the reaction  $\text{O}+\text{NO}$ .
- (l) Pulse radiolysis of  $\text{N}_2$  and NO mixtures; O atoms were measured by resonance emission.
- (m) Laser flash photolysis of NO at 160 nm was employed to generate O atoms.  $\text{NO}_2$  formation detected by  $\text{NO}_2$  chemiluminescence. Relative efficiencies of  $\text{M}; \text{N}_2:\text{He:NO:CH}_4 = 1.00:0.70:1.43:1.31$ , respectively.
- (n) Flash photolysis of NO over the range 300–1000 K; O atoms monitored by resonance fluorescence. Between 915 K and 1341 K a flash photolysis-shock tube technique was employed in which O atoms were detected by atomic resonance absorption spectroscopy. Collisional efficiencies  $\beta_c = 0.29, 0.26, 0.18$ , and 0.16 were derived at 300, 400, 1000, and 2000 K, respectively.
- (o) Laser flash photolysis study performed at 200, 300 and 400 K and at pressures between 2 and 200 bar  $\text{N}_2$ . O atoms generated by photolysis of  $\text{N}_2\text{O}$  at 193 nm.  $\text{NO}_2$  monitored by absorption at 405 nm. Neglecting the effects of the onset of diffusion control at high pressures, values of  $4.7 \cdot 10^{-11}, 4.0 \cdot 10^{-11}$ , and  $3.6 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  were obtained for  $k_\infty$  by extrapolations at 200, 300, and 400 K, respectively. The  $k_\infty$  values listed in the Table have been corrected for diffusional effects.
- (p) Evaluation of literature data up to 1972. Recommendations based on the results of Clyne and Thrush,<sup>20</sup> Kaufman and Kelso,<sup>21</sup> Hartley and Thrush,<sup>22</sup> Klein and Herron,<sup>23</sup> Atkinson and Cvitanovic;<sup>24</sup> relative efficiencies of  $\text{M}; \text{O}_2:\text{N}_2 = 1.0:1.4$ .
- (q) Recommendation based on the results of Schieferstein, Kohse-Höinghaus, and Stuhl<sup>13</sup> and their reanalysis of the data of Whytock, Michael, and Payne.<sup>7</sup>
- (r) Recommendation based on the data from Whytock, Michael, and Payne,<sup>7</sup> Michael, Payne, and Whytock,<sup>8</sup>

Anderson and Stephens,<sup>11</sup> Schieferstein, Kohse-Höinghaus, and Stuhl,<sup>13</sup> and Yarwood *et al.*<sup>14</sup>

## Preferred Values

$k_0 = 9.2 \cdot 10^{-28} T^{-1.6} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  for  $\text{M}=\text{N}_2$  over the range 200–2200 K.

$k_0 = 6.3 \cdot 10^{-28} T^{-1.6} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  for  $\text{M}=\text{Ar}$  over the range 200–2200 K.

$k_\infty = 4.9 \cdot 10^{-10} T^{-0.4} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 200–2200 K.

$F_c = 0.8$  for  $\text{M}=\text{N}_2$  over the range 200–2200 K.

$F_c = 0.8$  for  $\text{M}=\text{Ar}$  over the range 200–2200 K.

## Reliability

$\Delta \log k_0 = \pm 0.3$  for  $\text{M}=\text{N}_2$  over the range 200–2200 K.

$\Delta \log k_0 = \pm 0.3$  for  $\text{M}=\text{Ar}$  over the range 200–2200 K.

$\Delta \log k_\infty = \pm 0.3$  over the range 200–1000 K and  $\pm 0.5$  over the range 1000–2200 K.

$\Delta F_c = \pm 0.2$  for  $\text{M}=\text{N}_2$  over the range 200–2200 K.

$\Delta F_c = \pm 0.2$  for  $\text{M}=\text{Ar}$  over the range 200–2200 K.

## Comments on Preferred Values

Values for  $k_0$  for  $\text{M}=\text{N}_2$  have been obtained by combining the data from the IUPAC compilation<sup>18</sup> with the measurements of Endo, Glänzer, and Troe;<sup>10</sup> expressions for  $k_0$  for  $\text{M}=\text{Ar}$  are based on the measurements of Michael, Payne, and Whytock,<sup>8</sup> Atkinson, Perry, and Pitts,<sup>9</sup> Anderson and Stephens,<sup>11</sup> Yarwood *et al.*,<sup>14</sup> and Endo, Glänzer, and Troe.<sup>10</sup> The preferred value of  $k_\infty$  and of  $F_c$  are based on the measurements of Hippler *et al.*<sup>15</sup> which are supported by theoretical work from Harding *et al.*<sup>19</sup>

At high temperatures the reaction proceeds by the bimolecular channel,  $\text{O}+\text{NO} \rightarrow \text{O}_2+\text{N}$ , the data for which are evaluated on the data sheet preceding the present one.

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#### Thermodynamic Data

$$\begin{aligned}\Delta H^\circ_{298}(1) &= -150.6 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(1) &= 40.4 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 5.9 \cdot 10^4 T^{-0.883} \exp(+17790/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

$$\begin{aligned}\Delta H^\circ_{298}(2) &= -331.2 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(2) &= 15.7 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 2.48 \cdot 10^3 T^{-0.865} \exp(+39540/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$k_1 = k_2 = 7.5 \cdot 10^{-11} \exp(-12130/T)$	1640–3100	Soloukhin, 1972 <sup>1</sup>	(a)
$k_1 = 5.1 \cdot 10^{-11} \exp(-10971/T)$	2380–4080	Monat, Hanson, and Kruger, 1979 <sup>2,3</sup>	(b)
$1.42 \cdot 10^{-10} \exp(-12350/T)$	1680–2000	Sulzmann, Kline, and Penner, 1980 <sup>4</sup>	(c)
$k_1 = 2.32 \cdot 10^{-10} \exp(-15112/T)$	1700–2500	Zaslonko <i>et al.</i> , 1980 <sup>5</sup>	(d)
$k_1 = 4.8 \cdot 10^{-11} \exp(-11650/T)$	1680–2430	Davidson <i>et al.</i> , 1992 <sup>6</sup>	(e)
$k_2 = 2.3 \cdot 10^{-12} \exp(-5440/T)$	1940–3340		
$3.2 \cdot 10^{-11} \exp(-9686/T)$	1075–1140	Fontijn <i>et al.</i> , 2000 <sup>7</sup>	(f)
<i>Branching Ratio Measurements</i>			
See Fig. 2 and Comments on Preferred Values.			
<i>Reviews and Evaluations</i>			
$k_1 = k_2 = 1.7 \cdot 10^{-10} \exp(-14100/T)$	1200–2000	Baulch <i>et al.</i> , 1973 <sup>8</sup>	(g)
$k_1 = 1.15 \cdot 10^{-10} \exp(-13400/T)$	1200–4100	Hanson and Salimian, 1985 <sup>9</sup>	(h)
$k_2 = 1.7 \cdot 10^{-10} \exp(-14100/T)$	1200–3200	Tsang and Herron, 1991 <sup>10</sup>	(i)
$k_1 = 1.1 \cdot 10^{-10} \exp(-13400/T)$	1370–4080	Meagher and Anderson, 2000 <sup>11</sup>	(j)
$k_2 = 1.7 \cdot 10^{-10} \exp(-14100/T)$	1075–3340		

#### Comments

- (a) Shock tube study using incident and reflected shock waves in  $\text{N}_2\text{O}/\text{Ar}$  mixtures.  $[\text{N}_2\text{O}]$  monitored by luminescence at  $4.5 \mu\text{m}$ .  $k_1 = k_2$  was assumed and  $[\text{N}_2\text{O}]$  profiles were used to calculate values of the rate constants. This is effectively a determination of  $k (=k_1 + k_2)$ .
- (b) The cited expression is based on results from two shock tube studies. In the first, incident shock waves in mixtures of  $\text{N}_2\text{O}$  and various diluent gases ( $\text{Ar}, \text{Kr}, \text{N}_2, \text{O}_2$ ) were used.  $[\text{NO}]$  and  $[\text{N}_2\text{O}]$  were monitored by infrared emission at  $5.3 \mu\text{m}$  and  $4.5 \mu\text{m}$ , respectively, and a detailed kinetic model was used in deriving rate

constants from the  $[\text{N}_2\text{O}]$  and  $[\text{NO}]$  profiles. In the second study, which was also aimed at measuring the rate constant for the reaction  $\text{N}_2 + \text{O} \rightarrow \text{NO} + \text{N}$ ,  $\text{N}_2/\text{O}_2/\text{N}_2\text{O}/\text{Kr}$  mixtures were used.  $[\text{NO}]$  profiles were determined by monitoring infrared emissions at  $5.3 \mu\text{m}$  and by laser absorption at  $5.3 \mu\text{m}$ .

(c) Reflected shock waves in  $\text{N}_2\text{O}/\text{Ar}$  mixtures.  $[\text{N}_2\text{O}]$  monitored by infrared emission at  $4.52 \mu\text{m}$  and  $[\text{NO}]$  by UV absorption at  $226 \text{ nm}$ . As well as the expression for  $k$ , values of  $k_1/k_2$  were obtained giving  $k_1/k_2 = 0.92$  over the whole temperature range.

(d) Shock tube studies on  $\text{N}_2\text{O}/\text{CO}/\text{N}_2$ ,  $\text{He}$ , or  $\text{Ar}$  mixtures.  $[\text{N}_2\text{O}]$  and  $[\text{NO}]$  monitored by UV absorption at  $\sim 240 \text{ nm}$  and  $214.4 \text{ nm}$ , respectively. When  $\text{CO}$  was

- present,  $[O]$  was monitored using emissions at 405 nm from the O+CO combination reaction.  $k_1/k_2 = 5.4 \exp(-4030/T)$  was also derived.
- (e) Shock tube study on  $N_2O/Ar$  mixtures.  $[O_2]$  and  $[NO]$  monitored by laser absorption at 227.35 and 225.36 nm, respectively. In a later study from the same laboratory Rohrig *et al.*<sup>12</sup> find that the expression for  $k_2$  does not give good agreement with their studies of  $N_2O$  decomposition and prefer to use the values of  $k_1$  and  $k_2$  recommended by Hanson and Salimian.<sup>9</sup>
  - (f) Fast flow system used in which O atoms were generated by laser photolysis at 193 nm of  $SO_2$  or by broad band flash photolysis of  $SO_2$  (through a Supracil window) or  $O_2$  (through a quartz window).  $[O]$  was monitored by resonance fluorescence at 130.2–130.6 nm in the presence of a large excess of  $N_2O$ . The carrier gas was Argon at pressures in the range 130–500 mbar. The effects of traces of  $H_2O$  on the system were also studied.
  - (g) Expression for  $k_1$  based largely on the data of Fenimore and Jones.<sup>13</sup> Expression for  $k_2$  based on data for  $k_1/k_2$ .<sup>14–17</sup>
  - (h) As well as data available for the evaluation of Baulch *et al.*<sup>8</sup> the subsequent data of Nip,<sup>18</sup> Dove *et al.*,<sup>19</sup> Monat,<sup>20</sup> Dean and Steiner,<sup>21</sup> and Sulzmann *et al.*<sup>4</sup> are considered together with data on the reverse reaction. Expression for  $k_2$  of Baulch *et al.*<sup>8</sup> accepted but that for  $k_1$  modified slightly.
  - (i) The data available to Hanson and Salimian<sup>9</sup> together with the data of Hidaka *et al.*<sup>22</sup> were reviewed. Data of Hidaka *et al.*<sup>22</sup> considered to be erroneously high. Recommendations of Hanson and Salimian<sup>9</sup> accepted.
  - (j) Detailed review of the available data and previous evaluations. The recommendations from this review are the basis of our preferred values. See comments on Preferred Values.

### Preferred Values

$k_1 = 1.5 \cdot 10^{-10} \exp(-13930/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 1000–4000 K.

$k_2 = 6.1 \cdot 10^{-12} \exp(-8020/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 1000–2500 K.

### Reliability

$\Delta \log k_1 = \pm 0.2$  at 2000 K, rising to  $\pm 0.3$  at 4000 K and  $\pm 0.4$  at 1000 K.

$\Delta \log k_2 = \pm 0.2$  at 2000 K, rising to  $\pm 0.5$  at 1000 K and 2500 K.

### Comments on Preferred Values

The reaction of atomic oxygen with  $N_2O$  is very slow at ambient temperatures. Measurements of the rate constant<sup>1–7,13,16,17,19–27</sup> are only available for temperatures greater than 1000 K and the majority have been derived from shock tube or flame studies.

All of the studies have used the pyrolysis of  $N_2O$  as the O atom source and, in one case,<sup>25</sup>  $O_3$  was added to enhance and vary the O atom concentration. In most cases  $[N_2O]$  and  $[NO]$  were monitored and values of  $k$  and/or  $k_1$  derived. Most of the information on  $k_2$  comes from a knowledge of either  $k$  or  $k_1$  together with a measurement of  $k_1/k_2$ , usually from a determination of the  $O_2$  and  $N_2$  yields. There have been very few attempts to carry out time resolved studies of  $O_2$  production. Consequently the largest, and most consistent bodies of data pertain to  $k_1$  and  $k$ . All of the relevant studies have been carefully and critically reviewed by Meagher and Anderson.<sup>11</sup> Meagher and Anderson<sup>11</sup> show that the interpretation in most of the early studies is inadequate because of lack of reliable information on the secondary chemistry involved and, where possible, they have remodeled many of these systems using more recent rate data. We accept their conclusion and cite in the Table the studies that their analyses show to be the most reliable.

The data for  $k_1$  are shown in the Arrhenius diagram, Fig 1. Included there are values which have been derived from determinations of  $k$  and  $k_1/k_2$  in the same study. The preferred expression, also shown there, is that derived by Meagher and Anderson.<sup>11</sup> It is very similar to the expressions recommended in a number of previous evaluations.<sup>8–10</sup>

In principle it should also be possible to derive values of  $k_1$  from thermodynamic data and values of  $k_{-1}$ . However data on the reverse reaction are limited and the errors limits on the data are comparable with those on  $k_1$ . Meagher and Anderson<sup>11</sup> have also critically assessed the available data for  $k_{-1}$  and conclude that the studies of Kaufman *et al.*,<sup>28</sup> McCullough *et al.*,<sup>29</sup> Koshi and Asaba,<sup>30</sup> and Thielen and Roth<sup>31</sup> are the most reliable. These give an expression for  $k_{-1}$  which, when combined with the thermodynamic data, give values of  $k_1$  agreeing to better than a factor of 2 with those from the preferred expression. This is well within the error limits of the expressions for  $k_1$ ,  $k_{-1}$ , and  $K(1)$ , and gives strong support for the expression for  $k_1$  derived from the measured values.

Reliable information on  $k_2$  is extremely sparse. The experimental data for  $k_1/k_2$  are displayed in Fig. 2.<sup>4–6,14–18,22,23,26,27,32–34</sup> The error limits on most of the studies are substantial, typically  $\pm 20\%$ , often greater, and the scatter is large. Most of the experimental studies were interpreted satisfactorily on the basis of  $k_1 \approx k_2$  over a wide temperature range but Barton and Dove<sup>14</sup> observed a tendency for  $k_1/k_2$  to rise with increase in temperature and Zaslonko *et al.*<sup>5</sup> have given an expression for  $k_1/k_2$  which changes very rapidly with temperature. Further, values of  $k_1/k_2$  derived from the individual expressions for  $k_1$  and  $k_2$  obtained by Davidson *et al.*,<sup>6</sup> show a marked temperature dependence and the values of  $k$  obtained by Fontijn *et al.*<sup>7</sup> at  $\sim 1100$  K, when combined with the preferred expression for  $k_1$ , gives values of  $k_1/k_2$  of  $\sim 0.1$ . Meagher and Anderson<sup>11</sup> have used the data of Fontijn *et al.*<sup>7</sup> and Davidson *et al.*<sup>6</sup> to derive the expression for  $k_2$  cited in the Table. The expression so derived implies that  $k_1 = k_2$  at  $\sim 1850$  K, in accord with the general agreement among a number of studies in this tem-

perature region, but that channel (2) becomes dominant at low temperatures and channel (1) is the major channel at high temperatures. We accept the expression of Meagher and Anderson<sup>11</sup> as the most reliable assessment of  $k_2$  available but it should be noted (i) some doubt has been cast on the expression for  $k_2$  obtained by Davidson *et al.*<sup>7</sup> (and hence  $k_1/k_2$ ) by work in the same laboratory by Rohrig *et al.*<sup>12</sup> [see Comment (e)]. (ii) Dindi *et al.*<sup>27</sup> were able to model successfully the measured concentration profiles of CO, N<sub>2</sub>O, CO<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, and NO in their N<sub>2</sub>O/CO flames using  $k_1=k_2$  over the temperature range 1000–2000 K. (iii) in a low temperature (1245–1395 K) shock tube study of N<sub>2</sub>O decomposition,<sup>29</sup> values of  $k$  estimated from the measured [O] atom profiles were much lower than could be explained by the present, or previous, recommendations. Substantial error limits are therefore assigned to the expression for  $k_2$  at the extremes of its range.

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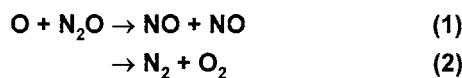
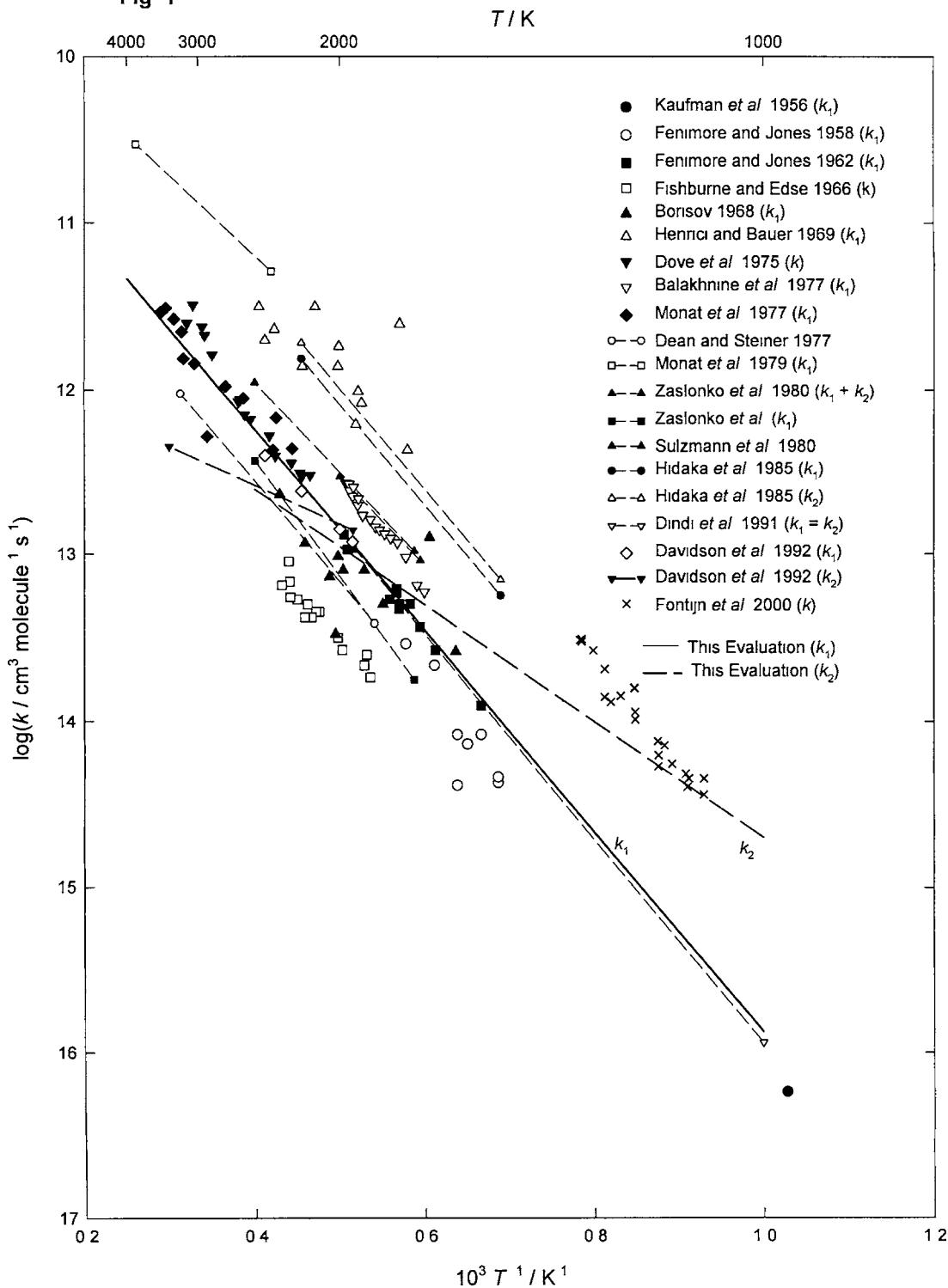


Fig. 1



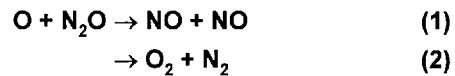
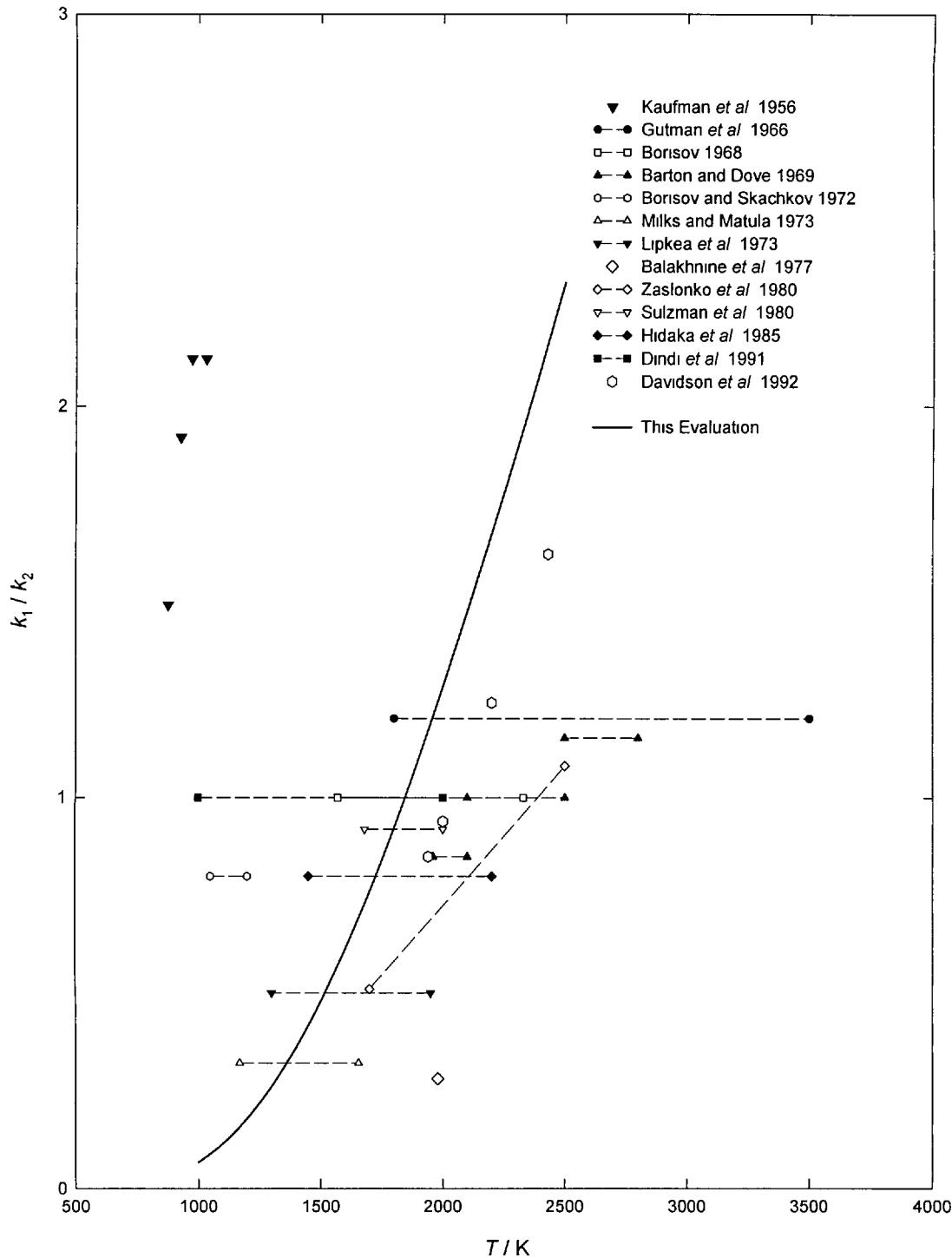


Fig. 2



*Thermodynamic Data*

$$\begin{aligned}\Delta H^\circ_{298}(1) &= -297.4 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(1) &= -16.9 \text{ J mol}^{-1} \text{ K}^{-1} \\ K_c(1) &= 3.87 \cdot 10^{-2} T^{0.174} \exp(+35840/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

$$\begin{aligned}\Delta H^\circ_{298}(2) &= -95.9 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(2) &= -5.3 \text{ J mol}^{-1} \text{ K}^{-1} \\ K_c(2) &= 0.904 T^{-0.076} \exp(+11500/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data

**Rate Coefficient Data ( $k = k_1 + k_2$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$1.5 \cdot 10^{-10}$	2728–3379	Mertens <i>et al.</i> , 1992 <sup>1</sup>	(a)
$k_2 < 1.66 \cdot 10^{-13}$	298	Hack, Wagner, and Zasypkin, 1994 <sup>2</sup>	(b)
$6.60 \cdot 10^{-11}$	295	Adamson <i>et al.</i> , 1994 <sup>3</sup>	(c)
<i>Reviews and Evaluations</i>			
$k_1 = 5 \cdot 10^{-11}$	200–2000	Cohen, and Westberg, 1991 <sup>4</sup>	(d)
$k_2 = 5 \cdot 10^{-12}$			
$1.50 \cdot 10^{-10}$	1000–3380	CEC, 1994 <sup>5</sup>	(e)

**Comments**

- (a) Shock tube study of HNCO/N<sub>2</sub>O/Ar mixtures. [NH] monitored with narrow linewidth laser absorption at 336 nm. Concentration of OH determined by absorption at 307 nm. Values of  $k$  obtained by fitting [NH] profiles to a detailed kinetic mechanism. The [NH] was sensitive to  $k$  but not to the branching ratio.
- (b) NH radicals were produced from the 248 nm pulsed laser photolysis of N<sub>3</sub>H and quenched to the ground state by collisions with Xe atoms. O atoms were produced by the reaction of N with NO where the N atoms were formed from a microwave discharge in N<sub>2</sub>/He mixtures. NH, OH, and NO were detected by pulsed LIF. Reaction pressures ranged from 15 to 20 mbar. The principal source of OH is from reaction of excited NH with O. The upper limit was set from reactions in the presence and absence of Xe.
- (c) Pulsed laser photolysis at 193 nm of reaction mixtures:  $(4\text{--}50.5) \cdot 10^{-3}$  mbar NH<sub>3</sub>,  $(2\text{--}42.6) \cdot 10^{-3}$  mbar O<sub>2</sub>,  $0.5 \cdot 10^{-3}$  mbar CH<sub>4</sub> in  $(3\text{--}4.66) \cdot 10^{-3}$  mbar He. NH<sub>2</sub>, NH, and OH transient absorption detected in the IR using a tunable infrared color center laser.  $k$  determined by fitting [NH] profiles.
- (d) Calculated value. Cohen and Westberg<sup>4</sup> assume that the N+OH channel is a metathesis reaction and, using the calculations of Melius and Binkley<sup>6</sup> suggesting a very small barrier, they recommend a characteristic exothermic O atom abstraction rate constant values.
- (e) Accepts the value of Mertens *et al.*<sup>1</sup>

**Preferred Values**

$$\begin{aligned}k &= 1.8 \cdot 10^{-10} \exp(-300/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the range } 295\text{--}3500 \text{ K.} \\ k_2 &< 1.7 \cdot 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}\end{aligned}$$

*Reliability*

$$\Delta \log k = \pm 0.5 \text{ over the range } 295\text{--}3500 \text{ K.}$$

*Comments on Preferred Values*

The two measurements<sup>1,3</sup> of the rate constant for the overall process are compatible with a fast reaction between two radical species and having a very small temperature coefficient. The preferred expression for  $k$  is based on these two studies<sup>1,3</sup> but substantial error limits are assigned.

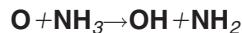
The major uncertainty is the branching ratio for the two channels. In this respect the work of Hack *et al.*<sup>2</sup> is particularly pertinent. Their result establishes that at room temperature the OH producing channel is more than 400 times slower than the overall process. Furthermore using the predicted rate constant of Cohen and Westberg<sup>4</sup> as the pre-exponential factor we find a minimum barrier of about 8.5 kJ mol<sup>-1</sup>, which in turn means that even at 3000 K this channel can make no more than a 3% contribution. In the absence of more detailed experimental evidence we limit our recommendations on the branching ratios to 298 K but it seems likely that channel (1) will predominate over the whole temperature range.

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#### Thermodynamic Data

$$\begin{aligned}\Delta H^\circ_{298} &= 23.4 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298} &= 24.7 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 6.47 \cdot 10^2 T^{-0.446} \exp(-3120/T) \\ &\quad (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$3.4 \cdot 10^{-11} \exp(-4529/T)$	448–841	Perry, 1984 <sup>1</sup>	(a)
$1.07 \cdot 10^{-10} \exp(-5613/T)$	765–1790	Sutherland <i>et al.</i> , 1990 <sup>2</sup>	(b)
<i>Reviews and Evaluations</i>			
$1.83 \cdot 10^{-18} T^{2.1} \exp(-2620/T)$	298–2000	Cohen and Westberg, 1991 <sup>3</sup>	(c)
$1.6 \cdot 10^{-11} \exp(-3670/T)$	500–2500	CEC, 1992; 1994 <sup>4</sup>	(d)

#### Comments

- (a) Pulsed laser photolysis of O<sub>2</sub>/NO/NH<sub>3</sub> mixtures at 157 nm and at total pressures of 100 mbar. [O] monitored by time resolved chemiluminescence from the O+NO reaction.
- (b) Flash photolysis and shock tube study. O atoms generated from the vacuum UV photolysis of NO in the presence of NH<sub>3</sub>. The N atoms also produced react with NO to form another O. Corrections were made for complications from the O+NO reaction. Total gas densities were in the range  $2\text{--}5 \cdot 10^{18}$  molecules cm<sup>-3</sup>. [O] monitored by resonance absorption. Mole fractions of NH<sub>3</sub>,  $1.5 \cdot 10^{-4}$  to  $4.2 \cdot 10^{-4}$  and of NO from  $1 \cdot 10^{-3}$  to  $3 \cdot 10^{-3}$ .
- (c) Expression for  $k$  taken from a comprehensive evaluation by Cohen<sup>5</sup> of previous experimental work. The expression for  $k$  was based on the experimental results of Perry<sup>1</sup> and transition state theory calculations.
- (d) Accepts the conclusion of Cohen<sup>5</sup> that the results of Perry<sup>1</sup> are likely to be the most reliable but the expression suggested for  $k$  also takes into account other studies.

#### Preferred Values

$$k = 2.7 \cdot 10^{-17} T^{1.85} \exp(-3250/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the range 300–2000 K.

#### Reliability

$\Delta \log k = \pm 0.2$  at 300 K increasing to  $\pm 0.3$  at 2000 K.

#### Comments on Preferred Values

Studies up to 1987<sup>1,2,6–17</sup> were very carefully evaluated by Cohen<sup>5</sup> and subsequently reviewed by Cohen and Westberg.<sup>4</sup>

They considered only the results of Perry<sup>1</sup> to be reliable. That conclusion is accepted. Since then Sutherland *et al.*<sup>3</sup> have studied the reaction over a wide temperature range obtaining results which agree well with those of Perry.<sup>1</sup>

The preferred expression for  $k$  is essentially that derived by Sutherland *et al.*<sup>3</sup> from their own results and those of Perry<sup>1</sup> but modified slightly to accommodate some of the older high temperature measurements.

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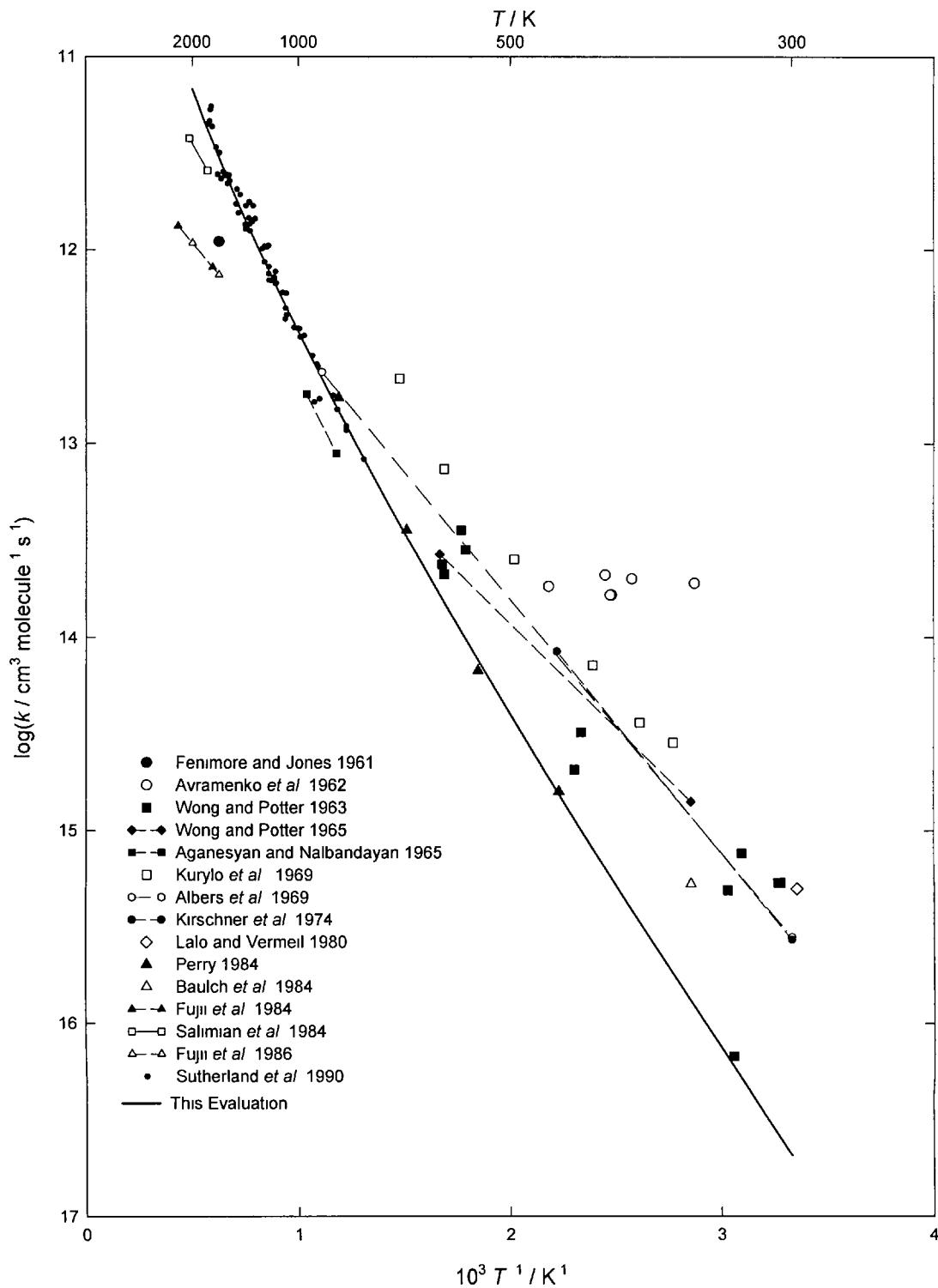
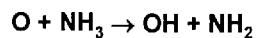
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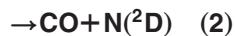
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#### Thermodynamic Data

$$\begin{aligned}\Delta H^\circ_{298}(1) &= -322.4 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(1) &= -12.87 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 0.624 T^{-0.150} \exp(+38710/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

$$\begin{aligned}\Delta H^\circ_{298}(2) &= -92.3 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(2) &= -9.51 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 0.935 T^{-0.150} \exp(+11034/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$2.0 \cdot 10^{-11}$	298	Schacke, Schmatjko, and Wolfrum, 1973 <sup>1</sup>	(a)
$2.0 \cdot 10^{-11}$	298–387	Albers <i>et al.</i> , 1975 <sup>2</sup>	(b)
$1.7 \cdot 10^{-11}$	298	Schmatjko and Wolfrum, 1978 <sup>3</sup>	(c)
$1.8 \cdot 10^{-11}$	295	Schmatjko and Wolfrum, 1978 <sup>4</sup>	(d)
$3.0 \cdot 10^{-11}$	2000	Louge and Hanson, 1984 <sup>5</sup>	(e)
$1.03 \cdot 10^{-11} \exp(1000/T)$	2510–3510	Lindackers, Burmeister, and Roth, 1990 <sup>6</sup>	(f)
$1.28 \cdot 10^{-10}$	3000–4500	Davidson <i>et al.</i> , 1991 <sup>7</sup>	(g)
$3.68 \cdot 10^{-11}$	298	Titarchuk and Halpern, 1995 <sup>8</sup>	(h)
<i>Branching Ratios</i>			
$k_2/k = 0.80$	298	Schmatjko and Wolfrum, 1978 <sup>3</sup>	(c)
$k_2/k = 0.85$	295	Schmatjko and Wolfrum, 1978 <sup>4</sup>	(d)
<i>Reviews and Evaluations</i>			
$k_1 = 3.4 \cdot 10^{-12}$	298	IUPAC, 1989 <sup>9</sup>	(i)
$k_2 = 1.4 \cdot 10^{-11}$			
$3.4 \cdot 10^{-11} \exp(-210/T)$	295–2000	Tsang, 1992 <sup>10</sup>	(j)
$1.7 \cdot 10^{-11}$	300–5000	CEC, 1992; 1994 <sup>11</sup>	(k)

#### Comments

- (a) Discharge flow-flash photolysis study in which CN radicals were produced by flash photolysis of  $\text{C}_2\text{N}_2$  and reacted with atomic oxygen from a discharge in a  $\text{He}/\text{O}_2$  mixture. [CN] was monitored by time resolved absorption spectroscopy at 421 nm. Vibrational excitation of the CN up to  $\nu=6$  had no effect on  $k$ .
- (b) Discharge flow-flash photolysis study; CN and O atom production as in (a). [CN] was monitored by time resolved absorption spectroscopy at 388.3 nm.
- (c) Discharge flow-flash photolysis study; CN and O atom production as in (a). [CO( $\nu$ )] monitored by time resolved resonance absorption spectroscopy using a CO laser. Branching ratios obtained from the bimodal vibrational distribution observed.
- (d) Technique as in (c) but  $\text{N}({}^2\text{P})$ ,  $\text{N}({}^2\text{D})$ , and  $\text{N}({}^4\text{S})$  also monitored.
- (e) Shock tube study on  $(\text{CN})_2/\text{O}_2/\text{Ar}$  mixtures. [CN] monitored by time resolved absorption at 388 nm. Values of  $k$  derived by computer simulation of [CN] profiles using a detailed mechanism.
- (f) Shock tube study on  $(\text{CN})_2/\text{CO}_2/\text{Ar}$  mixtures. [O] and [N] monitored by time resolved ARAS. Values of  $k$  obtained by computer simulation of the later stages of the reaction using a detailed mechanism.

- (g) Shock tube study on the pyrolysis of dilute mixtures of  $\text{N}_2\text{O}$  (200 ppm) and  $(\text{CN})_2$  (10 ppm) in Ar at pressures in the range 0.45–0.90 bar. [CN] monitored by time resolved cw laser absorption at 388.44 nm.
- (h) Photolysis study using Br CN as the source of CN radicals. Mixtures of  $\text{SO}_2/\text{BrCN}$  or  $\text{N}_2\text{O}/\text{BrCN}$  were photolyzed at 193 nm with the relative [CN] being monitored by LIF using 388 nm excitation. Values of  $k$  were obtained from the variation of the [CN] rate of decay with input energy.
- (i) Value for  $k$  based on an earlier evaluation by Baulch *et al.*<sup>12</sup> and branching ratio taken from Schmatjko and Wolfrum.<sup>3</sup>
- (j) Based on the study of Louge and Hanson.<sup>5</sup>
- (k) Based on Refs. 1–5 and the studies of Shaub and Bauer<sup>16</sup> and of Boden and Thrush.<sup>14</sup>

#### Preferred Values

$k = 5 \cdot 10^{-11} \exp(-200/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 295–4500 K.

#### Reliability

$\Delta \log k = \pm 0.5$  over the range 295–4500 K.

*Comments on Preferred Values*

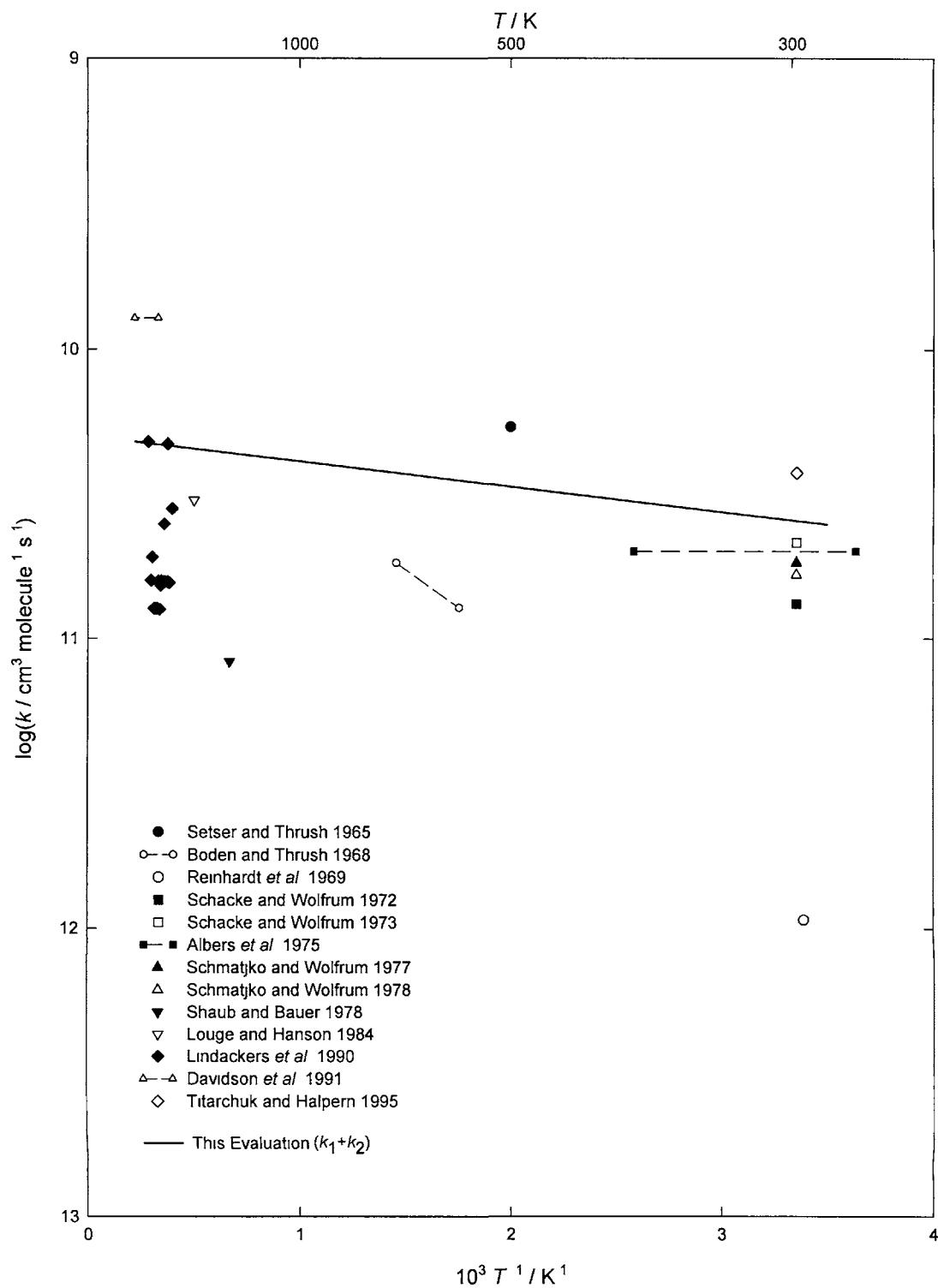
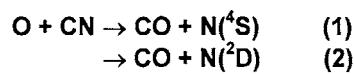
The experimental measurements of  $k^{1-8,13-17}$  cover a wide temperature range but are badly scattered reflecting the difficulty of generating and calibrating the concentrations of these two very labile reactants simultaneously. Within the substantial uncertainties the data suggest a relatively small temperature dependence. The preferred expression reflects this and is chosen to be compatible with the data cited in the Table.

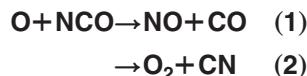
Measurements of the branching ratio suggest that ~80% of the overall reaction proceeds through Channel (2) but until more definitive measurements are available no recommendations are made.

Cobos<sup>18</sup> has carried out theoretical calculations on Channel (2) using the statistical adiabatic channel model. To establish absolute values for  $k_2$  the results are fitted to the results of Schmatjko and Wolfrum<sup>3</sup> at 298 K and a number of values of  $k_2$  calculated over the range 300–5000 K which can be fitted to the expression  $k_2 = 3.2 \cdot 10^{-12} \times \exp(-394/T)$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. This predicts a rather larger temperature dependence for the N(<sup>2</sup>D) forming channel than we propose for the overall rate constant but it extrapolates well to the high temperature data of Davidson *et al.*<sup>7</sup>

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*Thermodynamic Data*

$$\begin{aligned}\Delta H^\circ_{298}(1) &= -396.4 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(1) &= 15.0 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 8.02 \cdot 10^3 T^{-1.049} \exp(+47320/T) \\ &\quad (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

$$\begin{aligned}\Delta H^\circ_{298}(2) &= 59.3 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(2) &= 14.5 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 1.05 \cdot 10^3 T^{-0.783} \exp(-7390/T) \\ &\quad (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data ( $k = k_1 + k_2$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$9.34 \cdot 10^{-11}$	1450	Louge and Hanson, 1984 <sup>1</sup>	(a)
$5.25 \cdot 10^{-11}$	1680–2250	Higashihara, Saito, and Murakami, 1985 <sup>2</sup>	(b)
$7.83 \cdot 10^{-11}$	2180–3070	Mertens <i>et al.</i> , 1992 <sup>3</sup>	(c)
<i>Reviews and Evaluations</i>			
$k_1 = 7.5 \cdot 10^{-11}$	1000–2000	Tsang, 1992 <sup>4</sup>	(d)
$k_2 = 1.4 \cdot 10^{-6} T^{-1.43} \exp(-3501/T)$	1450–2600	CEC, 1992; 1994 <sup>5</sup>	(e)

**Comments**

- (a) Shock tube study on C<sub>2</sub>N<sub>2</sub>/O<sub>2</sub>/N<sub>2</sub>O mixtures. [NCO] monitored by time resolved absorption spectroscopy at 440.5 nm.
- (b) Shock tube study on BrCN/O<sub>2</sub>/Ar mixtures. [NO] monitored by time resolved infrared emission spectroscopy.
- (c) Shock tube study on HNCO/N<sub>2</sub>O/Ar mixtures at 1.1 bar. [NCO] monitored at 440.479 nm by time resolved absorption spectroscopy using a cw ring dye laser. Absorption coefficient of NCO at this wavelength determined in the same study.
- (d) Based on the data of Louge and Hanson<sup>1</sup> and Higashihara *et al.*<sup>2</sup>
- (e) Evaluation of accumulated work to 1991. The rate constant for Channel (2) was calculated from the data on the reverse reaction. Channel (2) was shown to be unimportant.

**Preferred Values**

$k_1 = 7.2 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 1450–3100 K.

$k_2 = 1.2 \cdot 10^{-8} T^{-0.783} \exp(-7390/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 290–4500 K.

*Reliability*

$\Delta \log k_1 = \pm 0.3$  over the range 1450–3100 K.

$\Delta \log k_2 = \pm 0.5$  over the range 290–4500 K.

*Comments on Preferred Values*

The only study since our previous evaluations<sup>3</sup> gives a value of  $k$  in good agreement with our previous

recommendations.<sup>5</sup> There have been a number of studies at temperatures above 1500 K,<sup>1–3,6–9</sup> all of which are based on measurements requiring substantial modeling to derive values of  $k$ , and which show considerable scatter. The preferred value is based on the most direct of the studies,<sup>1–3</sup> which are cited in the Table. Becker *et al.*<sup>10</sup> have studied the reaction at lower temperatures (302–757 K) by pulsed laser photolysis of CINCO/Ar mixtures at total pressures of a few mbar in the presence of an excess of O atoms produced by a discharge in O<sub>2</sub>/Ar mixtures, and with [NCO] monitored by LIF at 438.6 nm. They obtain,  $k = 4.3 \cdot 10^{-8} T^{-1.14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  which when extrapolated gives values of  $k$  an order of magnitude smaller than the high temperature measurements. However Becker *et al.*<sup>10</sup> also find that at 300 K the rate constant is pressure dependent which may, in large part, explain the apparent discrepancy between the low and high temperature results. Clearly more studies are desirable to clarify the pressure and temperature dependence of  $k$ .

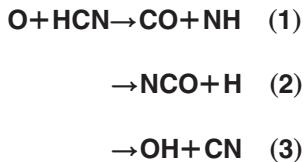
There are no measurements of the branching ratio. NO, which is observed as a major product, has been used to monitor the progress of the reaction in a number of the studies and it is usually assumed that Channel (1) predominates over the whole of the temperature range. Tsang's estimate of  $k_2$  based on the data on the reverse reaction, supports this.<sup>4</sup> We therefore identify measurements of  $k$  with  $k_1$  and we follow Tsang in deriving the expression for  $k_2$  based on  $k(\text{CN} + \text{O}_2)$  together with more recent thermodynamic data which makes Channel (2) even less competitive than indicated by Tsang.<sup>4</sup>

**References**

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<sup>9</sup>T. Higashihara, K. Saito, and I. Murakami, J. Phys. Chem. **87**, 3702 (1983).  
<sup>10</sup>K. H. Becker, R. Kurtenbach, F. Schmidt, and P. Wiesen, Combust. Flame **120**, 570 (2000).



#### Thermodynamic Data

$$\begin{aligned} \Delta H^{\circ}_{298}(1) &= -138.4 \text{ kJ mol}^{-1} \\ \Delta S^{\circ}_{298}(1) &= 15.9 \text{ J mol}^{-1} \text{ K}^{-1} \\ K_c(1) &= 1.58 \cdot 10^3 T^{-0.77} \exp(+16310/T) \\ &(300 \leq T/\text{K} \leq 5000) \end{aligned}$$

$$\begin{aligned} H^{\circ}_{298}(2) &= -39.4 \text{ kJ mol}^{-1} \\ \Delta S^{\circ}_{298}(2) &= -16.0 \text{ J mol}^{-1} \text{ K}^{-1} \\ K_c(2) &= 7.60 \cdot 10^{-3} T^{0.454} \exp(+4830/T) \\ &(300 \leq T/\text{K} \leq 5000) \end{aligned}$$

$$\begin{aligned} \Delta H^{\circ}_{298}(3) &= 88.4 \text{ kJ mol}^{-1} \\ \Delta S^{\circ}_{298}(3) &= 23.5 \text{ J mol}^{-1} \text{ K}^{-1} \\ K_c(3) &= 2.29 \cdot 10^3 T^{-0.696} \exp(-10900/T) \\ &(300 \leq T/\text{K} \leq 5000) \end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2 + k_3$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$8.6 \cdot 10^{-12} \exp(-4090/T)$	450–650	Davies and Thrush, 1968 <sup>1</sup>	(a)
$1.94 \cdot 10^{-10} \exp(-7460/T)$	1800–2500	Roth, Löhr, and Hermanns, 1980 <sup>2</sup>	(b)
$k_2 = 1.21 \cdot 10^{-10} \exp(-7460/T)$			
$9.8 \cdot 10^{-12} \exp(-4000/T)$	574–840	Perry and Melius, 1985 <sup>3</sup>	(c)
$k_2 = 8.3 \cdot 10^{-13}$	1440	Louge and Hanson, 1985 <sup>4</sup>	(d)
$k_1 = 3.7 \cdot 10^{-11} \exp(-7740/T)$	1800–2600	Szekeley, Hanson, and Bowman, 1985 <sup>5</sup>	(e)
$k_3 < 8.3 \cdot 10^{-11} \exp(-11000/T)$	2000–2500		
<i>Reviews and Evaluations</i>			
$k_1 = 9 \cdot 10^{-16} T^{1.21} \exp(-3850/T)$	500–2500	Tsang and Herron, 1991 <sup>6</sup>	(f)
$k_2 = 3.3 \cdot 10^{-16} T^{1.47} \exp(-3800/T)$			
$k_3 = 4.5 \cdot 10^{-15} T^{1.58} \exp(-13400/T)$			
$2.3 \cdot 10^{-18} T^{2.1} \exp(-3075/T)$	450–2500	CEC, 1992; 1994 <sup>7</sup>	(g)
$1 \cdot 10^{-11} \exp(-4000/T)$	200–300	NASA, 1997 <sup>8</sup>	(h)

#### Comments

- (a) Discharge flow study. O atoms generated by the N + NO reaction and [O] monitored by NO + O chemiluminescence. Stoichiometry of  $2.0 \pm 0.4$  for O removal interpreted as due to O + HCN → NCO + H, O + NCO → NO + CO but the possibility of contributions from other channels recognized.  
(b) Shock tube study HCN/N<sub>2</sub>O/Ar mixtures. [H] and [O] monitored by absorption at 121.6 nm and 130.5 nm, respectively.  
(c) Pulsed laser photolysis of O<sub>2</sub>, NO, or N<sub>2</sub>O at 157 nm to produce O atoms in the presence of a large excess of HCN. [O] monitored by O + NO chemiluminescence at 514.5 nm and [NCO] monitored by laser induced flu-

rescence at 416.81 nm. [NCO] measurements suggest Channel (2) to be a major route over the temperature range studied. Theoretical calculations suggest the following:  
 $k_1 = 9.0 \cdot 10^{-16} T^{1.21} \exp(-3800/T)$   
 $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,       $k_2 = 3.3 \cdot 10^{-16} T^{1.47}$   
 $\times \exp(-3850/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,       $k_3 = 4.5 \cdot 10^{-15} T^{1.58} \exp(-13300/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , and  
 $k = 9.8 \cdot 10^{-12} \exp(-4000/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 540–900 K.

- (d) Shock tube study on HCN/O<sub>2</sub>/N<sub>2</sub>O/Ar mixtures. [NCO] monitored by time-resolved laser absorption at 440.479 nm.  $k_2/k(O + \text{NCO}) = 2.4$  obtained from computer fit of [NCO] profiles.  $k(O + \text{NCO}) = 7.47 \cdot 10^{-12} \exp(-4440/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  used<sup>9</sup> to obtain  $k_2$ .

- (e) Shock tube study on HCN/N<sub>2</sub>O/Ar mixtures. [CN] and [NH] monitored by time-resolved absorption at 388 nm and 336 nm, respectively. [CN] and [NH] profiles fitted using a detailed mechanism (37 reactions).
- (f) Accepts the analysis of Perry and Melius.<sup>3</sup>
- (g) Based on the data in Refs. 1–5.
- (h) Based on the low temperature data of Davies and Thrush<sup>1</sup> and of Perry and Melius.<sup>3</sup>

### Preferred Values

$k = 2.3 \cdot 10^{-18} T^{2.1} \exp(-3075/T)$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>  
over the range 450–2500 K.

### Reliability

$\Delta \log k = \pm 0.2$  at 450 K rising to  $\pm 0.3$  at 2500 K.

### Comments on Preferred Values

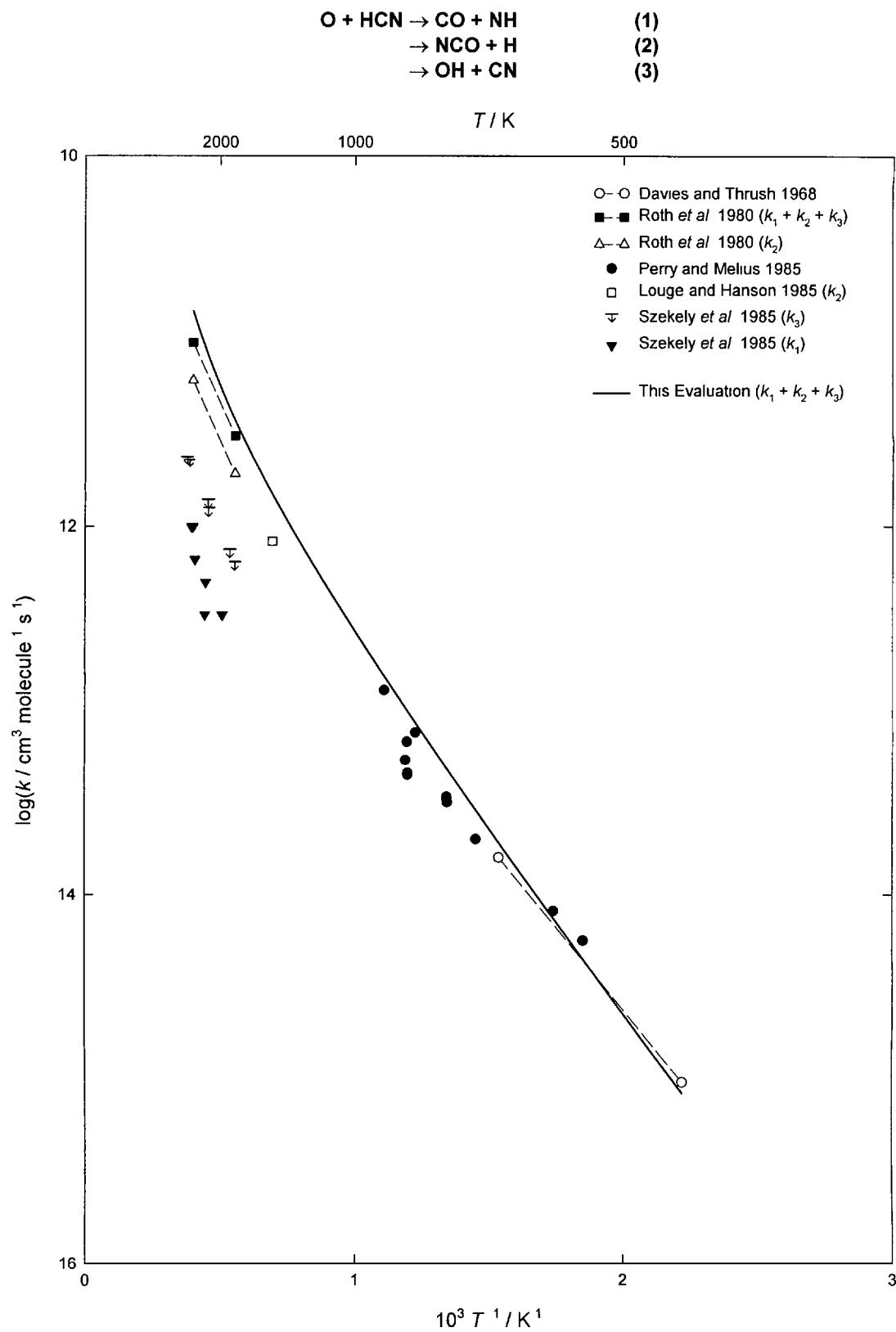
There have been no new experimental studies since our previous evaluations<sup>7</sup> and the Preferred Values are unchanged.

The overall rate constant is reasonably well defined over a wide temperature range, all of the experimental studies<sup>1–5</sup> being in good agreement. The preferred expression for  $k$  is based on all of them.

Experimental work and theoretical calculations<sup>3,10</sup> are in agreement that Channel (2) predominates over the whole temperature range with Channel (3) being negligible at low temperatures but becoming significant at high temperatures. There are insufficient experimental data to make recommendations for the branching ratios but the theoretically derived values of Perry and Melius<sup>3</sup> [Comment (c)] agree well with the little available experimental data and probably offer the best available guide to the relative values of  $k_1$ ,  $k_2$ , and  $k_3$ . They have also been recommended by Tsang and Herron<sup>6</sup> in their evaluation of the data on this reaction.

### References

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- <sup>2</sup>P. Roth, R. Löhr, and H. D. Hermanns, Ber Bunsenges. Phys. Chem. **84**, 835 (1980).
- <sup>3</sup>R. A. Perry and C. F. Melius, 20th Symp. (Int.) Combustion, 1985, p. 639.
- <sup>4</sup>M. Y. Louge and R. K. Hanson, 20th Symp. (Int.) Combustion, 1985, p. 665.
- <sup>5</sup>A. Szekely, R. K. Hanson, and C. T. Bowman, 20th Symp. (Int.) Combustion, 1985, p. 647.
- <sup>6</sup>W. Tsang and J. T. Herron, J. Phys. Chem. Ref. Data **20**, 609 (1991).
- <sup>7</sup>CEC, 1992; Supplement I, 1994 (see references in Introduction).
- <sup>8</sup>NASA, Evaluation No. 12 (see references in Introduction).
- <sup>9</sup>M. Y. Louge and R. K. Hanson, Int. J. Chem. Kinet. **16**, 231 (1984).
- <sup>10</sup>J. A. Miller, C. Parrish, and N. J. Brown, J. Phys. Chem. **90**, 3339 (1986).





#### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = 30.93 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = 16.07 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 49.3T^{-0.264} \exp(-3865/T) \\ (300 \leq T/\text{K} \leq 4000)$$

$$\Delta H^\circ_{298}(2) = -170.1 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = -17.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 6.35T^{-0.593} \exp(+20320/T) \\ (300 \leq T/\text{K} \leq 4000)$$

$$\Delta H^\circ_{298}(3) = -137.0 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = 6.25 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 6.17 \cdot 10^3 T^{-1.910} \exp(+16130/T) \\ (300 \leq T/\text{K} \leq 4000)$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2 + k_3$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$4.4 \cdot 10^{-12} \exp(-5183/T)$	679–741	Tully <i>et al.</i> , 1988 <sup>1</sup>	(a)
$k_1 = 1.1 \cdot 10^{-27} T^{4.55} \exp(890/T)$	1480–3200	He <i>et al.</i> , 1991 <sup>2</sup>	(b)
$k_2 = 3.2 \cdot 10^{-10} T^{-0.34} \exp(-6550/T)$			
$k_1 = 3.2 \cdot 10^{-11} \exp(-7150/T)$	2120–3190	Mertens <i>et al.</i> , 1992 <sup>3</sup>	(c)
$k_2 = 2.3 \cdot 10^{-10} \exp(-10300/T)$			
<i>Reviews and Evaluations</i>			
$k_1 = 3.7 \cdot 10^{-18} T^{2.11} \exp(-5750/T)$	295–2500	Tsang, 1992 <sup>4</sup>	(d)
$k_2 = 1.6 \cdot 10^{-14} T^{1.41} \exp(-4290/T)$			

#### Comments

- (a) Pulsed laser photolysis at 157 nm of NO/O<sub>2</sub>/HNCO/Ar mixtures or of NO/N<sub>2</sub>O/HNCO/Ar mixtures at 193 nm. Pressures were in the range 65–265 mbar. [O] monitored by time resolved chemiluminescence from the O+NO reaction. Expression for  $k$  based on measurements at only two temperatures.
- (b) Shock tube study on HNCO/NO/Ar mixtures at a total pressure of ~0.4 bar. [NO], [CO], and [H<sub>2</sub>O] monitored by time resolved laser absorption. Values of rate constants obtained by computer simulation of the detected species concentration profiles using a detailed mechanism. The authors' own data and those of Mertens *et al.*<sup>1</sup> were combined to give the expressions quoted. They also carried out a transition state theory calculation, using frequencies computed by the BAC-MP4 method, to derive expressions for  $k_1$ ,  $k_2$ , and  $k_3$ .
- (c) Shock tube study on HNCO/N<sub>2</sub>O/Ar mixtures at total pressures in the range 0.25–1.1 bar. [NH] and [OH] monitored by laser absorption at 336 nm and 307 nm, respectively. Values of rate constants obtained by computer simulation of [NH] and [OH] profiles using a detailed mechanism.
- (d) Accepts the expressions derived by He *et al.*<sup>2</sup> using transition state theory.

#### Preferred Values

$k_1 = 3.7 \cdot 10^{-18} T^{2.11} \exp(-5750/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 500–3000 K.

$k_2 = 1.6 \cdot 10^{-14} T^{1.41} \exp(-4290/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 500–3000 K.

#### Reliability

$\Delta \log k_1 = \pm 0.3$  over the range 500–3000 K.

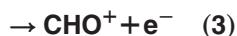
$\Delta \log k_2 = \pm 0.3$  over the range 500–3000 K.

#### Comments on Preferred Values

The expressions derived by He *et al.*<sup>2</sup> [Comment (b)] and recommended by Tsang<sup>4</sup> are consistent with all of the available data for this reaction and are accepted as our preferred expressions for  $k_1$  and  $k_2$ . A similar calculation by He *et al.*<sup>2</sup> for the very minor third channel [Channel (3)], for which there are no experimental data, gives  $k_3 = 2.5 \cdot 10^{-16} T^{1.57} \exp(-22150/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

#### References

- <sup>1</sup> F. P. Tully, R. A. Perry, L. R. Thorne, and M. D. Allendorf, 22nd Symp. (Int.) Combustion, 1988, p. 1101.
- <sup>2</sup> Y. He, M. C. Lin, C. H. Wu, and C. F. Melius, 24th Symp. (Int.) Combustion, 1992, p. 711.
- <sup>3</sup> J. D. Mertens, A. Y. Chang, R. K. Hanson, and C. T. Bowman, Int. J. Chem. Kinet. **24**, 279 (1992).
- <sup>4</sup> W. Tsang, J. Phys. Chem. Ref. Data **21**, 753 (1992).



#### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = -738.1 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = -31.83 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 6.20 \cdot 10^{-2} T^{-0.140} \exp(+88700/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(3) = -12.6 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = -119.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 4.16 \cdot 10^{-13} T^{2.026} \exp(+2290/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(2) = -91.8 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = -2.29 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 6.98 T^{-0.303} \exp(+10880/T) \\ (300 \leq T/\text{K} \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2 + k_3$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$k_3 = 2.8 \cdot 10^{-13}$	2000–2400	Peeters and Vinckier, 1975 <sup>1</sup>	(a)
$k_3 = 9.5 \cdot 10^{-13} \exp(-3020/T)$	1700–2100	Matsui and Nomaguchi, 1978 <sup>2</sup>	(b)
$k_3 = 2.4 \cdot 10^{-14}$	295	Vinckier, 1979 <sup>3</sup>	(c)
$k_1 = 9.4 \cdot 10^{-11}$	298	Messing <i>et al.</i> , 1980 <sup>4</sup>	(d)
$k_1 = 3.3 \cdot 10^{-11}$	298	Homann and Schweinfurth, 1981 <sup>5</sup>	(e)
$k_1 = (1.7–2.5) \cdot 10^{-10}$	1500–2500	Frank, Bhaskaran, and Just, 1988 <sup>6</sup>	(f)
<i>Reviews and Evaluations</i>			
$k_1 = 6.6 \cdot 10^{-11}$	300–2000	CEC, 1992; 1994 <sup>7</sup>	(g)
$k_3 = 4.2 \cdot 10^{-13} \exp(-850/T)$	300–2500		

#### Comments

- (a) Flat flames of  $\text{CH}_4$  and/or  $\text{C}_2\text{H}_4$  at pressures of 22 and 53 mbar; concentration profiles of several species determined by molecular beam sampling and mass spectrometry. Saturation ion currents measured and rate of ion generation found to be proportional to  $[\text{CH}] \cdot [\text{O}]$ .
- (b) Premixed  $\text{CH}_4$ /air flames;  $\text{OH}^*$ ,  $\text{CH}^*$  emissions and  $\text{CO} + \text{O}$  chemiluminescence measured.  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{CO}$ , and  $\text{CO}_2$  were determined by microprobe sampling and  $[\text{OH}]$  was obtained by ultraviolet (UV) absorption.
- (c) Fast flow discharge system used to study reaction of O atoms with  $\text{C}_2\text{H}_2$ .  $[\text{C}_2\text{H}_2]$ ,  $[\text{O}]$ ,  $[\text{O}_2]$ , and  $[\text{CH}]$  monitored by molecular beam sampling and mass spectrometry. Saturation current measured.
- (d) IR multiphoton decomposition of  $\text{CH}_3\text{OH}$  in the presence of an excess of O at total pressures of 6.6–13 mbar (bath gas, Ar).  $[\text{CH}]$  monitored by laser induced fluorescence (LIF).
- (e) Reaction of O and H atoms with  $\text{C}_2\text{H}_2$  in a discharge flow system studied at pressures of 1.4–8 mbar. Formation of  $\text{C}_3\text{H}_4$ ,  $\text{C}_4\text{H}_2$ , and  $\text{CH}_2\text{O}$  monitored by mass spectrometry. Computer modeling of reaction used to derive rate constant.

(f) Shock tube study on highly dilute  $\text{C}_2\text{H}_2 / \text{N}_2\text{O}/\text{Ar}$  mixtures.  $[\text{H}]$ ,  $[\text{O}]$ , and  $[\text{CO}]$  determined by resonance absorption spectroscopy.

(g) See Comments on Preferred Values.

#### Preferred Values

$k_1 = 6.6 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 295–2000 K.

$k_3 = 4.2 \cdot 10^{-13} \exp(-850/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 295–2500 K.

#### Reliability

$$\Delta \log k_1 = \pm 0.5 \text{ over the range 295–2000 K.}$$

$$\Delta \log k_3 = \pm 0.5 \text{ over the range 295–2500 K.}$$

#### Comments on Preferred Values

The preferred value for  $k_1$  is the mean of the values determined at 298 K by Messing *et al.*<sup>4</sup> and Homann and Schweinfurth<sup>5</sup> which differ by a factor of 3. The value of the rate constant is large and only a small temperature coefficient is expected, as indicated by the values of  $k_1$  obtained by Frank *et al.*<sup>6</sup> at 1500–2500 K, which are only a factor of 3–4 larger than the preferred value at 298 K.

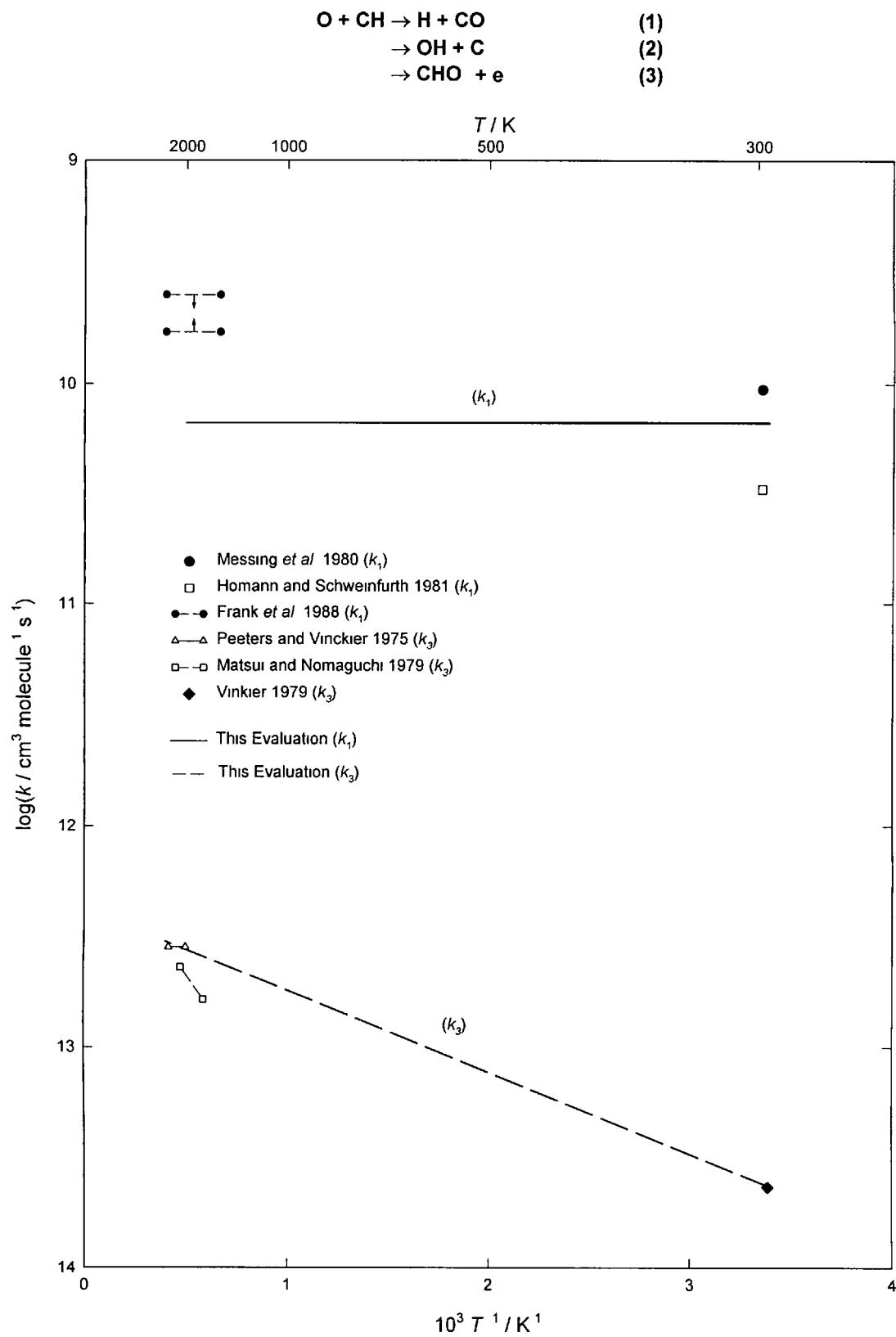
The preferred Arrhenius expression for  $k_3$  is based on the high temperature results of Peeters and Vinckier<sup>1</sup> and at low temperatures, the value at 295 K of Vinckier.<sup>3</sup> The absolute values of  $k_3$  obtained by Matsui and Nomaguchi<sup>2</sup> are in good agreement with those from the preferred expression despite the very different Arrhenius parameters which they obtain.

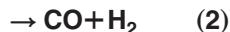
Murrell and Rodriguez<sup>8</sup> have carried out *ab initio* calculations on the reaction and obtain  $k_1 = 1.0 \cdot 10^{-10} \exp(-914/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the range 1600–6000 K which is consistent with the present recommendations. However, these authors also report a rate expression for the C+OH channel of  $k_2 = 2.52 \cdot 10^{-11} \exp(-2380/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  which gives a larger  $k_2$  at combustion temperatures than  $k_3$ , the rate constant of the  $\text{CHO}^+ + \text{e}^-$

channel. There are no measured values for  $k_2$  and in the absence of experimental data we make no recommendation.

## References

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- <sup>5</sup>K. H. Homann and H. Schweinfurth, Ber. Bunsenges. Phys. Chem. **85**, 569 (1981).
- <sup>6</sup>P. Frank, K. A. Bhaskaran, and Th. Just, 21st Symp. (Int.) Combustion, 1988, p. 885.
- <sup>7</sup>CEC, 1992; Supplement I, 1994 (see references in Introduction).
- <sup>8</sup>J. N. Murrell and J. A. Rodriguez, J. Mol. Struct. (Theochem.) **139**, 267 (1986).





#### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = -314.2 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = 70.79 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 1.12 \cdot 10^{23} T^{-0.050} \exp(+37860/T) \text{ molecule cm}^{-3}$$

(300 ≤  $T/\text{K}$  ≤ 5000)

$$\Delta H^\circ_{298}(2) = -750.1 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = -27.81 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 0.184 T^{-0.201} \exp(+90050/T)$$

(300 ≤  $T/\text{K}$  ≤ 5000)

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$1.3 \cdot 10^{-10}$	290–600	Vinckier and Debruyne, 1978, <sup>1</sup> 1979 <sup>2</sup>	(a)
$8 \cdot 10^{-11}$	298	Homann and Schweinfurth, 1981 <sup>3</sup>	(b)
$1.4 \cdot 10^{-10}$	296	Böhland, Temps, and Wagner, 1984 <sup>4</sup>	(c)
$k_1 = 2 \cdot 10^{-10}$	1500–2500	Frank, Bhaskaran, and Just, 1987 <sup>5</sup>	(d)
$k_2 = 1 \cdot 10^{-10}$			
<i>Reviews and Evaluations</i>			
$1.9 \cdot 10^{-11}$	298	Tsang and Hampson, 1986 <sup>6</sup>	(e)
$1.3 \cdot 10^{-10}$	300–2000	Herron, 1988 <sup>7</sup>	(f)
$2 \cdot 10^{-10}$	300–2500	CEC, 1992; 1994 <sup>8</sup>	(g)
$k_1/k = 0.6$			

#### Comments

- (a) Discharge flow study of O+C<sub>2</sub>H<sub>2</sub> with molecular beam sampling and mass spectrometric analysis. Rate coefficient determined from the approach of the [{}<sup>3</sup>CH<sub>2</sub>] signal to its steady state value.<sup>1</sup> The temperature dependence, corresponding to an “activation energy” of  $(-0.4 \pm 0.8) \text{ kJ mol}^{-1}$ , was determined from the steady state concentrations of <sup>3</sup>CH<sub>2</sub> and is based on an activation energy of  $(13 \pm 0.8) \text{ kJ mol}^{-1}$  for O + C<sub>2</sub>H<sub>2</sub>, close to the effective value recommended in this evaluation.
- (b) Discharge flow study of product formation in the C<sub>2</sub>H<sub>2</sub>/O/H system. Formation of C<sub>4</sub>H<sub>2</sub>, C<sub>3</sub>H<sub>4</sub>, and CH<sub>2</sub>O monitored by mass spectrometry. A number of other stable products and intermediates were detected. Rate coefficient based largely on the C<sub>3</sub>H<sub>4</sub> formation rate. Product profiles modeled using a 27 step reaction mechanism.
- (c) Discharge flow study using  $[{}^3\text{CH}_2] \approx (0.6–1.4) \cdot 10^{11} \text{ cm}^{-3}$  and  $[\text{O}^3\text{P}]_0/[{}^3\text{CH}_2]_0 = 2–20$ . <sup>3</sup>CH<sub>2</sub> radicals were generated either by reaction of O atoms with CH<sub>2</sub>CO or by 193 nm laser photolysis of CH<sub>2</sub>CO. [O<sup>3</sup>P] and [{}<sup>3</sup>CH<sub>2</sub>] were monitored by laser magnetic resonance (LMR). Secondary reactions of <sup>3</sup>CH<sub>2</sub> (e.g., with the wall, O<sub>2</sub>, H, <sup>3</sup>CH<sub>2</sub>) were carefully assessed.
- (d) Study using reflected shock waves in N<sub>2</sub>O/C<sub>2</sub>H<sub>2</sub>/Ar mixtures. [CO], [H], and [O] detected by resonance absorption. Values of  $k$  were obtained from numerical fits to a 14 reaction mechanism.
- (e) Based on an evaluation by Laufer<sup>9</sup> of the data from

Ref. 1 which, it was argued, gave a value of  $k({}^3\text{CH}_2 + \text{O})/k({}^3\text{CH}_2 + \text{C}_2\text{H}_2)$ . The analysis was dependent on a much larger value for  $k({}^3\text{CH}_2 + \text{C}_2\text{H}_2)$  than is now accepted and  $k$  is consequently too small.

(f) Based on the studies of Vinckier and Debruyne,<sup>1</sup> Böhland *et al.*,<sup>3</sup> and Frank and Just.<sup>10</sup>

(g) Based on the measurements of Refs. 1–4. NB, there were two typographical errors in the table in our CEC 1992<sup>8</sup> evaluation with the rate coefficients of Vinckier and Debruyne<sup>1</sup> and of Böhland *et al.*<sup>3</sup> being given values that are a factor of 10 too small.

#### Preferred Values

$k = 3.4 \cdot 10^{-10} \exp(-270/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 290–2500 K.

$k_1/k = 0.6$  over the range 290–2500 K.

#### Reliability

$\Delta \log k = \pm 0.2$  at 290 K, rising to  $\pm 0.3$  at 2500 K.

$\Delta(k_1/k) = \pm 0.3$  over the range 290–2500 K.

#### Comments on Preferred Values

The room temperature rate coefficient is based on the study of Böhland *et al.*<sup>4</sup> which is direct and is considered to be the most reliable. It is supported by the determinations in Refs. 1–3. A weakly positive  $T$  dependence has been adopted to reproduce the high temperature values of  $k$  obtained by Frank *et al.*<sup>5</sup> The rate constant ratio is based primarily on the study of Frank *et al.*,<sup>5</sup> although Tsang and

Hampson<sup>6</sup> have suggested  $k_1/k \approx 0.5$  based on the vibrational energy distribution in the product CO.<sup>11</sup> Both channels are highly exothermic and a constant rate coefficient ratio over the temperature range is reasonable.

## References

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- <sup>2</sup>C. Vinckier and W. DeBruyn, J. Phys. Chem. **83**, 2057 (1979).
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<sup>4</sup>T. Böhland, F. Temps, and H. Gg. Wagner, Ber. Bunsenges. Phys. Chem. **88**, 1222 (1984).

<sup>5</sup>P. Frank, K. A. Bhaskaran, and Th. Just, 21st Symp. (Int) Combustion, 1987, p. 885.

<sup>6</sup>W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data **15**, 1087 (1986).

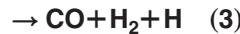
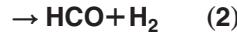
<sup>7</sup>J. T. Herron, J. Phys. Chem. Ref. Data **17**, 967 (1988).

<sup>8</sup>CEC, 1992; Supplement I, 1994 (see references in Introduction).

<sup>9</sup>A. H. Laufer, Rev. Chem. Intermed. **4**, 225 (1981).

<sup>10</sup>P. Frank and Th. Just, Proc. 14th Int. Symp. Shock Tubes and Waves, 1984, p. 705.

<sup>11</sup>W. M. Shaub, D. S. Y. Hsu, T. L. Birks, and M. C. Lin, 18th Symp. (Int.) Combustion, 1981, p. 811.



### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = -286.6 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = -21.65 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 1.43 \cdot 10^{-2} T^{0.2} \exp(+34634/T) \quad (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(2) = -352.5 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = -0.10 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 7.98 T^{-0.260} \exp(+42200/T) \quad (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(3) = -288.1 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = 87.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 6.30 \cdot 10^{25} T^{-0.680} \exp(+34420/T) \text{ molecule cm}^{-3} \quad (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(4) = 32.0 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(4) = 23.61 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(4) = 9.43 \cdot 10^2 T^{-0.543} \exp(-4130/T) \quad (300 \leq T/\text{K} \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data

### Rate Coefficient Data ( $k = k_1 + k_2 + k_3 + k_4$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$1.3 \cdot 10^{-10}$	1700–2300	Bhaskaran, Franck, and Just, 1979 <sup>1</sup>	(a)
$1.14 \cdot 10^{-10}$	295	Plumb and Ryan, 1982 <sup>2</sup>	(b)
$1.4 \cdot 10^{-10}$	294–900	Slagle, Sarzynski, and Gutman, 1987 <sup>3</sup>	(c)
$1.1 \cdot 10^{-10}$	298	Zellner <i>et al.</i> , 1988 <sup>4</sup>	(d)
$1.3 \cdot 10^{-10}$	300	Oser <i>et al.</i> , 1991 <sup>5</sup>	(e)
$0.94 \cdot 10^{-10}$	298	Seakins and Leone, 1992 <sup>6</sup>	(f)
$1.4 \cdot 10^{-10}$	1609–2002	Lim and Michael, 1993 <sup>7</sup>	(g)
$1.7 \cdot 10^{-10}$	298	Fockenberg <i>et al.</i> , 1999 <sup>8</sup>	(h)
<i>Branching Ratios</i>			
$k_1/k > 0.85$	300	Niki, Daby, and Weinstock, 1968 <sup>9</sup>	(i)
$k_2/k \leq 0.2$	300	Hoyermann and Sievert, 1979 <sup>10</sup>	(j)
$k_3/k = 0.4 \pm 0.2$	298	Seakins and Leone, 1992 <sup>6</sup>	(f)
$k_3/k = 0.17 \pm 0.11$	298	Fockenberg <i>et al.</i> , 1999 <sup>8</sup>	(h)
$k_3/k = 0.18 \pm 0.04$	298	Preses <i>et al.</i> , 2000 <sup>11</sup>	(k)
<i>Reviews and Evaluations</i>			
$1.4 \cdot 10^{-10}$	300–2500	CEC, 1992; 1994 <sup>12</sup>	(l)
$1.1 \cdot 10^{-10}$	259–341	NASA, 1997 <sup>13</sup>	(m)
$1.4 \cdot 10^{-10}$	290–900	IUPAC, 1999 <sup>14</sup>	(n)

### Comments

- (a) Shock-tube decomposition of  $\text{C}_2\text{H}_6/\text{O}_2$  mixtures with direct determination of  $[\text{H}]$  and  $[\text{O}]$  by atomic resonance absorption spectrometry. Rate coefficient derived from a computer simulation of  $[\text{H}]$  and  $[\text{O}]$  profiles.
- (b) Flow discharge with mass spectrometric detection of  $\text{O}$  and  $\text{CH}_3$ .  $k$  determined from decay of  $[\text{CH}_3]$  with  $[\text{O}] \gg [\text{CH}_3]$ .
- (c) Flow system with generation of  $\text{CH}_3$  and  $\text{O}({}^3\text{P})$  from the simultaneous *in situ* photolyses of  $\text{CH}_3\text{COCH}_3$  and  $\text{SO}_2$  and determination of  $[\text{CH}_3]$  and  $[\text{O}]$  by photoionization mass spectrometry. Experiments were performed under conditions such that  $[\text{O}]/[\text{CH}_3] > 20$  and the rate coefficients were determined from the decay of  $[\text{CH}_3]$ .  $k$  found to be independent of pressure over the range 1.3–15 mbar and its value was confirmed by measurement of the rate of formation of  $\text{HCHO}$ .  $\text{CHO}$  and  $\text{CH}_2$  were not detected as products and Channel (1) was assumed therefore to be the only important channel but the analytical system could not detect  $\text{CO}$  or  $\text{H}_2$ .
- (d) Laser photolysis at 193 nm of flowing mixtures of  $\text{N}_2/\text{N}_2\text{O}/(\text{CH}_3\text{N})_2$  to generate  $\text{O}({}^3\text{P})$  and  $\text{CH}_3$ .  $k$  was derived from the rate of formation of  $\text{HCHO}$  determined by LIF under conditions where  $[\text{O}] > [\text{CH}_3]$ . Mass balance estimates indicated that Channel (1) was predominant.
- (e) Discharge flow study using  $\text{He}/\text{O}_2$  mixtures with generation of  $\text{CH}_3$  from  $\text{F}+\text{CH}_4$  reaction at pressures of 0.25–1.00 mbar.  $k$  was derived from the decay of  $[\text{CH}_3]$  under conditions where  $[\text{O}]/[\text{CH}_3] > 10$ .
- (f) Pulsed laser cophotolysis at 193 nm of  $\text{SO}_2$  and acetone (or  $\text{CH}_3\text{I}$ ) mixtures was used to produce  $\text{O}$  atoms and  $\text{CH}_3$  radicals simultaneously in the presence of Ar, He, or  $\text{N}_2$  buffer gases. Time-resolved Fourier transform infrared (FTIR) emission spectroscopy was used to monitor products. The value of  $k$  was derived from the growth in  $[\text{HCHO}]$ . A number of tests were carried out to check that  $\text{CO}$  was a direct product of the reaction.
- (g) Pyrolysis/photolysis shock-tube system with decomposition of  $\text{CH}_3\text{Cl}$  in Ar followed by photolysis of  $\text{SO}_2$ .  $k$  determined from a computer simulation of O-atom profiles measured by resonance absorption.
- (h) Pulsed laser cophotolysis at 193 nm of  $\text{SO}_2$  and  $(\text{CH}_3)_2\text{CO}$  or  $\text{CH}_3\text{Br}$  at a total pressure of 0.13 mbar.  $[\text{CO}]$ ,  $[\text{HCHO}]$ , and  $[\text{CH}_3]$  were monitored by time-of-flight mass spectrometry under conditions of  $\text{O}$  in large excess over  $\text{CH}_3$ . Values of  $k$  were determined from both the decay in  $[\text{CH}_3]$  and growth in  $[\text{HCHO}]$  agreed to within 20%. The yield of  $\text{CO}$  was determined relative to that of  $\text{HCHO}$  which was, in turn, related to the yield of  $\text{CH}_3$  radicals.
- (i) Discharge flow-mass spectrometric study of the  $\text{O} + \text{C}_2\text{H}_4$  reaction, with  $\text{O}+\text{CH}_3$  observed as a secondary reaction.
- (j) Flow system with  $\text{CH}_3$  generated from the  $\text{F}+\text{CH}_4$  reaction and  $\text{O}$  by means of a microwave discharge. Electron impact mass spectrometric analysis of  $\text{CHO}$  and  $\text{HCHO}$ . No evidence found for Channel (4).
- (k) Pulsed laser cophotolysis at 193 nm of mixtures of  $\text{SO}_2$  and  $(\text{CH}_3)_2\text{CO}$  in Ar at a total pressure of  $\sim 7$  mbar.  $[\text{CO}]$  was determined by infrared diode laser absorption at  $\sim 2077 \text{ cm}^{-1}$ . The yields of  $\text{O}$  and  $\text{CH}_3$  were calculated using the UV absorption coefficients of  $(\text{CH}_3)_2\text{CO}$  and  $\text{SO}_2$ . Isotopic labeling was used to distinguish the  $\text{CO}$  produced by acetone photolysis from that from  $\text{O}+\text{CH}_3$ .
- (l) Based on data of Slagle *et al.*<sup>3</sup>
- (m)  $k$  at 298 K is the weighted average of the measurements of Washida and Bayes,<sup>15</sup> Washida,<sup>16</sup> and Plumb and Ryan,<sup>2</sup> and  $E/R$  is based on the results of Washida and Bayes.<sup>15</sup>
- (n) Mean of the results of Plumb and Ryan,<sup>2</sup> Slagle *et al.*,<sup>3</sup> Zellner *et al.*,<sup>4</sup> Oser *et al.*,<sup>5</sup> and Seakins and Leone.<sup>6</sup>

### Preferred Values

$$k = 1.4 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the range } 294\text{--}2500 \text{ K.}$$

$$k_1/k = 0.8; k_3/k = 0.2 \text{ at } 298 \text{ K.}$$

### Reliability

$$\Delta \log k = \pm 0.1 \text{ over the range } 294\text{--}2500 \text{ K.}$$

$$\Delta(k_1/k) = \Delta(k_3/k) = \pm 0.1 \text{ at } 298 \text{ K.}$$

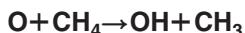
### Comments on Preferred Values

The recommended value of  $k$  is the mean of the results of Bhaskaran *et al.*,<sup>1</sup> Plumb and Ryan,<sup>2</sup> Slagle *et al.*,<sup>3</sup> Zellner *et al.*,<sup>4</sup> Oser *et al.*,<sup>5</sup> Seakins and Leone,<sup>6</sup> Lim and Michael,<sup>7</sup> and Fockenberg *et al.*<sup>8</sup> which are in agreement within their quoted error limits of  $\pm(20\% \text{--} 30\%)$ .

There is general agreement that Channel (1) is the predominant pathway. There is evidence that Channels (2) and (4) do not contribute to any extent<sup>3,10</sup> and a number of studies<sup>6,8,11,17</sup> suggest that  $\text{CO}$  is another primary product. A time-resolved FTIR study of the  $\text{CO}$  ( $v=1$ ) emissions together with a theoretical investigation of the reaction mechanism by Marcy *et al.*<sup>18</sup> suggests that the  $\text{CO}$  arises from dissociation of  $\text{HCO}$  produced by  $\text{H}_2$  elimination from highly vibrationally excited methoxy radicals. Measurements of the branching ratio,  $k_3/k$ , by Seakins and Leone<sup>6</sup> can only just be reconciled with those of Fockenberg *et al.*<sup>8</sup> and Preses *et al.*<sup>11</sup> at the extremes of their quoted error limits. The preferred branching ratios are based largely on the results of Preses *et al.*<sup>11</sup> and Fockenberg *et al.*<sup>8</sup> but substantial error limits are assigned. There is no direct information on the temperature dependence of the branching ratio but Slagle *et al.*<sup>3</sup> find Channel (1) predominant up to 600 K, it appears to remain important in the high temperature studies,<sup>1,7</sup> and the theoretical study of Marcy *et al.*<sup>18</sup> predicts little temperature dependence of the branching ratio.

## References

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### Thermodynamic Data

$$\begin{aligned}\Delta H_{298}^0 &= 9.25 \text{ kJ mol}^{-1} \\ \Delta S_{298}^0 &= 30.58 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 9.5 \cdot 10^2 T^{-0.345} \exp(-1510/T) \\ &\quad (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

### Rate Coefficient Data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$2.6 \cdot 10^{-10} \exp(-4000/T)$	1750–2575	Dean and Kistiakowski, 1971 <sup>1</sup>	(a)
$3.2 \cdot 10^{-10} \exp(-5900/T)$	1200–2000	Brabbs and Brokaw, 1975 <sup>2</sup>	(b)
$6.8 \cdot 10^{-10} \exp(-7030/T)$	1500–2250	Roth and Just, 1977 <sup>3</sup>	(c)
$2.63 \cdot 10^{-18} T^{2.36} \exp(-3730/T)$	420–1670	Felder and Fontijn, 1979 <sup>4</sup>	(d)
$2.01 \cdot 10^{-10} \exp(-5435/T)$	474–1156	Klemm <i>et al.</i> , 1981 <sup>5</sup>	(e)
$9.2 \cdot 10^{-19} T^{2.4} \exp(-2838/T)$	763–1755	Sutherland, Michael, and Klemm, 1986 <sup>6</sup>	(f)
$1.12 \cdot 10^{-9} \exp(-7750/T)$	1365–1840	Ohmori <i>et al.</i> , 1992 <sup>7</sup>	(g)
$4.70 \cdot 10^{-10} \exp(-6507/T)$	980–1520	Miyoshi <i>et al.</i> , 1994 <sup>8</sup>	(h)
<i>Reviews and Evaluations</i>			
$1.15 \cdot 10^{-15} T^{1.56} \exp(-4270/T)$	400–2250	Sutherland, Michael, and Klemm, 1986 <sup>6</sup>	(f)
$8.1 \cdot 10^{-18} T^{2.2} \exp(-3820/T)$	298–2500	Cohen and Westberg, 1991 <sup>9</sup>	(i)
$1.15 \cdot 10^{-15} T^{1.56} \exp(-4270/T)$	300–2500	CEC, 1992; 1994 <sup>10</sup>	(j)

### Comments

- (a) Shock tube study on CO/O<sub>2</sub>/CH<sub>4</sub>/Ar mixtures. CO and CO<sub>2</sub> infrared emissions at 4.02 and 5.03 μm behind incident shocks were monitored. Values of  $k$  were derived by computer fitting of the temporal [CO<sub>2</sub>] profile using a detailed mechanism.
- (b) Technique as in (d) but reaction progress monitored by detection of the CO flame band emissions. Values of  $k$  derived using a simplified mechanism and an analytical fitting procedure.
- (c) Shock tube study on N<sub>2</sub>O/CH<sub>4</sub>/Ar mixtures. The [O] was monitored behind reflected shocks by ARAS at 130.5 nm. Values of  $k$  were derived by computer fitting of the temporal [O] profile using a simplified mechanism.
- (d) Flash photolysis of slowly flowing CH<sub>4</sub>/O<sub>2</sub> (or

- CO<sub>2</sub>)/N<sub>2</sub> mixtures using a Xenon flash lamp ( $\lambda = 147$  nm). The [O] was monitored by resonance fluorescence at 130.5 nm (or at low temperatures by NO + O chemiluminescence) in the presence of large excess of CH<sub>4</sub>.
- (e) A flash photolysis technique similar to that described in (g) was used over the range 474–520 K. Over the range 548–1156 K the reaction was studied using a discharge flow technique in which O atoms were generated by a discharge in O<sub>2</sub>/He mixtures and the [O] monitored by resonance fluorescence.
- (f) Flash photolysis-shock tube technique applied to He/NO/CH<sub>4</sub> mixtures. O atoms were produced by flash photolysis of NO ( $\lambda > 145$  nm) behind reflected shocks and monitored by resonance absorption at 130.4 nm. Very pure CH<sub>4</sub> was used and checks were made by

computer simulation for the effects of secondary reactions. The results of previous studies were evaluated and a number of expressions for  $k$  were derived and checked. The finally recommended expression is adopted as our preferred expression. Similar experiments and results are described by Sutherland and Klemm.<sup>11</sup>

- (g) Flash photolysis-shock tube technique applied to Ar/CH<sub>4</sub>/O<sub>2</sub> mixtures. O atoms were produced by pulsed laser photolysis of the O<sub>2</sub> at 193 nm behind reflected shock waves and both [O] and [H] were monitored by ARAS at 130.6 and 121.6 nm, respectively. Computer simulations were used in extracting values of  $k$  from the [O] temporal profile and in checking the effects of secondary chemistry.
- (h) A flash photolysis-shock tube technique was applied to Ar/SO<sub>2</sub> (or NO)/CH<sub>4</sub> mixtures. O atoms were produced by pulsed laser photolysis of the SO<sub>2</sub> or NO at 193 nm behind reflected shock waves and [O] was monitored by ARAS at 130.6 nm. Computer simulations were used in extracting values of  $k$  from the [O] temporal profile and in checking the effects of secondary chemistry. Results reported here supersede those reported previously in a similar study.<sup>12</sup>
- (i) Based on a Transition State Theory calculation and selected experimental data.<sup>13</sup>
- (j) Accepts the expression derived by Sutherland *et al.*<sup>6</sup>

### Preferred Values

$$k = 7.3 \cdot 10^{-19} T^{2.5} \exp(-3310/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the range 400–2500 K.

### Reliability

$\Delta \log k = \pm 0.3$  over the temperature range 600–2500 K, rising to  $\pm 0.5$  at 400 K.

### Comments on Preferred Values

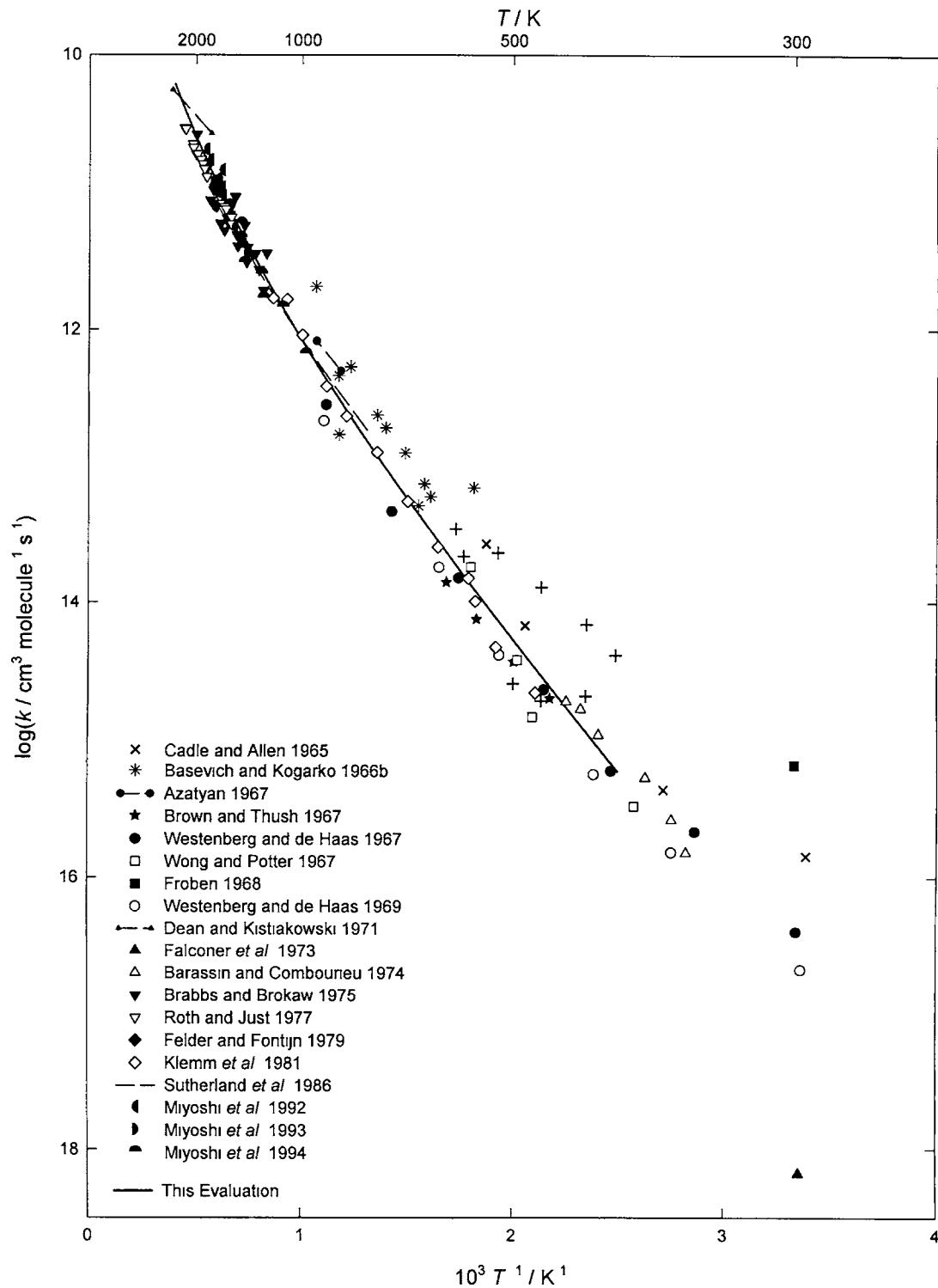
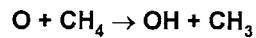
The preferred expressions for  $k$  are based on the studies cited in the table. The rate constant for the reaction is well defined at temperatures above 1000 K with only the study of Dean and Kistiakowsky<sup>1</sup> giving slightly high values. Further support comes from the shock tube study of Hidaka *et al.*<sup>14</sup> on CH<sub>4</sub> pyrolysis and oxidation in the range 1350–2400 K. In going to lower temperatures there is considerable scatter and none of the data at temperatures below 400 K<sup>15–22</sup> are considered reliable. Cohen<sup>23</sup> has analyzed in detail a number of the low temperature studies<sup>15–18</sup> and has shown that they have underestimated the effects of the secondary chemistry removing O atoms, leading to measured values of  $k$  that are

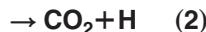
too high. This is reflected in our preferred expression, which is limited to temperatures above 400 K, and extrapolation of which predicts lower values than the experimental data at lower temperatures. In the intermediate range (400–1000 K) the studies of Felder and Fontijn<sup>4</sup> and of Klemm *et al.*<sup>5</sup> are considered the most reliable. The other studies either give rather high values of  $k$ <sup>22,24,25</sup> or there are doubts about the stoichiometry factors used in deriving the values of  $k$ .<sup>15–18,26</sup>

The expression derived by Cohen and Westberg<sup>9</sup> is in good agreement with our preferred expression at high temperatures but gives values lower by a factor of  $\sim 2$  at 400 K. Corchado *et al.*<sup>27</sup> have calculated values of  $k$  using *ab initio* methods and variational transition state theory with allowance for tunneling and obtain an expression which gives values of  $k$  some 30%–40% lower than our preferred expression throughout the recommended temperature range.

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#### Thermodynamic Data

$$\begin{aligned}\Delta H^{\circ}_{298}(1) &= -365.7 \text{ kJ mol}^{-1} \\ \Delta S^{\circ}_{298}(1) &= 4.11 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 21.1 T^{-0.481} \exp(+43740/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

$$\begin{aligned}\Delta H^{\circ}_{298}(2) &= -467.82 \text{ kJ mol}^{-1} \\ \Delta S^{\circ}_{298}(2) &= -57.05 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 9.96 \cdot 10^{-6} T^{0.682} \exp(+56500/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$k_1 = 5 \cdot 10^{-11}$	1000–1700	Browne <i>et al.</i> , 1969 <sup>1</sup>	(a)
$2.1 \cdot 10^{-10}$	297	Martinez, Washida, and Bayes, 1974 <sup>2</sup>	(b)
<i>Branching Ratios</i>			
$k_1/k = 0.8$	300	Niki, Daby, and Weinstock, 1969 <sup>3</sup>	(c)
$k_2/k_1 = 0.73$	298	Westenberg and de Haas, 1972 <sup>4</sup>	(d)
$k_2/k = 0.46$	300	Mack and Thrush, 1973 <sup>5</sup>	(e)
$k_1/k = 0.4$	425	Campbell and Handy, 1978 <sup>6</sup>	(f)
<i>Reviews and Evaluations</i>			
$k_1 = 5 \cdot 10^{-11}$	300–2000	Tsang and Hampson, 1986 <sup>7</sup>	(g)
$k_2 = 5 \cdot 10^{-11}$	300–2000	Herron, 1988 <sup>8</sup>	(h)
$1 \cdot 10^{-10}$	300–2500	CEC, 1992; 1994 <sup>9</sup>	(g)
$k_1 = 5 \cdot 10^{-11}$	300–2500	$k_2 = 5 \cdot 10^{-11}$	

#### Comments

- (a) Profiles of species in rich and lean acetylene/O<sub>2</sub> flames determined by optical absorption measurements (OH, CH, and C<sub>2</sub>) and stable products by GC (H<sub>2</sub>, Ar, O<sub>2</sub>) and mass spectrometry (C<sub>2</sub>H<sub>2</sub>, O<sub>2</sub>, Ar, CO, CO<sub>2</sub>, H<sub>2</sub>O). Fitting of the [CO] profile sensitive to reactions of HCO.
- (b) Discharge flow study of the reactions of O atoms with HCHO and C<sub>2</sub>H<sub>4</sub>. [H] and [O] monitored by ESR and products (CO, CO<sub>2</sub>) analyzed by gas chromatography (GC).
- (c) Discharge flow study of the O+C<sub>2</sub>H<sub>4</sub> reaction with time of flight mass spectrometric detection of C<sub>2</sub>H<sub>4</sub>, H, HCHO, and the final products, H<sub>2</sub> and CO<sub>2</sub> under conditions of an excess of O.
- (d) Discharge flow study of the reaction O+HCHO. [O] monitored by electron spin resonance (ESR) and [CO<sub>2</sub>] by mass spectrometry.
- (e) Discharge flow study of the reaction O+C<sub>2</sub>H<sub>4</sub>. [CHO] monitored by photoionization mass spectrometry.  $k$  derived from the rate of approach of [CHO] to the steady state.
- (f) Stirred flow reactor study of the O/H<sub>2</sub>/N<sub>2</sub> (or Ar) system with various amounts of added CO. [O] monitored by CO+O chemiluminescence.
- (g) See Comments on Preferred Values.
- (h) Recommends the value suggested by Warnatz.<sup>10</sup>

#### Preferred Values

$$\begin{aligned}k_1 &= 5 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the range } 300\text{--}2500 \text{ K.} \\ k_2 &= 5 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the range } 300\text{--}2500 \text{ K.}\end{aligned}$$

#### Reliability

$$\begin{aligned}\Delta \log k_1 &= \pm 0.3 \text{ over the range } 300\text{--}2500 \text{ K.} \\ \Delta \log k_2 &= \pm 0.3 \text{ over the range } 300\text{--}2500 \text{ K.}\end{aligned}$$

#### Comments on Preferred Values

There are no direct measurements of  $k$ . All of the studies have been made on systems in which O+HCO is a secondary reaction. The results obtained suggest that the value of the rate constant is large ( $\sim 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) with a small temperature coefficient and with both reaction channels making comparable contributions to the overall  $k$ . The preferred values are identical to those suggested by Tsang and Hampson.<sup>7</sup>

#### References

- <sup>1</sup> W. G. Browne, R. P. Porter, J. D. Verlin, and A. H. Clark, 12th Symp. (Int.) Combustion, 1969, p. 1035.
- <sup>2</sup> N. Washida, R. I. Martinez, and K. D. Bayes, Z. Naturforsch. A29, 251 (1974).

- <sup>3</sup>H. Niki, E. E. Daby, and B. Weinstock, 12th Symp. (Int.) Combustion, 1969, p. 277.  
<sup>4</sup>A. A. Westenberg and N. de Haas, J. Phys. Chem. **76**, 2215 (1972).  
<sup>5</sup>G. P. R. Mack and B. A. Thrush, J. Chem. Soc. Faraday Trans. I **69**, 208 (1972).  
<sup>6</sup>I. M. Campbell and B. J. Handy, J. Chem. Soc. Faraday Trans. I **74**, 316 (1978).

- <sup>7</sup>W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data **15**, 1087 (1984).  
<sup>8</sup>J. T. Herron, J. Phys. Chem. Ref. Data **17**, 967 (1988).  
<sup>9</sup>CEC, 1992; Supplement I, 1994 (see references in Introduction).  
<sup>10</sup>J. Warnatz, in *Combustion Chemistry*, edited by W. C. Gardiner, Jr. (Springer, New York, 1984).

### O+HCHO → OH+HCO

#### Thermodynamic Data

$$\Delta H_{298}^{\circ} = -60.4 \text{ kJ mol}^{-1}$$

$$\Delta S_{298}^{\circ} = 28.25 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c = 1.2 \cdot 10^3 T^{-0.454} \exp(+6900/T)$$

$$(300 \leq T/\text{K} \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$8.3 \cdot 10^{-11} \exp(-2300/T)$	1875–2240	Bowman, 1975 <sup>1</sup>	(a)
$2.8 \cdot 10^{-11} \exp(-1525/T)$	250–498	Klemm, 1979 <sup>2</sup>	(b)
$3.8 \cdot 10^{-11} \exp(-1583/T)$	296–437	Chang and Barker, 1979 <sup>3</sup>	(c)
$3.0 \cdot 10^{-11} \exp(-1554/T)$	298–748	Klemm et al., 1979 <sup>4</sup>	(d)
<i>Reviews and Evaluations</i>			
$6.9 \cdot 10^{-13} T^{0.57} \exp(-1390/T)$	250–2200	CEC, 1992; 1994 <sup>5</sup>	(e)

#### Comments

- (a) CH<sub>4</sub>/O<sub>2</sub>/Ar mixtures investigated in incident shock waves.  $k$  determined by computer fitting.
- (b) Flash photolysis; resonance fluorescence detection of O atoms.
- (c) Discharge flow; mass spectrometric detection of O atoms.
- (d) Discharge flow; resonance fluorescence detection of O atoms.
- (e) Based on high temperature data of Bowman<sup>1</sup> and low temperature data cited on this sheet.

#### Preferred Values

$k = 6.9 \cdot 10^{-13} T^{0.57} \exp(-1390/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$   
 over the range 250–2200 K.

#### Reliability

$\Delta \log k = \pm 0.1$  at 250 K, rising to  $\pm 0.3$  at 2200 K.

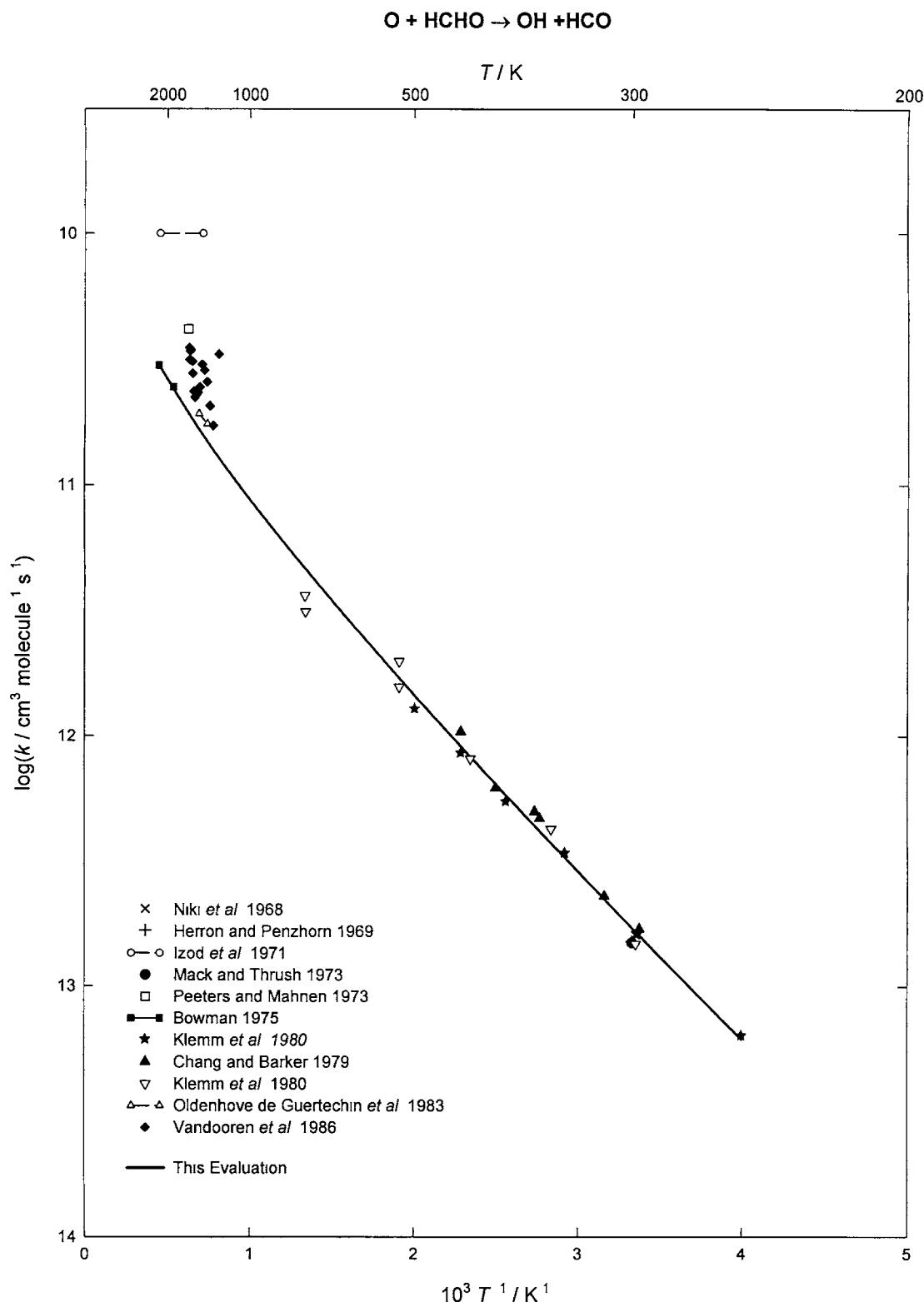
#### Comments on Preferred Values

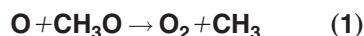
The preferred values, which are unchanged from the previous CEC evaluations,<sup>5</sup> are based on the high temperature determination of Bowman<sup>1</sup> and the low temperature data of

Klemm and co-workers<sup>2,4</sup> and of Chang and Barker.<sup>3</sup> The earlier room temperature measurements of Niki et al.,<sup>6</sup> Herron and Penzhorn,<sup>7</sup> and Mack and Thrush<sup>8</sup> are in good agreement with this expression. Other indirect determinations from high temperature flame studies<sup>9–11</sup> and the shock tube study of Izod et al.,<sup>12</sup> are considered unreliable, although more recent flame work<sup>10</sup> gives  $k$  values consistent with the preferred expression.

#### References

- C. T. Bowman, 15th Symp. (Int.) Combustion, 1975, p. 869.
- R. B. Klemm, J. Chem. Phys. **71**, 1987 (1979).
- J. S. Chang and J. R. Barker, J. Phys. Chem. **83**, 3059 (1979).
- R. B. Klemm, E. G. Skolnik, and J. V. Michael, J. Chem. Phys. **72**, 1256 (1980).
- CEC, 1992; Supplement I, 1994 (see references in Introduction).
- H. Niki, E. E. Daby, and B. Weinstock, J. Chem. Phys. **48**, 5729 (1968).
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- G. P. R. Mack and B. A. Thrush, J. Chem. Soc. Faraday Trans. I **69**, 208 (1973).
- J. Peeters and G. Mahnen, 14th Symp. (Int.) Combustion, 1973, p. 133.
- L. Oldenhove de Guertchin, J. Vandooren, and P. J. Van Tiggelen, Bull. Soc. Chim. Belg. **92**, 663 (1983).
- J. Vandooren, L. Oldenhove de Guertchin, and P. J. Van Tiggelen, Combust. Flame **64**, 127 (1986).
- P. J. Izod, G. B. Kistiakowsky, and S. Matsuda, J. Chem. Phys. **55**, 4425 (1971).





#### Thermodynamic Data

$$\begin{aligned}\Delta H^\circ_{298}(1) &= -120.0 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(1) &= 8.66 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 3.97 \cdot 10^2 T^{-0.703} \exp(+14170/T) \\ (200 \leq T/\text{K} \leq 6000) \end{aligned}$$

$$\begin{aligned}\Delta H^\circ_{298}(2) &= -337.9 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(2) &= 12.1 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 3.89 \cdot 10^3 T^{-0.971} \exp(+40240/T) \\ (300 \leq T/\text{K} \leq 5000) \end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$2.5 \cdot 10^{-11}$	298	Ewig, Rhäsa, and Zellner, 1987 <sup>1</sup>	(a)
<i>Branching Ratios</i>			
$k_2/k = 0.12$	298	Ewig, Rhäsa, and Zellner, 1987 <sup>1</sup>	(a)
$k_1/k = 0.65$	298	Heinemann-Fiedler and Hoyermann, 1988 <sup>2</sup>	(b)
<i>Reviews and Evaluations</i>			
$2.5 \cdot 10^{-11}$	300–1000	CEC, 1992; 1994 <sup>3</sup>	(c)

#### Comments

- (a) Laser photolysis of  $\text{CH}_3\text{ONO}/\text{O}_3/\text{N}_2$  mixtures at 248 nm.  $\text{CH}_3\text{O}$  detected by LIF in excess O. OH product detected by LIF.
- (b) Discharge flow system with molecular beam sampling into time-of-flight mass spectrometer.  $\text{CH}_3$  yield from  $\text{CH}_3\text{O}$  loss measured directly in presence of excess O.
- (c) Based on data of Ewig *et al.*<sup>1</sup>

$$\Delta(k_2/k) = {}^{+0.2}_{-0.1} \text{ at } 298 \text{ K.}$$

#### Comments on Preferred Values

The recommended value is based on the single experimental measurement<sup>1</sup> at 298 K with an assumed zero temperature dependence. The two estimates of the branching ratio<sup>1,2</sup> are in reasonable agreement and the recommended value at 298 K is a mean of the two determinations.

#### Preferred Values

$k = 2.5 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 298–1000 K.

$$k_2/k = 0.25 \text{ at } 298 \text{ K.}$$

#### Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K, rising to } \pm 0.7 \text{ at } 1000 \text{ K.}$$

#### References

- <sup>1</sup> F. Ewig, D. D. Rhäsa, and R. Zellner, Ber. Bunsenges. Phys. Chem. **91**, 708 (1987).
- <sup>2</sup> P. Heinemann-Fiedler and K. Hoyermann, Ber. Bunsenges. Phys. Chem. **92**, 1472 (1988).
- <sup>3</sup> CEC, 1992; Supplement I, 1994 (see references in Introduction).

*Thermodynamic Data*

$$\begin{aligned}\Delta H^{\circ}_{298}(1) &= -28.4 \text{ kJ mol}^{-1} \\ \Delta S^{\circ}_{298}(1) &= 26.78 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 3.58 \cdot 10^2 T^{-0.260} \exp(+3020/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

$$\begin{aligned}\Delta H^{\circ}_{298}(2) &= 6.63 \text{ kJ mol}^{-1} \\ \Delta S^{\circ}_{298}(2) &= 12.25 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 3.64 T^{0.097} \exp(-930/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data ( $k = k_1 + k_2$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$5.65 \cdot 10^{-11} \exp(-2750/T)$	300–1006	Grotheer and Just, 1981 <sup>1</sup>	(a)
$1.63 \cdot 10^{-11} \exp(-2267/T)$	297–544	Failes <i>et al.</i> , 1982 <sup>2</sup>	(b)
$2.70 \cdot 10^{-11} \exp(-2532/T)$	298–998	Keil <i>et al.</i> , 1987 <sup>3</sup>	(c)
<i>Reviews and Evaluations</i>			
$6.5 \cdot 10^{-19} T^{2.5} \exp(-1550/T)$ $k_1 > k_2$	300–1100	Tsang, 1987 <sup>4</sup>	(d)

**Comments**

- (a) Fast-flow discharge system with O atoms produced by titration of N atoms with NO. [O], [CH<sub>3</sub>OH], and the concentration of the products H<sub>2</sub>CO, H<sub>2</sub>O, H<sub>2</sub>, and O<sub>2</sub> were monitored by molecular beam sampling into a TOF mass spectrometer. Values of  $k$  were derived by modeling and fitting the concentration profiles.
- (b) Modulated photolysis–phase shift technique used. O atoms generated by modulated Hg photosensitized photolysis of N<sub>2</sub>O at 253.7 nm. [O] monitored by NO<sub>2</sub> chemiluminescence from O+NO reaction. Computer modeling used to correct for secondary reactions of O atoms.
- (c) Fast-flow discharge (298–998 K) and flash photolysis (329–527 K) with resonance fluorescence detection of O atoms used in both cases. Methanol was in large excess. O atoms were produced by photolysis of O<sub>2</sub> in the flash photolysis experiments, and in the flow system by a discharge through O<sub>2</sub>, or by titration of N atoms with NO. O<sub>2</sub> was added to suppress secondary chemistry caused by CH<sub>2</sub>OH production. Possible heterogeneous decomposition on the walls of the flow tube was detected at temperatures above ~450 K. Good agreement of results from the two techniques was obtained.
- (d) BEBO calculation carried out and activation energy adjusted to fit the results from Refs. 1–3 in the range 300–750 K.

**Preferred Values**

$k = 4.1 \cdot 10^{-11} \exp(-2670/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 350–1000 K.

**Reliability**

$\Delta \log k = \pm 0.2$  over the range 350–1000 K.

**Comments on Preferred Values**

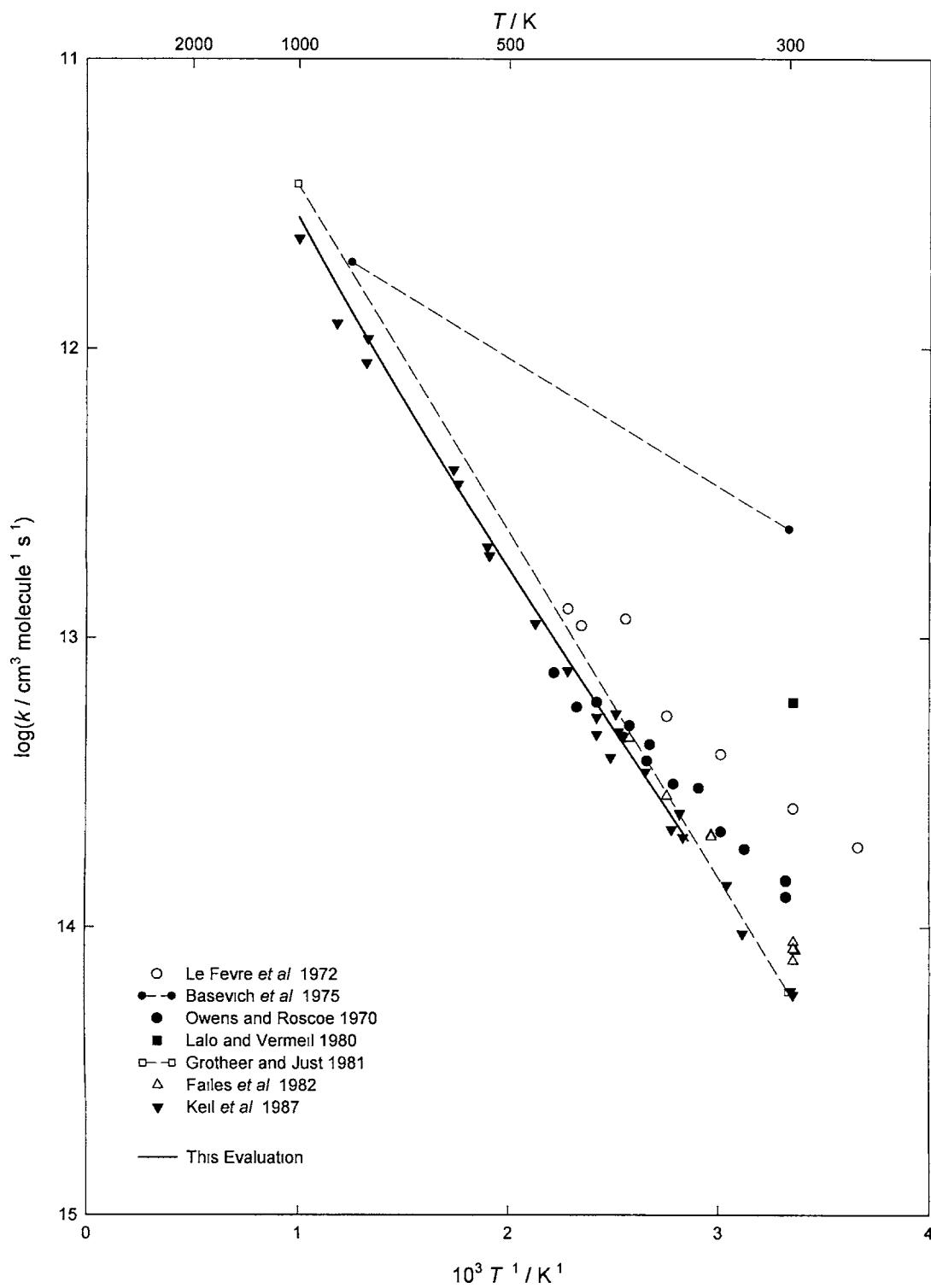
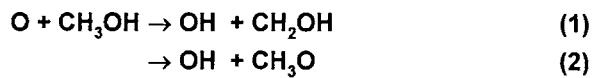
The preferred values are based on the data in Refs. 1–3 which are in good agreement over the range 350–1000 K. There are a number of other studies<sup>5–8</sup> which are not used in this evaluation. Those of Basevich *et al.*<sup>5</sup> and Lalo and Vermeil<sup>6</sup> give very high values of  $k$ . Those of Owens and Roscoe<sup>7</sup> and of Le Fevre *et al.*<sup>8</sup> give low activation energies and also slightly high values of  $k$ , possibly due to the difficulties in determining the stoichiometry factor in the discharge flow technique which they used.

All of the studies extend to lower temperatures but below 350 K they show increasing disagreement and no recommendations are made for the low temperature regime. The scatter on the data over the whole temperature range is such that any curvature on the Arrhenius plot is uncertain and the preferred expression for  $k$  contains no  $T^n$  dependence.

There is no experimental information on the channel branching ratios. Since the mechanism for both channels is likely to be direct hydrogen abstraction, Channel (1) is probably preferred under all conditions as it is the more exothermic and it involves three available hydrogens.

**References**

- <sup>1</sup>H. H. Grotheer and Th. Just, Chem. Phys. Lett. **78**, 71 (1981).
- <sup>2</sup>R. L. Failes, D. L. Singleton, G. Paraskevopoulos, and R. S. Irwin, Int. J. Chem. Kinet. **14**, 371 (1982).
- <sup>3</sup>D. G. Keil, T. Tanzawa, E. G. Skolnik, R. B. Klemm, and J. V. Michael, J. Chem. Phys. **75**, 2693 (1987).
- <sup>4</sup>W. Tsang, J. Phys. Chem. Ref. Data. **16**, 471 (1987).
- <sup>5</sup>V. Ya Basevich, S. M. Kogarko, and G. A. Furman, Bull. Acad. Sci. USSR **24**, 948 (1975).
- <sup>6</sup>C. Lalo and C. Vermeil, J. Chim. Phys. **27**, 131 (1980).
- <sup>7</sup>C. M. Owens and J. M. Roscoe, Can. J. Chem. **54**, 984 (1970).
- <sup>8</sup>H. F. Le Fevre, J. F. Meagher, and R. B. Timmons, Int. J. Chem. Kinet. **4**, 103 (1972).





#### Thermodynamic Data

$$\begin{aligned}\Delta H^\circ_{298}(1) &= -65.0 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(1) &= 20.37 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 1.70 \cdot 10^2 T^{-0.385} \exp(+7660/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

$$\begin{aligned}\Delta H^\circ_{298}(2) &= -28.4 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(2) &= 26.76 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 1.14 \cdot 10^2 T^{-0.127} \exp(+3140/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$1.06 \cdot 10^{-14}$	297	Vaghjiani and Ravishankara, 1990 <sup>1</sup>	(a)
<i>Reviews and Evaluations</i>			
$3.3 \cdot 10^{-11} \exp(-2390/T)$	300–1000	CEC, 1994 <sup>2</sup>	(b)

#### Comments

- (a) Pulsed photolysis of  $\text{O}_3$  at 532 nm in presence of excess  $\text{CH}_3\text{OOH}$ ;  $\text{O}(\text{P}^3)$  monitored by resonance fluorescence.
- (b) Based on the data of Vaghjiani and Ravishankara<sup>1</sup> (see Comments on Preferred Values).

#### Preferred Values

$$k = 4.1 \cdot 10^{-11} \exp(-2460/T) \text{ over the range } 297\text{--}1000 \text{ K.}$$

#### Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 297 \text{ K, rising to } \pm 0.5 \text{ at } 1000 \text{ K.}$$

#### Comments on Preferred Values

The room temperature data of Vaghjiani and

Ravishankara,<sup>1</sup> are the only reported experimental values of the rate constant for the  $\text{O}(\text{P}^3) + \text{CH}_3\text{OOH}$  reaction. The preferred temperature dependence is obtained assuming an A factor for this reaction equal to that for  $\text{O} + \text{CH}_3\text{OH}$  (this evaluation).

Comparison with the rate coefficient for the reaction:  $\text{O} + \text{H}_2\text{O}_2 \rightarrow \text{OH} + \text{HO}_2$  ( $1.7 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K) indicates that abstraction of the peroxide H atom is slower, suggesting that Channel (2) is dominant.

#### References

<sup>1</sup>G. L. Vaghjiani and A. R. Ravishankara, Int. J. Chem. Kinet. **22**, 351 (1990).

<sup>2</sup>CEC, Supplement I, 1994 (see references in Introduction).

**O+C<sub>2</sub>H→Products****Rate Coefficient Data**

<i>k/cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup></i>	<i>T/K</i>	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$2.4 \cdot 10^{-11} \exp(-1585/T)$	1400–2600	Shaub and Bauer, 1978 <sup>1</sup>	(a)
$\approx 1.7 \cdot 10^{-11}$	298	Homann and Schweinfurth, 1981 <sup>2</sup>	(b)
$\approx 1.2 \cdot 10^{-12}$	298	Grebe and Homann, 1982 <sup>3</sup>	(c)
$9.9 \cdot 10^{-11}$	600	Boullart <i>et al.</i> , 1996 <sup>4</sup>	(d)
$1.8 \cdot 10^{-11}$	295	Devriendt <i>et al.</i> , 1996 <sup>5</sup>	(e)
$2.4 \cdot 10^{-11} \exp(-230/T)$	290–925	Devriendt and Peeters, 1997 <sup>6</sup>	(f)
<i>Reviews and Evaluations</i>			
$3.0 \cdot 10^{-11}$	300–2500	Tsang and Hampson, 1986 <sup>7</sup>	(g)
$1.7 \cdot 10^{-11}$	300–2500	CEC, 1992; 1994 <sup>8</sup>	(h)

**Comments**(h) Based on the data of Homann and Schweinfurth.<sup>2</sup>

- (a) Shock tube study on C<sub>2</sub>H<sub>2</sub>/O<sub>2</sub>/Ar mixtures; final product concentrations measured by gas chromatography. Values of *k* determined by modeling assumed reaction mechanism of 17 reactions and fitting of product yields.
- (b) Discharge flow study on the C<sub>2</sub>H<sub>2</sub>/O system with and without added H. [C<sub>3</sub>H<sub>4</sub>], [C<sub>4</sub>H<sub>2</sub>], and [CH<sub>2</sub>O] monitored by mass spectrometry. *k* obtained by fitting of yields to a reaction mechanism of 27 reactions. Fit relatively insensitive to *k*.
- (c) Discharge flow study on the C<sub>2</sub>H<sub>2</sub>/O/H system. CH(A<sup>2</sup>Δ-X<sup>2</sup>Π) and C<sub>2</sub>(d<sup>3</sup>Π<sub>g</sub>-A<sup>3</sup>Π<sub>u</sub>) chemiluminescence monitored at 431.4 and 516.5 nm, respectively, and the quasi-continuous C<sub>2</sub>H\* emissions. Kinetics analyzed by modeling of a detailed reaction mechanism.
- (d) Discharge flow study on the C<sub>2</sub>H<sub>2</sub>/O/H system at 2.6 mbar total pressure of He. Molecular beam sampling mass spectrometry used to monitor relative concentrations of CH, C<sub>2</sub>H, C<sub>3</sub>H, and C<sub>3</sub>H<sub>2</sub> and absolute concentrations of C<sub>2</sub>H<sub>2</sub>, O, and H. From [C<sub>3</sub>H<sub>2</sub>]/[C<sub>2</sub>H] and [C<sub>3</sub>H]/[C<sub>2</sub>H], measured as a function of [C<sub>2</sub>H<sub>2</sub>]/[O], the ratio *k*/*k*(C<sub>2</sub>H+C<sub>2</sub>H<sub>2</sub>)+*k*(C<sub>2</sub>H+O<sub>2</sub>)/[O<sub>2</sub>]/[C<sub>2</sub>H<sub>2</sub>]) is obtained. Value of *k* derived using values of reference rate constants from the present evaluation.
- (e) The measured rate constant is for the channel forming CH(A<sup>2</sup>Δ). C<sub>2</sub>H and O were generated by co-photolysis of C<sub>2</sub>H<sub>2</sub> and N<sub>2</sub>O by 193 nm excimer laser pulses in the presence of a large excess of N<sub>2</sub>. Time resolved intensity of the CH(A<sup>2</sup>Δ-X<sup>2</sup>Π) luminescence was monitored and calibrated using the known photon yield of the NO+O+M→NO<sub>2</sub>\*+M reaction.
- (f) Discharge flow study of the C<sub>2</sub>H<sub>2</sub>/O/H system. [O] and [C<sub>2</sub>H] determined by mass spectrometry; CH(A<sup>2</sup>-X<sup>2</sup>Π) chemiluminescence monitored and used to derive *k* values. The measured rate constant is for the channel forming CH(A<sup>2</sup>Δ).
- (g) Based on analogy with O+C<sub>2</sub>H<sub>5</sub> and O+C<sub>2</sub>H<sub>3</sub> reactions.

**Preferred Values**

*k*= $9.9 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 290–2500 K.

**Reliability**

$\Delta \log k = \pm 0.5$  over the range 290–2500 K.

**Comments on Preferred Values**

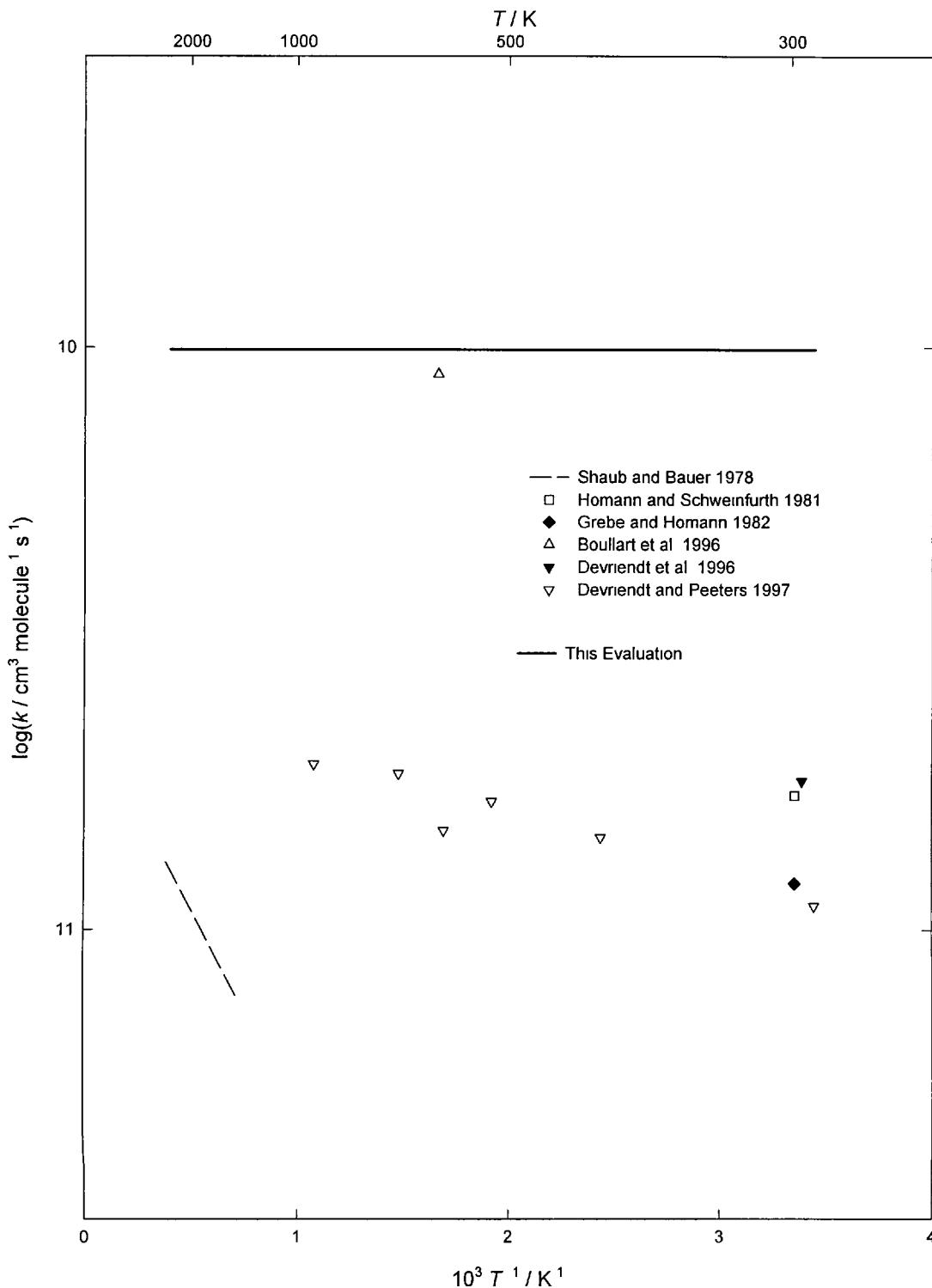
Prior to the studies of Boullart *et al.*,<sup>4</sup> Devriendt *et al.*,<sup>5</sup> and Devriendt and Peeters<sup>6</sup> the only available data on this reaction came from studies on systems in which the conditions were such that they were not very sensitive to the C<sub>2</sub>H+O reaction.<sup>1–3</sup> These studies gave only approximate values of *k* and little weight is given to them in assigning our preferred values. The only reasonably reliable measurement of the overall rate constant is that of Boullart *et al.*<sup>4</sup> at 600 K. The value obtained is close to collisional and only a very small temperature coefficient is to be expected. We therefore accept this value over a wide temperature range assigning substantial error limits until further studies are available.

The only reaction channel that has been positively identified is that leading to CH in its A<sup>2</sup>Δ state from which it undergoes a transition to the CH(X<sup>2</sup>Π) ground electronic state with emission of radiation in the 430 nm region. Other likely channels are those leading to CH(X<sup>2</sup>Π, X<sup>3</sup>Σ<sup>-</sup>, or a<sup>1</sup>Δ)+CO and C<sub>2</sub>O+H. The values of the rate constant for the CH(A<sup>2</sup>Δ) forming channel determined by Devriendt *et al.*<sup>5</sup> and Devriendt and Peeters<sup>6</sup> are in good agreement, and taken with the value of *k* determined by Boullart *et al.*,<sup>4</sup> indicate a yield of 0.2–0.4 for the CH(A<sup>2</sup>Δ).

## References

- <sup>1</sup> W. M. Shaub and S. H. Bauer, Comb. Flame **32**, 35 (1978).  
<sup>2</sup> K. H. Homann and H. Schweinfurth, Ber. Bunsenges. Phys. Chem. **85**, 569 (1981).  
<sup>3</sup> J. Grebe and K. H. Homann, Ber. Bunsenges. Phys. Chem. **86**, 587 (1981).

- <sup>4</sup> W. Boullart, K. Devriendt, R. Borms, and J. Peeters, J. Phys. Chem. **100**, 998 (1996).  
<sup>5</sup> K. Devriendt, H. Van Look, B. Ceursters, and J. Peeters, Chem. Phys. Lett. **261**, 450 (1996).  
<sup>6</sup> K. Devriendt and J. Peeters, J. Phys. Chem. A **101**, 2546 (1997).  
<sup>7</sup> W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data **15**, 1087 (1986).  
<sup>8</sup> CEC, 1992; Supplement I, 1994 (see references in Introduction).

 $\text{O} + \text{C}_2\text{H} \rightarrow \text{Products}$ 



#### Thermodynamic Data

$$\begin{aligned}\Delta H_{298}^{\circ}(1) &= -197.5 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ}(1) &= 30.47 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 1.03 \cdot 10^6 T^{-1.471} \exp(+23210/T) \\ &\quad (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

$$\begin{aligned}\Delta H_{298}^{\circ}(2) &= -84.09 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ}(2) &= -2.09 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 2.02 \cdot T^{-0.089} \exp(+9961/T) \\ &\quad (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$3.3 \cdot 10^{-11} \exp(-1641/T)$	230–450	Westenberg and de Haas, 1969 <sup>1</sup>	(a)
$2.0 \cdot 10^{-11} \exp(-1510/T)$	243–673	Hoyermann, Wagner, and Wolfrum, 1969 <sup>2</sup>	(b)
$2.4 \cdot 10^{-11} \exp(-1590/T)$	273–729	James and Glass, 1969 <sup>3</sup>	(c)
$k_1 = 2.0 \cdot 10^{-10} \exp(-3300/T)$	1500–2570	Löhr and Roth, 1981 <sup>4</sup>	(d)
$k_2 = 7.2 \cdot 10^{-10} \exp(-6100/T)$			
$3.0 \cdot 10^{-11} \exp(-1620/T)$	298–608	Aleksandrov, Arutyunov, and Kozlov, 1981 <sup>5</sup>	(e)
$2.7 \cdot 10^{-11} \exp(-1550/T)$	295–1330	Homann and Wellman, 1983 <sup>6</sup>	(f)
$k_1 = 2.7 \cdot 10^{-10} \exp(-4980/T)$	1500–2500	Frank, Bhaskaran, and Just, 1986 <sup>7</sup>	(g)
$k_2 = 6.6 \cdot 10^{-10} \exp(-5365/T)$			
$1.1 \cdot 10^{-19} T^{2.6} \exp(-330/T)$	290–1510	Mahmud and Fontijn, 1987 <sup>8</sup>	(h)
$6.5 \cdot 10^{-11} \exp(-1900/T)$	370–876	Russell <i>et al.</i> , 1988 <sup>9</sup>	(i)
$1.78 \cdot 10^{-10} \exp(-2710/T)$	850–1950	Michael and Wagner, 1990 <sup>10</sup>	(j)
$2.3 \cdot 10^{-11} \exp(-1530/T)$	200–284	Bohn and Stuhl, 1990 <sup>11</sup>	(k)
<i>Branching Ratios (<math>k_2/k</math>)</i>			
0.35	1500	Löhr and Roth, 1981 <sup>4</sup>	(d)
0.55	2570		
$0.5 \exp(-660/T)$	298–608	Aleksandrov, Arutyunov, and Kozlov, 1981 <sup>5</sup>	(e)
0.5	1000	Homann and Wellman, 1983 <sup>12</sup>	(l)
0.6	287,535	Peeters, Schaekers, and Vinckier, 1986 <sup>13</sup>	(m)
0.80	900–1200	Michael and Wagner, 1990 <sup>10</sup>	(j)
0.85	285	Boullart and Peeters, 1992 <sup>14</sup>	(n)
0.83	290	Peeters, Boullart, and Langhans, 1994 <sup>15</sup>	(o)
<i>Reviews and Evaluations</i>			
$1.2 \cdot 10^{-17} T^{2.1} \exp(-786/T)$	300–2500	CEC, 1994 <sup>16</sup>	(p)
$k_2/k = 0.7$			
$3.0 \cdot 10^{-11} \exp(-1600/T)$	200–300	NASA, 1997 <sup>17</sup>	(q)

#### Comments

- (a) Discharge flow study with [O] monitored by ESR. Stoichiometry of 2 O atoms removed for each C<sub>2</sub>H<sub>2</sub> molecule reacted established by ESR/mass spectrometry experiments.
- (b) Discharge flow study. O(<sup>3</sup>P) monitored by ESR and mass spectrometry used to detect H, C<sub>2</sub>H<sub>2</sub>, CO and minor hydrocarbon products.
- (c) Discharge flow study. Reaction progress followed by monitoring CH(<sup>2</sup>Δ → <sup>2</sup>Π) chemiluminescence.
- (d) Shock wave study using reflected shock waves in N<sub>2</sub>O/C<sub>2</sub>H<sub>2</sub>/Ar mixtures. [O] and [H] monitored by ARAS. Early stages of the reaction could be modeled with a simple reaction scheme to give the tabulated expressions for  $k_1$  and  $k_2$ .

- (e) Discharge flow study with O generated from N<sub>2</sub>O. H and O detected by resonance fluorescence with absolute calibration via equilibrium concentrations of H and O in H<sub>2</sub> and O<sub>2</sub> at 1300–1500 K.  $k$  determined from decay of the O signal;  $k_2/k$  obtained from the absolute H signal.
- (f) Discharge flow study on O/C<sub>2</sub>H<sub>2</sub> mixtures in He carrier with nozzle beam sampling and mass spectrometric detection. O atoms were prepared by a discharge in O<sub>2</sub> or by the N+NO reaction.  $k$  values were determined under conditions of a large excess of C<sub>2</sub>H<sub>2</sub>.
- (g) Reflected shock wave study of N<sub>2</sub>O/C<sub>2</sub>H<sub>2</sub>/Ar mixtures at 1.5–2 bar. O, H, and CO detected by resonance absorption. Profiles analyzed using a 14 reaction scheme, reduced from a 48 reaction scheme. Conditions were carefully chosen to ensure sensitivity of the profiles to

- both channels (1) and (2). Channel (2) was essential if the overall shape of the [H] profile was to be reproduced.
- (h) Flash photolysis study in which O was generated from the photolysis of O<sub>2</sub> or CO<sub>2</sub>. [O] was monitored by resonance fluorescence under conditions of excess C<sub>2</sub>H<sub>2</sub>.
- (i) Pulsed laser photolysis of SO<sub>2</sub>/C<sub>2</sub>H<sub>3</sub>Br mixtures at 193 nm to produce O atoms and C<sub>2</sub>H<sub>2</sub> from the SO<sub>2</sub> and C<sub>2</sub>H<sub>3</sub>Br, respectively. Conditions were chosen to give [O]>[C<sub>2</sub>H<sub>2</sub>] and the [C<sub>2</sub>H<sub>2</sub>] was monitored by mass spectrometry.
- (j) Flash photolysis, shock tube study. O generated from photolysis of NO (followed by the rapid N+NO reaction) and detected by ARAS. The branching yield was determined from the yield of H; the H signal was calibrated by reference to the O+H<sub>2</sub> reaction under identical conditions. The available overall rate coefficient data (Refs. 1–10) were analyzed over the temperature range 195–2500 K by giving equal weight to each study. Rate coefficients were calculated at 10 equally spaced values of K/T from the Arrhenius, and modified Arrhenius, expression from each of the 10 studies and the resulting 100 values were analyzed by nonlinear least squares, to give  $k=1.2 \cdot 10^{-17} T^{2.09} \times \exp(-786/T)$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.
- (k) O generated by the direct laser photolysis of NO at 160 nm and by the rapid N+NO reaction from the N atoms also produced in the photolysis. [O] was monitored by chemiluminescence (O+NO→NO<sub>2</sub><sup>\*</sup>) in the presence of an excess of C<sub>2</sub>H<sub>2</sub>.
- (l) Discharge flow with molecular beam sampling and mass spectrometric analysis. Analysis of data using a 30 reaction scheme. Channel yield determined via correlation of O removal and CO formation. Effect of H addition to the flow was also investigated.
- (m) Discharge flow with molecular beam sampling and mass spectrometric analysis. Steady-state [HCCO] detected and calibrated against [HCCO] formed in C<sub>3</sub>O<sub>2</sub>/H system. Analysis allowed for removal of HCCO by reaction with H, O, and O<sub>2</sub>.
- (n) Discharge flow/molecular beam sampling/mass spectrometry study of C<sub>2</sub>H<sub>2</sub>/H/O. The <sup>3</sup>CH<sub>2</sub> formed both in channel (1) and by deactivation of <sup>1</sup>CH<sub>2</sub> from the H+HCCO reaction was measured. The latter source was selectively eliminated by scavenging <sup>1</sup>CH<sub>2</sub> with CH<sub>4</sub>.
- (o) Discharge flow/molecular beam sampling/mass spectrometry study of the C<sub>2</sub>H<sub>2</sub>/O system. It was shown, using a 29 reaction scheme, that the shape of the relative CH<sub>2</sub> profile is sensitive to  $k_1/k_2$ .
- (p) Expression of Michael and Wagner<sup>10</sup> for  $k$  adopted.  $k_2/k$  based on the studies of Michael and Wagner,<sup>10</sup> Peeters *et al.*,<sup>13</sup> and Homann and Wellman.<sup>12</sup>
- (q)  $k(298\text{ K})$  based on the studies of Arrington *et al.*,<sup>18</sup> Sullivan and Warneck,<sup>19</sup> Brown and Thrush,<sup>20</sup> Hoyermann *et al.*,<sup>2</sup> Westenberg and de Haas,<sup>1,21</sup> James and

Glass,<sup>3</sup> Stuhl and Niki,<sup>22</sup> and Aleksandrov *et al.*<sup>5</sup> The temperature dependence of  $k$  was based on the studies of Westenberg and de Haas,<sup>1</sup> Hoyermann *et al.*,<sup>2</sup> and Aleksandrov *et al.*<sup>5</sup>

## Preferred Values

$k = 1.95 \cdot 10^{-15} T^{1.40} \exp(-1110/T)$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> over the range 200–2500 K.

$k_2/k = 0.8$  over the range 250–2500 K.

## Reliability

$\Delta \log k = \pm 0.2$  over the range 200–2000 K, rising to  $\pm 0.3$  at 2500.

$\Delta(k_2/k) = \pm 0.1$  over the range 250–2500 K.

## Comments on Preferred Values

The overall rate constant is well defined over a wide range of temperatures. The Arrhenius expression obtained in the analysis of the data in Refs. 1–10, by Michael and Wagner<sup>10</sup> [see Comment (j)] provided a good fit to the data available at that time but the more recent data of Bohn and Stuhl,<sup>11</sup> together with the lower temperature data of Ref. 1, suggest that the expression of Michael and Wagner<sup>10</sup> overestimates  $k$  slightly at temperatures below 300 K. Our preferred expression for  $k$  is very similar to that of Michael and Wagner<sup>10</sup> but modified to accommodate the low temperature data, and the curvature is reduced slightly to give a better representation of the data at very high temperatures.

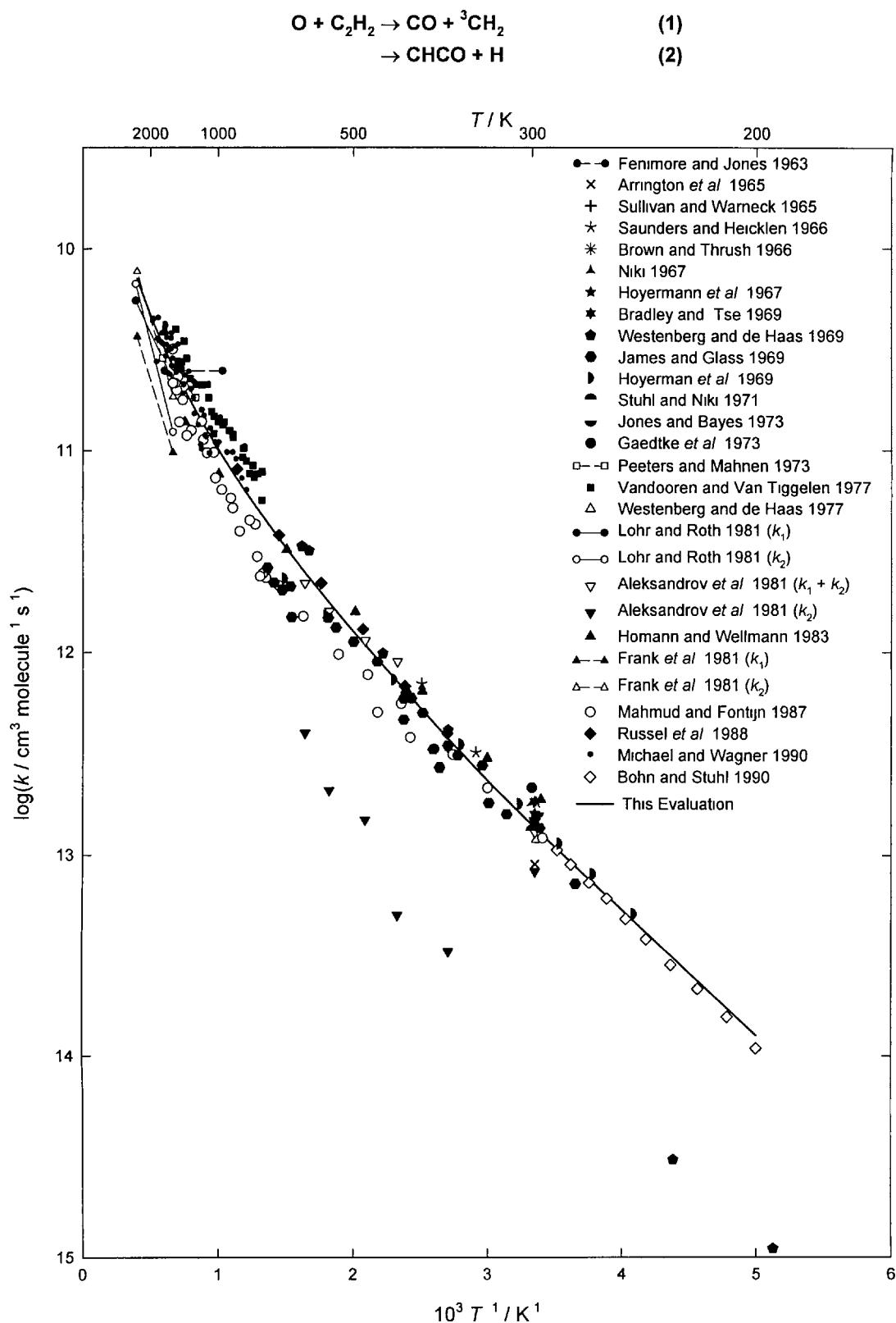
As well as the data cited in the Table there are a number of other studies,<sup>18–30</sup> shown on the Arrhenius diagram, in good agreement with the preferred expression for  $k$ . Most of the experimental data lie within  $\pm 35\%$  of the recommended expression but the data of Ref. 8 lies 40%–50% below the expression in the intermediate temperature range. Reference 10 contains a discussion of the detailed transition state/Rice–Ramsperger–Kassel–Marcus (RRKM) calculation of Harding and Wagner<sup>31</sup> including an analysis of the effects of variation of frequencies and barrier heights. The analysis shows that the model results differ significantly from the well-characterized experimental results. In particular, the model is unable to reproduce the substantial curvature in the Arrhenius plot.

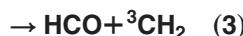
Early studies<sup>4,5,12,13</sup> generated low values of  $k_2/k$  because some of the secondary reactions were neglected. The more recent studies<sup>10,14,15</sup> are either direct or take quantitative account of secondary reactions. They show that Channel (2) is the more important and that there is little dependence on temperature. The calculations of Harding and Wagner<sup>31</sup> are qualitatively in accord with this conclusion.

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#### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = -283.6 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = -10.36 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 1.27 \cdot T^{-0.148} \exp(+33900/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(2) = -513.0 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = -3.50 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 1.24 \cdot 10^3 \cdot T^{-1.064} \exp(+61250/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(3) = -115.4 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = 24.22 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 2.35 \cdot 10^4 \cdot T^{-1.026} \exp(+13520/T) \\ (200 \leq T/\text{K} \leq 6000)$$

See Section 3 for the source of the Thermodynamic Data

#### Rate Coefficient Data ( $k = k_1 + k_2 + k_3$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficients Measurements</i>			
$3.3 \cdot 10^{-11}$	298	Homann and Schweinfurth, 1981 <sup>1</sup>	(a)
$5 \cdot 10^{-11}$	$\approx 200$	Heinemann <i>et al.</i> , 1986 <sup>2</sup>	(b)
<i>Reviews and Evaluations</i>			
$5 \cdot 10^{-11}$	300–2000	Warnatz, 1984 <sup>3</sup>	(c)
$1.6 \cdot 10^{-10}$	300–2500	Tsang and Hampson, 1986 <sup>4</sup>	(d)
$5 \cdot 10^{-11}$	300–2000	CEC, 1992; 1994 <sup>5</sup>	(e)

#### Comments

- (a) Discharge flow study of the  $\text{C}_2\text{H}_2/\text{H}/\text{O}$  system. The concentrations of a number of stable products were monitored and intermediates detected by mass spectrometry.  $k$  was one of several rate coefficients used to fit the product profiles to a numerical model. The products of the  $\text{O} + {}^3\text{CH}_2$  reaction were assumed to be  $\text{H} + \text{CH}_2 + \text{CO}$ .
- (b) Low pressure (0.3–4 mbar) measurements in a Laval nozzle reactor using mass spectrometric detection. The rate coefficient was measured relative to that for  $\text{O} + (\text{CH}_3)_3\text{C}$  which in turn had been measured relative to  $k(\text{O} + \text{CH}_3)$ . A value of  $1.2 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was assumed for  $k(\text{CH}_3 + \text{O})$ , in good agreement with the value recommended in this evaluation ( $1.3 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ). Both products of Channel (2) were detected and  $\text{CH}_2\text{CO}$  was also found showing that Channel (1) also operates. It was not possible to determine a branching ratio. The authors commented that it is difficult to determine the temperature in the Laval nozzle reactor, but a value of  $\approx 200$  K seems appropriate.
- (c) Based on Ref. 1 and a preliminary, private communication from the authors of Ref. 2.
- (d) Estimated by comparison with  $\text{O} + \text{CH}_3$ .
- (e) Based on Ref. 2, because of the more direct nature of the experimental technique.

#### Preferred Values

$$k = 5.0 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the range } 250\text{--}2000 \text{ K.}$$

#### Reliability

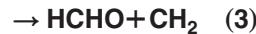
$$\Delta \log k = \pm 0.5 \text{ over the range } 250\text{--}2000 \text{ K.}$$

#### Comments on Preferred Values

A temperature independent value for  $k$  is recommended, based on the more direct measurements of Ref. 2. The data from Ref. 1 provides support well within the wide error limits given. It is not possible to assess the relative channel efficiencies. The preferred values are unchanged from our previous evaluations.<sup>5</sup>

#### References

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- <sup>5</sup>CEC, 1992; Supplement I, 1994 (see references in Introduction).



#### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = -73.2 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = 2.28 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 0.34 T^{0.285} \exp(+8690/T) \\ (300 \leq T/K \leq 5000)$$

$$\Delta H^\circ_{298}(2) = -112.1 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = 38.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 1.12 \cdot 10^5 T^{-0.933} \exp(+12940/T) \\ (300 \leq T/K \leq 5000)$$

$$\Delta H^\circ_{298}(3) = -19.8 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = 33.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 9.86 \cdot 10^4 T^{-1.035} \exp(+1890/T) \\ (300 \leq T/K \leq 5000)$$

$$\Delta H^\circ_{298}(4) = -349.1 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(4) = -7.75 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(4) = 1.28 T^{-0.022} \exp(+41630/T) \\ (300 \leq T/K \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2 + k_3 + k_4$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$1.4 \cdot 10^{-11} \exp(-800/T)$	223–613	Elias, 1963 <sup>1</sup>	(a)
$2.39 \cdot 10^{-13}$	195	Westenberg and de Haas, 1969 <sup>2</sup>	(b)
$3.40 \cdot 10^{-13}$	226		
$5.48 \cdot 10^{-13}$	273		
$7.47 \cdot 10^{-13}$	298		
$12.3 \cdot 10^{-13}$	381		
$29.5 \cdot 10^{-13}$	548		
$31.5 \cdot 10^{-13}$	555		
$56.4 \cdot 10^{-13}$	715		
$5.41 \cdot 10^{-12} \exp(-569/T)$	232–500	Davis <i>et al.</i> , 1972 <sup>3</sup>	(c)
$1.15 \cdot 10^{-11} \exp(-845/T)$	298–486	Singleton and Cvetanovic, 1976 <sup>4</sup>	(d)
$9.23 \cdot 10^{-12} \exp(-742/T)$	298–439	Atkinson and Pitts, 1977 <sup>5</sup>	(e)
$1.12 \cdot 10^{-11} \exp(-1870/T)$	298–500	Nicovitch and Ravishankara, 1982 <sup>6</sup>	(f)
$2.65 \cdot 10^{-12}$	552		
$3.99 \cdot 10^{-12}$	695		
$3.85 \cdot 10^{-12}$	708		
$4.48 \cdot 10^{-12}$	736		
$4.98 \cdot 10^{-12}$	811		
$5.81 \cdot 10^{-12}$	835		
$6.97 \cdot 10^{-12}$	944		
$8.40 \cdot 10^{-12} \exp(-757/T)$	197–372	Browarzik and Stuhl, 1984 <sup>7</sup>	(g)
$2.12 \cdot 10^{-13} T^{0.63} \exp(-689/T)$	260–860	Perry, 1984 <sup>8</sup>	(h)
$1.02 \cdot 10^{-11} \exp(-753/T)$ + $2.75 \cdot 10^{-10} \exp(-4220/T)$	244–1052	Klemm <i>et al.</i> , 1987 <sup>9</sup>	(i)
$1.3 \cdot 10^{-10} \exp(-2770/T)$	1052–2284	Klemm <i>et al.</i> , 1990 <sup>10</sup>	(j)
$k_1 = 1.12 \cdot 10^{-12} \exp(-352/T)$	1100–2100	Hidaka <i>et al.</i> , 1999 <sup>11</sup>	(k)
$k_2 = 2.2 \cdot 10^{-17} T^{1.9} \exp(-302/T)$			
$k_3 = 3 \cdot 10^{-11} \exp(-2013/T)$			
<i>Branching Ratios</i>			
$k_1/k = 0.36$	298	Hunzicker, Kneppen, and Wendt, 1981 <sup>12</sup>	(l)
$k_2/k = 0.52–0.58$			
$k_1/k = 0.27$	300	Smalley, Nesbitt, and Klemm, 1986 <sup>13</sup>	(m)
$k_1/k = 0.37$	769		
$k_2/k_1 = 1.2$	298	Koda <i>et al.</i> , 1987 <sup>14,15</sup>	(n)
$k_2/k_1 = 6.0$ (ethylene d <sub>4</sub> )			
$k_1/k = 0.30$	298	Anastasi <i>et al.</i> , 1994 <sup>16</sup>	(o)
<i>Reviews and Evaluations</i>			
$1.07 \cdot 10^{-11} \exp(-800/T)$	200–500	Cvetanovic, 1987 <sup>17</sup>	(p)
$5 \cdot 75 \cdot 10^{-17} T^{1.88} \exp(-92/T)$	300–2000	CEC, 1992; 1994 <sup>18</sup>	(q)
$k_1/k = 0.35$ ; $k_2/k = 0.60$	>300		
$k_4/k = 0.05$			

### Comments

- (a) Discharge flow. O atoms produced by discharge in He/O<sub>2</sub> mixtures or by N+NO titration. Relative [O] monitored by O+NO chemiluminescence. [C<sub>2</sub>H<sub>4</sub>] determined by mass spectrometry.
- (b) Discharge flow. O atoms produced by discharge in He/O<sub>2</sub> mixtures or by N+NO titration. ESR detection of O(<sup>3</sup>P). [C<sub>2</sub>H<sub>4</sub>] monitored by mass spectrometry. Experiments carried out with both O and C<sub>2</sub>H<sub>4</sub> in excess. Measured stoichiometry used to derive values of *k*. Authors note curved Arrhenius plot.
- (c) Flash photolysis of O<sub>2</sub>/C<sub>2</sub>H<sub>4</sub>/He mixtures at a total pressure of 70 mbar. [O] monitored by resonance fluorescence. Other experiments were carried out using resonance absorption detection of O and discharge flow with mass spectrometric detection of C<sub>2</sub>H<sub>4</sub>. *k* was found to be independent of pressure in the range covered (1.7–325 mbar).
- (d) Molecular modulation; Hg photosensitized decomposition of N<sub>2</sub>O in He bath gas used as the O atom source. O detected by O+NO chemiluminescence. *k* obtained from phase difference between amplitude of the chemiluminescence and 254 nm photolytic radiation. *k* independent of pressure in the range studied (40–120 mbar).
- (e) Pulsed vacuum UV photolysis of O<sub>2</sub> or NO in Ar/C<sub>2</sub>H<sub>4</sub> mixtures. Total pressure, approximately 45 mbar. [O] monitored by O+NO chemiluminescence.
- (f) Flash photolysis of O<sub>2</sub>/C<sub>2</sub>H<sub>4</sub>/Ar mixtures with 145–165 nm radiation. [O] monitored by resonance fluorescence. *k* independent of pressure in the range covered (53–265 mbar). Non-Arrhenius behavior was found above 500 K.
- (g) Pulsed laser photolysis of NO/C<sub>2</sub>H<sub>4</sub>/N<sub>2</sub> mixtures at 160 nm; O+NO chemiluminescence used to monitor [O]. Total pressure, approximately 8 mbar.
- (h) Pulsed laser photolysis at 157 nm of O<sub>2</sub> or NO in C<sub>2</sub>H<sub>4</sub>/Ar mixtures; O+NO chemiluminescence used to monitor [O]. Total pressures in the range 66–132 mbar.
- (i) Two techniques used: (i) flash photolysis of O<sub>2</sub> or NO in C<sub>2</sub>H<sub>4</sub>/Ar mixtures at pressures in the range 65–130 mbar and temperature range 244–1052 K, with resonance fluorescence detection of O; (ii) discharge flow using O<sub>2</sub> or O+NO as the O atom source, with resonance fluorescence detection of O and covering the temperature range 298–1017 K.
- (j) High temperature study using combined flash photolysis-shock tube technique. O atoms produced by flash photolysis of NO and monitored by atomic resonance absorption.
- (k) Shock tube study on the pyrolysis and oxidation of C<sub>2</sub>H<sub>4</sub> using a range of C<sub>2</sub>H<sub>4</sub>/O<sub>2</sub>/Ar mixtures at pressures in the range 1.5–4.5 bar. Three shock tubes were used. The first had facilities for resolved time resolved and single pulse product analysis studies. IR emissions at 4.24 μm, and 3.48 μm were monitored, and reactants and products could be sampled and analyzed by GC. The second shock tube was equipped for laser absorption at 3.39 μm and IR emission studies behind reflected shocks. The third was equipped to monitor UV absorption at 230 nm behind reflected shocks. The emission profiles at 4.24 μm and 3.48 μm and the laser absorption profiles were sensitive to *k*<sub>1</sub>, *k*<sub>2</sub>, and *k*<sub>3</sub> and were simulated using a detailed mechanism. The [H] and [O] profiles reported in the shock tube study of Frank and Just<sup>19</sup> could also be modeled using these expressions.
- (l) Photochemical modulation spectroscopy was applied to 253.7 nm Hg photosensitized decomposition of N<sub>2</sub>O in N<sub>2</sub>O/C<sub>2</sub>H<sub>4</sub>/N<sub>2</sub> mixtures. CH<sub>2</sub>CHO radicals were detected by UV and infrared absorption. CH<sub>2</sub>CHO yields were determined by absorption measurements at 347.7 nm and comparison with the corresponding absorption following the Hg-sensitized decomposition of CH<sub>3</sub>OC<sub>2</sub>H<sub>3</sub>, which generates CH<sub>2</sub>CHO with unit quantum yield. HCO was detected in absorption at 563.2 nm.
- (m) Branching ratio for the H+CH<sub>2</sub>CHO product channel determined from measured H and O atom profiles in flash photolysis-resonance fluorescence study at pressures in the range 66–132 mbar. The O atoms were produced by broadband ( $\lambda > 160$  nm) flash photolysis of O<sub>2</sub> or NO in the presence of an excess of C<sub>2</sub>H<sub>4</sub>. The branching ratio increased slightly with temperature over the range 300–769 K.
- (n) Branching ratio determined from measurement of CHO/(CDO) and CH<sub>2</sub>CHO/(CD<sub>2</sub>CDO) yields by time-resolved microwave spectroscopy in pulsed Hg photosensitized reaction of N<sub>2</sub>O/C<sub>2</sub>H<sub>4</sub> mixtures at a total pressure of approximately 0.04 mbar.
- (o) Pulse radiolysis at 1 bar total pressure; UV absorption detection of CH<sub>3</sub>, HCO, and CH<sub>2</sub>CHO.
- (p) Considered 33 literature sources up to 1984. Assumed linear Arrhenius plot up to 500 K.
- (q) Accepts expression derived by Klemm *et al.*<sup>10</sup> from data in Refs. 1–10. Branching ratios were based on the data from Refs. 12–15.

### Preferred Values

$$k = 2.25 \cdot 10^{-17} T^{1.88} \exp(-92/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the range 220–2000 K.

$$k_1/k = 0.35; k_2/k = 0.6; k_4/k = 0.05, \text{ at } 298 \text{ K and for } P < 1 \text{ bar.}$$

### Reliability

$\Delta \log k = \pm 0.1$  over the range 300–1000 K, rising to  $\pm 0.3$  at 220 K and 2000 K.

$\Delta(k_1/k) = \pm 0.05; \Delta(k_2/k) = \pm 0.1; \Delta(k_4/k) = \pm 0.1$ , all at 298 K.

*Comments on Preferred Values*

There is a large experimental data base covering a wide range of experimental conditions for this reaction. The data up to 1984 have been reviewed by Cvetanovic.<sup>17</sup>

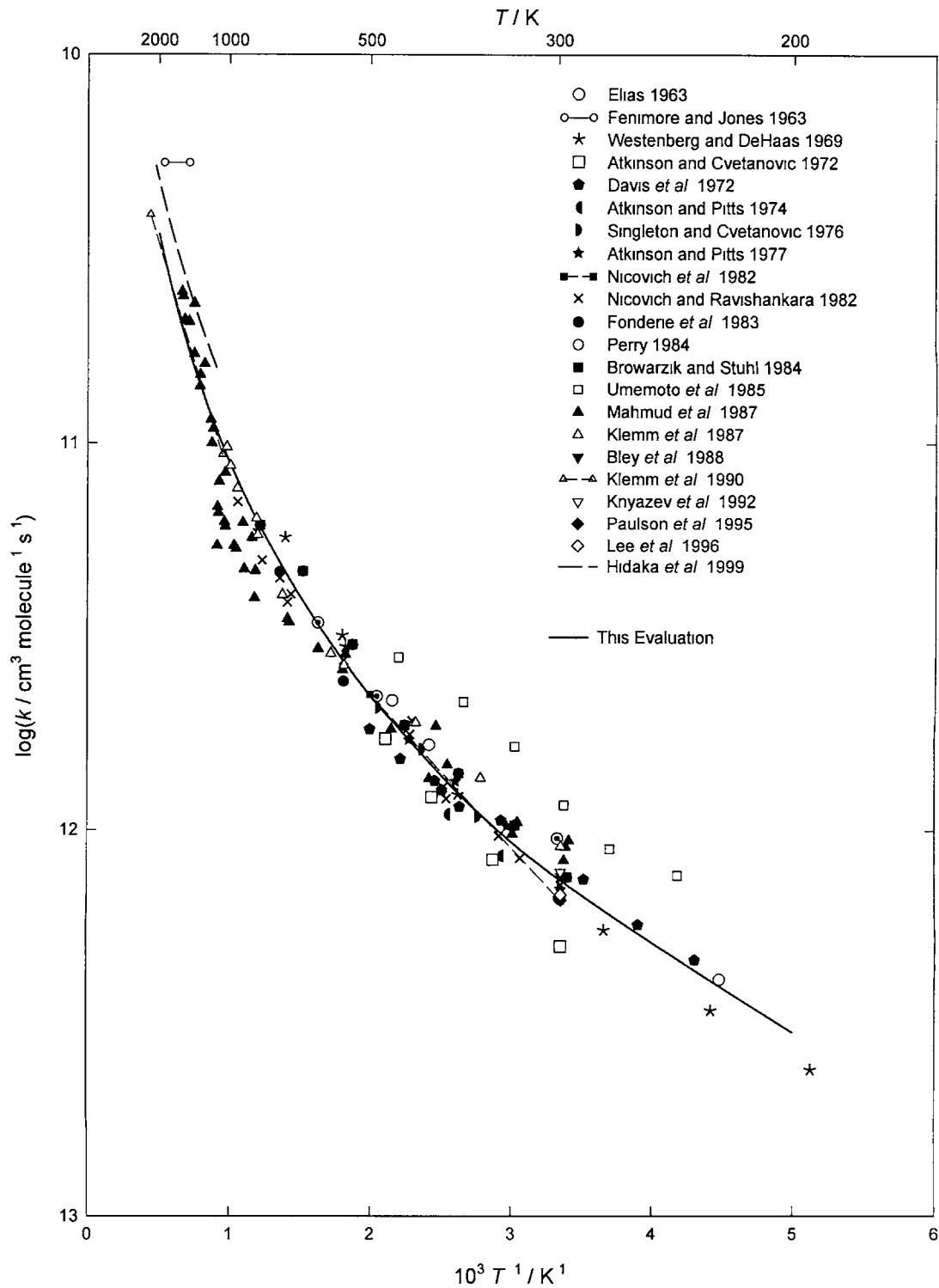
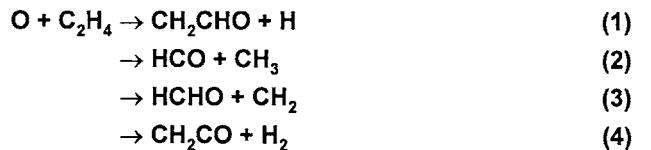
The preferred expression, which is unchanged from our previous evaluations<sup>18</sup> is derived from a fit to the 3 parameter expression  $k = AT^n \exp(B/T)$ , of the curve generated from the bi-exponential expression of Klemm *et al.*<sup>10</sup> over the range 300–2000 K, which was derived from the data in Refs. 1–10. A large number of other measurements<sup>13,21–27</sup> are consistent with the expression derived. However the values of  $k$  obtained by Umemoto *et al.*<sup>27</sup> seem to be systematically high and those of Mahmud *et al.*<sup>20</sup> are low in the middle of the temperature range covered (290–1510 K).

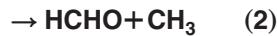
The reaction mechanism involves addition of the O atom to the double bond forming an energy rich triplet diradical which can decompose or cross to the singlet state, isomerize, and then decompose.<sup>17,28</sup> A variety of experiments over a wide pressure range have shown that the principle channels are (1) and (2). On the basis of their own results<sup>29</sup> and those from a number of earlier studies,<sup>30–32</sup> Knyazev *et al.*<sup>29</sup> have suggested that at pressures below  $\sim 15$  mbar the branching ratio is strongly pressure dependent. But, on the low pressure side of this range, under single collision conditions Schmoltner *et al.*<sup>28</sup> have measured CHO and CH<sub>2</sub>CHO yields and find  $k_2/k_1 = 2.5 \pm 0.9$  and at 0.04 mbar Kendo *et al.*<sup>14,15</sup> find  $k_1/k = 0.37$ , while on the high pressure side, studies up to 1000 mbar by discharge flow, pulsed photolysis, pulse radiolysis, and molecular modulation techniques, employing a variety of detection methods,<sup>12–16</sup> have also yielded values of  $k_1/k$  of 0.27–0.37 with sufficient scatter to mask any pressure variation in that range. The only direct study of the temperature dependence of the branching ratios is that of Smalley *et al.*<sup>13</sup> who found a small increase in  $k_1/k$  of 0.27 to 0.35 in going from 300 K to 798 K. At high temperatures the expressions derived by Hidaka *et al.*<sup>11</sup> for the range 1100–2100 K are in reasonable agreement with the preferred expression for  $k$  and, extrapolated to lower temperatures, also give branching ratios compatible with our recommendations at room temperature. These expressions suggest that Channel (3) becomes competitive with the other channels above 1000 K. However the expressions of Hidaka *et al.*<sup>11</sup> were derived from a complex system and our preferred values for the branching ratios are based mainly on the more direct low temperature studies<sup>12–16</sup> and are limited to pressures of less than 1 bar. There are also minor contributions ( $\sim 5\%$ ) from other channels.

At yet higher pressures the stabilization products, acetaldehyde and ethylene oxide, have been observed. Bley *et al.*<sup>33</sup>

have measured the yields of these two products as a function of pressure over the range 4–70 bar. They find at 70 bar  $[\text{CH}_3\text{CHO}]/[\text{C}_2\text{H}_4\text{O}] = 2.2$  but at this pressure the high pressure limiting value of this ratio has still not been reached.

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#### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = -318.3 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = 29.6 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 1.85 \cdot 10^{-3} T^{0.423} \exp(+38370/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(3) = -280.6 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = -5.26 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 7.25 T^{-0.367} \exp(+33590/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(5) = -334.2 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(5) = 113.90 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(4) = 2.26 \cdot 10^{30} T^{-1.641} \exp(+39510/T) \text{ molecule cm}^{-3} \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(2) = -331.8 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = 4.55 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 4.94 \cdot 10^2 T^{-0.810} \exp(+39620/T) \\ (200 \leq T/\text{K} \leq 6000)$$

$$\Delta H^\circ_{298}(4) = -337.5 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(4) = -90.02 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(4) = 5.31 \cdot 10^{27} T^{-1.303} \exp(+40280/T) \text{ molecule cm}^{-3} \\ (300 \leq T/\text{K} \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2 + k_3 + k_4 + k_5$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$2.2 \cdot 10^{-10}$	295–600	Slagle <i>et al.</i> , 1988 <sup>1</sup>	(a)
<i>Branching Ratios</i>			
$k_1/k = 0.4 \pm 0.04$	298–450	Slagle <i>et al.</i> , 1988 <sup>1</sup>	(a)
$k_2/k = 0.32 \pm 0.07$	298–450		
$k_3/k = 0.23 \pm 0.07$	298–450		
<i>Reviews and Evaluations</i>			
$1 \cdot 10^{-10}$	300–2500	CEC, 1992; 1994 <sup>2</sup>	(b)
$k_2/k = 0.17$	300		

#### Comments

- (a) Flow system with generation of  $\text{C}_2\text{H}_5$  and  $\text{O}({}^3\text{P})$  from the simultaneous *in situ* photolysis of  $\text{C}_2\text{H}_5\text{COC}_2\text{H}_5$  and  $\text{SO}_2$  and measurement of  $[\text{C}_2\text{H}_5]$  and  $[\text{O}]$  by photoionization mass spectrometry.  $k$  determined from  $\text{C}_2\text{H}_5$  decay profile with  $[\text{O}]/[\text{C}_2\text{H}_5] > 20$ , and shown to be independent of pressure over the range 1–10 mbar. Branching ratios were determined by analyses of  $\text{CH}_3\text{CHO}$ ,  $\text{HCHO}$ , and  $\text{C}_2\text{H}_4$  products.
- (b) Value of  $k$  based on unpublished data of Peeters and Caymax. The branching ratio is from Hoyermann and Sievert.<sup>3</sup>

#### Preferred Values

$k = 2.2 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 298–1000 K.

$k_1/k = 0.4$  over the range 298–450 K.

$k_2/k = 0.3$  over the range 298–450 K.

$k_3/k = 0.2$  over the range 298–450 K.

#### Reliability

$\Delta \log k = \pm 0.3$  at 298 K, rising to  $\pm 0.5$  at 1000 K.

$\Delta(k_1/k) = \pm 0.05$ ;  $\Delta(k_2/k) = \pm 0.1$ ;  $\Delta(k_3/k) = \pm 0.1$ , all over the range 298–450 K.

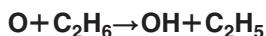
#### Comments on Preferred Values

The preferred values for  $k$  and the branching ratios are based on the study of Slagle *et al.*<sup>1</sup> Hoyermann and Sievert<sup>3</sup> carried out a discharge flow/mass-spectrometric study on this reaction and obtained results at variance with those of Slagle *et al.*,<sup>1</sup> but in a later study, using more direct techniques, Hoyermann *et al.*<sup>4</sup> obtain branching ratios in agreement with those of Slagle *et al.*<sup>1</sup> and accept that the values of Slagle *et al.*<sup>1</sup> are to be preferred. Lindner *et al.*<sup>5</sup> have measured the

vibrational distribution in the OH produced [Channel (3)] and conclude that the OH is probably formed by direct abstraction rather than by an addition/decomposition process. The production of CO ( $v=1-9$ ) has also been observed by Reid *et al.*,<sup>6</sup> using time-resolved Fourier transform infrared emission spectroscopy. They suggest that it arises directly from a hitherto unidentified reaction channel. The branching ratio was not determined but it was comparable with that for the corresponding O+CH<sub>3</sub> reaction (i.e., ~0.2). This finding remains to be confirmed but there may be a minor, but significant channel, not accounted for in the present recommendations.

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### Thermodynamic Data

$$\begin{aligned}\Delta H_{298}^{\circ}(1) &= -7.30 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ}(1) &= 40.8 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 7.2 \cdot 10^3 T^{-0.511} \exp(+538/T) \\ &\quad (300 \leq T/\text{K} \leq 4000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

### Rate Coefficient Data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$1.39 \cdot 10^{-10} \exp(-3770/T)$	853–933	Azatyan, Nalbandyan, and Meng-yuan, 1962 <sup>1</sup>	(a)
$3.2 \cdot 10^{-10} \exp(-4806/T)$	600–1030	Caymax and Peeters, 1983 <sup>2</sup>	(b)
$6.6 \cdot 10^{-11} \exp(-3410/T)$	308–410	Mix and Wagner, 1983 <sup>3</sup>	(c)
$1.9 \cdot 10^{-31} T^{6.5} \exp(-138/T)$	297–1232	Mahmud, Marshall, and Fontijn, 1988 <sup>4</sup>	(d)
$6.59 \cdot 10^{-10} \exp(-5051/T)$	938–1192	Miyoshi <i>et al.</i> , 1994 <sup>5</sup>	(e)
<i>Reviews and Evaluations</i>			
$2.0 \cdot 10^{-12} T^{0.6} \exp(-3680/T)$	500–1000	Tsang and Hampson, 1986 <sup>6</sup>	(f)
$1.9 \cdot 10^{-10} \exp(-3950/T)$	400–1100	Herron, 1988 <sup>7</sup>	(g)
$4.5 \cdot 10^{-18} T^{2.4} \exp(-2940/T)$	1100–2000		
$1.9 \cdot 10^{-31} T^{6.5} \exp(-140/T)$	298–1300	Cohen and Westberg, 1991 <sup>8</sup>	(h)
$4.32 \cdot 10^{-9} \exp(-7010/T)$	1300–3000		
$1.66 \cdot 10^{-12} T^{1.5} \exp(-2920/T)$	300–1200	CEC, 1992; 1994 <sup>9</sup>	(i)

### Comments

- (a) The pressure and temperature of the lower explosion limit for CO/O<sub>2</sub>/C<sub>2</sub>H<sub>6</sub> mixtures was determined for a range of concentrations of C<sub>2</sub>H<sub>6</sub> and O<sub>2</sub>. Values of  $k$  depend upon calculated values of the rate of reaction of O atoms with the vessel walls which were coated with MgO.
- (b) Discharge flow study under conditions of [O]  $\gg$  [C<sub>2</sub>H<sub>6</sub>]. O atoms were generated by a discharge in O<sub>2</sub>/He mixtures and their concentration calibrated by means of the N+NO reaction. The [C<sub>2</sub>H<sub>6</sub>] was monitored by molecular beam sampling into a mass spectrometer.
- (c) Discharge flow study with [O]/[C<sub>2</sub>H<sub>6</sub>] in the range 18–21. O atoms were generated by a discharge in O<sub>2</sub>/He mixtures and the [C<sub>2</sub>H<sub>6</sub>] was monitored by molecular beam sampling into a mass spectrometer.
- (d) A fast flow discharge system was used to study the

reaction under conditions of [O]  $\gg$  [C<sub>2</sub>H<sub>6</sub>]. O atoms were generated by flash photolysis of O<sub>2</sub> or CO<sub>2</sub> introduced into the flow tube together with the C<sub>2</sub>H<sub>6</sub> and carrier gas (Ar) at total pressures in the range 128–817 mbar. The [O] was monitored by atomic resonance fluorescence

- (e) A pulsed laser photolysis-shock tube technique was applied to Ar/SO<sub>2</sub> (or NO)/C<sub>2</sub>H<sub>6</sub> mixtures. O atoms were produced by pulsed laser photolysis of the SO<sub>2</sub> or NO at 193 nm behind reflected shock waves and [O] was monitored by ARAS at 130.6 nm. Computer simulations were used in extracting values of  $k$  from the [O] temporal profile and in checking the effects of secondary chemistry. Results reported here supersede those reported previously in a similar study.<sup>10</sup>
- (f) Expression derived by Cohen<sup>11</sup> recommended.
- (g) For the range 400–1100 K an expression suggested by

Michael<sup>12</sup> is recommended and for the range 1100–2000 K the recommended expression is that of Cohen and Westberg.<sup>13</sup>

- (h) The expression derived by Mahmud *et al.*<sup>4</sup> is recommended for the range 298–1300 K and the expression recommended for the range 1300–3000 K is based on a Transition State Theory calculation with corrections for tunneling.
- (i) Based on the high temperature data of Caymax and Peeters<sup>2</sup> and Cohen's analysis<sup>14</sup> of the low temperature data.

### Preferred Values

$$k = 3.0 \cdot 10^{-19} T^{2.8} \exp(-2920/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the range 500–1400 K.

### Reliability

$\Delta \log k = \pm 0.15$  in the range 500–1100 K, rising to  $\pm 0.3$  at 1400 K.

### Comments on Preferred Values

In the temperature range 500–1150 K the relatively recent studies of Caymax and Peeters,<sup>2</sup> Mahmud *et al.*,<sup>4</sup> and Miyoshi *et al.*<sup>5</sup> are in fair agreement with the scatter in values of  $k$  corresponding to factor of about 2. The values derived from the earlier explosion limits studies of Azatyan<sup>1,22</sup> are also in this range.

Below 500 K the data are more scattered. At these temperatures the rate constant is small and difficult to measure, with secondary reactions and impurities in the C<sub>2</sub>H<sub>6</sub> presenting major experimental difficulties. Cohen<sup>14</sup> has evaluated in some detail the low temperature studies of Saunders and Heicklen,<sup>15</sup> Westenberg and de Haas,<sup>16,17</sup> and Papadopoulos *et al.*<sup>18</sup> and comes to the conclusion that none of them can be considered reliable because of the uncertain effects of secondary chemistry, which are likely to lead to measured values of  $k$  being too high. He also points out that in the experiments of Herron and Huie<sup>19</sup> very small changes in [C<sub>2</sub>H<sub>6</sub>] had to be measured so that the values of  $k$  which they derived cannot be considered very precise. The remaining low temperature studies are those of Avramenko *et al.*,<sup>20</sup> Mahmud *et al.*,<sup>4</sup> Mix and Wagner,<sup>3</sup> and Gal and Bar-Ziv.<sup>21</sup> The reliability of the early discharge flow study of Avramenko *et al.*<sup>20</sup> which used H<sub>2</sub>O and O<sub>2</sub> as the O atom source and analysis of product yields is very uncertain. The studies of Mahmud *et al.*<sup>4</sup> and of Mix and Wagner<sup>3</sup> appear to be the most reliable of the low temperature studies but at 298 K the values of  $k$  obtained by Mahmud *et al.*<sup>4</sup> is approaching a factor of 2 higher than that of Mix and Wagner.<sup>3</sup> Gal and

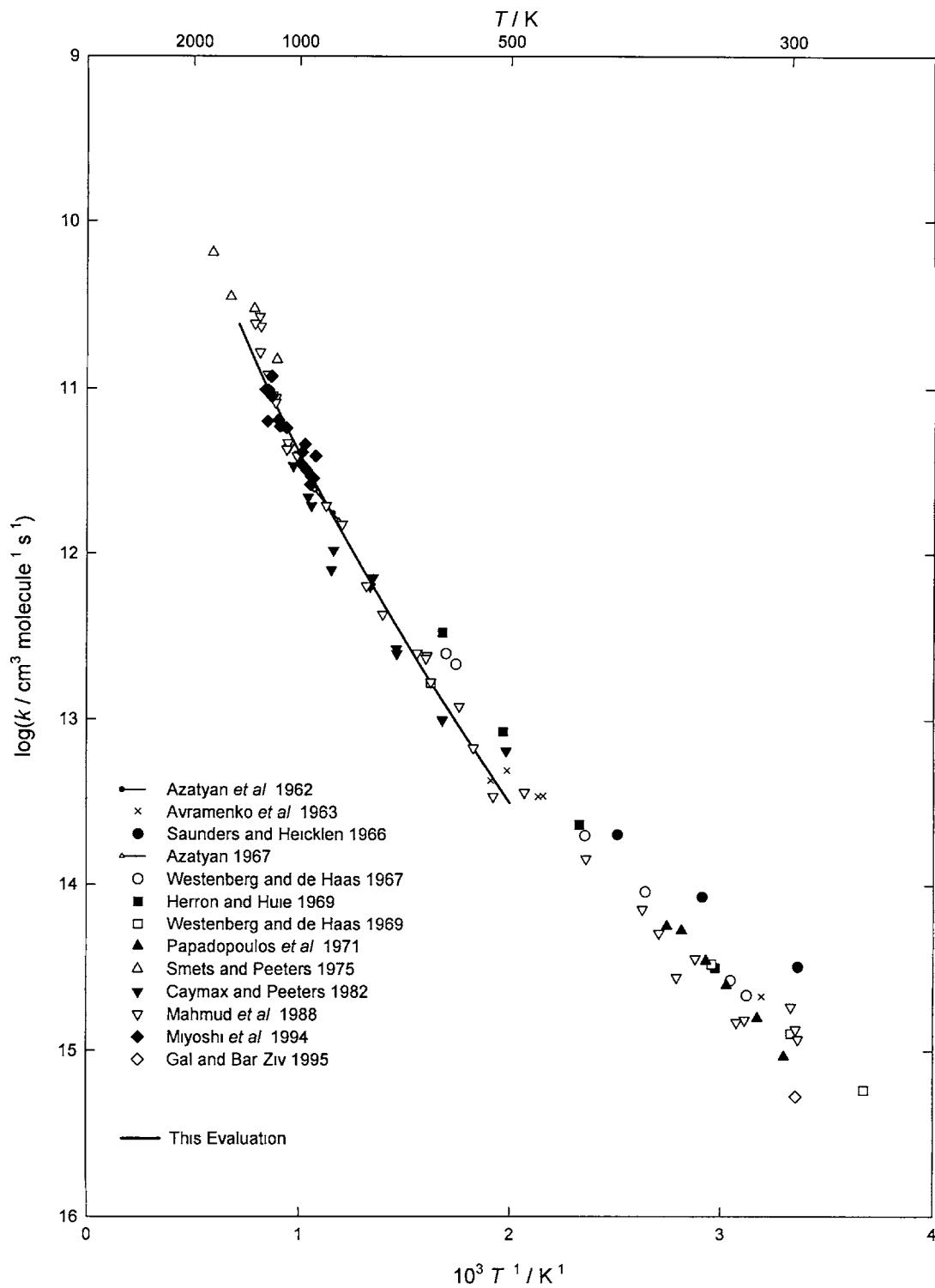
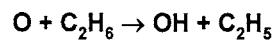
Bar-Ziv's<sup>21</sup> determination of  $k$  at 298 K was indirect, being derived from modeling measured [OH] temporal profiles in a discharge flow study of the O+C<sub>2</sub>H<sub>6</sub> system, and the value of  $k$  obtained ( $5.3 \cdot 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) is also much lower than that of Mahmud *et al.*<sup>4</sup>

As well as the uncertainty of the value of  $k$  at low temperatures another major problem is the extent of curvature of the Arrhenius plot. Mahmud *et al.*<sup>4</sup> obtain a pre-exponential factor varying as  $T^{6.5}$  in their expression for  $k$  over the range 297–1237 K. Such a temperature dependence is larger than found for O atom reactions with other alkanes and, in all of the other studies of the temperature dependence of  $k$ ,<sup>1–3,5,12,16–20</sup> albeit over smaller ranges of temperature and with less precision, linear Arrhenius plots have been obtained. The large  $T^n$  term in the expression for  $k$  obtained by Mahmud *et al.*<sup>4</sup> is due, in part, to their high values of  $k$  at low temperatures which they have justified as being due to contributions from tunneling. However the extent of such contributions is controversial and the status of the low temperature data and the temperature dependence remain uncertain.

The preferred expression for  $k$  is limited to temperatures above 500 K and is derived from the studies of Caymax and Peeters,<sup>2</sup> Mahmud *et al.*,<sup>4</sup> and Miyoshi *et al.*<sup>5</sup> and, on this basis  $k$  is well defined up to 1100 K. The preferred expression is very similar to that recommended for the closely related reaction O+CH<sub>4</sub> (see data sheet).

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- <sup>19</sup>J. T. Herron and R. E. Huie, J. Phys. Chem. **73**, 3327 (1969).
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*Thermodynamic Data*

$$\Delta H_{298}^\circ(1) = -427.6 \text{ kJ mol}^{-1}$$

$$\Delta S_{298}^\circ(1) = 103.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 5.72 \cdot 10^{28} T^{-1.432} \exp(+51110/T) \text{ molecule cm}^{-3}$$

(300 ≤ T/K ≤ 5000)

$$\Delta H_{298}^\circ(2) = 62.34 \text{ kJ mol}^{-1}$$

$$\Delta S_{298}^\circ(2) = -22.14 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 8.65 \cdot 10^5 T^{-2.793} \exp(-8330/T)$$

(300 ≤ T/K ≤ 6000)

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data ( $k = k_1 + k_2 + k_3$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$3.2 \cdot 10^{-10} \exp(-300/T)$	285–535	Vinckier, Schaekers, and Peeters, 1985 <sup>1</sup>	(a)
$1.6 \cdot 10^{-10}$	1500–1700	Frank, Bhaskaran, and Just, 1986 <sup>2</sup>	(b)
$(k_2 + k_3) = 8.0 \cdot 10^{-12}$	290	Peeters <i>et al.</i> , 1994 <sup>3</sup>	(c)
$(k_2 + k_3) = 4.9 \cdot 10^{-11} \exp(-560/T)$	404–960	Peeters, Boullart, and Devriendt, 1995 <sup>4</sup>	(c)
<i>Reviews and Evaluations</i>			
$1.6 \cdot 10^{-10}$	300–2500	CEC, 1992; 1994 <sup>5</sup>	(d)

**Comments**

- (a) Discharge flow study of the O+C<sub>2</sub>H<sub>2</sub> reaction. O atoms were produced by a microwave discharge in He/O<sub>2</sub> mixtures and their concentration determined from the initial concentration of the O<sub>2</sub> or by titration. The concentrations of C<sub>2</sub>H<sub>2</sub> and a number of radicals produced in the reaction were monitored by molecular beam sampling into a quadrupole mass spectrometer. Values of  $k/k(\text{O} + \text{C}_2\text{H}_2 \rightarrow \text{CHCO} + \text{H})$  were determined from the steady state values of [CHCO] over the range 285–535 K. These were combined with the measured value at 535 K of the rate constant for the reference reaction, and its activation energy, to derive the cited expression for  $k$ .
- (b) Shock tube study using reflected shocks in C<sub>2</sub>H<sub>2</sub>/N<sub>2</sub>O/Ar mixtures with simultaneous measurement of [H], [O], and [CO] by atomic and molecular absorption spectrometry. The O+CHCO reaction is important in the later stages of the reaction. Values of  $k$  were determined by fitting the [O] profile under optimized conditions using a detailed mechanism.
- (c) The same technique was used in Refs. 3 and 4. Both studies used the O+C<sub>2</sub>H<sub>2</sub> reaction carried out in a discharge flow system. O atoms were produced by a microwave discharge in He/N<sub>2</sub>O mixtures. Concentrations of radicals and stable species were monitored by molecular beam sampling into a quadrupole mass spectrometer. Values of  $(k_2 + k_3)/k$  were determined by fitting the measured CO<sub>2</sub> profile using a detailed reaction mechanism.  $k = 2.0 \cdot 10^{-10} \exp(-120/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , which corresponds closely to the preferred value in the present evaluation, was used to derive the cited expression for  $(k_2 + k_3)$ .
- (d) Based on the studies of Vinckier *et al.*<sup>1</sup> and Frank *et al.*<sup>2</sup>

**Preferred Values**

$k = 1.6 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 280–2500 K.

$(k_2 + k_3) = 4.9 \cdot 10^{-11} \exp(-560/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 280–1000 K.

*Reliability*

$\Delta \log k = \pm 0.2$  over the range 280–2500 K.

$\Delta \log(k_2 + k_3) = \pm 0.3$  over the range 280–1000 K.

*Comments on Preferred Values*

The preferred value for  $k$  is unchanged from our previous evaluations<sup>5</sup> and is based on the studies of Vinckier *et al.*<sup>1</sup> and Frank *et al.*<sup>2</sup>; the earlier study of Jones and Bayes<sup>6</sup> appears to give erroneously low values of the rate constant for the reaction of CHCO with both O and H.

The major channel for the reaction is that leading to the formation of CO and H [Channel (1)] but Peeters *et al.*<sup>3,4</sup> have also identified a contribution from Channel (3) and/or Channel (2) which is small at room temperature but rises with temperature sufficiently rapidly to suggest that it may be important under combustion conditions. The preferred expression for  $(k_2 + k_3)$  is that determined by Peeters *et al.*<sup>4</sup> with enhanced error limits until confirmatory studies are made. The experimental and theoretical studies<sup>3,4</sup> have not been able to identify the separate contributions of the two channels [(2) and (3)].

**References**

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- <sup>2</sup>P. Frank, K. A. Bhaskaran, and Th. Just, 21st Symp. (Int.) Combustion, 1986, p. 885.
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- <sup>5</sup>CEC, 1992; Supplement I, 1994 (see references in Introduction).
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#### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = -420.8 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = 13.36 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 1.41 \cdot 10^4 T^{-1.214} \exp(+50320/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(3) = -115.5 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = 45.71 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 5.70 \cdot 10^5 T^{-1.147} \exp(+13540/T) \\ (200 \leq T/\text{K} \leq 6000)$$

$$\Delta H^\circ_{298}(2) = -51.13 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = 133.5 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 7.63 \cdot 10^8 T^{-0.539} \exp(+5724/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(4) = -204.8 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(4) = -15.68 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(4) = 4.91 \cdot 10^2 T^{-0.808} \exp(+24360/T) \\ (300 \leq T/\text{K} \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2 + k_3 + k_4$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$4.6 \cdot 10^{-13}$	296	Gaffney, Atkinson, and Pitts, 1975 <sup>1</sup>	(a)
$2.92 \cdot 10^{-12} \exp(-680/T)$	230–449	Washida <i>et al.</i> , 1983 <sup>2</sup>	(b)
$4.3 \cdot 10^{-13}$	298		(c)
<i>Branching Ratios</i>			
$k_1/k = 0.15$	298	Washida <i>et al.</i> , 1983 <sup>2</sup>	(c)
$(k_2 + k_3)/k = 0.1$			
<i>Reviews and Evaluations</i>			
$3.0 \cdot 10^{-12} \exp(-680/T)$	230–449	Cvetanovic, 1987 <sup>3</sup>	(d)
$3.8 \cdot 10^{-12} \exp(-680/T)$	230–500	CEC, 1992; 1994 <sup>4</sup>	(e)

#### Comments

- (a) Relative rate study with  $k$  determined relative to  $k(\text{O} + \text{cyclopentene}) = 1.92 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . O atoms produced by Hg photosensitized photolysis of  $\text{N}_2\text{O}$  at total pressures in the range 270–660 mbar.
- (b) Experiments based on pulse radiolysis of  $\text{CO}_2/\text{CH}_2\text{CO}/\text{Ar}$  mixtures at total pressures of 660 mbar. [O] monitored by resonance absorption.
- (c) Discharge flow system study using a large excess of O atoms over the ketene. Photoionization mass spectrometry was used to detect the ketene and products to obtain both the rate coefficient and the product yields (HCO and HCHO).
- (d) Based on the studies of Carr *et al.*,<sup>5</sup> Jones and Bayes,<sup>6</sup> Mack and Thrush,<sup>7</sup> and Washida *et al.*<sup>2</sup>
- (e) Based on the studies of Mack and Thrush<sup>7</sup> and of Washida *et al.*<sup>2</sup>

#### Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 296 \text{ K, rising to } \pm 1.0 \text{ at } 1000 \text{ K.}$$

$$\Delta(k_1/k) = \Delta[(k_2 + k_3)/k] = \pm 0.1, \text{ at } 298 \text{ K.}$$

$$\Delta(k_4/k) = \pm 0.2 \text{ at } 298 \text{ K.}$$

#### Comments on Preferred Values

Under the conditions used in the early discharge flow studies<sup>5–7</sup> there is considerable uncertainty in the reaction stoichiometry, which introduces corresponding uncertainty into the values of  $k$  obtained. This objection does not apply to relative rate measurement of Gaffney *et al.*<sup>1</sup> and the discharge flow study of Washida *et al.*<sup>2</sup> which are accepted as the basis for our preferred expression. There are no direct measurements of  $k$  at flame temperatures. Hidaka *et al.*<sup>8</sup> studied ketene oxidation by  $\text{O}_2$  and  $\text{N}_2\text{O}$  behind shock waves at 1050–2050 K and found that to model their system a value of  $k_4 = 1.5 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was required. This is an order of magnitude greater than the value obtained by extrapolation of our preferred expression for  $k$ .

The recommended branching ratios are based on the study of Washida *et al.*,<sup>2</sup> in which direct measurements of the product yields were made, and on the unpublished results of Bley *et al.*, quoted in Ref. 9, which are in reasonable agreement.

#### Preferred Values

$k = 3.0 \cdot 10^{-12} \exp(-680/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 296–1000 K.

$k_1/k = 0.2$ ;  $(k_2 + k_3)/k = 0.2$ ;  $k_4/k = 0.6$ , at 298 K.

## References

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<sup>3</sup>R. J. Cvetanovic, *J. Phys. Chem. Ref. Data* **16**, 261 (1987).  
<sup>4</sup>C. E. C. 1992; Supplement I, 1994 (see references in Introduction).  
<sup>5</sup>R. W. Carr, I. D. Gay, G. P. Glass, and H. Niki, *J. Chem. Phys.* **49**, 846 (1968).

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<sup>7</sup>G. P. R. Mack and B. A. Thrush, *J. Chem. Soc. Faraday Trans. 1* **70**, 187 (1974).  
<sup>8</sup>Y. Hidaka, K. Kimura, K. Hattori, and T. Okuno, *Combust. Flame* **106**, 155 (1996).  
<sup>9</sup>U. Bley, F. Temps, H. Gg. Wagner, and M. Wolf, *Ber. Bunsenges. Phys. Chem.* **96**, 1043 (1992); reference is made to the conference poster, U. Bley, M. Koch, C. Oehlers, F. Temps, and H. Gg. Wagner, 23rd Symp (Int.) Combustion Proceedings, 1990, p. 105.



## Thermodynamic Data

$$\Delta H^\circ_{298}(1) = -249.6 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = -2.88 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 0.198 T^{0.24} \exp(+29980/T)$$

$$(300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(2) = -486.3 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = -20.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 9.22 \cdot 10^{-2} T^{-0.011} \exp(+58480/T)$$

$$(300 \leq T/\text{K} \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$5.1 \cdot 10^{-10}$	295	Miyoshi, Matsui, and Washida, 1989 <sup>1</sup>	(a)
$1.78 \cdot 10^{-10}$	298	Bartels, Edelbeuttel-Einhaus, and Hoyermann, 1990 <sup>2</sup>	(b)
<i>Branching Ratios</i>			
$k_1/k = 0.22$	295	Miyoshi, Matsui, and Washida, 1989 <sup>1</sup>	(c)
$k_2/k = 0.76$			
$k_2/k > 0.7$	298	Bartels, Edelbeuttel-Einhaus, and Hoyerman, 1990 <sup>2</sup>	(d)
<i>Reviews and Evaluations</i>			
$1 \cdot 10^{-10}$	300–2000	Herron, 1988 <sup>3</sup>	(e)
$3.2 \cdot 10^{-10}$	298–1500	CEC, 1994 <sup>4</sup>	(f)
$k_1/k = 0.2; k_2/k = 0.8$	298		

## Comments

- (a) Discharge flow system. Reactants and products monitored by photoionization mass spectrometry.  $k$  measured relative to  $k(\text{CH}_3\text{CO} + \text{O}_2)$ .  $k_{\text{ref}}/k = (6.3 \pm 0.5) \cdot 10^{-3}$  obtained from effect of  $\text{O}_2$  on the yield of  $\text{CH}_3\text{CO}$  in the  $\text{O} + \text{CH}_3\text{CHO}$  reaction with excess  $\text{O}$ . Value given uses  $k_{\text{ref}} = 3.2 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (this evaluation).  
(b) Discharge flow with molecular beam sampling and REMPI mass spectrometry or electron impact mass spectrometry.  $\text{CH}_3\text{CO}$  from reaction of  $\text{F}$  or  $\text{Cl}$  with  $\text{CH}_3\text{CHO}$ . Pressure 0.5–10 mbar.  $k$  measured relative to  $k(\text{O} + \text{C}_2\text{H}_5)$ .  $k/k_{\text{ref}} = 0.81$  obtained. Value of  $k$  derived using  $k(\text{O} + \text{C}_2\text{H}_5) = 2.2 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (this evaluation).  
(c) Branching ratio  $k_1/k$  from the yield of ketene;  $k_2/k$  from yield of  $\text{CH}_3$ . Both were measured independently in the experiments described in (a).

- (d) Based on yield of  $\text{CH}_3$ .  
(e) Based on analogy with other reactions of  $\text{O}$  atoms with organic radicals.  
(f) Based on results of Miyoshi *et al.*<sup>1</sup>

## Preferred Values

$$k = 3.5 \cdot 10^{-10} \text{ over the range } 295\text{--}1000 \text{ K.}$$

$$k_1/k = 0.25; k_2/k = 0.75 \text{ at } 298 \text{ K.}$$

## Reliability

$$\Delta \log k = \pm 0.3 \text{ over the range } 295\text{--}1000 \text{ K.}$$

$$\Delta(k_1/k) = \Delta(k_2/k) = \pm 0.2, \text{ at } 298 \text{ K.}$$

## Comments on Preferred Values

The preferred value of  $k$  is a simple mean of the experimental values of Miyoshi *et al.*<sup>1</sup> and Bartels *et al.*,<sup>2</sup> which are in reasonable agreement, considering the substantial un-

certainties in the reference reactions used. In view of the large value of  $k$ , it is expected to have little, if any, temperature dependence.

The branching ratios are based on the measurements of Miyoshi *et al.*,<sup>1</sup> with which the data of Bartels *et al.*<sup>2</sup> are consistent.

## References

- <sup>1</sup> A. Miyoshi, H. Matsui, and N. Washida, J. Phys. Chem. **93**, 5813 (1989).
- <sup>2</sup> M. Bartels, J. Edelbuettel-Einhäusl, and K. Hoyermann, 23rd Symp. (Int) Combustion, 1990, p. 131.
- <sup>3</sup> J. T. Herron, J. Phys. Chem. Ref. Data **17**, 967 (1988).
- <sup>4</sup> CEC, Supplement I (1994).



### Thermodynamic Data

$$\begin{aligned}\Delta H^{\circ}_{298}(1) &= -55.9 \text{ kJ mol}^{-1} \\ \Delta S^{\circ}_{298}(1) &= 26.2 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 7.03 \cdot 10^4 T^{-1.075} \exp(+6120/T) \\ (300 \leq T/K \leq 5000)\end{aligned}$$

$$\begin{aligned}\Delta H^{\circ}_{298}(2) &= -35.4 \text{ kJ mol}^{-1} \\ \Delta S^{\circ}_{298}(2) &= 26.6 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 1.98 \cdot 10^3 T^{-0.550} \exp(+3850/T) \\ (300 \leq T/K \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

### Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$4.8 \cdot 10^{-13}$	300	Mack and Thrush, 1974 <sup>1</sup>	(a)
$4.9 \cdot 10^{-13}$	298	Michael and Lee, 1977 <sup>2</sup>	(b)
$1.2 \cdot 10^{-11} \exp(-990/T)$	298–472	Singleton <i>et al.</i> , 1977 <sup>3</sup>	(c)
<i>Reviews and Evaluations</i>			
$9.7 \cdot 10^{-12} \exp(-910/T)$	298–1500	CEC, 1992; 1994 <sup>4</sup>	(d)

### Comments

- (a) Discharge flow study.  $[\text{O}(\text{P}^3)]$  was monitored by electron paramagnetic resonance (EPR) and chemiluminescence from the  $\text{NO} + \text{O} + \text{M}$  reaction.
- (b) Discharge flow study.  $[\text{O}(\text{P}^3)]$  was monitored by resonance fluorescence.
- (c) Modulated photolysis of  $\text{N}_2\text{O}/\text{CH}_3\text{CHO}$  mixtures.  $[\text{O}]$  was monitored by chemiluminescence from the  $\text{O} + \text{NO} + \text{M}$  reaction.
- (d) Based on the data of Mack and Thrush,<sup>1</sup> Michael and Lee,<sup>2</sup> and Singleton *et al.*<sup>3</sup>

### Preferred Values

$k = 9.7 \cdot 10^{-12} \exp(-910/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 298–1500 K.

### Reliability

$\Delta \log k = \pm 0.1$  at 298 K, rising to  $\pm 0.5$  at 1500 K.

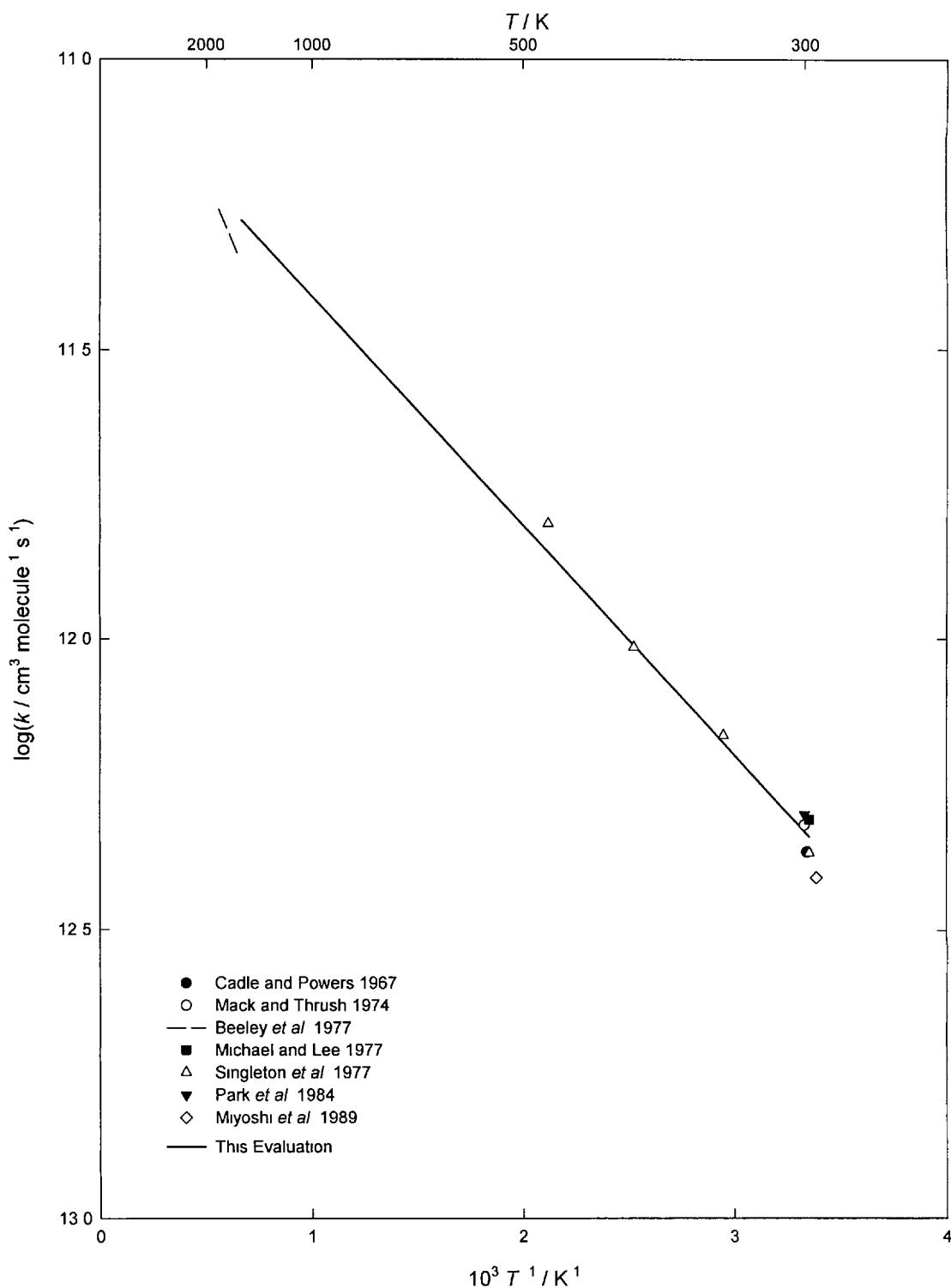
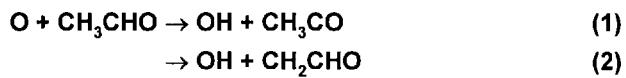
### Comments on Preferred Values

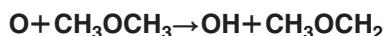
The preferred values are based on the low temperature data of Mack and Thrush,<sup>1</sup> Michael and Lee,<sup>2</sup> and Singleton

*et al.*<sup>3</sup> Room temperature data of Cadle and Powers,<sup>5</sup> Miyoshi *et al.*,<sup>6</sup> and Park *et al.*<sup>7</sup> are consistent with the preferred expression. Although the high temperature data of Beeley *et al.* (1550–1850 K)<sup>8</sup> agree with the extrapolation of our simple Arrhenius expression, the determination was indirect and subject to uncertainty. There are no experimental data on the branching ratio. If it is assumed that  $k_2 = \frac{1}{2}k(\text{O} + \text{C}_2\text{H}_6)$  then the second channel only becomes significant ( $k_2/k > 0.1$ ) at  $T > 700$  K but extrapolation of this estimation to higher temperatures gives values a factor of 2 higher than the overall rate coefficient given by Beeley *et al.*<sup>8</sup>

## References

- <sup>1</sup> G. P. R. Mack and B. A. Thrush, J. Chem. Soc. Faraday 1 **70**, 178 (1974).
- <sup>2</sup> J. V. Michael and J. H. Lee, Chem. Phys. Lett. **51**, 303 (1977).
- <sup>3</sup> D. L. Singleton, R. S. Irwin, and R. J. Cvitanovic, Can. J. Chem. **55**, 3321 (1977).
- <sup>4</sup> CEC, 1992; Supplement 1, 1994 (see references in Introduction).
- <sup>5</sup> R. D. Cadle and J. W. Powers, J. Phys. Chem. **71**, 1702 (1967).
- <sup>6</sup> A. Miyoshi, H. Matsui, and N. Washida, J. Phys. Chem. **93**, 5813 (1989).
- <sup>7</sup> J. Y. Park, P. F. Sawyer, M. C. Heaven, and D. Gutman, J. Phys. Chem. **88**, 2821 (1984).
- <sup>8</sup> P. Beeley, J. F. Griffiths, B. A. Hunt, and A. Williams, 16th Symp. (Int) Combustion, 1976, p. 1013.



*Thermodynamic Data*

$$\begin{aligned}\Delta H_{298}^{\circ} &= -28.2 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= 37.2 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 6.5 \cdot 10^3 T^{-0.540} \exp(+2990/T) \\ &\quad (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$8.3 \cdot 10^{-12} \exp(-1430/T)$	217–366	LeFevre, Meagher, and Timmons, 1972 <sup>1</sup>	(a)
$5.4 \cdot 10^{-12} \exp(-1320/T)$	240–400	Liu <i>et al.</i> 1990 <sup>2</sup>	(b)

**Comments**

- (a) Discharge flow study. O atoms were produced by a microwave discharge in He/O<sub>2</sub> mixtures or by the N + NO reaction. In one set of studies ESR was used to monitor [O] in an excess of CH<sub>3</sub>OCH<sub>3</sub>. In other experiments [CH<sub>3</sub>OCH<sub>3</sub>] was monitored by mass spectrometry in an O-atom excess. A similar temperature dependence for  $k$  was obtained in each of the two studies but different absolute values of  $k$ , which was attributed to differences in reaction stoichiometry in the two sets of experiments. The expression tabulated is based on the ESR results and a stoichiometry of 2 estimated in the paper from a comparison of the results from the two studies.
- (b) Flash photolysis study. Vacuum UV photolysis of flowing Ar/O<sub>2</sub> mixtures was used as the O atom source and [O] was monitored at 130.3 nm by resonance fluorescence in the presence of a large excess of CH<sub>3</sub>OCH<sub>3</sub>.

**Preferred Values**

$$k = 5.4 \cdot 10^{-12} \exp(-1320/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the range } 220\text{--}450 \text{ K.}$$

*Reliability*

$$\Delta \log k = \pm 0.2 \text{ over the temperature range } 220\text{--}450 \text{ K.}$$

*Comments on Preferred Values*

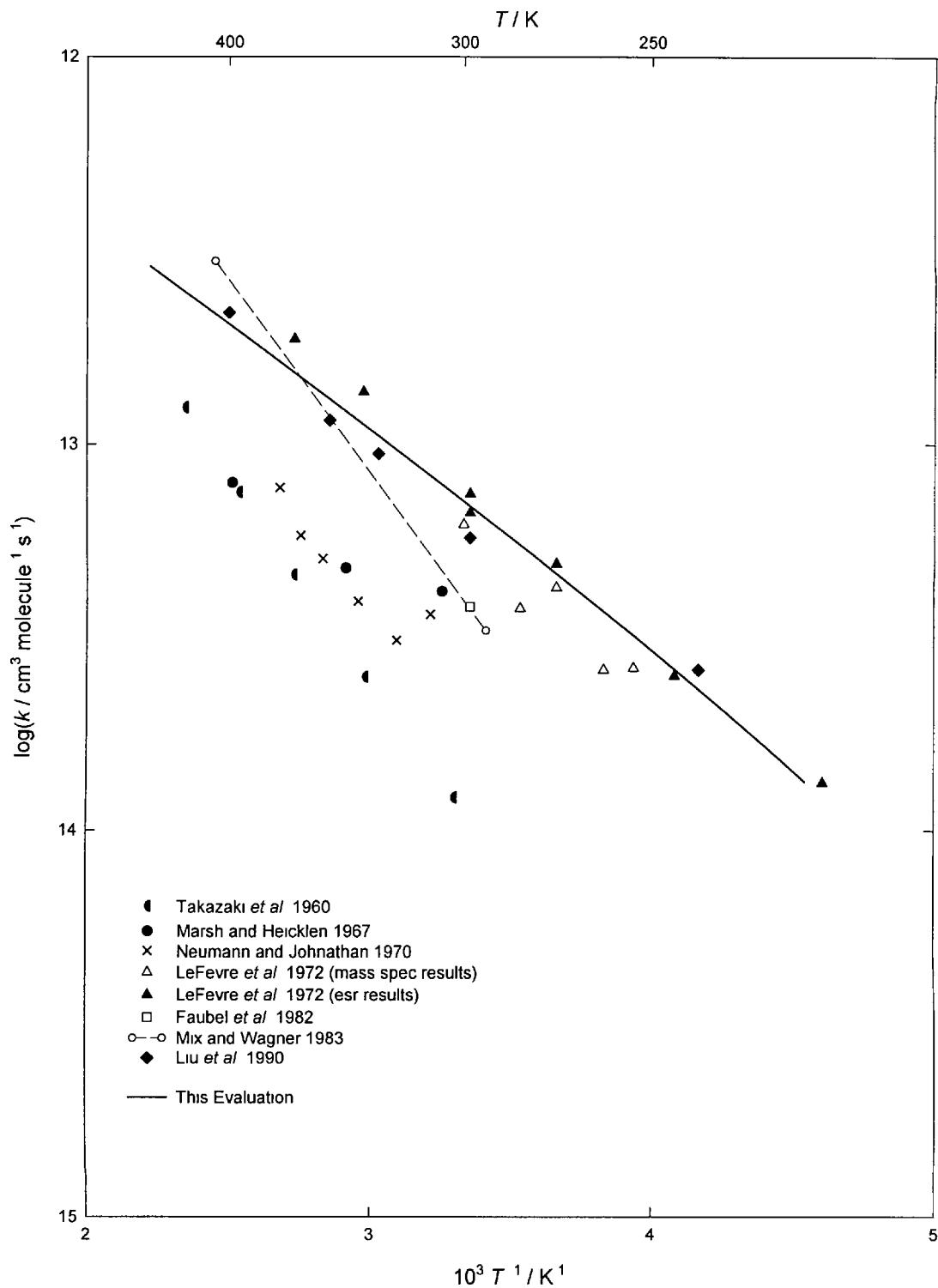
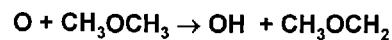
The expression derived by Liu *et al.*<sup>2</sup> from their flash photolysis study is taken as the preferred expression for  $k$ . Of the several studies of the reaction this is the only one in which the effects of secondary chemistry are likely to have been eliminated.

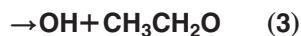
There are a number of older, relative rate studies<sup>3–5</sup> employing photolysis of N<sub>2</sub>O as a source of atomic O in a steady state system. The results from these studies given on the Arrhenius diagram have been recalculated using more recent values for the reference rate constants but, although there is fair agreement among them, they all give values of  $k$  much lower than predicted by the preferred expression. This suggests a common source of error almost certainly associated with uncertainties in the secondary chemistry in such systems.

The discharge flow studies of Mix and Wagner<sup>6</sup> and of Faubel *et al.*<sup>7</sup> may also have suffered from complicating secondary chemistry. Such complications were recognized by Le Fevre *et al.*<sup>1</sup> in their discharge flow work. Thus their absolute values of  $k$  are suspect because of uncertainties in the stoichiometry, but the temperature dependence of  $k$  obtained from their studies, using both ESR and mass spectrometry, provide good support for the value obtained by Liu *et al.*<sup>2</sup> which is the basis of our preferred values.

**References**

- <sup>1</sup> H. F. LeFevre, J. F. Meagher, and R. B. Timmons, Int. J. Chem. Kinet. **4**, 103 (1972).
- <sup>2</sup> R. Liu, P. Dagaut, R. E. Huie, and M. J. Kurylo, Int. J. Chem. Kinet. **22**, 711 (1990).
- <sup>3</sup> G. Marsh and J. Heicklen, J. Phys. Chem. **71**, 250 (1967).
- <sup>4</sup> Y. Takazaki, S. Mori, and H. Kawasaki, Bull. Chem. Soc. Jpn. **39**, 1643 (1960).
- <sup>5</sup> M. G. Neumann and N. Jonathan, J. Chem. Soc. B 167 (1970).
- <sup>6</sup> K. H. Mix and H. Gg. Wagner, Oxid. Commun. **5**, 321 (1983).
- <sup>7</sup> C. Faubel, K. Hoyermann, and H. Gg. Wagner, Z. Phys. Chem. N.F. **130**, 1 (1982).





#### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = -28.8 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = 23.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 4.8 \cdot 10^3 T^{-0.764} \exp(+3030/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(3) = 7.66 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = 16.5 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 38.8 T^{-0.199} \exp(-1090/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(2) = -13.13 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = 17.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 0.77 T^{0.468} \exp(+1440/T) \\ (300 \leq T/\text{K} \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2 + k_3$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$9.9 \cdot 10^{-19} T^{2.46} \exp(-932/T)$	298–886	Grotheer, Nesbitt, and Klemm, 1986 <sup>1</sup>	(a)
<i>Reviews and Evaluations</i>			
$1.0 \cdot 10^{-18} T^{2.46} \exp(-930/T)$	300–1000	Herron, 1988 <sup>2</sup>	(b)

#### Comments

- (a) Fast-flow discharge (298–706 K) and flash photolysis (297–886 K) were used with resonance fluorescence detection of O atoms in both cases. O atoms were produced by photolysis of O<sub>2</sub> or NO in the flash photolysis experiments and, in the fast-flow technique, by a discharge through O<sub>2</sub> or by titration of N atoms with NO. Total pressures were in the range 2.2–132 mbar with He or Ar as the bath gas. O<sub>2</sub> was added in the discharge flow experiments to suppress secondary chemistry and wall reactions at high temperatures. Good agreement between results from the two techniques was obtained.
- (b) Accepts the expression of Grotheer *et al.*<sup>1</sup>

#### Preferred Values

$$k = 1 \cdot 10^{-18} T^{2.5} \exp(-930/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the range } 298\text{--}1000 \text{ K.}$$

#### Reliability

$$\Delta \log k = \pm 0.2 \text{ over the range } 298\text{--}1000 \text{ K.}$$

#### Comments on Preferred Values

The preferred expression is based on the results of Grotheer *et al.*<sup>1</sup> There are a number of other studies<sup>3–6</sup> which appear suspect and which have not been used in this evaluation. Owens and Roscoe<sup>3</sup> used much smaller [C<sub>2</sub>H<sub>5</sub>OH]/[O] ratios than Grotheer *et al.*<sup>1</sup> and their technique required measured values of the stoichiometry to allow for the secondary chemistry and to derive values of  $k$ . The

results of Owens and Roscoe<sup>3</sup> (later reanalyzed by Ayub and Roscoe<sup>4</sup>) give values of  $k$  similar in magnitude to those of Grotheer *et al.*<sup>1</sup> but the two studies give widely different values for the temperature dependence of  $k$ . It is likely that the relative rate study of Kato and Cvetanovic,<sup>5</sup> which gives a high value of  $k$  at 298 K, was also affected by secondary reactions. However it is more difficult to see why Washida<sup>6</sup> obtains a value of  $k$  approximately a factor of 3 larger than that of Grotheer *et al.*<sup>1</sup> at 298 K.

Kato and Cvetanovic<sup>5</sup> found that the major product from their steady state photolysis study of the reaction was 2,3-butandiol, the dimer of the radical formed via reaction Channel (1). Similarly, from a mass-spectrometric study of the reaction products from a number of isotopically labeled ethanol, Washida<sup>6</sup> concluded that at 298 K Channel (1) accounts for 99% of the reaction. There are no kinetic studies of the branching ratios at higher temperatures but the curvature on the Arrhenius plot found by Grotheer *et al.*<sup>1</sup> may indicate the growth in importance of Channels (2) and (3) as the temperature is raised. This view is supported by a crossed beam molecular beam study of Dutton *et al.*<sup>7</sup> who examined the relative importance of the H-atom abstraction at the various sites by O atoms at relative translational temperatures of 3500 K. The results at such temperatures indicate a branching ratio for abstraction from the OH site more than twice that from each of the CH sites (see Marinov<sup>8</sup> for a discussion of these results).

#### References

<sup>1</sup> H. Grotheer, F. L. Nesbitt, and R. B. Klemm, *J. Phys. Chem.* **90**, 2512 (1986).

<sup>2</sup>J. T. Herron, J. Phys. Chem. Ref. Data **17**, 967 (1988).

<sup>3</sup>C. M. Owens and J. M. Roscoe, Can. J. Chem. **54**, 984 (1976).

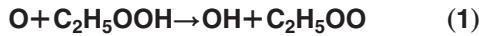
<sup>4</sup>A. L. Ayub and J. M. Roscoe, Can. J. Chem. **57**, 1269 (1979).

<sup>5</sup>A. Kato and R. J. Cvetanovic, Can. J. Chem. **45**, 1845 (1967).

<sup>6</sup>N. Washida, J. Chem. Phys. **75**, 2715 (1981).

<sup>7</sup>N. J. Dutton, I. W. Fletcher, and J. C. Whitehead, J. Phys. Chem. **89**, 569 (1985).

<sup>8</sup>N. M. Marinov, Int. J. Chem. Kinet. **31**, 183 (1999).



#### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = -67.4 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = 17.5 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 5.8 \cdot 10^3 T^{-0.970} \exp(+7800/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(3) = -7.05 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = 37.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 1.32 \cdot 10^4 T^{-0.656} \exp(+460/T) \\ (300 \leq T/\text{K} \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data

There are no experimental data for this reaction.

#### Preferred Values

$$k = 1.10 \cdot 10^{-10} \exp(-2090/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad \text{over the range } 298\text{--}1000 \text{ K.}$$

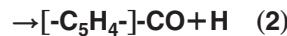
#### Reliability

$$\Delta \log k = \pm 0.5 \text{ at } 298 \text{ K, rising to } \pm 0.7 \text{ at } 1000 \text{ K.}$$

#### Comments on Preferred Values

In the reaction of O atoms with CH<sub>3</sub>OOH attack on the alkyl group predominates. This is also expected to be the

case for C<sub>2</sub>H<sub>5</sub>OOH, where the presence of secondary H atoms is expected to lead to enhanced reactivity compared with CH<sub>3</sub>OOH, and hence Channel (2) is expected to dominate at ambient and slightly higher temperatures. Comparison of  $k(\text{O} + \text{CH}_3\text{OH})$  with  $k(\text{O} + \text{C}_2\text{H}_5\text{OH})$  shows  $k(\text{O} + \text{C}_2\text{H}_5\text{OH})$  to be enhanced over  $k(\text{O} + \text{CH}_3\text{OH})$  by a factor of 10 at 300 K and a factor of 4 at 1000 K. In the absence of experimental data for the reaction of O with C<sub>2</sub>H<sub>5</sub>OOH the preferred expression for  $k$  has been estimated by use of  $k(\text{O} + \text{CH}_3\text{OOH})$  and assuming the same degree of enhancement at 300 K and 1000 K that is observed for the corresponding alcohols.



#### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = -436.2 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = 13.36 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 7.02 \cdot 10^2 T^{-0.637} \exp(+52070/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(2) = -232.3 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = 19.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 5.17 \cdot 10^{-2} T^{0.919} \exp(+27900/T) \\ (300 \leq T/\text{K} \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$(1.5\text{--}1.8) \cdot 10^{-10}$	1050–1500	Frank <i>et al.</i> , 1994 <sup>1</sup>	(a)

## Comments

- (a) Shock tube study using measurements behind reflected shock waves. Phenyl radicals were generated by decomposition of nitroso- or iodobenzene. [O] measured by ARAS. [O] profile simulated with a kinetic model; the position of the maximum [O]<sub>1</sub> was found to be sensitive to the reactions C<sub>6</sub>H<sub>5</sub>+O<sub>2</sub>→C<sub>6</sub>H<sub>5</sub>O+O and C<sub>6</sub>H<sub>5</sub>+O→products.

## Preferred Values

$k = 1.7 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 1050–1500 K.

### Reliability

$\Delta \log k = \pm 0.3$  over the range 1050–1500 K.

### Comments on Preferred Values

The only published study to date is that of Frank *et al.*<sup>1</sup>. We therefore accept the average of the range reported with

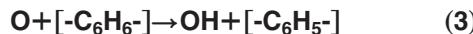
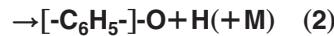
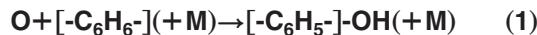
wide error limits. The high rate coefficient agrees with an unpublished value<sup>2</sup> determined at room temperature,  $k = 1 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

Since this is a radical-radical reaction no entrance barrier for the reaction is expected and, therefore, the high rate coefficient observed seems plausible. The reactants probably form an excited phenoxy radical adduct which isomerizes to generate the products. According to Frank *et al.*,<sup>1</sup> there is a barrier of at least 200 kJ mol<sup>-1</sup> in Channel (2) relative to Cyclopentadienyl+CO, so that  $k_1(E) \gg k_2(E)$ ; thus it is likely that the reaction proceeds almost entirely by Channel (1).

## References

<sup>1</sup> P. Frank, J. Herzler, Th. Just, and C. Wahl, 25th Symp. (Int.) Combustion, 1994, p. 833.

<sup>2</sup> K. Hoyermann (University of Göttingen, Germany, private communication, 1993).



### Thermodynamic Data

$$\Delta H_{298}^{\circ}(1) = -428.1 \text{ kJ mol}^{-1}$$

$$\Delta S_{298}^{\circ}(1) = -115.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 9.57 \cdot 10^{-29} T^{1.059} \exp(+51490/T) \text{ cm}^3 \text{ molecule}^{-1}$$

(300 ≤ T/K ≤ 5000)

$$\Delta H_{298}^{\circ}(2) = -59.96 \text{ kJ mol}^{-1}$$

$$\Delta S_{298}^{\circ}(2) = -3.55 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 7.4 \cdot 10^{-2} T^{0.441} \exp(+7075/T) \text{ cm}^3 \text{ molecule}^{-1}$$

(300 ≤ T/K ≤ 3000)

$$\Delta H_{298}^{\circ}(3) = 43.4 \text{ kJ mol}^{-1}$$

$$\Delta S_{298}^{\circ}(3) = 42 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 2.48 \cdot 10^4 T^{-0.679} \exp(-5590/T)$$

(300 ≤ T/K ≤ 5000)

See Section 3 for the source of the Thermodynamic Data.

## Rate Coefficient Data ( $k = k_1 + k_2 + k_3$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$2.5 \cdot 10^{-10} \exp(-2768/T)$	883–963	Mkryan, Oganesyan, and Nalbandyan, 1971 <sup>1</sup>	(a)
$k_3 = 5.3 \cdot 10^{-10} \exp(-3019/T)$	1300–1700	Fujii and Asaba, 1972 <sup>2</sup>	(b)
$2.4 \cdot 10^{-14}$	300	Atkinson and Pitts, 1974 <sup>3</sup>	(c)
$1.8 \cdot 10^{-11} \exp(-2214/T)$	298–462	Colussi <i>et al.</i> , 1975 <sup>4</sup>	(d)
$1.8 \cdot 10^{-11} \exp(-2003/T)$	299–392	Atkinson and Pitts, 1975 <sup>5</sup>	(d)
$1.7 \cdot 10^{-11} \exp(-2010/T)$	299–440	Atkinson and Pitts, 1975 <sup>6</sup>	(e)
$4.6 \cdot 10^{-11} \exp(-2470/T)$	298–867	Nicovich, Gump, and Ravishankara, 1982 <sup>7</sup>	(f)
$k_3 = 5.3 \cdot 10^{-10} \exp(-3020/T)$	1600–2300	Hsu, Lin, and Lin, 1984 <sup>8</sup>	(g)
$3.5 \cdot 10^{-11} \exp(-2550/T)$	300–670	Tappe, Schiephake, and Wagner, 1989 <sup>9</sup>	(h)
$k_1 = 4.0 \cdot 10^{-11} \exp(-2350/T)$	1200–1450	Leidreiter and Wagner, 1989 <sup>10</sup>	(i)
$k_1 = 5.4 \cdot 10^{-11} \exp(-2611/T)$	600–1300	Ko, Adusei, and Fontijn, 1991 <sup>11</sup>	(j)
<i>Reviews and Evaluations</i>			
$5.9 \cdot 10^{-23} T^{3.8} \exp(-473/T)$	300–2000	CEC 1992; 1994 <sup>12</sup>	(k)
$k_1 = 3.7 \cdot 10^{-11} \exp(-2280/T)$	298–1400		

### Comments

- (a) Evaluation of an overall rate coefficient from a flow reactor study.
- (b) Single-pulse shock tube study to investigate the kinetic behavior of benzene/argon mixtures containing small amounts of oxygen. Gas chromatographic analysis of stable products and absorption/emission measurements O<sub>2</sub>, CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and [-C<sub>6</sub>H<sub>6</sub>-] during course of reaction.
- (c) Pulse radiolysis with product analysis by gas chromatography. O atoms generated from radiolysis of CO<sub>2</sub> and NO<sub>2</sub> at high pressures. Rate coefficient derived from absorption profiles of transient species.
- (d) Phase shift-O+NO chemiluminescence. O atoms generated by Hg photosensitized decomposition of NO<sub>2</sub>.
- (e) Flash-photolysis resonance fluorescence study. O atoms generated by pulsed vacuum ultraviolet (VUV) photolysis of O<sub>2</sub> and NO.
- (f) Flash-photolysis resonance fluorescence study. O atoms generated by pulsed VUV photolysis of O<sub>2</sub>.
- (g) Shock tube study behind reflected shock waves under fuel lean conditions. CO production monitored with a stabilized cw CO laser. [CO] profile fitted with a 25-step reaction mechanism. The rate coefficient for Channel (2) was taken from Fujii and Asaba.<sup>2</sup>
- (h) Flow reactor study. O atoms generated by microwave discharge of O<sub>2</sub>. O atom in 32–80 fold excess. [O] determined by mass spectrometry. Experiments conducted over the pressure range 2.4–11.6 mbar and temperature range 300–870 K. For  $T > 670$  K strong upward curvature of the Arrhenius plot is observed, the authors therefore recommended a rate expression only to 670 K.
- (i) Shock tube study. O atoms generated from decomposition of (6–25 ppm) ozone in the presence of low concentrations of benzene (100–160 ppm). O atoms monitored by ARAS at 130.5 nm.
- (j) High temperature fast flow reactor study. O(<sup>3</sup>P) was generated by 193 nm photolysis of SO<sub>2</sub> and monitored by resonance fluorescence in excess of benzene. The results for the rate of removal of O(<sup>3</sup>P) are consistent with low temperature data and with the results of Leidreiter and Wagner.<sup>10</sup> It was concluded that the same reaction channel is dominant up to 1400 K.
- (k) See Comments on Preferred Values.

### Preferred Values

$(k_1 + k_2) = 3.7 \cdot 10^{-11} \exp(-2280/T)$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> over the range 298–1400 K.

### Reliability

$\Delta \log(k_1 + k_2) = \pm 0.3$  over the range 298–1400 K.

### Comments on Preferred Values

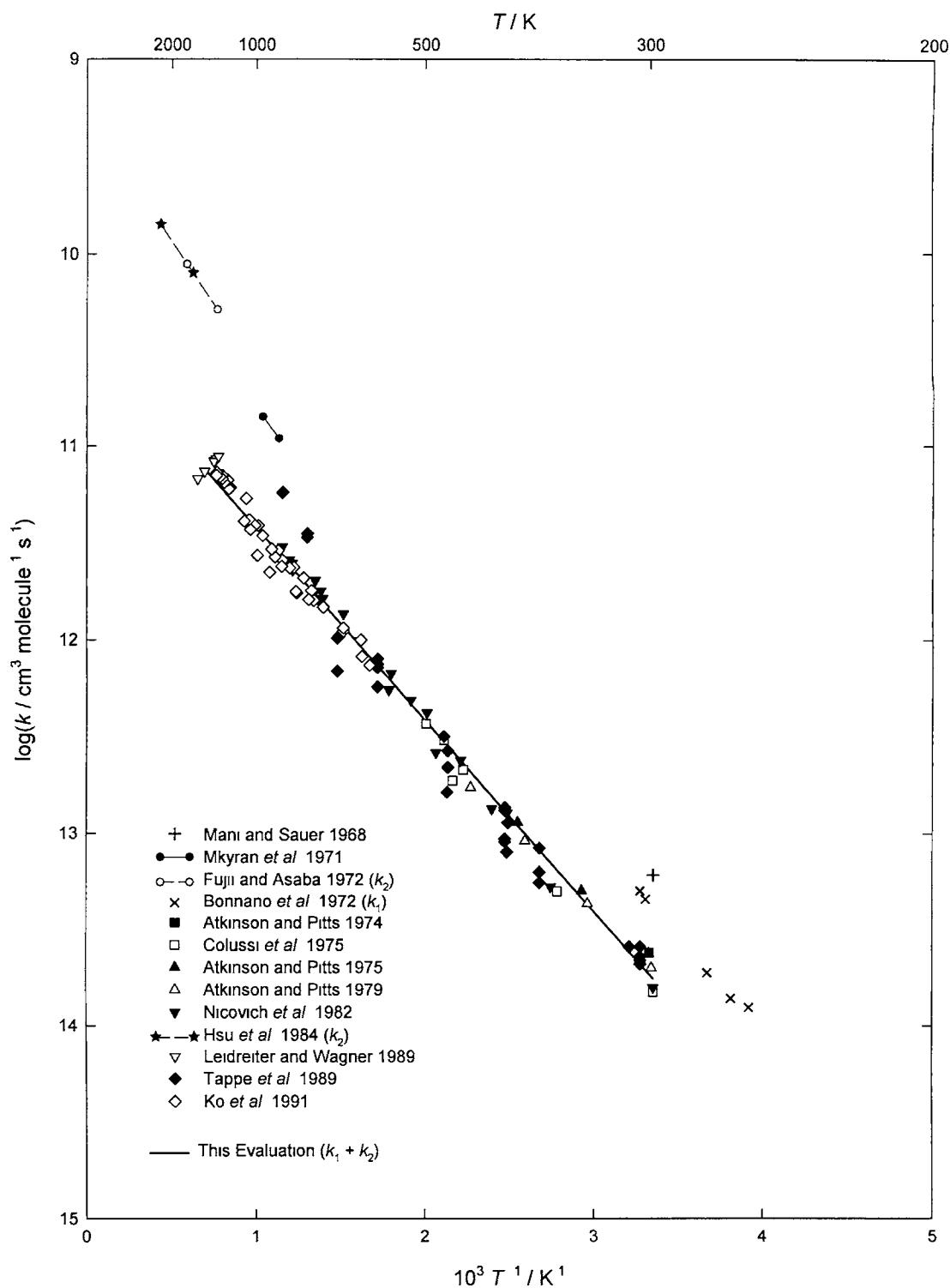
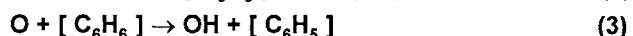
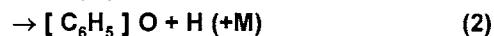
There are a number of studies on benzene oxidation in the lower temperature range, up to about 900 K. The preferred values for ( $k_1 + k_2$ ) remain unchanged from our previous evaluation<sup>12</sup> and are based on the data of Atkinson and Pitts,<sup>3,5,6</sup> Colussi *et al.*,<sup>4</sup> Nicovich, Gump, and Ravishankara,<sup>7</sup> Tappe, Schliephake, and Wagner,<sup>9</sup> and Leidreiter and Wagner.<sup>10</sup> The data of Ko, Adusei, and Fontijn<sup>11</sup> determined over the temperature range 600–1300 K are in close agreement with the recommended expression, and the lower temperature data of Mani and Sauer<sup>13</sup> and Bonnano *et al.*<sup>14</sup> are also in reasonable agreement.

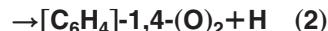
The addition of O(<sup>3</sup>P) to benzene is highly exothermic and there are a number of possible decomposition channels for the adduct. Experimental information on the likely products is very limited but *ab initio* calculations by Hodgson *et al.*<sup>15</sup> suggest that formation of C<sub>6</sub>H<sub>5</sub>O+H, C<sub>5</sub>H<sub>5</sub>CHO, and C<sub>5</sub>H<sub>5</sub>+CHO are the most likely. In a flow reactor study performed at 405 K and low pressures, Bajaj and Fontijn<sup>16</sup> have found that the main products are phenoxy radicals and H, whereas phenol is a minor product.

In the figure we show additionally the data points of Mkryan, Oganesyan, and Nalbandyan,<sup>1</sup> Fujii and Asaba,<sup>2</sup> and Hsu *et al.*<sup>8</sup> These data are based upon rather crude models of benzene oxidation. Whether there is a contribution of Channel (3) at high temperatures cannot be stated, due to the present lack of a sound kinetic basic for reactions at temperatures  $> 1400$  K.

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- <sup>2</sup>N. Fujii and T. Asaba, 14th Symp. (Int.) Combustion, 1972, p. 433.
- <sup>3</sup>R. Atkinson and J. N. Pitts, Jr., J. Phys. Chem. **78**, 1780 (1974).
- <sup>4</sup>A. J. Colussi, D. L. Singleton, R. S. Irwin, and R. J. Cvetanovic, J. Phys. Chem. **79**, 1900 (1975).
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- <sup>9</sup>M. Tappe, V. Schliephake, and H. G. Wagner, Z. Phys. Chem. N.F. **162**, 129 (1989).
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- <sup>13</sup>I. Mani and M. C. Sauer, Adv. Chem. Ser. **82**, 142 (1968).
- <sup>14</sup>R. A. Bonnano, P. Kim, J. H. Lee, and R. B. Timmons, J. Chem. Phys. **57**, 1377 (1972).
- <sup>15</sup>D. Hogson, H-Y. Zhang, M. R. Nimlos, and J. T. McKinnon, J. Phys. Chem. A **105**, 4316 (2000).
- <sup>16</sup>P. N. Bajaj and A. Fontijn, Combust. Flame **105**, 239, (1996).





#### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = -183.4 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = -23.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 1.88 \cdot 10^{-2} T^{0.196} \exp(+22080/T) \\ (300 \leq T/\text{K} \leq 4000)$$

$$\Delta H^\circ_{298}(2) = -201.8 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = -26.6 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 2.72 \cdot 10^{-2} T^{0.079} \exp(+24260/T) \\ (300 \leq T/\text{K} \leq 4000)$$

$$\Delta H^\circ_{298}(3) = -435.8 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = -44.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 1.36 \cdot 10^{13} T^{-5.131} \exp(+50414/T) \\ (300 \leq T/\text{K} \leq 3000)$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2 + k_3$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$2.8 \cdot 10^{-10}$	295	Buth <i>et al.</i> , 1994 <sup>1</sup>	(a)

#### Comments

- (a) Measurements in a dual discharge-flow reactor at low pressures of  $\sim 1\text{--}5$  mbar. O atoms were generated from highly dilute  $\text{O}_2/\text{He}$  mixtures. Phenoxy radicals were generated by the reaction  $[-\text{C}_6\text{H}_5]-\text{OH} + \text{Cl}$ ; Cl atoms were generated in a microwave discharge of  $\text{Cl}_2/\text{He}$  mixtures and the products were analyzed by molecular-beam sampling-mass spectrometry. The rate coefficient was measured relative to  $k(\text{O} + \text{C}_2\text{H}_5 \rightarrow \text{products}) = 2.2 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (this evaluation).

#### Preferred Values

$k = 2.8 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 295–1500 K.

#### Reliability

$\Delta \log k = \pm 0.3$  over the range 295–1500 K.

#### Comments on Preferred Values

The only published experimental data for this reaction are those of Buth *et al.*<sup>1</sup> at 295 K. We have revised the reported

relative rate coefficient to include the value of the rate coefficient for the reference reaction  $k(\text{O} + \text{C}_2\text{H}_5)$  recommended in this evaluation. This radical-atom reaction is rapid, Channels 1–3 are exothermic, and the rate coefficient is unlikely to be appreciably temperature dependent.

Quinones,  $\text{C}_5\text{H}_5$ , and  $\text{CO}_2$  were detected as products. The isomeric form of the quinones could not be distinguished, product recovery was poor (35%), and therefore a branching ratio could not be given by the authors. However,  $\text{CO}_2$  appeared as a minor component, and therefore it is concluded that Channels (1) and (2) are the major channels. This conclusion agrees with the potential energy surface calculated by Lin and Mebel.<sup>2</sup> The reactants may react to form an adduct in a barrierless reaction which may isomerize to yield the products of Channels (1) and (2), whereas there is a substantial barrier (about 60 kJ mol<sup>-1</sup>) to formation of the adduct which leads to  $\text{CO}_2$  production [Channel (3)].

#### References

<sup>1</sup>R. Buth, K. H. Hoyermann, and J. Seeba, 25th Symp. (Int.) Combustion, 1994, p. 841.

<sup>2</sup>M. C. Lin and A. M. Mebel, J. Phys. Org. Chem. **8**, 407 (1995).

**O+[-C<sub>6</sub>H<sub>5</sub>-]-OH→Products****Rate Coefficient Data**

<i>k/cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup></i>	<i>T/K</i>	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$2.82 \cdot 10^{-11} \exp(-1540/T)$	298–870	Koch, Stucken, and Wagner, 1992 <sup>1</sup>	(a)
<i>Reviews and Evaluations</i>			
$2.1 \cdot 10^{-11} \exp(-1455/T)$	292–600	CEC, 1992; 1994 <sup>2</sup>	(b)

**Comments**

- (a) Flow reactor study in He bath gas at pressures between 2.3 and 5.0 mbar. O atoms generated by discharge in O<sub>2</sub>/He mixtures. O atoms monitored by mass spectrometry. Data of Frerichs *et al.*<sup>3</sup> reanalyzed and included in determining *k*. Supersedes study of Frerichs *et al.*<sup>3</sup>
- (b) Preferred value based on the data of Frerichs *et al.*<sup>3</sup>

**Preferred Values**

$$k = 2.82 \cdot 10^{-11} \exp(-1540/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad \text{over the range 298–870 K.}$$

**Reliability**

$$\Delta \log k = \pm 0.3 \text{ over the range 298–870 K.}$$

*Comments on Preferred Values*

The preferred value is based on the revised data of Koch, Stucken, and Wagner.<sup>1</sup> The upward curvature apparent in the earlier study<sup>3</sup> has been corrected by a reinterpretation of the earlier data. The recommendation now covers the full temperature range of the experimental studies.<sup>1,3</sup>

**References**

- <sup>1</sup>R. Koch, D. K. Stucken, and H. G. Wagner, 24th Symp. (Int.) Combustion, 1992, p. 675.  
<sup>2</sup>CEC, 1992; Supplement I, 1994 (see references in Introduction).  
<sup>3</sup>H. Frerichs, R. Koch, V. Schiepake, M. Tappe, and H. G. Wagner, Z. Phys. Chem. N.F. **166**, 145 (1990).

**Thermodynamic Data**

$$\begin{aligned}\Delta H^\circ_{298}(1) &= -331.4 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(1) &= 13.3 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 1.05 \cdot 10^6 T^{-1.890} \exp(+39440/T) \\ (300 \leqslant T/\text{K} \leqslant 5000)\end{aligned}$$

$$\begin{aligned}\Delta H^\circ_{298}(2) &= -275.9 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(2) &= -29.6 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 2.79 \cdot 10^{-1} T^{-0.380} \exp(+33180/T) \\ (300 \leqslant T/\text{K} \leqslant 5000)\end{aligned}$$

$$\begin{aligned}\Delta H^\circ_{298}(3) &= -227.7 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(3) &= 27.0 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(3) &= 2.17 \cdot 10^7 T^{-2.115} \exp(+26940/T) \\ (300 \leqslant T/\text{K} \leqslant 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data (*k*=*k*<sub>1</sub>+*k*<sub>2</sub>+*k*<sub>3</sub>)**

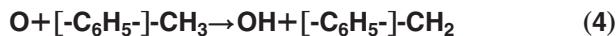
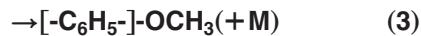
<i>k/cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup></i>	<i>T/K</i>	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$k_3 = 1.7 \cdot 10^{-11}$	1700–2800	McLain, Jachimowski, and Wilson, 1979 <sup>1</sup>	(a)
$(k_1 + k_2) = 5.5 \cdot 10^{-10}$	298	Bartels, Edelbuettel-Einhaus, and Hoyermann, 1988 <sup>2</sup>	(b)
<i>Reviews and Evaluations</i>			
$(k_1 + k_2) = 5.5 \cdot 10^{-10}$	298	CEC, 1992; 1994 <sup>3</sup>	(c)

## Comments

- (a) Investigation of benzene and toluene/oxygen/argon mixtures behind incident shock waves by monitoring UV and IR emission of CO, CO<sub>2</sub>, and the product [O]·[CO]. Rate coefficient for channel (2) estimated from reaction model.
- (b) Reactions of benzyl with H, O and O<sub>2</sub> were studied at low pressures (around 1 mbar) in a multiple discharge flow reactor by a molecular beam sampling technique and mass spectrometric detection. The rate coefficient ( $k_1 + k_2$ ) was determined relative to  $k(O + CH_3) = 1.4 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (this evaluation).
- (c) See Comments on Preferred Values.

## Preferred Values

$$(k_1 + k_2) = 5.5 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$



## Thermodynamic Data

$$\Delta H^\circ_{298}(1) = -428.3 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = -128.6 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 2.40 \cdot 10^{-27} T^{0.413} \exp(+51130/T) \text{ cm}^3 \text{ molecule}^{-1} \\ (300 \leq T/K \leq 5000)$$

$$\Delta H^\circ_{298}(3) = -367.6 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = -130.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 2.78 \cdot 10^{-30} T^{1.311} \exp(+44300/T) \text{ cm}^3 \text{ molecule}^{-1} \\ (300 \leq T/K \leq 5000)$$

$$\Delta H^\circ_{298}(5) = 43.3 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(5) = 30.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(5) = 4.92 \cdot 10^3 T^{-0.642} \exp(-5560/T) \\ (300 \leq T/K \leq 5000)$$

$$\Delta H^\circ_{298}(2) = -424.5 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = -130.5 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 7.32 \cdot 10^{-30} T^{1.168} \exp(+51140/T) \text{ cm}^3 \text{ molecule}^{-1} \\ (300 \leq T/K \leq 5000)$$

$$\Delta H^\circ_{298}(4) = -54.7 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(4) = 21.6 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(4) = 3.66 T^{0.354} \exp(+6310/T) \\ (300 \leq T/K \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

## Rate Coefficient Data ( $k = k_1 + k_2 + k_3 + k_4 + k_5$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$2.4 \cdot 10^{-11} \exp(-1640/T)$	393–495	Jones and Cvetanovic, 1961 <sup>1</sup>	(a)
$1.3 \cdot 10^{-13}$	303	Grovenstein and Mosher, 1970 <sup>3</sup>	(b)
$7.5 \cdot 10^{-14}$	300	Atkinson and Pitts, 1974 <sup>4</sup>	(c)
$3.8 \cdot 10^{-11} \exp(-1942/T)$	298–462	Colussi <i>et al.</i> , 1975 <sup>5</sup>	(c)
$1.4 \cdot 10^{-11} \exp(-1560/T)$	299–392	Atkinson and Pitts, 1974 <sup>6</sup>	(c)
$8.3 \cdot 10^{-12} \exp(-1359/T)$	373–648	Furuyama and Ebara, 1975 <sup>7</sup>	(d)
$1.6 \cdot 10^{-11} \exp(-1535/T)$	299–440	Atkinson and Pitts, 1979 <sup>8</sup>	(e)
$1.7 \cdot 10^{-10} \exp(-3625/T)$	1700–2800	McLain, Jachimowski, and Wilson, 1979 <sup>9</sup>	(f)
$4.3 \cdot 10^{-11} \exp(-1910/T)$	298–932	Nicovich, Gump, and Ravishankara, 1982 <sup>10</sup>	(g)
$2.8 \cdot 10^{-11} \exp(-1770/T)$	305–873	Tappe, Schliephake, and Wagner, 1989 <sup>11</sup>	(h)
$5.1 \cdot 10^{-11} \exp(-2000/T)$	1100–1350	Hoffmann, Klatt, and Wagner, 1990 <sup>12</sup>	(i)

$k/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$	T/K	Reference	Comments
<i>Reviews and Evaluations</i>			
$5.3 \cdot 10^{-15} T^{1.21} \exp(-1260/T)$	298–2800	CEC, 1992; 1994 <sup>13</sup>	(j)

### Comments

- (a) O atoms generated from Hg photosensitized decomposition of N<sub>2</sub>O.  $k$  determined relative to  $k(\text{O}+[-\text{C}_5\text{H}_6^-])=2.4 \cdot 10^{-12} \exp(-1640/T) \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$  evaluated by Cvetanovic.<sup>2</sup>
- (b) Same method as in (a).  $k$  determined relative to  $k(\text{O}+[-\text{C}_6\text{H}_5^-])=5.9 \cdot 10^{-23} T^{3.8} \exp(-473/T) \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$  (this evaluation).
- (c) Phase shift-O+NO chemiluminescence. O atoms generated from Hg photosensitized decomposition of N<sub>2</sub>O.
- (d) Microwave discharge-fast flow reactor. O atoms generated by the reaction N+NO. Products analyzed by gas chromatography.
- (e) Flash photolysis-resonance fluorescence. O atoms generated by VUV photolysis of O<sub>2</sub> and NO.
- (f) Incident shock wave investigation of the oxidation mechanism of [-C<sub>6</sub>H<sub>6</sub><sup>-</sup>]/O<sub>2</sub>/Ar and [-C<sub>6</sub>H<sub>5</sub><sup>-</sup>]-CH<sub>3</sub>/O<sub>2</sub>/Ar mixtures by monitoring UV and IR emission of CO, CO<sub>2</sub>, and the product [O]·[CO]. Arrhenius expression for Channel (1) by comparison with data for benzene.
- (g) Flash photolysis-resonance fluorescence study. O atoms generated by VUV photolysis of O<sub>2</sub>.
- (h) Low pressure discharge flow experiments with molecular beam sampling and mass spectral analysis of reactants and products.
- (i) Shock tube study behind incident shock waves. O atoms generated by pyrolysis of 10–20 ppm ozone in presence of 290–360 ppm toluene in Ar bath gas. O atom concentration determined by VUV absorption at 131.5 nm. OH production monitored by laser absorption at 308.417 nm and corrected for benzyl radical absorption by estimating benzyl radical concentration from computer fit. Rate coefficient extracted by fitting with a 23-step mechanism. Data combined with those of Nicovich, Gump, and Ravishankara,<sup>10</sup> Colussi *et al.*,<sup>5</sup> and Tappe, Schliephake, and Wagner<sup>11</sup> to derive rate expression given in table.
- (j) Preferred value based on the data of Refs. 1–10, and 14. See also Comments on Preferred Values.

### Preferred Values

$$k = 5.3 \cdot 10^{-15} T^{1.21} \exp(-1260/T) \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$$

over the range 298–2800 K.

### Reliability

$\Delta \log k = \pm 0.1$  at 298 K, rising to  $\pm 0.3$  at 2800 K.

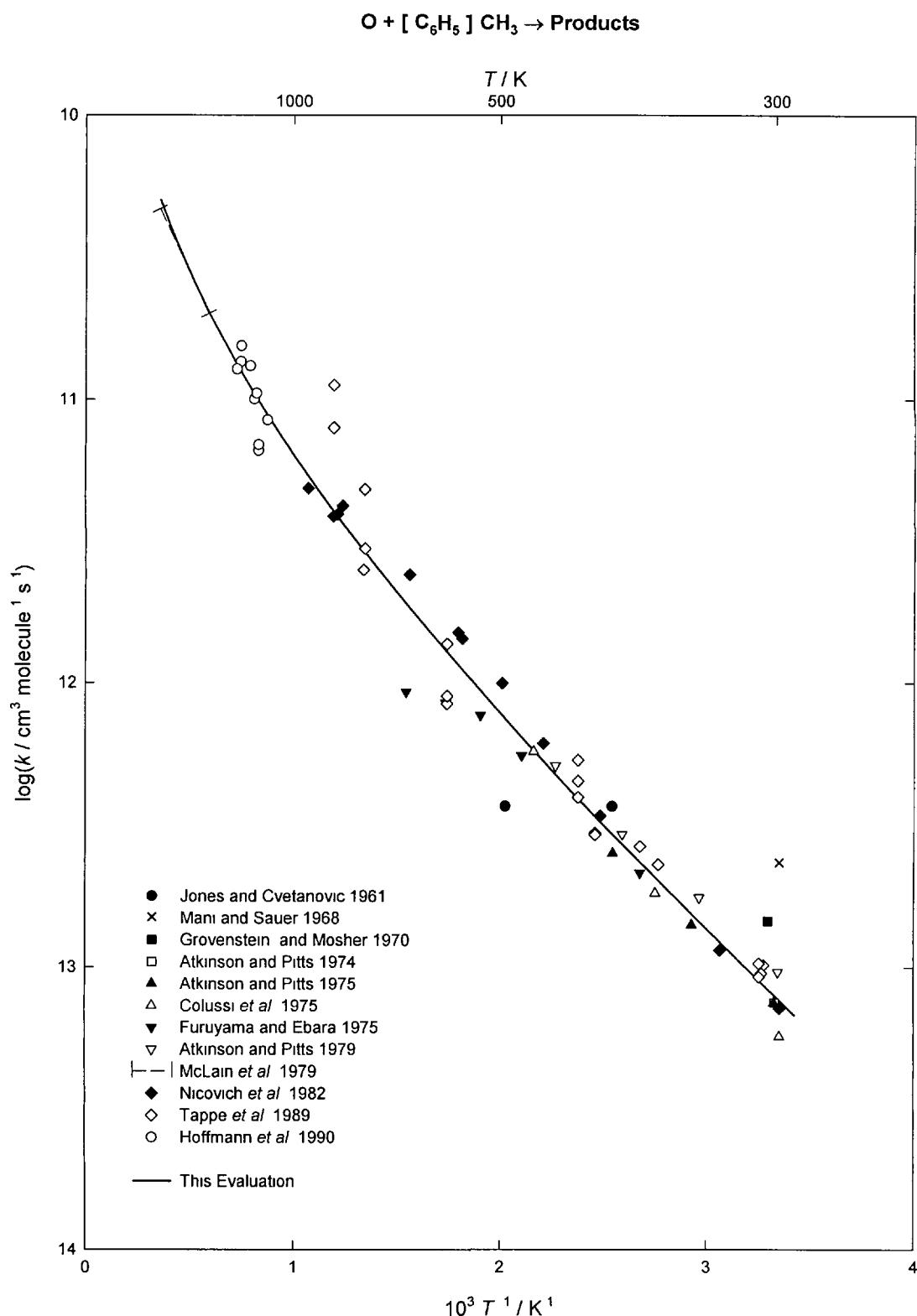
### Comments on Preferred Values

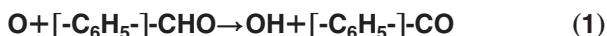
The preferred expression for  $k$  remains unchanged from our previous evaluation. The data of Hoffmann, Klatt, and Wagner<sup>12</sup> confirm the value of the rate coefficient at high temperatures from the previous evaluation which was based solely on the value estimated by McLain, Jachimowski, and Wilson<sup>10</sup> from modeling a complex reaction system. We have adjusted the error limits of the preferred values accordingly. All of the available experimental data are in good agreement except the room temperature value of Mani and Sauer<sup>14</sup> which is a factor of 3 greater than the recommendation.

Hoffmann, Klatt, and Wagner<sup>12</sup> found that the OH radical yield accounted for approximately 10% of the overall reaction at 1300 K with  $(k_4 + k_5) = 1.0 \cdot 10^{-12} \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$  over the range 1150–1350 K. The branching ratio  $k_5/k_4$  is estimated to be 0.1 based on thermodynamic considerations. The contributions of Channels (4) and (5) are small under normal combustion conditions. Cresols are the most probable products generated by O atom insertion into the aromatic C-H bonds [channels (1) and (2)]. At combustion temperatures such cresols are most likely to decompose to generate H atoms and methylphenoxy radicals.

### References

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- <sup>2</sup>R. J. Cvetanovic, J. Phys. Chem. Ref. Data **16**, 261 (1987).
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- <sup>11</sup>M. Tappe, V. Schliephake, and H. G. Wagner, Z. Phys. Chem. N.F. **162**, 129 (1989).
- <sup>12</sup>A. Hoffmann, M. Klatt, and H. G. Wagner, Z. Phys. Chem. N.F. **168**, 1 (1990).
- <sup>13</sup>CEC, 1992; Supplement I, 1994 (see references in Introduction).
- <sup>14</sup>I. Mani and M. C. Sauer, Adv. Chem. Ser. **82**, 142 (1968).





#### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = -54.1 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = 26.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 1.85 \cdot 10^2 T^{-0.197} \exp(+6180/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(2) = 52.4 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = 161.443 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 5.44 \cdot 10^{-5} T^{-2.951} \exp(-1750/T) \\ (300 \leq T/\text{K} \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2 + k_3$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$4.8 \cdot 10^{-13}$	298	Filby and Gusten, 1978 <sup>1</sup>	(a)
<i>Reviews and Evaluations</i>			
$1.1 \cdot 10^{-11} \exp(-910/T)$	298–1500	CEC, 1994 <sup>2</sup>	(b)

#### Comments

- (a) Discharge flow technique with time resolved EPR detection of O atoms in excess benzaldehyde. Total pressure of 6.3 mbar He bath gas.
- (b) See Comments on Preferred Values.

#### Preferred Values

$k_1 = 1.1 \cdot 10^{-11} \exp(-910/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 298–1500 K.

#### Reliability

$\Delta \log k_1 = \pm 0.3$  at 298 K, rising to  $\pm 0.7$  at 1500 K.

#### Comments on Preferred Values

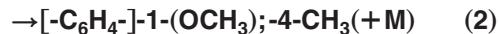
The preferred values remain unchanged from our previous evaluation.<sup>2</sup> The only experimental kinetic data for this reac-

tion are at room temperature. The  $k$  value is essentially identical to that for the reaction of O atoms with acetaldehyde, indicating that the main channel is H abstraction from the carbonyl group. The preferred rate expression applies to Channel (1) and is based on the room temperature measurements<sup>1</sup> and the temperature dependence for O + CH<sub>3</sub>CHO (see this evaluation). There is no direct information on the alternative channels [(2) and (3)] in which O attacks the aromatic ring. The importance of these channels can be assessed from the O + [-C<sub>6</sub>H<sub>5</sub>-] reaction. Applying the recommended expression from this evaluation of  $k(\text{O} + [\text{C}_6\text{H}_6]) = 1.42 \cdot 10^{19} T^{2.82} \exp(-1280/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  to the other channels, ( $k_2 + k_3$ ) is approximately a factor 28 lower than  $k_1$  at 298 K but they become equal at 750 K.

#### References

<sup>1</sup> W. G. Filby and H. Gusten, Atmos. Environ. **12**, 1563 (1978).

<sup>2</sup> CEC, Supplement I, 1994 (see references in Introduction).



#### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = -425.9 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = -118.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 4.14 \cdot 10^{-32} T^{1.995} \exp(+51910/T) \text{ cm}^3 \text{ molecule}^{-1}$$

(300 ≤ T/K ≤ 5000)

$$\Delta H^\circ_{298}(2) = -317.2 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = -119.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 5.06 \cdot 10^{-33} T^{2.289} \exp(+45430/T) \text{ cm}^3 \text{ molecule}^{-1}$$

(300 ≤ T/K ≤ 5000)

$$\Delta H^\circ_{298}(3) = -54.3 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = 11.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 1.31 \cdot 10^{-4} T^{1.463} \exp(+7190/T)$$

(300 ≤ T/K ≤ 5000)

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2 + k_3$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$1.8 \cdot 10^{-13}$	300	Atkinson and Pitts, 1974 <sup>1</sup>	(a)
$1.3 \cdot 10^{-11} \exp(-1280/T)$	299–392	Atkinson and Pitts, 1975 <sup>2</sup>	(a)
$3.9 \cdot 10^{-11} \exp(-1540/T)$	298–600	Nicovich, Gump, and Ravishankara, 1982 <sup>3</sup>	(b)
$4.3 \cdot 10^{-11} \exp(-1540/T)$	298–868	Frerichs <i>et al.</i> , 1989 <sup>4</sup>	(c)
<i>Reviews and Evaluations</i>			
$5.1 \cdot 10^{-11} \exp(-1630/T)$	298–600	CEC, 1992; 1994 <sup>5</sup>	(d)

#### Comments

- (a) Phase shift in modulated photolysis followed using O + NO chemiluminescence. O atoms generated from Hg photosensitized decomposition of N<sub>2</sub>O. Total pressure 72 mbar.
- (b) Flash photolysis-resonance fluorescence study. O atoms generated by pulsed photolysis of O<sub>2</sub> in N<sub>2</sub> or Ar diluent at 76 mbar total pressure.
- (c) Flow reactor study. O atoms generated by microwave discharge in O<sub>2</sub>; [O] in 45–172 fold excess. Total pressures in the range 2.2–4.5 mbar. [O] determined by mass spectrometry.
- (d) Preferred values based on the data of Refs. 1–4 and the review of Cvetanovic.<sup>6</sup> See Comments on Preferred Values.

#### Preferred Values

$k = 5.1 \cdot 10^{-11} \exp(-1630/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 298–1000 K.

#### Reliability

$\Delta \log k = \pm 0.3$  over the range 298–1000 K.

#### Comments on Preferred Values

The preferred values remain unchanged from our previous evaluation and are based on the experimental data of Atkinson and Pitts,<sup>1,2</sup> Nicovich, Gump, and Ravishankara,<sup>3</sup> and Frerichs *et al.*<sup>4</sup> The room temperature value of Mani and Sauer<sup>7</sup> is considerably higher than other room temperature determinations of  $k$  and has not been included in deriving the preferred expression. The recommended values are restricted to  $T < 1000$  K; at higher temperatures the results of Nicovich, Gump, and Ravishankara,<sup>2</sup> and Frerichs *et al.*<sup>4</sup> indicate an upward curvature of the Arrhenius plot, which requires further investigation. Channels (1)–(3) are exothermic and, by analogy with the reaction O+[-C<sub>6</sub>H<sub>5</sub>]-CH<sub>3</sub>, Channel (1) is the most probable product channel.

#### References

<sup>1</sup> R. Atkinson and J. N. Pitts, Jr., *J. Phys. Chem.* **78**, 1780 (1974).

<sup>2</sup> R. Atkinson and J. N. Pitts, Jr., *J. Phys. Chem.* **79**, 295 (1975).

<sup>3</sup> J. M. Nicovich, C. A. Gump, and R. A. Ravishankara, *J. Phys. Chem.* **86**, 1648 (1982).

<sup>4</sup> H. Frerichs, V. Schliephake, M. Tappe, and H. G. Wagner, *Z. Phys. Chem. N. F.* **165**, 9 (1989).

<sup>5</sup> CEC, 1992; Supplement I, 1994 (see references in Introduction).

<sup>6</sup> R. J. Cvetanovic, *J. Phys. Chem. Ref. Data* **16**, 261 (1987).

<sup>7</sup> I. Mani and M. C. Sauer, *Adv. Chem. Ser.* **82**, 142 (1968).

*Thermodynamic Data*

$$\begin{aligned}\Delta H^\circ_{298} &= -70.7 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298} &= 1.53 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 4.01 \cdot 10^{-1} T^{0.213} \exp(+8460/T) \\ &(300 \leq T/\text{K} \leq 3000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$3.7 \cdot 10^{-11} \exp(-1912/T)$	298–875	Frerichs <i>et al.</i> , 1991 <sup>1</sup>	(a)
<i>Reviews and Evaluations</i>			
$2.8 \cdot 10^{-11} \exp(-1840/T)$	298–600	CEC, 1992; 1994 <sup>2</sup>	(b)

**Comments**

- (a) Flow reactor experiments with 2.9–4.9 mbar He carrier gas. O atoms generated by microwave discharge, ethyl benzene concentration monitored by mass spectrometry. O atom concentration in excess over ethyl benzene. Supersedes the study of Tappe *et al.*<sup>3</sup> by the same technique.
- (b) Preferred value based on the data of Tappe *et al.*<sup>3</sup> which, at 300 K, is in reasonable agreement with the data of Grovenstein and Mosher.<sup>4</sup>

**Preferred Values**

$k = 3.7 \cdot 10^{-11} \exp(-1910/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 298–900 K.

*Reliability*

$\Delta \log k = \pm 0.2$  over the range 298–900 K.

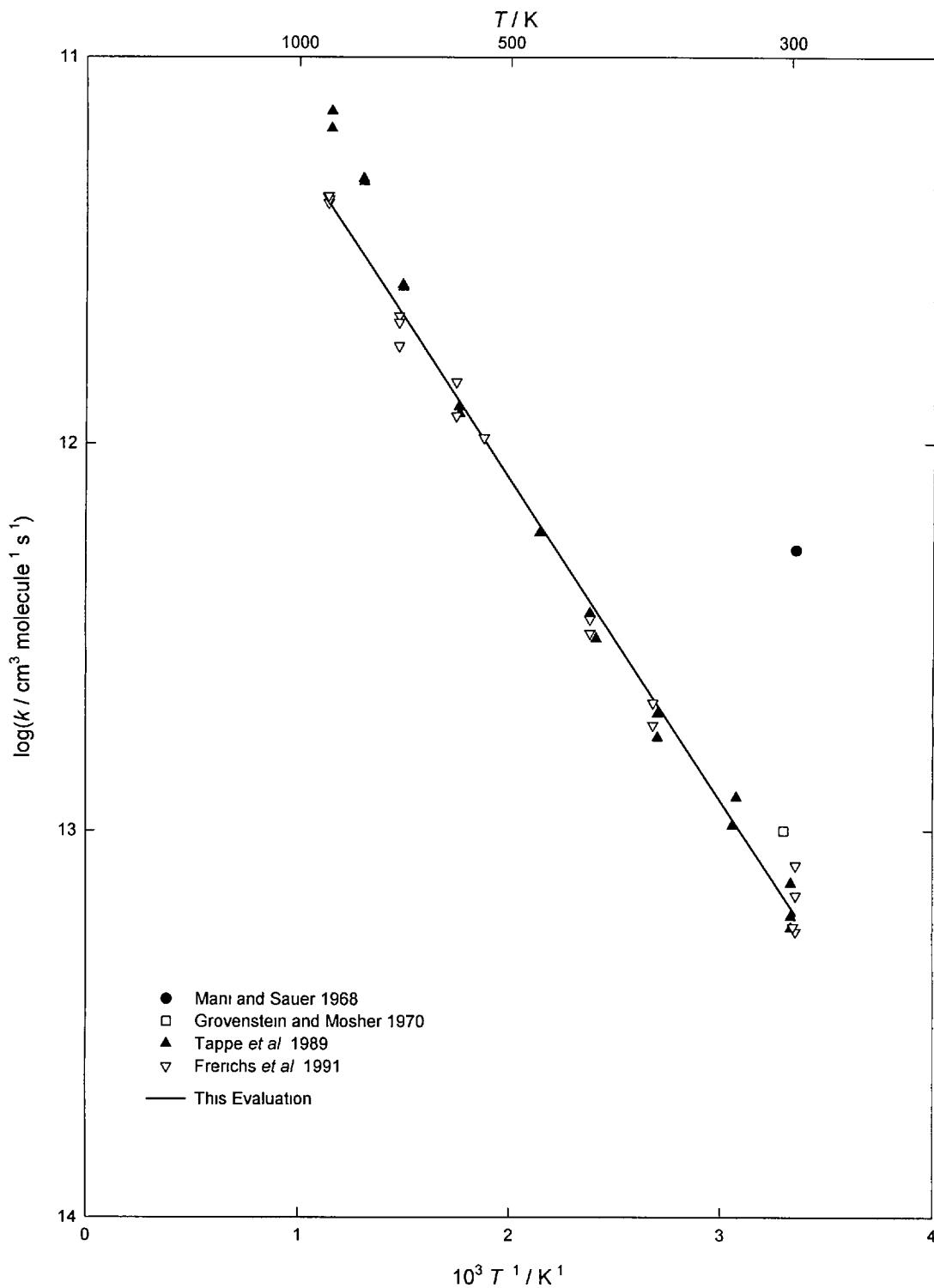
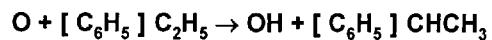
*Comments on Preferred Values*

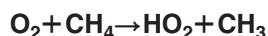
In an earlier study by Tappe *et al.*<sup>3</sup> non-Arrhenius behav-

ior was observed at  $T > 700$  K. The data obtained in the later study of Frerichs *et al.*,<sup>1</sup> with an improved flow reactor technique, are more accurate and do not exhibit non-Arrhenius behavior at higher temperatures. We take the more recent data of Frerichs *et al.*<sup>1</sup> as the basis of our preferred values. The earlier study of Grovenstein and Mosher<sup>4</sup> is also in reasonable agreement but the value of Mani and Sauer<sup>5</sup> is unacceptably high. The products of this reaction are not known. The H-atom abstraction reaction, above, is energetically the most exothermic channel and is assumed to be the major reaction pathway but there is no experimental evidence to support this.

**References**

- <sup>1</sup>H. Frerichs, D. V. Stucken, M. Tappe, and H. Gg. Wagner, Z. Phys. Chem. N. F. **174**, 1 (1991).
- <sup>2</sup>CEC, 1992; Supplement I, 1994 (see references in Introduction).
- <sup>3</sup>M. Tappe, V. Schliephake, and H. Gg. Wagner, Z. Phys. Chem. N. F. **162**, 129 (1989).
- <sup>4</sup>E. Grovenstein and A. J. Mosher, J. Am. Chem. Soc. **92**, 3810 (1970).
- <sup>5</sup>I. Mani and M. C. Sauer, Adv. Chem. Ser. **82**, 142 (1968).





#### Thermodynamic Data

$$\begin{aligned}\Delta H_{298}^{\circ} &= 235.9 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= 31.9 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 85.4 T^{-0.003} \exp(-28580/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
No direct experimental measurements have been made.			
<i>Reviews and Evaluations</i>			
$3.4 \cdot 10^{-11} \exp(-19600/T)$	500–2000	Walker, 1975 <sup>1</sup>	(a)
$6.6 \cdot 10^{-11} \exp(-28630/T)$	500–2000	CEC, 1992; 1994 <sup>2</sup>	(b)

#### Comments

- (a) Based on the experimental value of  $k(\text{O}_2 + \text{HCHO}) = 3.4 \cdot 10^{-22} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 773 K by Baldwin *et al.*,<sup>3</sup> which was effectively  $3.4 \cdot 10^{-11} \exp(-\Delta H/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Assuming equal A factors the expression for  $k$  was calculated using the then available thermodynamic data. This expression is also recommended by Tsang and Hampson.<sup>4</sup>
- (b) Derived using the method of Walker<sup>1</sup> [see Comment (a)] using more recent thermodynamic data.

#### Preferred Values

$$k = 8.1 \cdot 10^{-19} T^{2.5} \exp(-26370/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the range 500–2000 K.

#### Reliability

$\Delta \log k = \pm 0.5$  over the range 500–1000 K, rising to  $\pm 0.7$  at 2000 K.

#### Comments on Preferred Values

The preferred expression for  $k$  is an estimate based on the expression  $k = 8.1 \cdot 10^{-19} T^{2.5} \exp(-26370/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the rate constant of the reaction  $\text{O}_2 + \text{HCHO} \rightarrow \text{HO}_2 + \text{CHO}$ , which is recommended on the basis of reliable experimental studies at low and high temperatures (this evaluation).

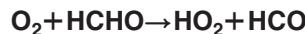
The energy barrier for the  $\text{O}_2 + \text{HCHO}$  reaction is  $13.7 \text{ kJ mol}^{-1}$  lower than the enthalpy of reaction. This same

difference is applied, with the same  $T^{2.5}$  dependence, in arriving at the expression for  $k$  for  $\text{O}_2 + \text{CH}_4$ . These terms are combined with an A factor adjusted for the differences in path degeneracies for the two reactions.

Zhu and Lin<sup>5</sup> have modeled the reverse reaction using *ab initio* molecular orbital theory and variational RRKM theory, deriving expression for  $k_{-1}$  over the range 300–2000 K. Their finding of a “negative activation energy” of  $15.6 \text{ kJ mole}^{-1}$  are consistent with the energy difference used in our estimate, and combining their theoretical values with the thermodynamic data gives values of  $k$  within a factor of  $\sim 3$  over the range 500–2000 K. There is further support for our preferred expression from the study of Reid *et al.*<sup>6</sup> who required values of  $k$  similar to our preferred values to model the ignition of  $\text{CH}_4$ /air mixtures, as did Hidaka *et al.*<sup>7</sup> in modeling some features of their shock tube study on  $\text{CH}_4$  pyrolysis and oxidation at temperatures of 1350–2400 K.

#### References

- <sup>1</sup>R. W. Walker, in *Reaction Kinetics*, edited by P. G. Ashmore, Specialist Periodical Rep. (The Chemical Society, London, 1975), Vol. 1, p. 161.
- <sup>2</sup>CEC, 1992; Supplement I, 1994 (see references in Introduction).
- <sup>3</sup>R. R. Baldwin, A. R. Fuller, D. Longthorn, and R. W. Walker, *J. Chem. Soc. Faraday Trans. 1* **70**, 1257 (1974).
- <sup>4</sup>W. Tsang and R. F. Hampson, *J. Phys. Chem. Ref. Data* **15**, 11087 (1986).
- <sup>5</sup>R. Zhu and M. C. Lin, *J. Phys. Chem. A* **105**, 6243 (2001).
- <sup>6</sup>I. A. B. Reid, C. Robinson, and D. B. Smith, 20th Symp. (Int.) Combustion, 1984, p. 1833.
- <sup>7</sup>Y. Hidaka, K. Sato, Y. Henmi, H. Tanaka, and K. Inami, *Combust. Flame* **118**, 340 (1999).

*Thermodynamic Data*

$$\begin{aligned}\Delta H_{298}^{\circ} &= 165.3 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= 29.5 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 1.08 \cdot 10^2 T^{-0.112} \exp(-20050/T) \\ &\quad (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$3.4 \cdot 10^{-11} \exp(-19580/T)$	713–813	Baldwin <i>et al.</i> , 1974 <sup>1</sup>	(a)
$7.5 \cdot 10^{-11} \exp(-20630/T)$	878–952	Vardanyan <i>et al.</i> , 1975 <sup>2</sup>	(b)
$2.04 \cdot 10^{-18} T^3 \exp(-26170/T)$	1160–1890	Hidaka <i>et al.</i> , 1993 <sup>3</sup>	(c)
$4.8 \cdot 10^{-8} \exp(-28476/T)$	1608–2091	Michael <i>et al.</i> , 1999 <sup>4</sup>	(d)
$1.6 \cdot 10^{-5} \exp(-40940/T)$	1633–2027	Michael <i>et al.</i> , 2001 <sup>5</sup>	(e)
<i>Reviews and Evaluations</i>			
$6.7 \cdot 10^{-11} \exp(-20100/T)$	650–900	Walker, 1975 <sup>6</sup>	(f)
$3.4 \cdot 10^{-11} \exp(-19600/T)$	300–2000	Tsang and Hampson, 1986 <sup>7</sup>	(g)
$1.0 \cdot 10^{-10} \exp(-20460/T)$	700–1000	CEC, 1992; 1994 <sup>8</sup>	(h)

**Comments**

- (a) Oxidation of HCHO was studied using HCHO/O<sub>2</sub>/N<sub>2</sub> mixtures in KCl coated vessels under conditions where the chain length of the reaction is close to unity. The [CO] was monitored as a function of time by gas chromatography and the products were tested for the presence of CO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>. Values of  $k$  were derived by computer modeling of the data using a detailed mechanism.
- (b) Thermal oxidation of HCHO studied. The expression for  $k$  is cited from earlier work published in the Armenian Chemical Journal.<sup>9</sup>
- (c) Shock tube study of the pyrolysis and oxidation of HCHO using HCHO/O<sub>2</sub>/Ar mixtures at total pressures in the range 1.4–2.5 bar. Two shock tubes were used, one equipped to monitor [HCHO] behind reflected shocks by time-resolved IR laser absorption at 3.39 μm, and the other employing time resolved IR emission at 3.48 μm to monitor [HCHO]. Values of  $k$  were derived by modeling the induction periods, and the changes in [HCHO] with time, using a detailed reaction mechanism.
- (d) Shock tube study of the reaction CH<sub>3</sub>+O<sub>2</sub> behind reflected shock waves using CH<sub>3</sub>I/O<sub>2</sub>/He mixtures at total pressures of 8–16 mbar. [O] was monitored by ARAS. The reaction O<sub>2</sub>+HCHO was required to model the [O] at long reaction times and values of  $k$  were obtained by modeling the [O] profiles.
- (e) Shock tube study using reflected shocks in trioxane as the source of the HCHO. [O] was monitored by ARAS. Mixtures highly dilute in HCHO were used so that secondary reactions made little contribution. Good agreement was obtained with the results of their previous study<sup>4</sup> particularly at high pressures. *Ab initio* calcula-

tions confirmed that the only products are HO<sub>2</sub>+CHO and gave the expression  $k = 4.49 \cdot 10^{-20} T^{2.92} \exp(-18692/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (see Comments on Preferred Values).

- (f) Based on the data of Ref. 1. Arrhenius parameters for the general reaction RH+O<sub>2</sub>→R+HO<sub>2</sub> are derived by taking  $E = \Delta H^{\circ}$  and an  $A$  factor adjusted to fit the experimental value of  $k = 3.4 \cdot 10^{-22} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 773 K. Accuracy is estimated to be  $\pm$  a factor of 2–4 in the temperature range 650–900 K.
- (g) Accepts the expression of Baldwin *et al.*<sup>1</sup>
- (h) Expression derived using the method of Walker<sup>6</sup> using the then accepted  $\Delta H^{\circ}$  and an  $A$  factor adjusted to fit the value of  $k = 3.4 \cdot 10^{-22} \text{ cm}^3 \text{ molecule}^{-1}$  at 773 K from Ref. 1.

**Preferred Values**

$$k = 4.05 \cdot 10^{-19} T^{2.5} \exp(-18350/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the range 600–2500 K.

**Reliability**

$$\Delta \log k = \pm 0.3 \text{ at } 600 \text{ K rising to } \pm 0.5 \text{ at } 2500 \text{ K.}$$

**Comments on Preferred Values**

The preferred expression in our previous evaluations was based<sup>8</sup> on the results of Baldwin *et al.*<sup>1</sup> covering the range 713–813 K, which were considered reliable. Since then there has been a shock tube study of the reaction by Hidaka *et al.*<sup>3</sup> over the range 1120–1890 K and the studies of Michael *et al.*<sup>4,5</sup> Hidaka *et al.*<sup>3</sup> showed that their results at 1250 K could be satisfactorily modeled using the expression obtained by Baldwin *et al.*<sup>1</sup> but at higher temperatures (~1590 K) much higher values of  $k$  than predicted by the expression of Baldwin *et al.*<sup>1</sup> were needed. The expression

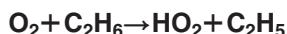
given by Hidaka *et al.*<sup>3</sup> with its high temperature dependence is, however, incompatible with the experimental data of both Baldwin *et al.*<sup>1</sup> and of Michael *et al.*<sup>4,5</sup> The values of  $k$  obtained in the later of the two studies of Michael *et al.*<sup>4,5</sup> are considered the more reliable because of the more direct nature of the technique, but the authors point out the possibility of contributions from HCHO decomposition at the highest temperatures used, tending to increase values of  $k$ , and this may be relevant to the high value of  $E/R$  obtained in their later study.<sup>5</sup>

The preferred expression is based on the results of Baldwin *et al.*<sup>1</sup> and Michael *et al.*<sup>4,5</sup> The theoretical expression derived by Michael *et al.*<sup>5</sup> [see Comment (e)] gives an excellent fit to the results of Baldwin *et al.*<sup>1</sup> but favors only the highest temperature results of Michael *et al.*<sup>4,5</sup> In contrast our previously recommended expression fits the results of Baldwin *et al.*<sup>1</sup> and the lowest temperature results of Michael *et al.*,<sup>4,5</sup> seriously underestimating those above 1750 K. The preferred expression is an optimum fit to the data of both

Baldwin *et al.*<sup>1</sup> and of Michael *et al.*<sup>4,5</sup> but differs substantially from that of Hidaka *et al.*<sup>3</sup>

## References

- <sup>1</sup>R. R. Baldwin, A. R. Fuller, D. Longthorn, and R. W. Walker, J. Chem. Soc. Faraday Trans. 1 **70**, 1257 (1974).
- <sup>2</sup>I. A. Vardanyan, G. A. Sachyan, and A. B. Nalbandyan, Int. J. Chem. Kinet. **7**, 23 (1975).
- <sup>3</sup>Y. Hidaka, T. Taniguchi, H. Tanaka, T. Kamesawa, K. Inami, and H. Kawano, Combust. Flame **92**, 365 (1993).
- <sup>4</sup>J. V. Michael, S. S. Kumaran, and M.-C. Su, J. Phys. Chem. A **103**, 5942 (1999).
- <sup>5</sup>J. V. Michael, M.-C. Su, J. W. Sutherland, D. C. Fang, L. B. Harding, and A. F. Wagner, Abstract 4-B03 "Work in Progress" Posters, 28th Symp. (Int.) Combustion, 2001.
- <sup>6</sup>R. W. Walker, in *Reaction Kinetics*, edited by P. G. Ashmore, Spec. Per. Reports (The Chemical Society, London, 1975), Vol. 1, p. 165.
- <sup>7</sup>W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data **15**, 1087 (1986).
- <sup>8</sup>CEC, 1992; Supplement I, 1994 (see references in Introduction).
- <sup>9</sup>I. A. Vardanyan, G. A. Sachyan, and A. B. Nalbandyan, Arm. Chem. J. **25**, 281 (1972).



### Thermodynamic Data

$$\begin{aligned}\Delta H_{298}^{\circ} &= 218.4 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= 42.1 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 7.69 \cdot 10^2 T^{-0.190} \exp(-26430/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

### Rate Coefficient Data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
No experimental measurements have been made.			
<i>Reviews and Evaluations</i>			
$6.7 \cdot 10^{-11} \exp(-25620/T)$	500–2000	Walker, 1975 <sup>1</sup>	(a)
$1.0 \cdot 10^{-10} \exp(-26100/T)$	500–2000	CEC, 1992; 1994 <sup>2</sup>	(b)

### Comments

- (a) Based on the experimental value of  $k(\text{O}_2 + \text{HCHO}) = 3.4 \cdot 10^{-22} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 773 K obtained by Baldwin *et al.*,<sup>3</sup> which was effectively  $3.4 \cdot 10^{-11} \exp(-\Delta H/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The expression for  $k$  was calculated using the then available thermodynamic data. This expression is also recommended by Tsang and Hampson.<sup>4</sup>
- (b) Derived using the method of Walker<sup>1</sup> [see Comment (a)] using more recent thermodynamic data.

### Reliability

$\Delta \log k = \pm 0.5$  over the range 500–1000 K, rising to  $\pm 1.0$  at 2000 K.

### Comments on Preferred Values

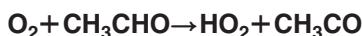
The expression for  $k$  is an estimate based on the recommended expression for  $k(\text{O}_2 + \text{HCHO})$  and derived in an analogous manner to that for  $k(\text{O}_2 + \text{CH}_4)$ , in which the activation energy is related to the enthalpy of reaction and the  $A$  factor is related to the number of abstractable hydrogens (see the  $\text{O}_2 + \text{CH}_4$  data sheet).

## References

- <sup>1</sup>R. W. Walker, in *Reaction Kinetics*, edited by P. G. Ashmore, Specialist Periodical Rep. (The Chemical Society, London, 1975), Vol. 1, p. 161.
- <sup>2</sup>CEC, 1992; Supplement I, 1994 (see references in Introduction).
- <sup>3</sup>R. R. Baldwin, A. R. Fuller, D. Longthorn, and R. W. Walker, J. Chem. Soc. Faraday Trans. 1 **70**, 1257 (1974).
- <sup>4</sup>W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data **15**, 11087 (1986).

### Preferred Values

$k = 1.21 \cdot 10^{-18} T^{2.5} \exp(-24740/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 500–2000 K.

*Thermodynamic Data*

$$\begin{aligned}\Delta H^\circ_{298} &= 170.8 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298} &= 27.5 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 6.33 \cdot 10^3 T^{-0.733} \exp(-20950/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Reviews and Evaluations</i>			
$5.0 \cdot 10^{-11} \exp(-19700/T)$	600–1100	CEC, 1992; 1994 <sup>1</sup>	(a)

**Comments**

- (a) Based on the previously accepted value for the reaction enthalpy change and an assumed  $A$  factor based on the previously recommended  $k(\text{O}_2 + \text{HCHO})$ .

**Preferred Values**

$$k = 2.0 \cdot 10^{-19} T^{2.5} \exp(-18900/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the range 600–1500 K.

*Reliability*

$\Delta \log k = \pm 0.4$  over the range 600–1000 K, rising to  $\pm 0.7$  at 1500 K.

*Comments on Preferred Values*

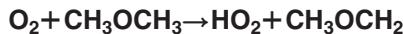
The only reported experimental data are obtained from

analyses of complex mechanisms and are therefore subject to considerable uncertainty.<sup>2</sup> The preferred expression is an estimate based on the recommended value of  $k(\text{O}_2 + \text{HCHO})$ , which is considered accurate over the range 600–2000 K (see data sheet), by allowing for differences in reaction path degeneracy and the small difference in the enthalpies of reaction.

**References**

<sup>1</sup> CEC, 1992; Supplement I, 1994 (see references in Introduction).

<sup>2</sup> R. W. Walker and C. Morley, in *Comprehensive Chemical Kinetics*, Volume 35, Low Temperature Combustion and Autoignition, edited by M. J. Pilling (Elsevier, Amsterdam, 1997).

*Thermodynamic Data*

$$\begin{aligned}\Delta H^\circ_{298} &= 197.6 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298} &= 38.5 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 5.85 \cdot 10^2 T^{-0.198} \exp(-23960/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
No experimental measurements of $k$ have been made.			

*Reviews and Evaluations*

$$6.8 \cdot 10^{-11} \exp(-22600/T)$$

650–1300

Curran *et al.*, 1998<sup>1</sup>

(a)

**Comments****Preferred Values**

- (a) Estimated expression based on the expression for  $k(\text{O}_2 + \text{CH}_3\text{OH})$  (modified to allow for reaction path degeneracy) derived by Tsang<sup>2</sup> using the estimation method of Walker.<sup>3</sup> Used by Curran *et al.*<sup>1</sup> in a modeling study of  $\text{CH}_3\text{OCH}_3$  oxidation

$$k = 1.21 \cdot 10^{-18} T^{2.5} \exp(-22240/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the range 500–2000 K.

*Reliability*

$\Delta \log k = \pm 0.5$  in the range 500–1000 K, rising to  $\pm 0.7$  at 2000 K.

*Comments on Preferred Values*

The preferred expression for  $k$  is an estimate based on the non-Arrhenius expressions,  $k = AT^n \exp(-B/T)$ , derived in the present evaluation for the analogous reactions,  $O_2 + HCHO$  and  $O_2 + CH_4$ , for which reliable experimental and theoretical information is available. The  $A$  factor is adjusted for path degeneracy and the activation energy is based on the

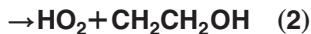
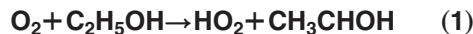
enthalpy of reaction in the same way as for the  $O_2 + HCHO$  and  $O_2 + CH_4$  reactions.

**References**

<sup>1</sup>H. J. Curran, W. J. Pitz, C. K. Westbrook, P. Dagaut, J.-C. Boettner, and M. Cathonnet, Int. J. Chem. Kinet. **30**, 229 (1998).

<sup>2</sup>W. Tsang, J. Phys. Chem. Ref. Data **16**, 471 (1987).

<sup>3</sup>R. W. Walker, in *Reaction Kinetics*, edited by P. G. Ashmore, Spec. Per. Reports (The Chemical Society, London, 1974), Vol. 1, p. 161.

*Thermodynamic Data*

$$\Delta H^o_{298}(1) = 197.0 \text{ kJ mol}^{-1}$$

$$\Delta S^o_{298}(1) = 24.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 4.32 \cdot 10^2 T^{0.422} \exp(-23930/T) \\ (300 \leq T/K \leq 5000)$$

$$\Delta H^o_{298}(3) = 233.3 \text{ kJ mol}^{-1}$$

$$\Delta S^o_{298}(3) = 17.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 3.49 T^{0.143} \exp(-28040/T) \\ (300 \leq T/K \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

$$\Delta H^o_{298}(2) = 212.5 \text{ kJ mol}^{-1}$$

$$\Delta S^o_{298}(2) = 18.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 6.96 \cdot 10^{-2} T^{0.810} \exp(-25510/T) \\ (300 \leq T/K \leq 5000)$$

**Rate Coefficient Data ( $k = k_1 + k_2 + k_3$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
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*Rate Coefficient Measurements*

No experimental measurements of the rate constants have been made.

**Preferred Values**

$k_1 = 4.0 \cdot 10^{-19} T^{2.5} \exp(-22170/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 500–2000 K.

$k_2 = 6.0 \cdot 10^{-19} T^{2.5} \exp(-24030/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 500–2000 K.

$k_3 = 2.0 \cdot 10^{-19} T^{2.5} \exp(-26530/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 500–2000 K.

*Reliability*

$\Delta \log k_1 = \Delta \log k_2 = \pm 0.5$  over the range 500–1000 K, rising to  $\pm 0.7$  at 2000 K.

$\Delta \log k_3 = \pm 1.0$  over the range 500–2000 K.

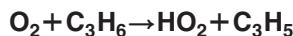
*Comments on Preferred Values*

The preferred expressions for  $k_1$ ,  $k_2$ , and  $k_3$  are estimates based on the non-Arrhenius expressions,  $k = AT^{2.5}$

$\times \exp(-B/T)$ , derived in the present evaluation for the analogous reactions,  $O_2 + HCHO$  and  $O_2 + CH_4$ , for which reliable experimental and theoretical information is available. The  $A$  factor is adjusted for path degeneracy and the activation energy is based on the enthalpy of reaction in the same way as for the  $O_2 + HCHO$  and  $O_2 + CH_4$  reactions. The error limits are set higher for  $k_3$  than for  $k_1$  and  $k_2$  because an O-H rather than a C-H bond is broken. However, even at 2000 K, with the expressions given,  $k_1 \sim 20k_3$  so that, unless the  $O_2$  pressure is extremely high, Channel (3) will be of negligible importance compared with initiation by C-C homolysis at such a temperature.<sup>1</sup>

**References**

<sup>1</sup>R. W. Walker and C. Morley, in *Comprehensive Chemical Kinetics*, Vol. 35, Low-Temperature Combustion and Autoignition, edited by M. J. Pilling (Elsevier, Amsterdam, 1997).

*Thermodynamic Data*

$$\begin{aligned}\Delta H_{298}^{\circ} &= 164.3 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= 16.93 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 3.43 T^{0.134} \exp(-19750/T) \\ (300 \leqslant T/\text{K} \leqslant 5000)\end{aligned}$$

Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$3.2 \cdot 10^{-12} \exp(-19670/T)$	673–793	Stothard and Walker, 1991 <sup>1</sup>	(a)
<i>Reviews and Evaluations</i>			
$1 \cdot 10^{-10} \exp(-23950/T)$	300–2500	Tsang, 1991 <sup>2</sup>	(b)
$3.2 \cdot 10^{-12} \exp(-19700/T)$	600–1000	CEC, 1994 <sup>3</sup>	(c)

**Comments**

- (a) Oxidation of  $\text{C}_3\text{H}_6$  was studied using  $\text{C}_3\text{H}_6/\text{O}_2/\text{N}_2$  mixtures in boric acid coated vessels with gas chromatographic analysis of the products. Conditions were chosen so that the chain length was small. Values of  $k$  were obtained by equating the rate of initiation to the rate of termination which was measured directly. Minor corrections (<20%) were made for radical branching reactions.
- (b) Estimate based on the assumption that the rate should be similar to the rate of abstraction of secondary hydrogens from alkanes.
- (c) See Comments on Preferred Values.

**Preferred Values**

$$k = 1.8 \cdot 10^{-20} T^{2.5} \exp(-17980/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the range 600–1500 K.

**Reliability**

$\Delta \log k = \pm 0.3$  in the range 600–800 K, rising to  $\pm 0.5$  at 1000 K and falling back to  $\pm 0.3$  at 1500 K.

**Comments on Preferred Values**

Although only a single set of experimental data exist for this reaction (see Table), they are in excellent agreement with the data for the corresponding reaction with  $(\text{CH}_3)_2\text{C}=\text{CH}_2$  which gives  $k[\text{O}_2 + (\text{CH}_3)_2\text{C}=\text{CH}_2 \rightarrow \text{HO}_2 + \text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2] = 7.9 \cdot 10^{-12} \exp(-19390/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the same temperature range.<sup>4</sup> The derivation of the preferred values also reflects the fact that the Arrhenius expressions for the initiation reactions,  $\text{O}_2 + \text{RH} \rightarrow \text{HO}_2 + \text{R}$ , when based on low temperature data, tend to underestimate the rate constants at temperatures above 1000 K. This is most clearly seen in the case of  $\text{O}_2 + \text{HCHO} \rightarrow \text{HO}_2 + \text{HCO}$ , but is also clear from a number of modeling studies and particularly from *ab initio* theoretical

calculations<sup>5</sup> of the rate constant of  $\text{CH}_3 + \text{HO}_2 \rightarrow \text{CH}_4 + \text{O}_2$ , coupled with the equilibrium constant (this evaluation) between 500 K and 3000 K.

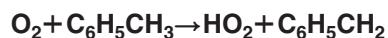
The preferred expression for  $k$  is obtained by fitting the experimental results of Stothard and Walker<sup>1</sup> between 673 K and 793 K using a fixed  $T$  exponent of 2.5. It is pertinent to compare the preferred expression with that of  $k(\text{O}_2 + \text{HCHO} \rightarrow \text{HO}_2 + \text{HCO}) = 4.0 \cdot 10^{-19} T^{2.5} \exp(-18352/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

recommended in the present evaluation over the temperature range 600–2500 K. The almost identical exponential terms are consistent with the two reactions having the same enthalpy change within  $\sim 2 \text{ kJ mol}^{-1}$ , and the significantly lower  $A$  factor for  $\text{O}_2 + \text{C}_3\text{H}_6$  is consistent with the loss of entropy of activation due to electron delocalization in the emerging allyl radical. Although this effect becomes less important as the temperature rises, probably leading to a higher temperature exponent, in the absence of additional experimental evidence a 2.5 exponent is preferred.

While the above comments support the validity of the expression for  $k(\text{O}_2 + \text{C}_3\text{H}_6)$  it has significantly different parameters from  $k(\text{O}_2 + \text{C}_6\text{H}_5\text{CH}_2) = 1.9 \cdot 10^{-17} T^{2.5} \times \exp(-17980/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , required to express results over the range 770–1400 K (see data sheet), despite the similar enthalpies of reaction and the formation of delocalised radicals in both reactions. Thus, although the preferred expression is considered reliable over the temperature range of the experimental data it may seriously underestimate  $k$  above 1000 K if the experimental data for  $k(\text{O}_2 + \text{C}_6\text{H}_5\text{CH}_2)$  are correct.

**References**

- N. D. Stothard and R. W. Walker, J. Chem. Soc. Faraday Trans. **87**, 241 (1991).
- W. Tsang, J. Phys. Chem. Ref. Data **20**, 231 (1991).
- CEC, Supplement I, 1994 (see references in Introduction).
- T. Ingham, R. W. Walker, and R. E. Woolford, 25th Symp. (Int.) Combustion, 1994, p. 764.
- R. Zhu and M. C. Lin, J. Phys. Chem. A **105**, 6243 (2001).

*Thermodynamic Data*

$$\begin{aligned}\Delta H^\circ_{298} &= 171.1 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298} &= 22.9 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 0.329 T^{0.696} \exp(-20650/T) \\ (300 \leqslant T/\text{K} \leqslant 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$5 \cdot 10^{-10} \exp(-20800/T)$	1000–1200	Emdee, Brezinsky, and Glassman, 1992 <sup>1</sup>	(a)
$\leqslant 6.0 \cdot 10^{-23}$	773	Ingham, Walker, and Woolford, 1994 <sup>2</sup>	(b)
$5 \cdot 10^{-10} \exp(-21650/T)$	1050–1400	Eng <i>et al.</i> , 1998 <sup>3</sup>	(c)
<i>Reviews and Evaluations</i>			
$3 \cdot 10^{-12} \exp(-20000/T)$	700–1200	CEC, 1994 <sup>4</sup>	(d)

**Comments**

- (a) Based on a computer modeling fit to data on the oxidation of toluene at atmospheric pressure obtained by Brezinsky *et al.*<sup>5</sup> and Lovell *et al.*<sup>6</sup> In the model the rate of consumption of toluene is highly sensitive to  $k$ . The activation energy is estimated from the reaction endothermicity and the pre-exponential factor is adjusted to achieve the best fit to the rate of toluene consumption. The mechanism used is complex but incomplete. For example, the reactions  $\text{HO}_2 + \text{C}_6\text{H}_5\text{CH}_3 \rightarrow \text{H}_2\text{O}_2 + \text{C}_6\text{H}_5\text{CH}_2$  and H abstraction at the ring by OH radicals are omitted, both leading to branching. The values of  $k$  are, therefore, probably too high and are a factor of 2 greater than those calculated from the expression of Eng *et al.*<sup>3</sup>
- (b) Addition of small amounts of toluene to  $\text{C}_3\text{H}_6/\text{O}_2/\text{N}_2$  mixtures in boric acid coated vessels at total pressures of 79 mbar. Products analyzed by GC [see  $\text{O}_2 + \text{C}_3\text{H}_6$  data sheet, Comment (a)]. With small corrections for secondary initiation, the primary initiation rate is equal to the rate of termination, which was measured directly. When a compound, RH, with a labile H atom is added to the  $\text{C}_3\text{H}_6/\text{O}_2/\text{N}_2$  mixtures, the increased rate of termination is equal to the rate of initiation from  $\text{O}_2 + \text{RH} \rightarrow \text{R} + \text{HO}_2$ , after minor corrections. Very successful experiments were carried out with a number of additives, but the increase in termination rate with toluene was small and difficult to measure. It was concluded that  $k/k(\text{O}_2 + \text{C}_3\text{H}_6)$  was in the range 1–2(max) at 773 K.
- (c) Shock tube study on toluene/ $\text{O}_2/\text{Ar}$  mixtures. Benzyl radical concentrations were monitored by UV absorption at 257 nm behind reflected shocks at total pressures between 2 and 4 bar. Initially the benzyl concentration profiles were analyzed using a detailed mechanism but this analysis showed that a simplified

mechanism applied and this was used to derive values of  $k$ . Consequently, the values of  $k$  derived may be slightly high due to some branching.

(d) Activation energy obtained by Emdee *et al.*<sup>1</sup> accepted and combined with an  $A$  factor based on the value for the  $\text{C}_3\text{H}_6 + \text{O}_2$  reaction as reported by Stothard and Walker<sup>7</sup> (see data sheet for  $\text{O}_2 + \text{C}_6\text{H}_6$  reaction).

**Preferred Values**

$$k = 1.9 \cdot 10^{-17} T^{2.5} \exp(-22620/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the range 500–2000 K.

*Reliability*

$\Delta \log k = \pm 0.4$  over the range 500–1400 K, rising to  $\pm 0.6$  at 2000 K.

*Comments on Preferred Values*

In our previous evaluation<sup>4</sup> it was argued that the  $A$  factor of the  $\text{O}_2 + \text{C}_6\text{H}_5\text{CH}_3$  reaction should be similar to that for the  $\text{O}_2 + \text{C}_3\text{H}_6$  reaction since both involve H abstraction with similar entropies of activation arising from the electron delocalization in the emerging radical. On this basis the  $A$  factor for the  $\text{O}_2 + \text{C}_6\text{H}_5\text{CH}_3$  reaction was assigned a value of  $3 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , the  $A$  factor obtained by Stothard and Walker<sup>7</sup> for  $\text{O}_2 + \text{C}_3\text{H}_6$  over the range 673–793 K. This is a factor of  $\sim 100$  smaller than the values obtained by Emdee *et al.*<sup>1</sup> and Eng *et al.*<sup>3</sup> but over a significantly different temperature range.

The values of  $k$  of Emdee *et al.*<sup>1</sup> are a factor of 2 higher than those of Eng *et al.*<sup>3</sup> and were obtained from a very complex simulation of toluene oxidation where a number of potentially important branching reactions were not included in the mechanism. Although their method is direct, the values of Eng *et al.*<sup>3</sup> may also be slightly high because some branching may have been present despite their careful

analysis of the system. The value of Ingham *et al.*<sup>2</sup> is also slightly uncertain [see Comment (b)] and for present purposes their maximum value is taken. When this value is combined with the results of Eng *et al.*<sup>3</sup> the Arrhenius function  $k = 7.4 \cdot 10^{-9} \exp(-25064/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  fits the results well but the activation energy of 208 kJ mol<sup>-1</sup> is considerably higher than the enthalpy of reaction, suggesting that a non-Arrhenius expression is required. Although it may be argued that the temperature exponent of 2.5 adopted in this evaluation for the reactions  $\text{O}_2 + \text{RH} \rightarrow \text{HO}_2 + \text{R}$ , where R is an electron-localized radical, should be enhanced by about a factor of 4 for a delocalized radical arising from decreased effects on the pre-exponential factor at high temperatures, 2.5 is maintained for consistency and the risk of

overestimating  $k$  at temperatures above those used in the study of Eng *et al.*,<sup>3</sup> the values of which are probably high by about a factor of 2.

<sup>1</sup>J. L. Emdee, K. Brezinsky, and I. Glassman, J. Phys. Chem. **96**, 2151 (1992).

<sup>2</sup>T. Ingham, R. W. Walker, and R. E. Woolford, 25th Symp. (Int.) Combustion, 1994, p. 767.

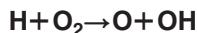
<sup>3</sup>R. A. Eng, C. Fittschen, A. Gebert, P. Hibomvschi, H. Hippler, and A.-N. Unterreiner, 27th Symp. (Int.) Combustion, 1998, p. 211.

<sup>4</sup>CEC, Supplement I, 1994 (see references in Introduction).

<sup>5</sup>K. Brezinsky, T. A. Litzinger, and I. Glassman, Int. J. Chem. Kinet. **16**, 1053 (1984).

<sup>6</sup>A. B. Lovell, K. Brezinsky, and I. Glassman, 22nd Symp. (Int.) Combustion, 1989, p. 1063.

<sup>7</sup>N. D. Stothard and R. W. Walker, J. Chem. Soc. Faraday Trans. **87**, 241 (1991).



#### Thermodynamic Data

$$\Delta H_{298}^\circ = 68.29 \text{ kJ mol}^{-1}$$

$$\Delta S_{298}^\circ = 25.04 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c = 2.88 \cdot 10^2 T^{-0.367} \exp(-8390/T)$$

$$(300 \leq T/\text{K} \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$2.0 \cdot 10^{-10} \exp(-8107/T)$	1000–2500	Pamidimukkala and Skinner, 1982 <sup>1</sup>	(a)
$1.78 \cdot 10^{-10} \exp(-7400/T)$	1000–1350	Vandooren, Nelson da Cruz, and Van Tiggelen, 1988 <sup>2</sup>	(b)
$2.8 \cdot 10^{-10} \exp(-8118/T)$	962–1705	Pirraglia <i>et al.</i> , 1989 <sup>3</sup>	(c)
$1.55 \cdot 10^{-10} \exp(-7448/T)$	1450–3370	Masten, Hanson, and Bowman, 1990 <sup>4</sup>	(d)
$2.64 \cdot 10^{-7} T^{-0.927} \exp(-8493/T)$	1050–2700	Yuan <i>et al.</i> , 1991 <sup>5</sup>	(e)
$1.15 \cdot 10^{-10} \exp(-6917/T)$	1103–2055	Shin and Michael, 1991 <sup>6</sup>	(f)
$1.55 \cdot 10^{-10} \exp(-7270/T)$	2050–5300	Du and Hessler, 1992 <sup>7</sup>	(g)
$1.38 \cdot 10^{-10} \exp(-7253/T)$	1336–3370	Yu <i>et al.</i> , 1994 <sup>8</sup>	(h)
$1.66 \cdot 10^{-10} \exp(-7690/T)$	1850–3550	Yang <i>et al.</i> , 1994 <sup>9</sup>	(i)
$1.18 \cdot 10^{-10} \exp(-6957/T)$	1050–2500	Ryu, Hwang, and Rabinowitz, 1995 <sup>10</sup>	(j)
<i>Reviews and Evaluations</i>			
$2.77 \cdot 10^{-7} T^{-0.9} \exp(-8750/T)$	300–2500	Cohen and Westberg, 1983 <sup>11</sup>	(k)
$1.62 \cdot 10^{-10} \exp(-7470/T)$	300–2500	CEC, 1992; 1994 <sup>12</sup>	(l)

#### Comments

- (a) Shock tube study on rich and stoichiometric  $\text{H}_2/\text{O}_2/\text{Ar}$  mixtures at pressures of 1.5–2.5 bar. [O] monitored by time-resolved resonance absorption.
- (b) Lean low-pressure (46 mbar)  $\text{CO}/\text{H}_2/\text{O}_2/\text{Ar}$  premixed flame.  $k$  derived from fit of  $\text{O}_2$  reaction rate from  $[\text{O}_2]$  profiles measured by molecular beam sampling/mass spectrometry.
- (c) Shock tube study in which H atoms were produced by flash photolysis of  $\text{NH}_3$  or  $\text{H}_2\text{O}$  in the reflected shock regime. Total pressures 13–40 mbar. [H] monitored by time-resolved resonance absorption.
- (d) Shock tube study using rich  $\text{H}_2/\text{O}_2/\text{Ar}$  mixtures at total pressures of 0.3–2.6 bar. [H] monitored by ARAS in

incident shock experiments; absolute [OH] obtained by cw laser absorption.  $k$  derived by numerical simulations using a 23-reaction mechanism.

(e) Shock tube study using reflected shocks in  $\text{H}_2/\text{O}_2/\text{Ar}$  mixtures at total pressures of 1.4–3.4 bar. Relative [OH] monitored by time-resolved cw laser absorption.  $k$  obtained by numerical simulations using a 19-reaction mechanism.

(f) Shock tube study using reflected shocks in  $\text{O}_2/\text{H}_2\text{O}$  or  $\text{NH}_3/\text{Ar}$  mixtures at total pressures of 0.3–1 bar. H produced by excimer laser photolysis of  $\text{H}_2\text{O}$  or  $\text{NH}_3$ . [H] monitored by time-resolved ARAS under pseudo first order conditions.

(g) Shock tube study using incident shocks in rich  $\text{H}_2/\text{O}_2/\text{Ar}$  mixtures at total pressures of 0.75–1.6 bar.

- [OH] determined by pulsed laser absorption.  $k$  obtained by using numerical simulations of a 17-reaction mechanism to fit the [OH] profile.
- (h) Reinterpretation of experimental data of Yuan *et al.*,<sup>5</sup> and Masten *et al.*<sup>4</sup>
  - (i) Shock tube study using reflected shocks in rich H<sub>2</sub>/O<sub>2</sub>/Ar mixtures at pressures of 2.4–3.9 bar. Relative [OH] monitored by time resolved cw laser absorption.  $k$  obtained by using numerical simulations of an 11-reaction mechanism to fit the [OH] profile.
  - (j) Shock tube study using reflected shocks in rich H<sub>2</sub>/O<sub>2</sub>/Ar mixtures at total pressures of 0.7–4.0 bar. Relative [OH] monitored by cw laser absorption.  $k$  obtained using numerical simulations of a 20-reaction mechanism to fit the [OH] profile.
  - (k) Based on low temperature data for the reverse reaction and a number of shock tube and flame studies. Recommended expression is accepted by Tsang and Hampson.<sup>13</sup>
  - (l) Accepts the expression of Baulch *et al.*<sup>14</sup> adjusted to fit data of Frank and Just<sup>15</sup> and Pirraglia *et al.*<sup>3</sup>

### Preferred Values

$$k = 3.43 \cdot 10^{-10} T^{-0.097} \exp(-7560/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the range } 800\text{--}3500 \text{ K.}$$

### Reliability

$\Delta \log k = \pm 0.1$  at 800 K, rising to  $\pm 0.2$  at 3500 K.

### Comments on Preferred Values

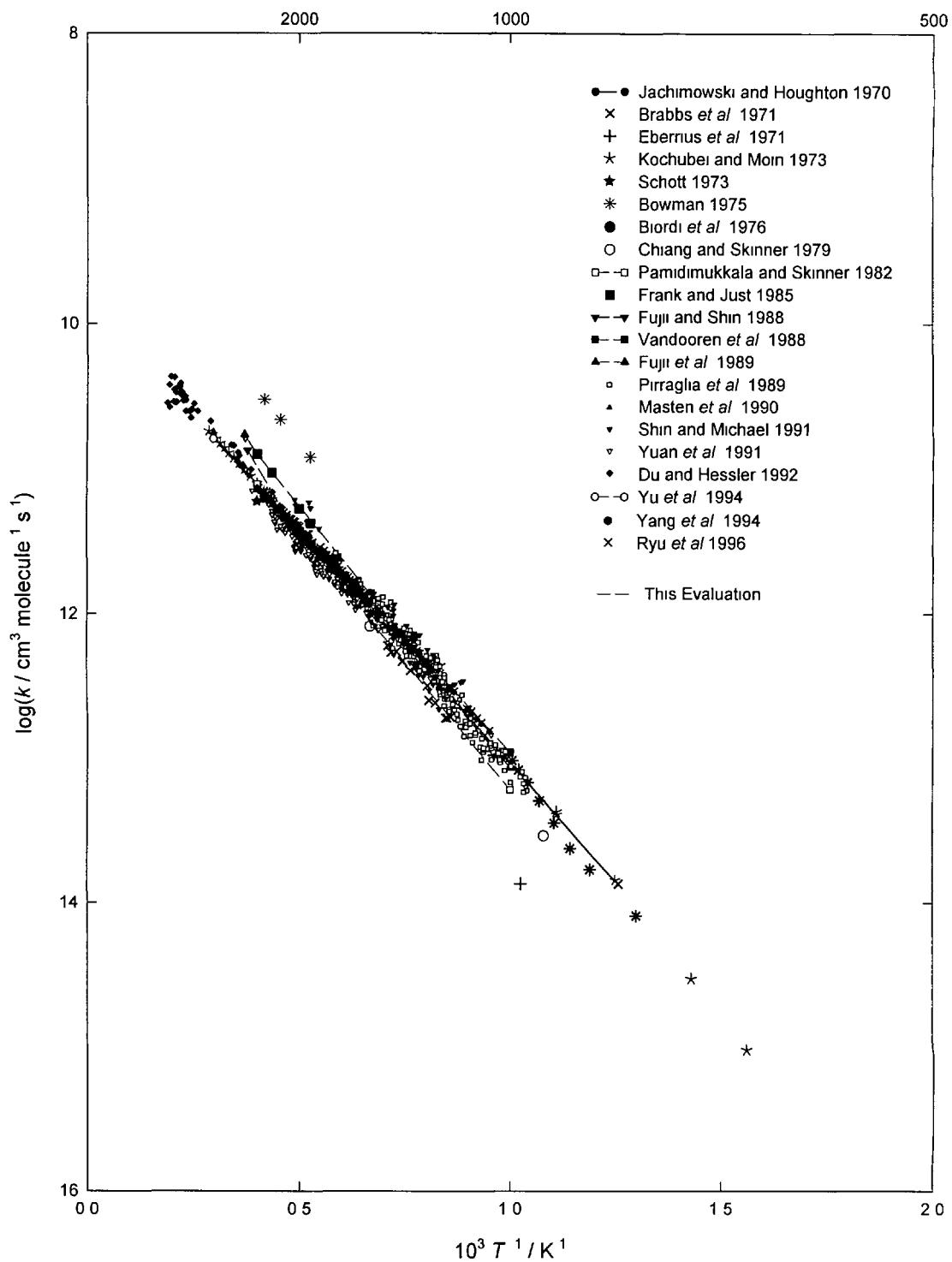
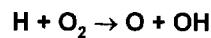
There have been numerous studies of this reaction. For clarity, only data since 1970 have been included in the Arrhenius diagram although some of the earlier data are in good agreement with those obtained more recently. The early studies have been evaluated by Baulch *et al.*<sup>14</sup> and by Cohen and Westberg.<sup>11</sup> The review of Tsang and Hampson<sup>13</sup> accepts the recommendations of Cohen and Westberg.<sup>11</sup>

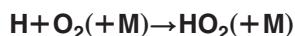
There are no direct measurements of  $k$  below 500 K and the recommended values are based on data obtained at temperatures above 800 K. The majority of the determinations of  $k$  have been made using shock tube techniques and, generally, are in good agreement.<sup>1–10,15–25</sup> There is a trend in the

more recent studies<sup>1–10</sup> to give slightly lower values of  $E/R$  than most of the older determinations.<sup>11,5–25</sup> Our preferred expression for  $k$  is based on the more recent studies, which are cited in the Table. The expression derived gives values very similar to the expression used by Smith *et al.*<sup>26</sup> in modeling studies using the GRI mechanism.

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*Thermodynamic Data*

$$\Delta H^{\circ}_{298} = -202.4 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298} = -90.64 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c = 2.76 \cdot 10^{-25} T^{1.786} \exp(+24310/T) \text{ cm}^3 \text{ molecule}^{-1}$$

(300 ≤ T/K ≤ 5000)

See Section 3 for the source of the Thermodynamic data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	[M]/molecule cm <sup>-3</sup>	Reference	Comments
<i>Rate Coefficient Measurements</i>				
<i>Low Pressure Range</i>				
[Ar] 3.9 · 10 <sup>-33</sup>	1500	(4.1–26) · 10 <sup>18</sup>	Getzinger and Schott, 1965 <sup>1</sup>	(a)
[Ar] 3.0 · 10 <sup>-33</sup>	1400–2600	(4.4–23) · 10 <sup>18</sup>	Gay and Pratt, 1971 <sup>2</sup>	(b)
[Ar] 6.6 · 10 <sup>-33</sup> exp(238/T)	203–404	(0.18–18) · 10 <sup>18</sup>	Kurylo, 1972 <sup>3</sup>	(c)
[Ar] 6.8 · 10 <sup>-33</sup> exp(345/T)	220–360	(0.26–22) · 10 <sup>18</sup>	Wong and Davis, 1974 <sup>4</sup>	(d)
[N <sub>2</sub> ] 1.5 · 10 <sup>-32</sup> exp(390/T)	220–298	(0.26–16) · 10 <sup>18</sup>		
[Ar] 2.5 · 10 <sup>-32</sup>	293	1.2 · 10 <sup>17</sup>	Hack, 1977 <sup>5</sup>	(e)
[N <sub>2</sub> ] 9.1 · 10 <sup>-33</sup>	980–1176	1.4 · 10 <sup>19</sup>	Slack, 1977 <sup>6</sup>	(f)
[Ar] 6.1 · 10 <sup>-32</sup>	964–1075	1.4 · 10 <sup>9</sup>		
[Ar] 2.8 · 10 <sup>-32</sup>	298	(0.24–48) · 10 <sup>18</sup>	Cobos, Hippler, and Troe, 1985 <sup>7</sup>	(g)
[N <sub>2</sub> ] 6.5 · 10 <sup>-32</sup>		(1.2–41) · 10 <sup>20</sup>		
[N <sub>2</sub> ] 8.0 · 10 <sup>-28</sup> T <sup>-1.66</sup>	298–639	(7.1–97) · 10 <sup>16</sup>	Hsu, Durant, and Kaufman, 1989 <sup>8</sup>	(h)
[Ar] 7.1 · 10 <sup>-33</sup>	746–987	(9.5–40) · 10 <sup>16</sup>	Pirraglia <i>et al.</i> , 1989 <sup>9</sup>	(i)
[N <sub>2</sub> ] 0.99 · 10 <sup>-32</sup>	800	(1.2–2.9) · 10 <sup>18</sup>	Hanning–Lee, Pilling, and Warr, 1991 <sup>10</sup>	(j)
[N <sub>2</sub> ] 2.95 · 10 <sup>-32</sup>	825	(1.2–29) · 10 <sup>18</sup>		
[N <sub>2</sub> ] 3.45 · 10 <sup>-32</sup>	850	(1.2–29) · 10 <sup>18</sup>		
[Ar] 2.1 · 10 <sup>-32</sup>	298	(1.6–16) · 10 <sup>19</sup>	Carleton, Kessler, and Marinelli, 1993 <sup>11</sup>	(k)
[N <sub>2</sub> ] 2.9 · 10 <sup>-33</sup> exp(825/T)	298–580	(2–18) · 10 <sup>18</sup>		
[H <sub>2</sub> O] 3.9 · 10 <sup>-32</sup> exp(600/T)	575–750	(1.2–4.9) · 10 <sup>17</sup>		
[Ar] 1.9 · 10 <sup>-30</sup> T <sup>-0.8</sup>	1260–1376	(2.6–6.5) · 10 <sup>20</sup>	Davidson <i>et al.</i> , 1996 <sup>12</sup>	(l)
[Ar] 7.2 · 10 <sup>-29</sup> T <sup>-1.24</sup>	1278–1375	(2.6–6.5) · 10 <sup>20</sup>		
[Ar] 3.5 · 10 <sup>-33</sup> exp(680/T)	725–900	(8–9.6) · 10 <sup>18</sup>	Ashman and Haynes, 1998 <sup>13</sup>	(m)
[N <sub>2</sub> ] 6.2 · 10 <sup>-33</sup> exp(680/T)	750–900			
[H <sub>2</sub> O] 6.6 · 10 <sup>-32</sup> exp(680/T)	750–900			
[N <sub>2</sub> ] 9.7 · 10 <sup>-32</sup> T <sup>-0.41</sup> exp(562/T)	800–900	(8–12) · 10 <sup>19</sup>	Mueller, Yetter, and Dryer, 1998 <sup>14</sup>	(n)
[Ar] 1.88 · 10 <sup>-29</sup> T <sup>-1.2</sup>	1050–1250	(0.7–8.9) · 10 <sup>20</sup>	Bates <i>et al.</i> , 2001 <sup>15</sup>	(o)
[N <sub>2</sub> ] 7.3 · 10 <sup>-29</sup> T <sup>-1.3</sup>		(0.5–2) · 10 <sup>20</sup>		
[H <sub>2</sub> O] 1.02 · 10 <sup>-28</sup> T <sup>-1.0</sup>				
[Ar] 1.26 · 10 <sup>-29</sup> T <sup>-1.12</sup>	482–712	(1.3–6.5) · 10 <sup>18</sup>	Michael <i>et al.</i> , 2002 <sup>16</sup>	(p)
[N <sub>2</sub> ] 4.82 · 10 <sup>-29</sup> T <sup>-1.23</sup>	296–698	(0.75–3.9) · 10 <sup>18</sup>		
[H <sub>2</sub> O] 5.0 · 10 <sup>-31</sup>	296	(0.6–2.15) · 10 <sup>16</sup>		
<i>Intermediate Fall-off Range</i>				
1.2 · 10 <sup>-12</sup>	298	2.4 · 10 <sup>19</sup> (N <sub>2</sub> )	Cobos, Hippler, and Troe, 1985 <sup>7</sup>	(g)
4.8 · 10 <sup>-12</sup>		1.2 · 10 <sup>20</sup>		
1.4 · 10 <sup>-11</sup>		6.0 · 10 <sup>20</sup>		
1.9 · 10 <sup>-11</sup>		1.2 · 10 <sup>21</sup>		
3.3 · 10 <sup>-11</sup>		2.4 · 10 <sup>21</sup>		
3.9 · 10 <sup>-11</sup>		4.8 · 10 <sup>21</sup>		
2.3 · 10 <sup>-12</sup>		1.2 · 10 <sup>20</sup> (Ar)		
1.2 · 10 <sup>-11</sup>		1.2 · 10 <sup>21</sup>		
2.3 · 10 <sup>-11</sup>		4.1 · 10 <sup>21</sup>		
3.3 · 10 <sup>-13</sup>	1050–1250	7.3 · 10 <sup>19</sup> (Ar)	Bates <i>et al.</i> , 2001 <sup>15</sup>	(o)
8.0 · 10 <sup>-13</sup>		2.1 · 10 <sup>20</sup>		
1.6 · 10 <sup>-12</sup>		5.8 · 10 <sup>20</sup>		
1.9 · 10 <sup>-12</sup>		8.9 · 10 <sup>20</sup>		
3.4 · 10 <sup>-13</sup>		5.0 · 10 <sup>19</sup> (N <sub>2</sub> )		
1.2 · 10 <sup>-12</sup>		2.0 · 10 <sup>20</sup>		
6.9 · 10 <sup>-12</sup>		9.3 · 10 <sup>19</sup> (H <sub>2</sub> O)		
1.5 · 10 <sup>-11</sup>		2.4 · 10 <sup>20</sup>		
<i>High Pressure Range</i>				

$k/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$	T/K	[M]/molecule cm $^{-3}$	Reference	Comments
$7.5 \cdot 10^{-11}$	298		Cobos, Hippler, and Troe, 1985 <sup>7</sup>	(g)
$6.2 \cdot 10^{-11}$	1200		Bates <i>et al.</i> 2001 <sup>15</sup>	(o)
$9.6 \cdot 10^{-11}$	300–500		Hahn <i>et al.</i> 2002 <sup>17</sup>	(q)
<i>Reviews and Evaluations</i>				
$k_0 = [\text{Ar}] 1.7 \cdot 10^{-30} T^{-0.8}$	300–2000		CEC, 1992; 1994 <sup>18</sup>	(r)
$k_0 = [\text{N}_2] 3.9 \cdot 10^{-30} T^{-0.8}$				
$k_0 = [\text{Ar}] 2.9 \cdot 10^{-29} T^{-1.257}$	300–2500		Marinov, Westbrook, and Pitz, 1996 <sup>19</sup>	(s)
$k_0 = [\text{N}_2] 5.6 \cdot 10^{-28} T^{-1.59}$				
$k_0 = [\text{Air}] 5.2 \cdot 10^{-28} T^{-1.6}$	220–600		NASA, 1997 <sup>20</sup>	(t)
$k_0 = [\text{N}_2] 1.55 \cdot 10^{-27} T^{-1.8}$	200–600		IUPAC, 1997 <sup>21</sup>	(u)
$k_0 = [\text{N}_2] 1.59 \cdot 10^{-28} T^{-1.4}$	300–2000		Troe, 2000 <sup>22</sup>	(v)
$k_0 = [\text{Ar}] 2.1 \cdot 10^{-29} T^{-1.2}$	300–2000			
$k_\infty = [7.84(T/300)^{0.56} + 1.79(T/300)^{-1.7}] \cdot 10^{-11}$	300–1500			

### Comments

- (a) Shock tube study using lean H<sub>2</sub>/O<sub>2</sub>/Ar mixtures. [OH] monitored by UV absorption.
- (b) Shock tube study using H<sub>2</sub>/O<sub>2</sub>/Ar(or N<sub>2</sub>) mixtures. [OH] monitored by UV absorption spectroscopy. Relative efficiencies of third bodies estimated to be  $k(\text{Ar}):k(\text{N}_2):k(\text{H}_2\text{O})=1:2:22$ .
- (c) Flash photolysis of CH<sub>4</sub>(or C<sub>3</sub>H<sub>8</sub>)/O<sub>2</sub>/He, Ar, or N<sub>2</sub> mixtures. [H] monitored by Lyman- $\alpha$  resonance fluorescence at pressures in the range 13–530 mbar.
- (d) Discharge flow study. [H], [OH], and [O] monitored by ESR.
- (e) Vacuum UV flash photolysis of CH<sub>4</sub>/O<sub>2</sub>/Ar, He, H<sub>2</sub>, or N<sub>2</sub> mixtures. [H] monitored by Lyman- $\alpha$  resonance fluorescence at pressures in the range 13–660 mbar.
- (f) Shock tube study using reflected shocks in H<sub>2</sub>/O<sub>2</sub>/N<sub>2</sub> mixtures. Induction times were measured by monitoring emissions from OH radicals. The results of similar experiments of Skinner and Ringrose<sup>23</sup> using Ar as the bath gas were reanalyzed to give the value of  $k$  cited for the range 964–1075 K.
- (g) Pulsed laser photolysis at 193 nm of NH<sub>3</sub> in the presence of O<sub>2</sub> and N<sub>2</sub>, Ar, or CH<sub>4</sub>. [HO<sub>2</sub>] monitored by absorption at 230 nm. Experiments over the range 1–200 bar allowed construction of fall-off curves and extrapolation to give a broadening factor  $F_c$  of 0.55 for N<sub>2</sub> and  $k_\infty = 2.4 \cdot 10^{-12} T^{0.6} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .
- (h) Discharge flow study at pressures in the range 6–90 mbar. [H] monitored by resonance absorption and [OH] by resonance fluorescence. Detailed numerical simulations of species profiles.
- (i) Combined flash photolysis and shock tube study.
- (j) Flow reactor study in which H was generated by means of a microwave discharge or by thermal decomposition of H<sub>2</sub> on a W filament. [H] was monitored by resonance absorption and [OH] by resonance fluorescence.
- (k) Flow reactor study with excimer laser photolysis production of H atoms from H<sub>2</sub>S. [H] monitored by LIF and ARAS. Detailed numerical simulations of H-atom decay. Total pressures, 65–650 mbar.
- (l) Shock tube study using reflected shocks in stoichio-
- metric H<sub>2</sub>/O<sub>2</sub>/Ar and H<sub>2</sub>/O<sub>2</sub>N<sub>2</sub>/Ar mixtures at total pressures in the range 50–120 bar. Quantitative measurements of [OH] were made by cw laser absorption. Numerical simulations performed using a detailed reaction mechanism. Experimental conditions chosen to emphasize sensitivity to the title reaction.
- (m) N<sub>2</sub>/O<sub>2</sub>/H<sub>2</sub>/NO mixtures were passed through a heated flow reactor at a total pressure of 1 bar. [NO<sub>x</sub>], [NO], [H<sub>2</sub>O], and [H<sub>2</sub>] were monitored. Species profiles were fitted by detailed numerical simulations using a detailed reaction mechanism. As well as N<sub>2</sub> several other gases were used as third bodies; relative efficiencies obtained were  $k(\text{N}_2):k(\text{Ar}):k(\text{CO}_2):k(\text{H}_2\text{O}) = 1.0:0.56:2.4:10.6$ .
- (n) Technique as in (m) but higher pressures were used. [NO<sub>x</sub>], [NO], [H<sub>2</sub>O], [O<sub>2</sub>], and [H<sub>2</sub>] were monitored. The expression cited was obtained by fitting their own data from this study with that of Getzinger and Blair,<sup>24</sup> Hsu *et al.*,<sup>8</sup> Cobos *et al.*,<sup>7</sup> Ashmore and Tyler,<sup>13</sup> Wong and Davis,<sup>4</sup> Kurylo *et al.*,<sup>3</sup> and Davidson *et al.*<sup>12</sup>
- (o) H<sub>2</sub>/O<sub>2</sub>/NO/bath gas mixtures were heated by reflected shock waves at total pressures in the range 7–152 bar. Narrow linewidth laser absorption of NO<sub>2</sub> at 472.7 nm was used to measure quasi-steady NO<sub>2</sub> concentration plateaus in experiments designed so that the plateau was sensitive only to the H+O<sub>2</sub>+M→HO<sub>2</sub>+M reaction rate and to the relatively well-known HNO<sub>2</sub>→NO+OH and HO<sub>2</sub>→OH+O reaction rates.
- (p) Laser photolysis-shock tube experiments. H atoms were generated by ArF excimer laser photolysis (193 nm) of dilute mixtures of NH<sub>3</sub> in O<sub>2</sub> and a bath gas. The H-atom detection technique was atomic resonance absorption spectrometry. At room temperature, the shock tube was used as a static reactor. At high temperatures, the experiments were conducted behind reflected shock waves. Extrapolation to the high pressure limit as carried out using  $F_c=0.7$  for M=Ar and N<sub>2</sub> and using  $F_c=0.8$  for M=H<sub>2</sub>O.
- (q) Technique as in (g) with extension of the accessible range of temperatures and pressures and temperatures.

Fall-off curve extrapolated with  $F_c = 0.5$  and  $k_\infty = 9.6 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  from the theoretical modeling in Ref. 22.

- (r) Based largely on the recommendations of Baulch *et al.*<sup>25</sup>
- (s) Fits to multiple data sets.
- (t) Based on the data of Kurylo,<sup>3</sup> Wong and Davis,<sup>4</sup> Hsu *et al.*,<sup>8</sup> and Cobos *et al.*<sup>7</sup>
- (u) Based on the data of Kurylo,<sup>3</sup> Wong and Davis,<sup>4</sup> Cobos *et al.*,<sup>7</sup> Hsu *et al.*,<sup>8</sup> and Carleton *et al.*<sup>11</sup> A high pressure limit of  $k_\infty = 2.45 \cdot 10^{-12} T^{0.6} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  together with  $F_c(\text{N}_2) = 0.5$  and  $F_c(\text{Ar}) = 0.45$  were used for the fitting.
- (v) Based on the data of Getzinger and Schott,<sup>1</sup> Gay and Pratt,<sup>2</sup> Wong and Davis,<sup>3</sup> Hack,<sup>5</sup> Slack,<sup>6</sup> Cobos *et al.*,<sup>7</sup> Hsu *et al.*,<sup>8</sup> Pirraglia *et al.*,<sup>9</sup> Hanning-Lee *et al.*,<sup>10</sup> Carleton *et al.*,<sup>11</sup> Davidson *et al.*,<sup>12</sup> Ashman and Haynes,<sup>13</sup> and Mueller *et al.*<sup>14</sup> Values of  $k_\infty$  are from theoretical modeling by Harding, Troe, and Ushakov<sup>26</sup> on an *ab initio* potential surface. Modeled values of  $F_c = 0.81$  for  $\text{M} = \text{H}_2\text{O}$ ,  $F_c = 0.51$  for  $\text{M} = \text{Ar}$ , and  $F_c = 0.57$  for  $\text{N}_2$  are recommended for the range 300 to 1500 K.

### Preferred Values

$k_0 = 1.9 \cdot 10^{-29} T^{-1.2} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  for  $\text{M} = \text{Ar}$  over the range 298–2000 K.

$k_0 = 7.3 \cdot 10^{-29} T^{-1.3} \text{ cm}^6 \text{ molecules}^{-2} \text{ s}^{-1}$  for  $\text{M} = \text{N}_2$  over the range 298–2000 K.

$k_0 = 1.0 \cdot 10^{-28} T^{-1.0} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  for  $\text{M} = \text{H}_2\text{O}$  over the range 298–2000 K.

$k_\infty = [0.32 T^{0.56} + 2.9 \cdot 10^4] T^{-1.7} \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 298–1500 K.

$F_c = 0.51$  for  $\text{M} = \text{Ar}$  over the range 298–1500 K.

$F_c = 0.57$  for  $\text{M} = \text{N}_2$  over the range 298–1500 K.

$F_c = 0.81$  for  $\text{M} = \text{H}_2\text{O}$  over the range 298–1500 K.

### Reliability

$\Delta \log k_0 = \pm 0.1$  at 298 K, rising to  $\pm 0.2$  at 2000 K for  $\text{M} = \text{Ar}$  and for  $\text{M} = \text{N}_2$ .

$\Delta \log k_0 = \pm 0.1$  at 298 K, rising to  $\pm 0.3$  at 2000 K for  $\text{M} = \text{H}_2\text{O}$ .

$\Delta \log k_\infty = \pm 0.5$  over the range 298–1500 K.

$\Delta F_c(\text{Ar}) = \Delta F_c(\text{N}_2) = \Delta F_c(\text{H}_2\text{O}) = \pm 0.1$  over the range 298–1500 K.

### Comments on Preferred Values

There have been many studies of this reaction and only the recent studies, and a number of older studies on which our recommendations are based, are cited in the Table. The large majority of studies of the kinetics of the reaction<sup>1–17,23,24,27–40</sup> have been carried out with Ar or N<sub>2</sub> as the third body and the citations in the Table have been restricted to these two collision partners together with the limited data<sup>1,8,11,13,16,32,41,42</sup> for the important collision partner,

H<sub>2</sub>O. The relative efficiency of other third bodies is, however, also considered later in this section.

The reaction is relevant to atmospheric chemistry and, consequently, there have been a number of low temperature studies with N<sub>2</sub> as the third body. These low temperature studies have been evaluated by the NASA<sup>20</sup> and the IUPAC<sup>21</sup> Panels whose findings we accept. Over a wider temperature range, the preferred values of  $k_0$  for M=Ar and N<sub>2</sub> are those given in the study of Bates *et al.*<sup>15</sup> which are in good agreement with the data of Michael *et al.*<sup>16</sup> and a number of other studies. The preferred values for  $k_\infty$  and  $F_c$  are from the theoretical modeling studies of Troe<sup>22</sup> and Harding *et al.*<sup>26</sup>

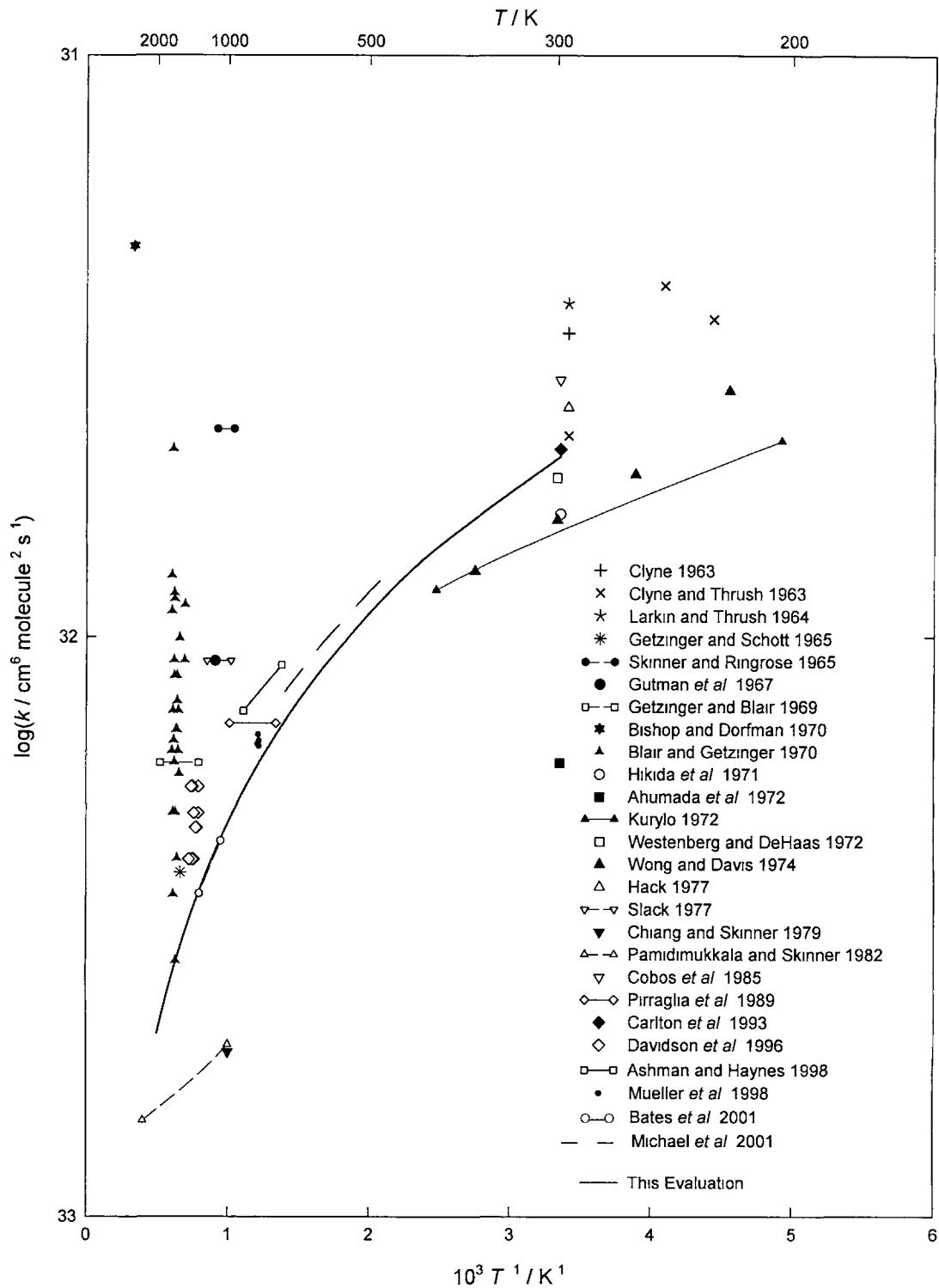
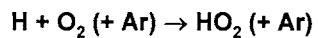
Early studies involving H<sub>2</sub>O as third body in the reaction, evaluated by Baulch *et al.*,<sup>25</sup> suggested it to be very efficient, with  $k(\text{M} = \text{H}_2\text{O})/k(\text{M} = \text{N}_2) \approx 16$ . The more recent studies cited in the Table confirm this [N.B. a value of  $k(\text{M} = \text{H}_2\text{O})/k(\text{M} = \text{N}_2) = 1.1$  was erroneously reported in our previous evaluations<sup>21</sup>]. Our preferred expression for  $k_0(\text{M} = \text{H}_2\text{O})$  is based on the data of Bates *et al.*<sup>15</sup> which are in good agreement with those of Michael *et al.*<sup>16</sup> and compatible with the results of Hsu *et al.*,<sup>8</sup> Ashman and Haynes,<sup>13</sup> and Carleton *et al.*<sup>11</sup> The preferred expressions suggest only a small temperature dependence for the relative efficiencies of the third bodies e.g.,  $k(\text{M} = \text{H}_2\text{O})/k(\text{M} = \text{N}_2) = 1.36 T^{0.4}$ .

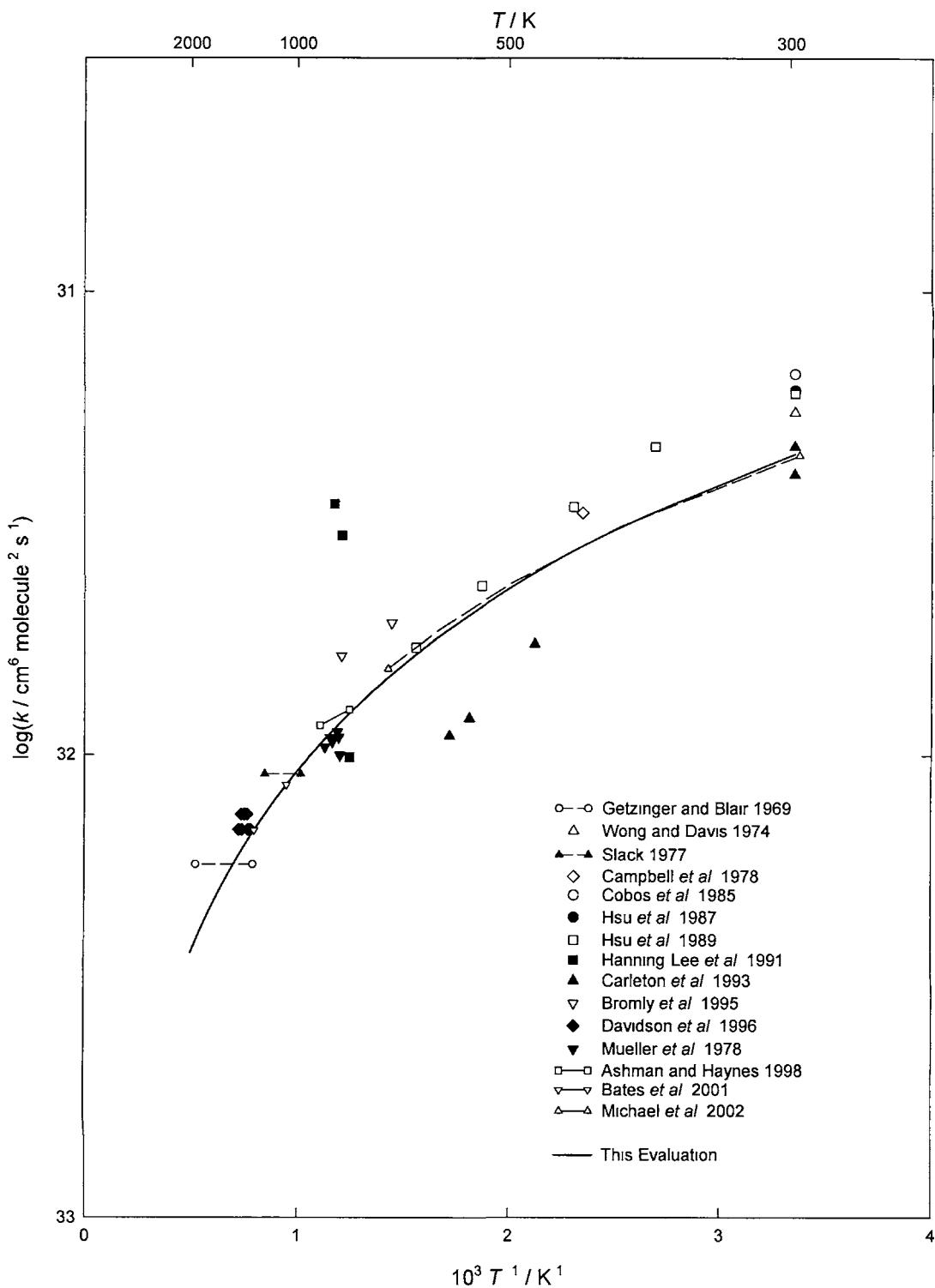
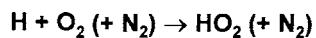
There have been far fewer studies for other third bodies. For M=CO<sub>2</sub>, early work, reviewed by Baulch *et al.*,<sup>25</sup> in which both  $k(\text{M} = \text{CO}_2)$  and  $k(\text{M} = \text{N}_2)$  were measured in the same study, gave values of  $k(\text{M} = \text{CO}_2)/k(\text{M} = \text{N}_2)$  in the range 2.5–3.5 at temperatures of ~700–800 K. More recently Ashman and Haynes<sup>13</sup> obtain  $k(\text{M} = \text{CO}_2)/k(\text{M} = \text{N}_2) = 2.4$  at similar temperatures. For O<sub>2</sub>, a collision efficiency identical with that of N<sub>2</sub> is often assumed, but there are a number of older studies which suggest that O<sub>2</sub> is a slightly less efficient collision partner (see Ref. 25) and in a recent direct measurement Michael *et al.*<sup>16</sup> obtain  $k_0(\text{M} = \text{O}_2) = 1.57 \cdot 10^{-29} T^{-1.09} \text{ cm}^6 \text{ molecule}^{-1} \text{ s}^{-1}$  and a value of  $k(\text{M} = \text{O}_2)/k(\text{M} = \text{N}_2) = 0.72$  at room temperature.

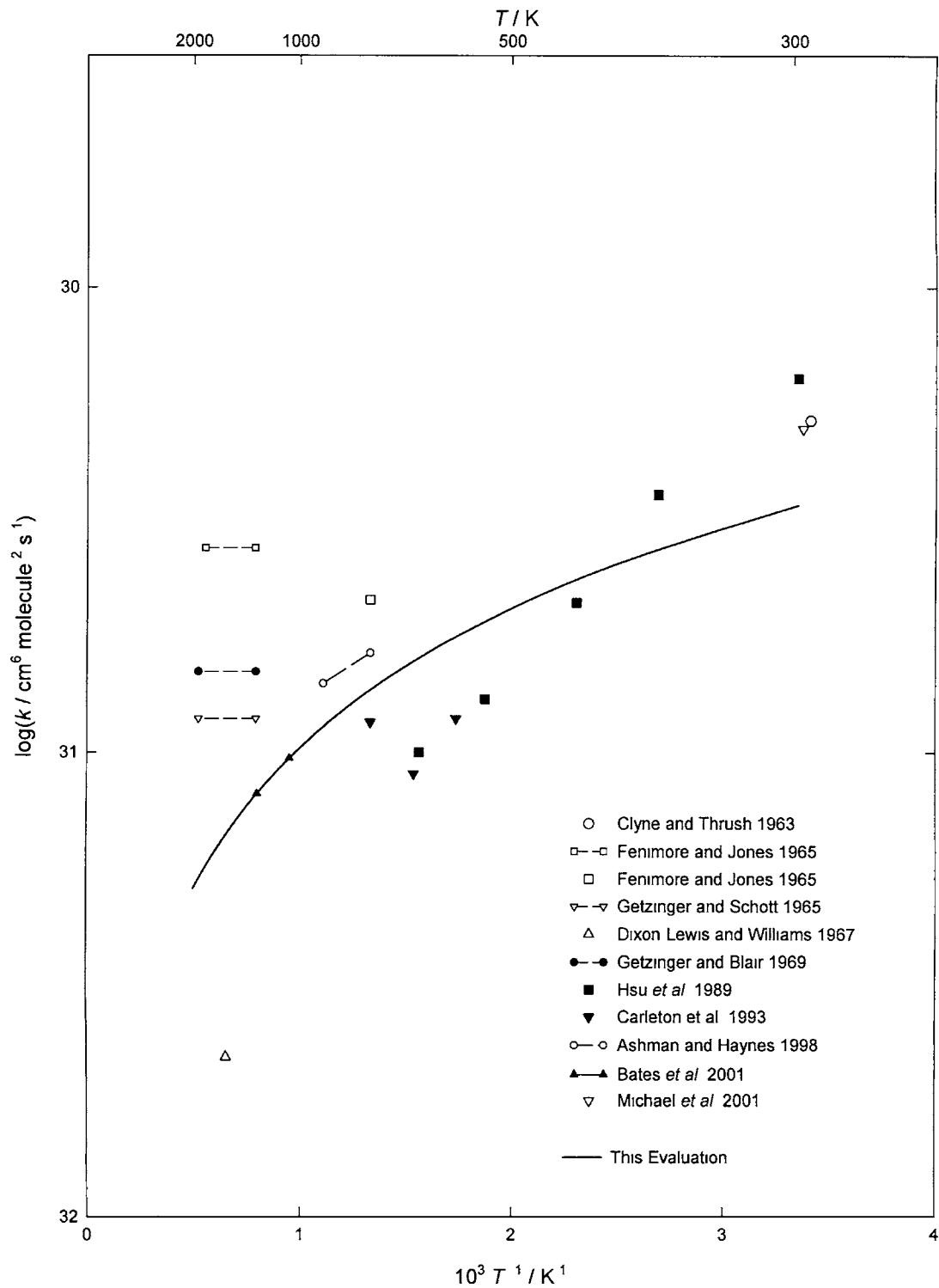
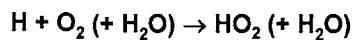
### References

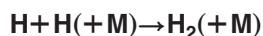
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*Thermodynamic Data*

$$\begin{aligned}\Delta H_{298}^{\circ} &= -435.9 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= -98.6 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 1.64 \cdot 10^{-24} T^{-0.151} \exp(+52190/T) \text{ cm}^3 \text{ molecule}^{-1} \\ (300 \leqslant T/\text{K} \leqslant 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Measurements**

$k/\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$	T/K	M	Reference	Comments
<i>Rate Coefficient Measurements</i>				
$9.6 \cdot 10^{-33}$	293	H <sub>2</sub>	Larkin and Thrush, 1964, <sup>1</sup> 1965; <sup>2</sup> Larkin, 1968 <sup>3</sup>	(a)
$6.3 \cdot 10^{-33}$	293	Ar		
$2.1 \cdot 10^{-33}$	1259–1912	Ar	Getzinger and Blair, 1969 <sup>4</sup>	(b)
$3.0 \cdot 10^{-31} T^{-0.6}$	79–298	H <sub>2</sub>	Ham, Trainor, and Kaufman, 1970 <sup>5</sup>	(c)
$8.1 \cdot 10^{-33}$	298	H <sub>2</sub>	Trainor, Ham, and Kaufman, 1973 <sup>6</sup>	(c)
$9.2 \cdot 10^{-33}$	298	Ar		
$2.5 \cdot 10^{-31} T^{-0.6}$	77–295	H <sub>2</sub>	Walkauskas and Kaufman, 1975 <sup>7</sup>	(c)
$9.2 \cdot 10^{-31} T^{-0.81}$	77–295	Ar		
$8.5 \cdot 10^{-33}$	298	H <sub>2</sub>	Lynch, Schwab, and Michael, 1975 <sup>8</sup>	(d)
$8.0 \cdot 10^{-33}$	298	Ar		
<i>Reviews and Evaluations</i>				
$2.8 \cdot 10^{-31} T^{-0.6}$	50–5000	H <sub>2</sub>	Cohen and Westberg, 1983 <sup>9</sup>	(e)
$1.9 \cdot 10^{-30} T^{-1.0}$	77–5000	Ar		
$2.8 \cdot 10^{-31} T^{-0.6}$	100–5000	H <sub>2</sub>	CEC, 1992; 1994 <sup>10</sup>	(f)
$1.8 \cdot 10^{-30} T^{-1.0}$	300–2500	Ar		

**Comments**

- (a) Discharge flow studies using pure H<sub>2</sub> or H<sub>2</sub> in an Ar carrier gas. [H] determined using a calorimetric probe and in some of the studies<sup>2,3</sup> checked by the H+NO emission method. Total pressures over the range 1.3–9.3 mbar.
- (b) Shock tube study using H<sub>2</sub>/O<sub>2</sub>/Ar (or N<sub>2</sub>) mixtures. [OH] monitored by UV absorption. Partial equilibrium assumed between [H] and [OH].
- (c) Flow system in which H atoms were generated by dissociation of H<sub>2</sub> on a hot tungsten filament. [H] profile monitored by means of a calorimetric probe. Pure H<sub>2</sub> or H<sub>2</sub>/Ar mixtures used; total pressures covered in the three studies,<sup>5–7</sup> 2.7–20 mbar.
- (d) Pulsed photolysis system using Hg photosensitization of H<sub>2</sub> to generate H atoms. [H] monitored as a function of time by Lyman- $\alpha$  absorption spectroscopy. Total pressures were in the range 0.66–2.0 bar.
- (e) Expressions based on the earlier evaluation of Baulch *et al.*<sup>11</sup> modified to take into account more recent data. Expressions are also given for  $k(M=N_2)$ ,  $k(M=H)$ , and  $k(M=H_2O)$ .
- (f) Accepts the expressions from the evaluations of Baulch *et al.*<sup>11</sup> for  $k(M=Ar)$  and of Cohen and Westberg<sup>9</sup> for  $k(M=H_2)$ .

**Preferred Values**

$k_0 = 2.8 \cdot 10^{-31} T^{-0.6} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  for M=H<sub>2</sub> over the range 200–5000 K.

$k_0 = 1.8 \cdot 10^{-30} T^{-1.0} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  for M=Ar over the range 200–2500 K.

*Reliability*

$\Delta \log k_0 = \pm 0.5$  for M=H<sub>2</sub> over the range 200–5000 K.

$\Delta \log k_0 = \pm 0.5$  for M=Ar over the range 200–2500 K.

*Comments on Preferred Values*

The data on this reaction have been thoroughly evaluated by Baulch *et al.*<sup>11</sup> and by Cohen and Westberg.<sup>9</sup> The later reviews by Tsang and Hampson,<sup>12</sup> by Warnatz,<sup>13</sup> and the CEC Panel<sup>10</sup> have accepted the conclusion of these two earlier evaluations, as do we in the present evaluation.

There have been many measurements of the rate constant of the reaction with a variety of third bodies. The data for M=H<sub>2</sub> and M=Ar are the most extensive and reliable.<sup>1–8,14–39</sup> but even so the data show substantial scatter.

In reviewing the data for  $k(M=H_2)$ , Cohen and Westberg<sup>9</sup> concluded that the discharge flow studies prior to 1960 and the flame studies could not be considered reliable, and based their recommendations on the studies cited in the Table together with the high temperature data of Sutton,<sup>40</sup>

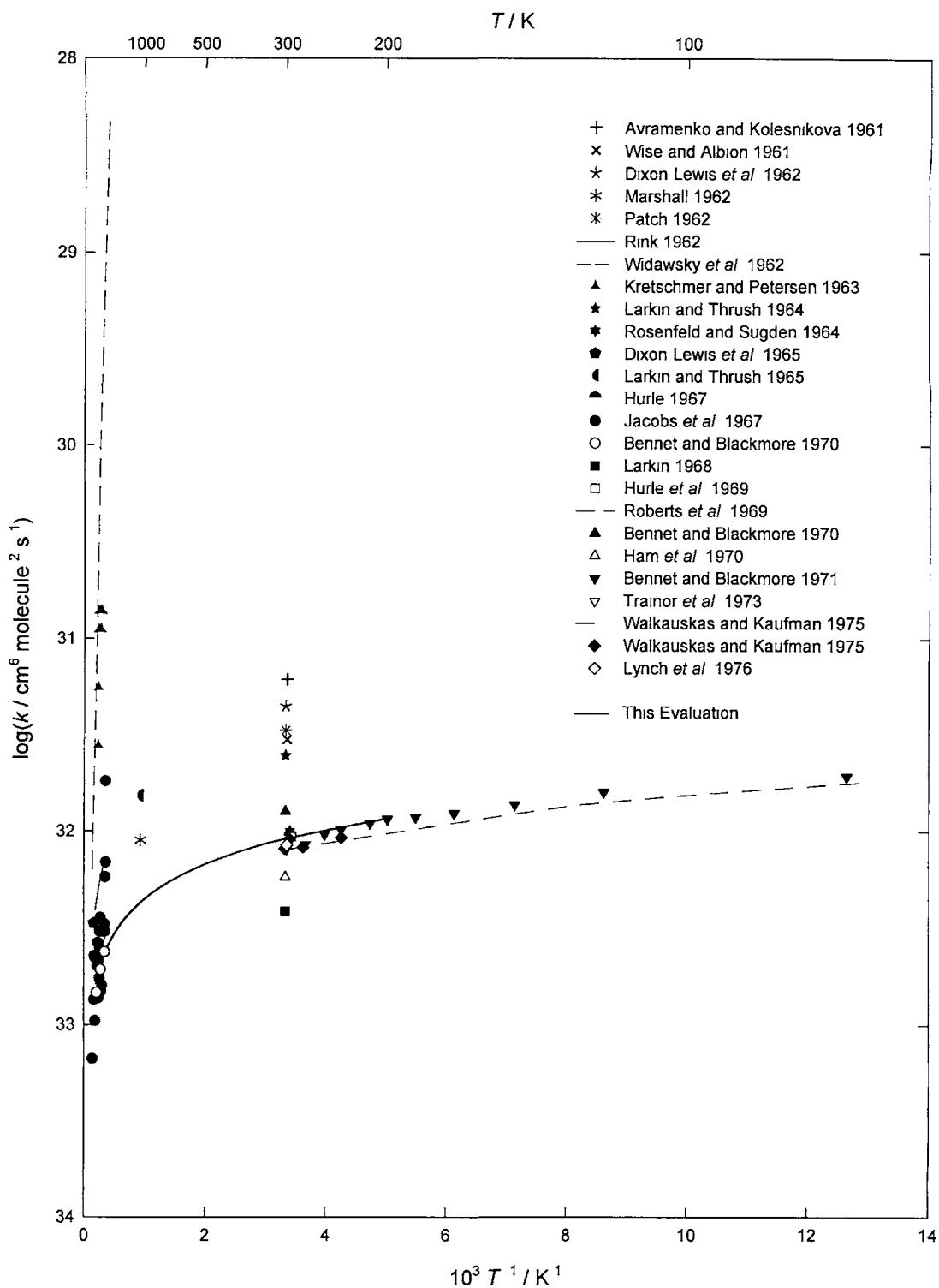
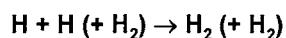
which in the present evaluation is used in evaluating the data for the reverse reaction,  $k(\text{H}_2 + \text{M})$ . The expression for  $k$  proposed by Cohen and Westberg<sup>9</sup> is adopted as our preferred expression, which is unchanged from our previous evaluations.<sup>10</sup> The rate constant and its temperature coefficient are reasonably well defined at temperatures close to 300 K but at higher temperatures substantial error limits must be accepted until better data are available.

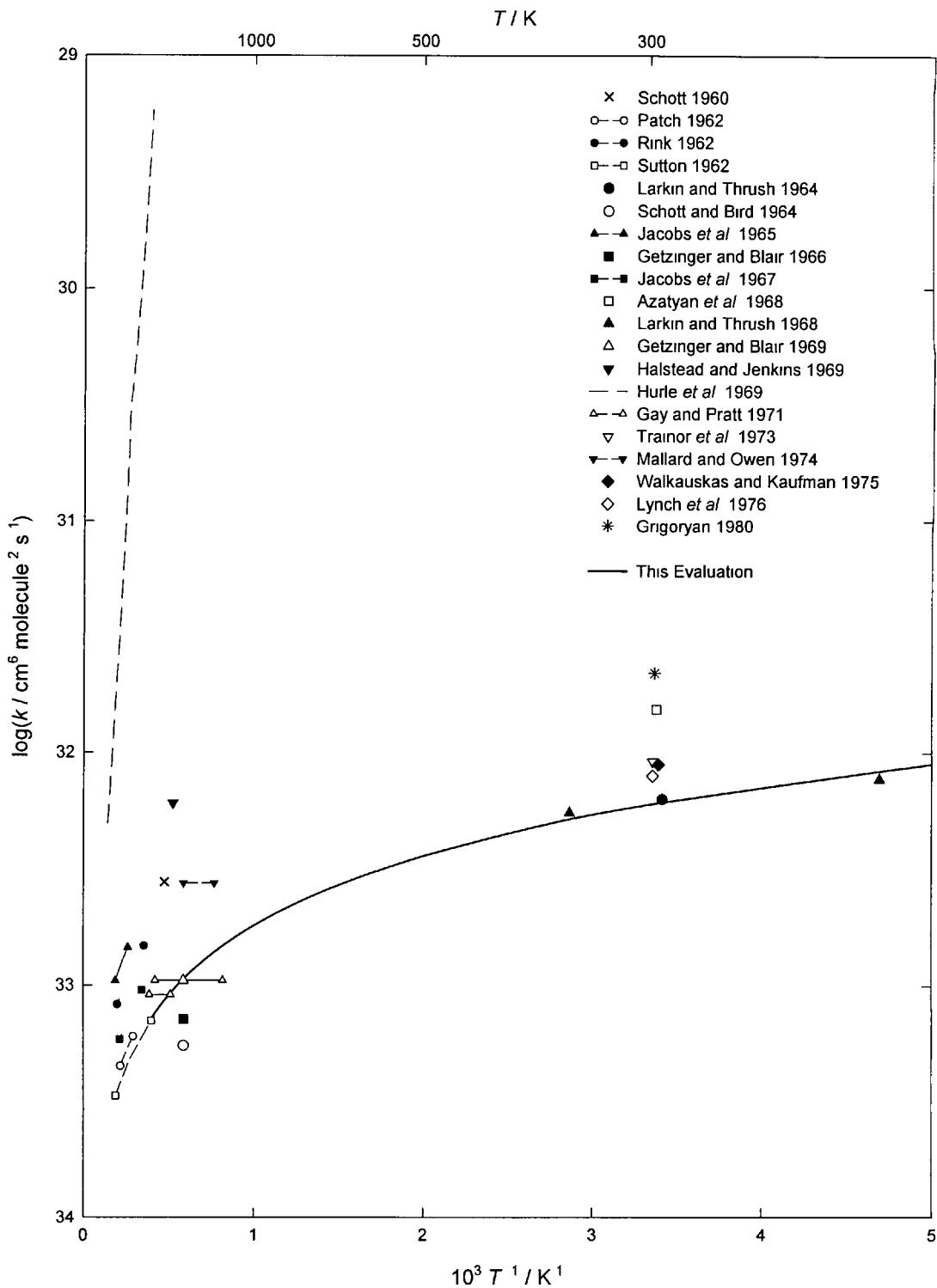
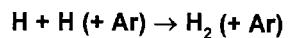
For  $k(\text{M} = \text{Ar})$  a number of the low temperature studies, cited in the Table, are in reasonable agreement. At higher temperatures Baulch *et al.*<sup>11</sup> conclude that some reliance can be placed on the shock tube study of Getzinger and Blair<sup>31</sup> and their data are supported by similar results from Schott and Bird.<sup>23</sup> Beyond 2000 K the data for the reverse reaction combined with the equilibrium constant offer the best guide. A  $T^{-1.0}$  dependence of the rate constant is compatible with the low and high temperature data. The expression recommended by Baulch *et al.*<sup>11</sup> is accepted as our preferred expression which is unchanged from our previous evaluations.<sup>10</sup>

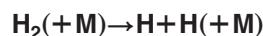
The data for other third bodies ( $\text{N}_2$ ,<sup>4,7,8,24,26,31,35,36</sup>  $\text{H}_2\text{O}$ ,<sup>2,3,4,17,24,26,36,41</sup>  $\text{H}$ ,<sup>19,20,27,28,32,40</sup>  $\text{He}$ ,<sup>6,8,31,33,35,36,37,41,43</sup>  $\text{Ne}$ ,<sup>7</sup>  $\text{Kr}$ ,<sup>7,42</sup>  $\text{NH}_3$ ,<sup>44</sup>) are very uncertain.  $\text{H}_2\text{O}$  is believed to be a very efficient collision partner. However, Baulch *et al.*<sup>11</sup> conclude that the scatter on the data are such that all that can be said is that  $k(\text{M} = \text{H}_2\text{O})/k(\text{M} = \text{Ar})$  lies between 10 and 20, a finding with which Cohen and Westberg<sup>9</sup> concur. For  $\text{M} = \text{N}_2$ , both high and low temperature data suggest that  $k(\text{M} = \text{N}_2) \approx k(\text{M} = \text{H}_2)$ . No recommendations are made for these third bodies until more data are available.

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*Thermodynamic Data*

$$\begin{aligned}\Delta H_{298}^{\circ} &= 435.9 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= 98.6 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 6.09 \cdot 10^{23} T^{0.151} \exp(-52190/T) \text{ molecule cm}^{-3} \\ &(300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	M	Reference	Comments
<i>Rate Coefficient Measurements</i>				
$4.17 \cdot 10^{-10} \exp(-48790/T)$	2500–5300	Ar	Sutton, 1962 <sup>1</sup>	(a)
$4.77 \cdot 10^{-10} \exp(-48780/T)$	3430–4600	Ar	Patch, 1962 <sup>2</sup>	(b)
$5.7 \cdot 10^{-10} \exp(-48330/T)$	2900–4700	Ar	Jacobs, Geidt, and Cohen, 1967 <sup>3</sup>	(c)
$3.7 \cdot 10^{-12} T^{0.5} \exp(-46600/T)$	2300–3740	Ar	Myerson and Watt, 1968 <sup>4</sup>	(d)
$1.6 \cdot 10^{-10} \exp(-44740/T)$	3500–8000	Ar	Breshears and Bird, 1973 <sup>5</sup>	(e)
$1.66 \cdot 10^{-9} \exp(-48790/T)$	2600–5400	H <sub>2</sub>	Sutton, 1962 <sup>1</sup>	(a)
$1.96 \cdot 10^{-9} \exp(-48880/T)$	2800–5000	H <sub>2</sub>	Rink, 1962 <sup>6</sup>	(f)
$1.43 \cdot 10^{-9} \exp(-48330/T)$	2900–4700	H <sub>2</sub>	Jacobs, Geidt, and Cohen, 1967 <sup>3</sup>	(c)
$5.5 \cdot 10^{-9} \exp(-52990/T)$	3500–8000	H <sub>2</sub>	Breshears and Bird, 1973 <sup>5</sup>	(e)
<i>Reviews and Evaluations</i>				
$3.7 \cdot 10^{-10} \exp(-48350/T)$	2500–5000	Ar	Baulch <i>et al.</i> , 1972; <sup>7</sup> CEC, 1992; 1994 <sup>8</sup>	(g)
$1.5 \cdot 10^{-9} \exp(-48350/T)$	2500–5000	H <sub>2</sub>		
$9.69 \cdot 10^{-6} T^{-1.1} \exp(-52530/T)$	600–5000	Ar	Cohen and Westberg, 1983 <sup>9</sup>	(h)
$1.43 \cdot 10^{-6} T^{-0.7} \exp(-52530/T)$	600–5000	H <sub>2</sub>		

**Comments**

- (a) Shock tube study on H<sub>2</sub>/Ar mixtures. Dissociation of H<sub>2</sub> monitored by following density changes by interferometry. System modeled to obtain  $k(\text{H}+\text{H}+\text{M})$ . Expression for  $k$  obtained using  $K_c$ .
- (b) Shock tube study on H<sub>2</sub>/Ar mixtures. H<sub>2</sub> monitored by UV absorption. System modeled to obtain  $k(\text{H}+\text{H}+\text{M})$  from [H<sub>2</sub>] profiles. Arbitrary  $T^{-1.0}$  dependence chosen for  $k(\text{H}+\text{H}+\text{M})$  in modeling the system. Results presented as  $k(\text{H}+\text{H}+\text{M})$  and converted here to  $k$  using  $K_c$ .
- (c) Shock tube study on H<sub>2</sub>/HCl/Ar mixtures. [H] monitored by IR emission from HCl assuming the equilibrium HCl+H $\rightleftharpoons$ H<sub>2</sub>+Cl to be established. Arbitrary  $T^{-1.0}$  dependence chosen for  $k(\text{H}+\text{H}+\text{M})$  in fitting [H] profiles. Results presented as  $k(\text{H}+\text{H}+\text{M})$  and converted here to  $k$  using  $K_c$ .
- (d) Shock tube study on H<sub>2</sub>/Ar mixtures. [H] monitored by absorption spectroscopy using the Lyman- $\alpha$  line.
- (e) Shock tube study on H<sub>2</sub>/Ar mixtures. Dissociation of H<sub>2</sub> monitored by following density changes using a laser schlieren technique.
- (f) Shock tube study on H<sub>2</sub>/Ar mixtures. Dissociation of H<sub>2</sub> monitored by following density profile using x-ray densitometer. Arbitrary  $T^{-1.0}$  dependence chosen for  $k(\text{H}+\text{H}+\text{M})$  in modeling the reaction. Results presented as  $k(\text{H}+\text{H}+\text{M})$  and converted here to  $k$  using  $K_c$ .

- (g) Survey of literature to 1972. Recommendations based on the data of Myerson and Watt,<sup>3</sup> Patch,<sup>2</sup> and Sutton.<sup>1</sup> These findings accepted by CEC Panel.<sup>8</sup>
- (h) Survey of literature to 1982. Recommendations based on data of Sutton<sup>1</sup> at high temperatures and data at lower temperatures derived from values of  $k(\text{H}+\text{H}+\text{M})$  and  $K_c$ . These findings accepted by Tsang and Hampson.<sup>10</sup>

**Preferred Values**

$k_0 = 3.7 \cdot 10^{-10} \exp(-48350/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 2500–8000 K for M=Ar.

$k_0 = 1.5 \cdot 10^{-9} \exp(-48350/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 2500–8000 K for M=H<sub>2</sub>.

**Reliability**

$\Delta \log k_0 = \pm 0.3$  over the range 2500–8000 K for M=Ar.

$\Delta \log k_0 = \pm 0.5$  over the range 2500–8000 K for M=H<sub>2</sub>.

**Comments on Preferred Values**

The literature on this reaction has been thoroughly evaluated in previous reviews by Baulch *et al.*<sup>7</sup> and Cohen and Westberg.<sup>9</sup> The later review by Tsang and Hampson<sup>10</sup> and our previous CEC evaluations<sup>8</sup> largely accept the findings of these earlier evaluations. Results from the only recent experimental study, that of Du and Hessler,<sup>11</sup> with M=Kr, generally support the previous recommendations.

This reaction will occur as a second order process at all but extremely high pressures. Direct measurements of the rate constant are only available from shock tube studies at high temperatures. In a number of cases the dissociation of H<sub>2</sub> was followed by measuring changes in density, and in the subsequent modeling of the system to derive rate parameters, both  $k$  and  $k(H+H+M)$  were used. The results from such studies are usually presented as values of  $k(H+H+M)$ . However in evaluating data for  $k$ , these values of  $k(H+H+M)$  at high temperatures have been combined with  $K_c$  to give the  $k$  values displayed on the Arrhenius diagram, and where appropriate, cited in the Table.

The most reliable data are for Ar and H<sub>2</sub> as the bath gas gases. The preferred expression for  $k_0(M=Ar)$ , which is unchanged from our previous evaluations,<sup>8</sup> is supported by the data of Sutton,<sup>1</sup> Patch,<sup>2</sup> Jacobs *et al.*,<sup>3</sup> Myerson and Watt,<sup>4</sup> and Breshears and Bird.<sup>5</sup>

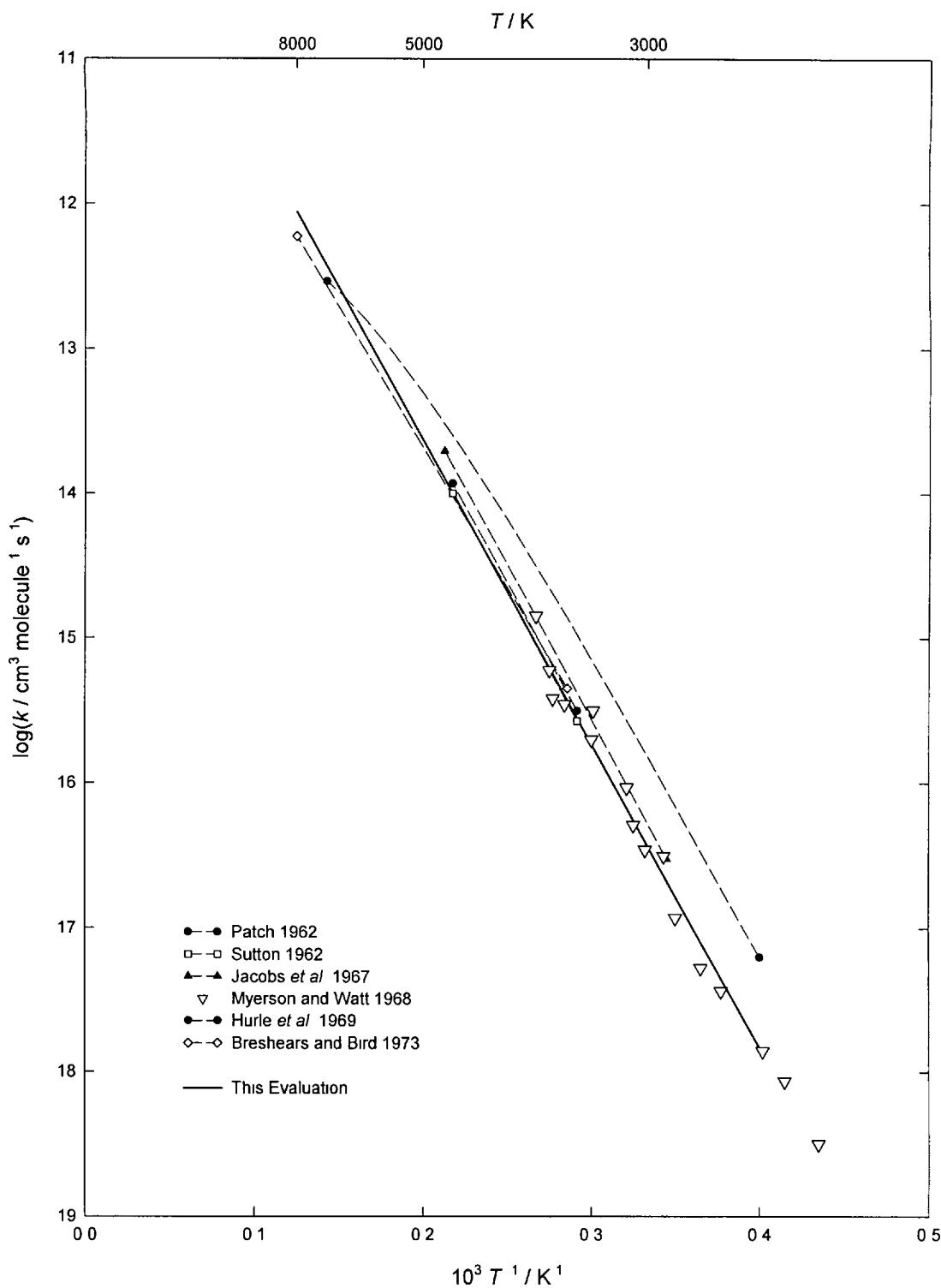
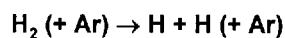
The preferred expression for  $k_0(M=H_2)$  is based on the data of Sutton,<sup>1</sup> Jacobs *et al.*,<sup>6</sup> Breshears and Bird,<sup>5</sup> and Rink,<sup>6</sup> which are in good agreement. The data of Hurle *et al.*<sup>12</sup> differ substantially from other studies both for Ar and H<sub>2</sub>.

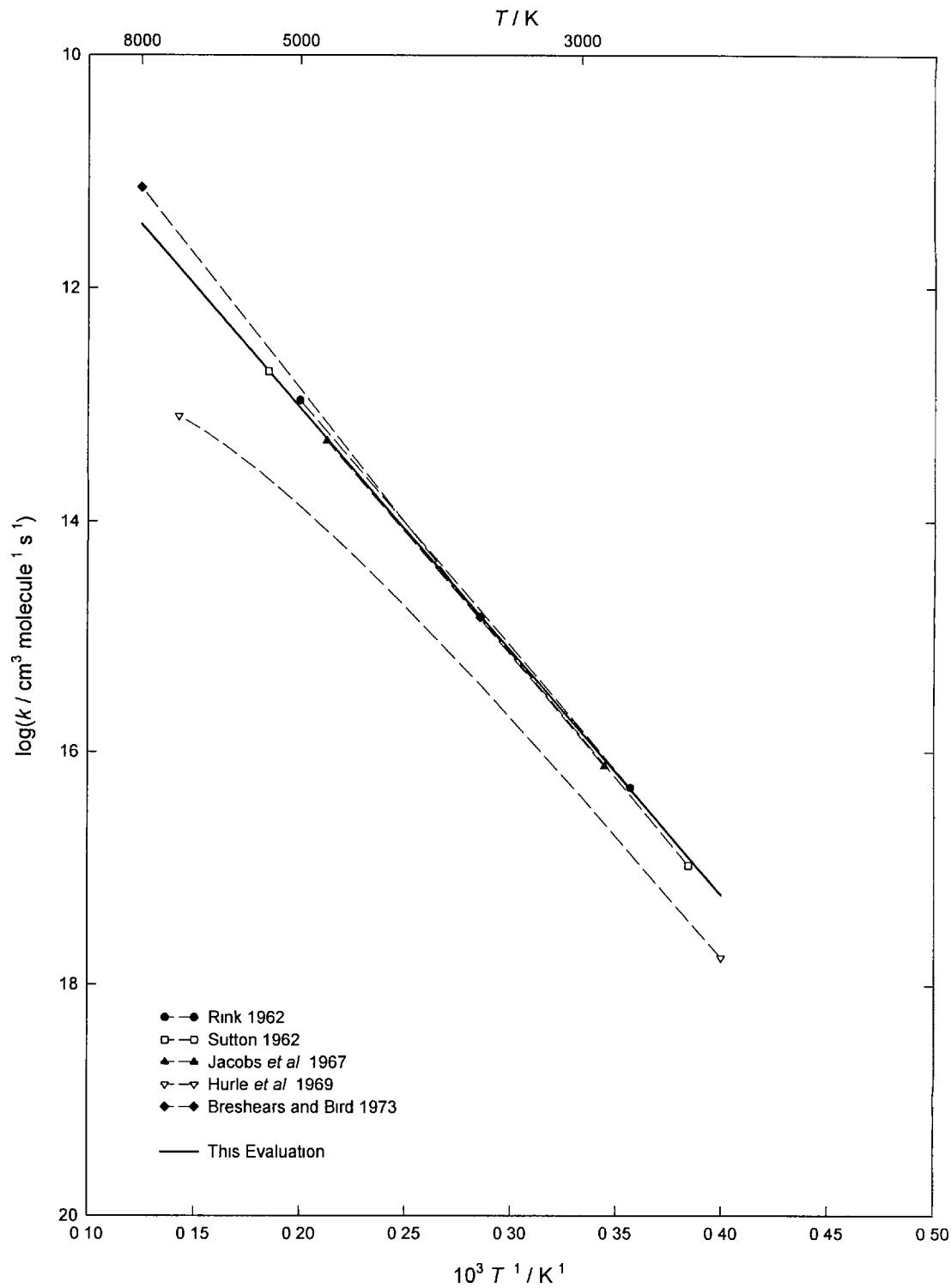
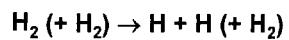
Information on the relative efficiencies of other third bodies is sparse and drawn largely from low temperature studies

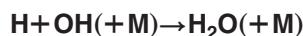
on H atom combination. In their review Cohen and Westberg<sup>9</sup> derive the expressions  $k_0(M=N_2)=7.60 \cdot 10^{-5} T^{-1.4} \exp(-52530/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k_0(M=H_2O)=1.4 \cdot 10^{-4} T^{-1.1} \exp(-52530/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , both over the range 600–2000 K, which are also accepted by Tsang and Hampson,<sup>10</sup> and probably represent the best currently available assessments.

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- <sup>5</sup>W. D. Breshears and P. F. Bird, 14th Symp. (Int.) Combustion, 1973, p. 211.
- <sup>6</sup>J. P. Rink, J. Chem. Phys. **36**, 262 (1962).
- <sup>7</sup>D. L. Baulch, D. D. Drysdale, D. G. Horne, and A. C. Lloyd, *Evaluated Kinetic Data for High Temperature Reactions*, Vol. 1, Homogeneous Gas Phase Reactions of the H<sub>2</sub>-O<sub>2</sub> System (London, Butterworths, 1972).
- <sup>8</sup>CEC, 1992; Supplement I, 1994 (see references in Introduction).
- <sup>9</sup>N. Cohen and K. Westberg, J. Phys. Chem. Ref. Data **12**, 531 (1983).
- <sup>10</sup>W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data **15**, 1987 (1986).
- <sup>11</sup>H. Du and J. P. Hessler, J. Chem. Phys. **96**, 1077 (1992).
- <sup>12</sup>I. R. Hurle, A. Jones, and J. L. J. Rosenfeld, Proc. R. Soc. London, Ser. A **310**, 253 (1969).





*Thermodynamic Data*

$$\begin{aligned}\Delta H^\circ_{298} &= -496.9 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298} &= -109.5 \text{ J K}^{-1} \text{ mol}^1 \\ K_c &= 1.03 \cdot 10^{25} T^{0.010} \exp(+59700/T) \text{ cm}^3 \text{ molecule}^{-1} \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$	T/K	M	Reference	Comments
<i>Rate Coefficient Measurements</i>				
$1.4 \cdot 10^{-31}$	1400	N <sub>2</sub>	Rosenfeld and Sugden, 1964 <sup>1</sup>	(a)
$2.8 \cdot 10^{-31}$	1400	H <sub>2</sub> O		
$2.3 \cdot 10^{-32}$	1518–1912	N <sub>2</sub>	Getzinger and Blair, 1969 <sup>2</sup>	(b)
$1.8 \cdot 10^{-31}$	1633–1768	H <sub>2</sub> O		
$9.1 \cdot 10^{-33}$	1633–1768	Ar		
$8.8 \cdot 10^{-33}$	~1900	N <sub>2</sub>	Halstead and Jenkins, 1970 <sup>3</sup>	(c)
$7.4 \cdot 10^{-32}$	~1900	H <sub>2</sub> O		
$8.8 \cdot 10^{-33}$	~1900	Ar		
<i>Reviews and Evaluations</i>				
$6.1 \cdot 10^{26} T^{-2.0}$	300–3000	N <sub>2</sub>	Tsang and Hampson, 1986 <sup>4</sup>	(d)
$2.3 \cdot 10^{-26} T^{-2.0}$	1000–3000	Ar	CEC, 1992; 1994 <sup>5</sup>	(d)
$6.1 \cdot 10^{-26} T^{-2.0}$	1000–3000	N <sub>2</sub>		
$3.9 \cdot 10^{-25} T^{-2.0}$	1000–3000	H <sub>2</sub> O		

**Comments**

- (a) [H] decay rate measured in post flame gases in fuel rich H<sub>2</sub>/O<sub>2</sub>/N<sub>2</sub> flames burning at atmospheric pressure. [H] monitored by Pb chemiluminescence calibrated using Li/LIOH technique.
- (b) Shock tube study on H<sub>2</sub>/O<sub>2</sub> mixtures in N<sub>2</sub> or Ar + H<sub>2</sub>O. [OH] monitored by UV absorption.
- (c) Study on fuel rich atmospheric pressure H<sub>2</sub>/O<sub>2</sub> flames diluted with N<sub>2</sub>, Ar, H<sub>2</sub>O and a range of other gases. [H] monitored by the Li/LIOH technique. Results reported in Ref. 6 and reanalyzed in Ref. 3.
- (d) Accepts the recommendations of Baulch *et al.*<sup>7</sup>

**Preferred Values**

$k_0 = 2.3 \cdot 10^{-26} T^{-2.0} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  for M=Ar over the range 300–3000 K.

$k_0 = 6.1 \cdot 10^{-26} T^{-2.0} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  for M=N<sub>2</sub> over the range 300–3000 K.

$k_0 = 3.9 \cdot 10^{-25} T^{-2.0} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  for M=H<sub>2</sub>O over the range 300–3000 K.

*Reliability*

$\Delta \log k_0 = \pm 0.3$  for M=Ar over the range 300–3000 K.

$\Delta \log k_0 = \pm 0.5$  for M=N<sub>2</sub> over the range 300–3000 K.

$\Delta \log k_0 = \pm 0.5$  for M=H<sub>2</sub>O over the range 300–3000 K.

*Comments on Preferred Values*

The kinetics of this reaction will be third order in combustion systems and all of the studies of the kinetics have been

carried under third order conditions. Most of the data<sup>1–3,8–24</sup> have been obtained with Ar, N<sub>2</sub>, or H<sub>2</sub>O as the “third body” in the reaction. The data are badly scattered. Baulch *et al.*<sup>7</sup> have thoroughly evaluated the available data and, in common with Tsang and Hampson,<sup>4</sup> we accept their findings. They conclude that the high temperature data of Rosenfeld and Sugden,<sup>1</sup> Getzinger and Blair,<sup>2</sup> and Halstead and Jenkins<sup>3</sup> are probably the most reliable. The results of these three studies together with the lower limits of the studies of Dixon-Lewis *et al.*<sup>8</sup> and Zeegers and Alkemade<sup>9</sup> suggest a substantial negative temperature dependence for  $k$ . On this basis Baulch *et al.*<sup>7</sup> suggest the expression for  $k(M=H_2O)$  which we accept as our preferred expression.

Despite the scatter in the absolute values of  $k$  the data on the relative efficiencies of Ar, N<sub>2</sub>, and H<sub>2</sub>O as third bodies are in reasonable agreement. The expressions for  $k(M=Ar)$  and  $k(M=N_2)$  are based on the relative efficiencies suggested by Baulch *et al.*<sup>7</sup> combined with the expression for  $k(M=H_2O)$ . The only studies carried out since the evaluation of Baulch *et al.*<sup>7</sup> are those of Goodings and Hayhurst,<sup>24</sup> at 1600–2200 K with M=N<sub>2</sub>, and that of Zellner *et al.*,<sup>25</sup> at 220–300 K with M=He. Both give higher values than might be expected from the preferred expressions but within the fairly substantial error limits.

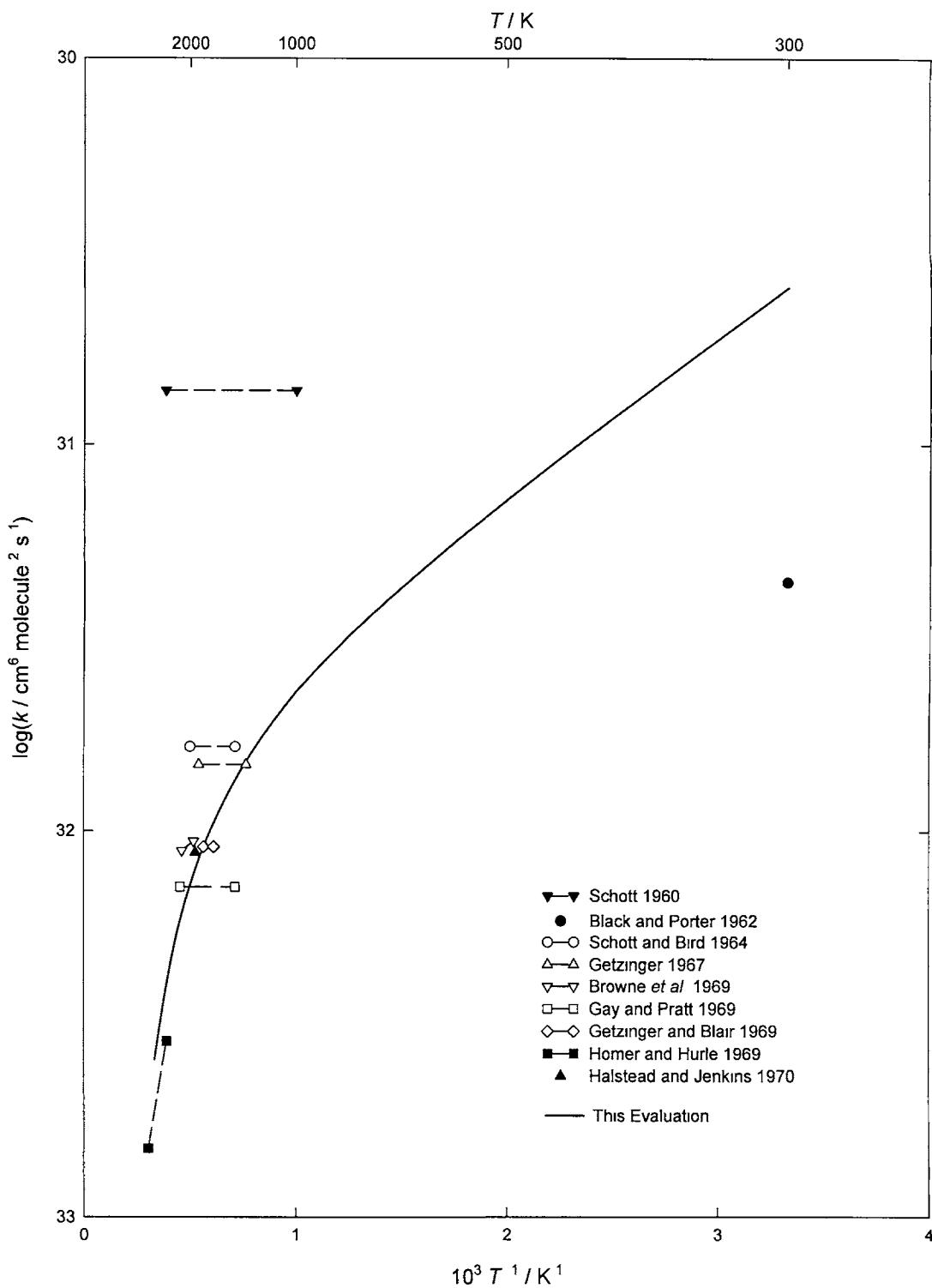
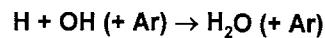
**References**

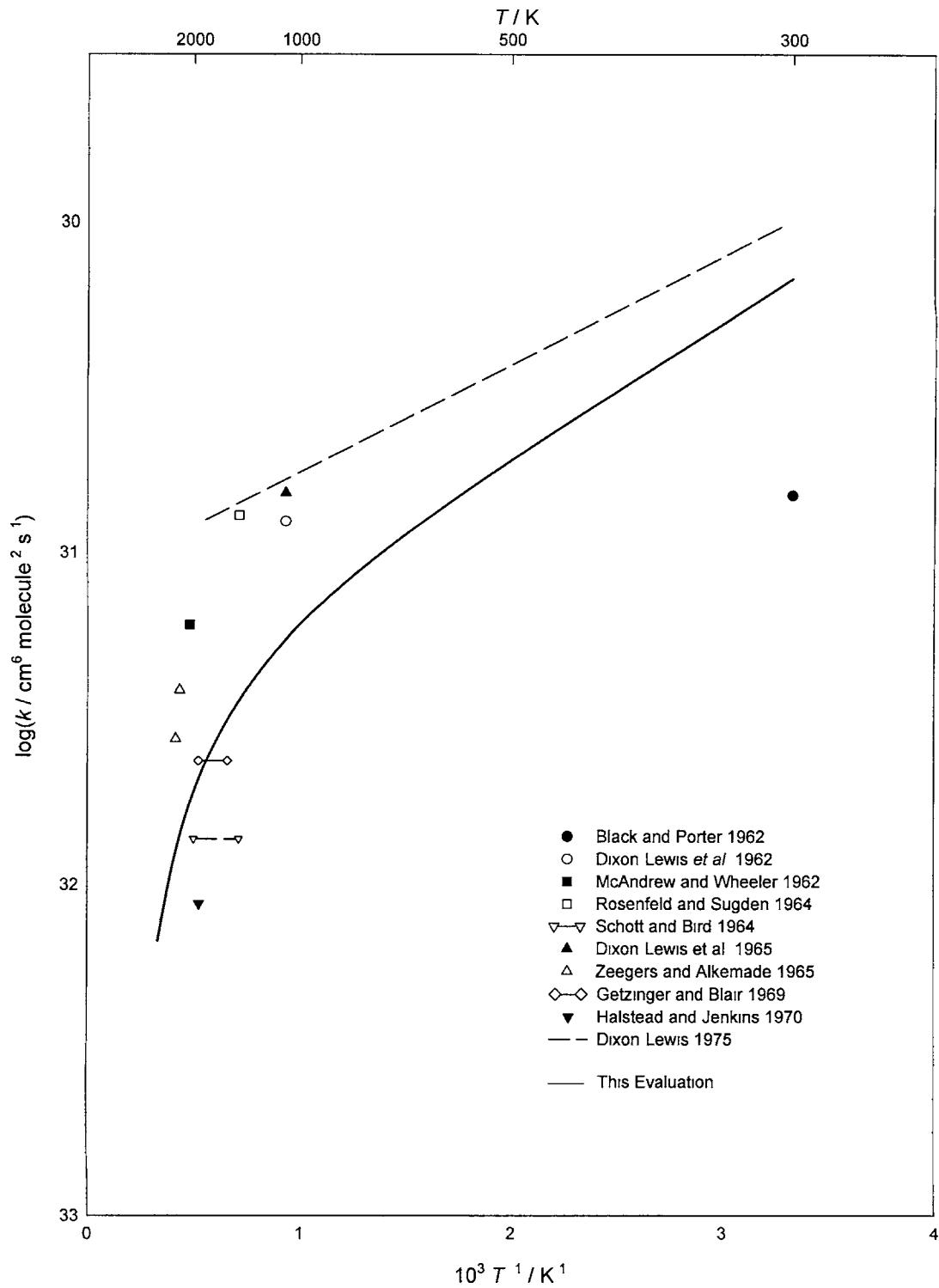
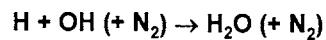
<sup>1</sup>J. L. J. Rosenfeld and T. M. Sugden, Comb. Flame **8**, 44 (1964).

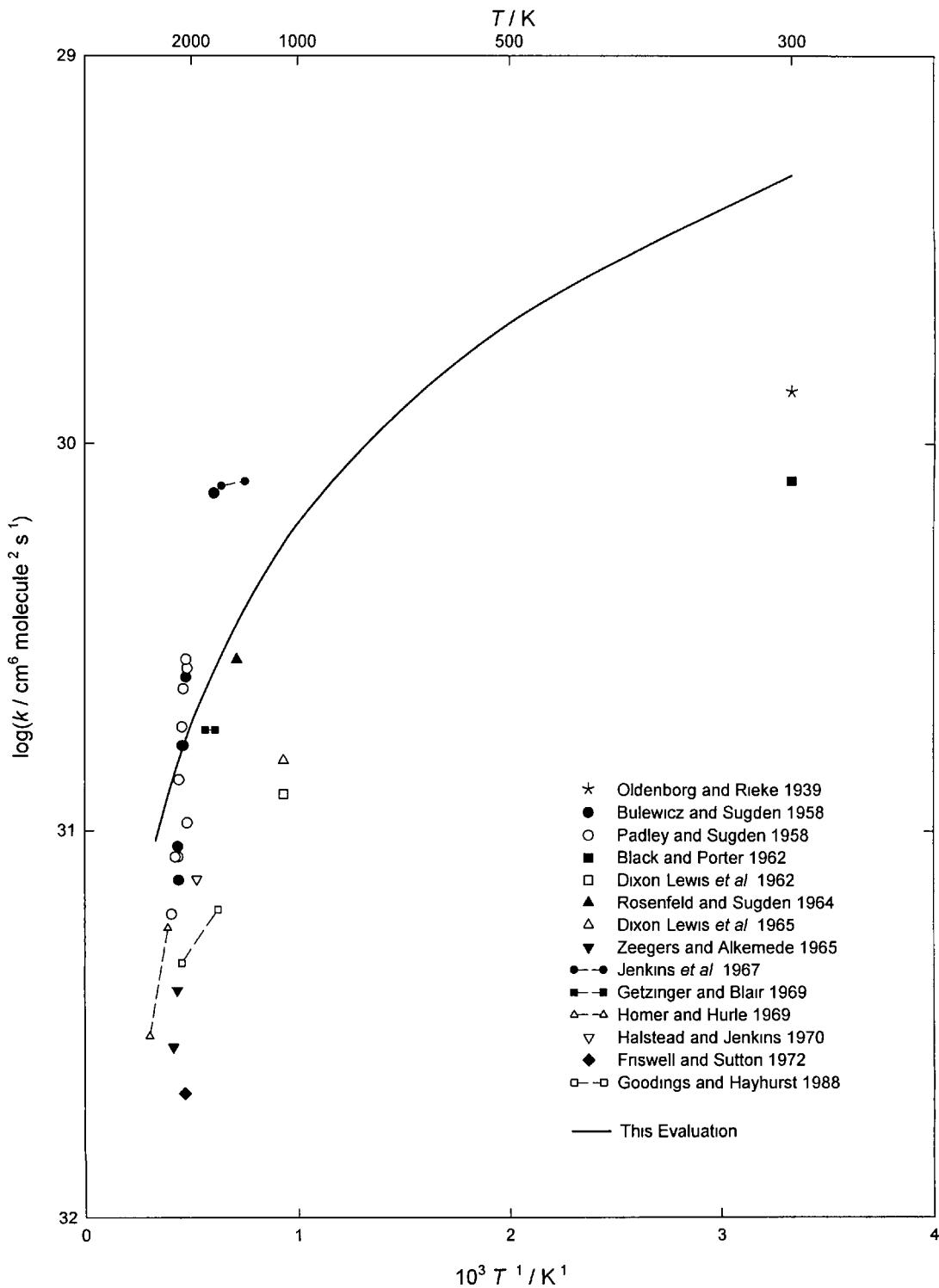
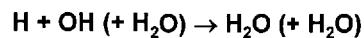
<sup>2</sup>R. W. Getzinger and L. S. Blair, Comb. Flame **13**, 271 (1969).

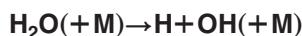
<sup>3</sup>C. J. Halstead and D. R. Jenkins, Comb. Flame **14**, 321 (1970).

- <sup>4</sup> W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data **15**, 1087 (1986).  
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<sup>8</sup> O. Oldenborg and F. F. Rieke, J. Chem. Phys. **7**, 485 (1939).  
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<sup>18</sup> R. W. Getzinger, 11th Symp. (Int.) Combustion, 1967, p. 117.  
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<sup>21</sup> J. B. Homer and I. R. Hurle, Proc. R. Soc. London, Ser. A **314**, 585 (1969).  
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<sup>23</sup> N. J. Frizwell and M. M. Sutton, Chem. Phys. Lett. **15**, 108 (1972).  
<sup>24</sup> J. M. Goodings and A. N. Hayhurst, J. Chem. Soc. Faraday Trans. 2, **84**, 745 (1988).  
<sup>25</sup> R. Zellner, K. Erler, and D. Field, 16th Symp. (Int.) Combustion, 1977, p. 939.









#### Thermodynamic Data

$$\begin{aligned}\Delta H_{298}^{\circ} &= 496.9 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= 109.5 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 9.7 \cdot 10^{24} T^{-0.010} \exp(-59700/T) \text{ molecule cm}^{-3} \\ &(300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	M	Reference	Comments
<i>Rate Coefficient Measurements</i>				
$8.3 \cdot 10^{-10} \exp(-52800/T)$	2700–6000	Ar	Olschewski, Troe, and Wagner, 1967 <sup>1</sup>	(a)
$1.83 \cdot 10^{-9} \exp(-52900/T)$	2570–3290	Ar	Homer and Hurle, 1970 <sup>2</sup>	(b)
$3.7 \cdot 10^{-8} \exp(-52900/T)$	2570–3290	$\text{H}_2\text{O}$		
$1.49 \cdot 10^{-9} \exp(-52800/T)$	2000–2400	Ar	Cathroe and Mackie, 1972 <sup>3</sup>	(c)
$3.0 \cdot 10^{-8} \exp(-52800/T)$	2000–4000	$\text{H}_2\text{O}$		
$2.1 \cdot 10^{-10} \exp(-50323/T)$	3600–4800	Ar	Bopp, Kern, and Nicki, 1978 <sup>4</sup>	(d)
<i>Reviews and Evaluations</i>				
$5.8 \cdot 10^{-9} \exp(-52920/T)$	2000–6000	$\text{N}_2$	Baulch <i>et al.</i> , 1972 <sup>5</sup>	(e)
$2.2 \cdot 10^{-9} \exp(-52920/T)$	2000–6000	Ar		
$3.7 \cdot 10^{-8} \exp(-52920/T)$	2000–6000	$\text{H}_2\text{O}$		
$5.8 \cdot 10^{-9} \exp(-52920/T)$	2000–6000	$\text{N}_2$	Tsang and Hampson, 1986 <sup>6</sup>	(f)
$5.8 \cdot 10^{-9} \exp(-52920/T)$	2000–6000	$\text{N}_2$	CEC, 1992; 1994 <sup>7</sup>	(f)

#### Comments

- (a) Shock tube study on  $\text{H}_2\text{O}/\text{Ar}$  mixtures.  $[\text{H}_2\text{O}]$  and  $[\text{OH}]$  monitored by IR emission and UV absorption spectroscopy, respectively.
- (b) Shock tube study on  $\text{H}_2\text{O}/\text{Ar}$  mixtures.  $[\text{OH}]$  monitored by UV absorption spectroscopy.
- (c) Shock tube study on  $\text{H}_2\text{O}/\text{Ar}$  mixtures seeded with LiOH.  $[\text{Li}]$  monitored by atomic absorption spectroscopy.  $[\text{H}]$  profiles derived from  $[\text{Li}]$  determinations and fitted to  $\text{H}_2/\text{O}_2$  mechanism by computer modeling.
- (d) Shock tube study using reflected shocks in  $\text{D}_2/\text{CO}_2$  (or  $\text{O}_2$ )/Kr/Ar mixtures.  $[\text{D}_2\text{O}]$  monitored by infrared emission at  $3.8 \mu\text{m}$ . Computer simulation used to check fitting of  $[\text{D}_2\text{O}]$  profile.
- (e) Based on the data of Homer and Hurle<sup>2</sup> together with data on the reverse reaction.
- (f) Accepts the recommendations of Baulch *et al.*<sup>5</sup>

#### Preferred Values

$k_0 = 8 \cdot 10^{-9} \exp(-52920/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for M =  $\text{N}_2$  over the range 2000–6000 K.

#### Reliability

$\Delta \log k_0 = \pm 0.5$  for M =  $\text{N}_2$  over the range 2000–6000 K.

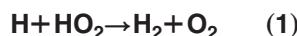
#### Comments on Preferred Values

The preferred expression for  $k_0(\text{M}=\text{N}_2)$  is that proposed by Baulch *et al.*<sup>5</sup> and is unchanged from our previous evaluations.<sup>7</sup>

There have been no direct determinations of  $k$  for M =  $\text{N}_2$  but there have been a number of determinations of  $k$  for M =  $\text{H}_2\text{O}$  and M = Ar, which are in reasonable agreement and which are cited in the Table. Only the stirred reactor study of Jenkins *et al.*<sup>8</sup> appears to give unacceptably high results. Baulch *et al.*<sup>5</sup> therefore obtain their expression for  $k_0(\text{M}=\text{N}_2)$  by combining the data of Homer and Hurle<sup>2</sup> for  $k(\text{M}=\text{H}_2\text{O})$  with the third body efficiencies of Ar:N<sub>2</sub>:H<sub>2</sub>O = 1.0:2.6:16.8 obtained from measurements of  $k(\text{H}+\text{OH}+\text{M})$ .

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*Thermodynamic Data*

$$\Delta H^\circ_{298}(1) = -232.6 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = -7.97 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 5.95 T^{-0.365} \exp(+27770/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(2) = -158.4 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = 23.76 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 3.20 \cdot 10^3 T^{-0.709} \exp(+18410/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(3) = -225.2 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = 6.18 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 1.08 \cdot 10^2 T^{-0.570} \exp(+26890/T) \\ (300 \leq T/\text{K} \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data ( $k = k_1 + k_2 + k_3$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$k_1 = 4.6 \cdot 10^{-11}$	773	Baldwin and Walker, 1979 <sup>1</sup>	(a)
$(k_2 + k_3) = 3.0 \cdot 10^{-10}$			
$k_1 = 6.7 \cdot 10^{-12}$	296	Sridharan, Qiu, and Kaufman, 1982 <sup>2</sup>	(b)
$k_2 = 6.4 \cdot 10^{-11}$			
$k_3 = 3.0 \cdot 10^{-12}$			
$k_1 = 7 \cdot 10^{-12}$	245–300	Keyser, 1986 <sup>3</sup>	(c)
$k_2 = 7.8 \cdot 10^{-11}$			
$k_3 = 2 \cdot 10^{-12}$			
<i>Reviews and Evaluations</i>			
$k_1 = 1.1 \cdot 10^{-10} \exp(-1070/T)$	300–2500	Tsang and Hampson, 1986 <sup>4</sup>	(d)
$k_2 = 2.8 \cdot 10^{-10} \exp(-440/T)$			
$k_1 = 7.1 \cdot 10^{-11} \exp(-710/T)$	300–1000	CEC, 1992; 1994 <sup>5</sup>	(e)
$k_2 = 2.8 \cdot 10^{-10} \exp(-440/T)$			
$k_3 = 5.0 \cdot 10^{-11} \exp(-866/T)$			
$k = 8.1 \cdot 10^{-11}$	245–300	NASA, 1997 <sup>6</sup>	(f)
$k_1 = 5.6 \cdot 10^{-12}$	245–300	IUPAC, 1997 <sup>7</sup>	(f)
$k_2 = 7.2 \cdot 10^{-11}$			
$k_3 = 2.4 \cdot 10^{-12}$			

**Comments**

- (a) Revision of previous measurements<sup>8–11</sup> from the same laboratory of the rate constants of a number of reactions in the  $\text{H}_2\text{-O}_2$  system to allow for self heating, reactions of O atoms with  $\text{H}_2\text{O}_2$ , and other refinements in the mechanism. The values of  $k_1$  and  $(k_2 + k_3)$  are combined with published low temperature data to obtain values of the temperature coefficients of the rate constants given in the paper.
- (b) Discharge flow study in which  $\text{HO}_2$  was generated by the  $\text{F} + \text{H}_2\text{O}_2$  reaction.  $[\text{H}]$  and  $[\text{O}]$  monitored by VUV resonance fluorescence,  $[\text{OH}]$  by LIF, and  $[\text{HO}_2]$  by quantitative conversion to OH with excess NO.
- (c) Discharge flow study in which  $\text{HO}_2$  was generated by the  $\text{F} + \text{H}_2\text{O}_2$  reaction.  $[\text{H}]$ ,  $[\text{O}]$ , and  $[\text{OH}]$  monitored by resonance fluorescence, and  $[\text{HO}_2]$  by quantitative conversion to OH with an excess of NO.
- (d) Based on the data of Sridharan *et al.*<sup>2</sup> and Baldwin and Walker.<sup>1</sup>

(e) See Comments on Preferred Values.

(f) Based on the data of Sridharan *et al.*<sup>2</sup> and Keyser.<sup>3</sup>

**Preferred Values**

$k_1 = 1.75 \cdot 10^{-10} \exp(-1030/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 250–1000 K.

$k_2 = 7.4 \cdot 10^{-10} \exp(-700/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 250–1000 K.

$k_3 = 2.4 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

**Reliability**

$\Delta \log k_1 = \pm 0.3$  over the range 250–1000 K.

$\Delta \log k_2 = \pm 0.15$  over the range 250–1000 K.

$\Delta \log k_3 = \pm 0.5$  at 298 K.

**Comments on Preferred Values**

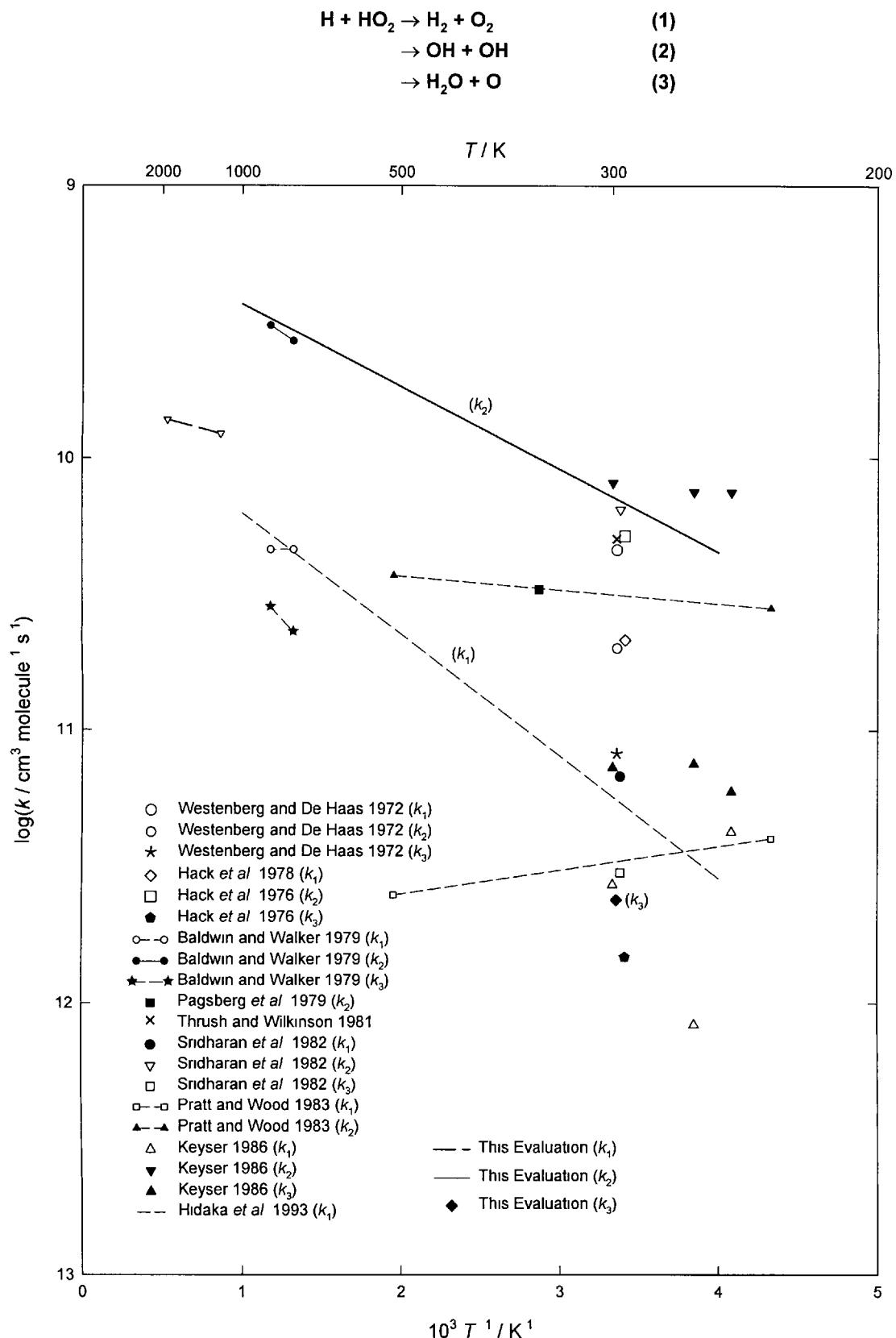
The overall rate constant is reasonably well established at

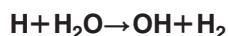
low temperatures and the data in this region<sup>2,3,12–19</sup> have been evaluated by the NASA and IUPAC Panels whose findings we accept. They base their recommended values on the data of Sridharan *et al.*<sup>2</sup> and Keyser.<sup>3</sup> The values of  $k$  obtained by Vaghjiani and Ravishankara,<sup>19</sup> Hack *et al.*,<sup>12,13</sup> and Thrush and Wilkinson<sup>14</sup> are in reasonable agreement.

At higher temperatures there are few data and the scatter is large. In agreement with Tsang and Hampson<sup>4</sup> we accept the data of Baldwin *et al.*<sup>1</sup> as being the most reliable and combine their data for  $k_1$  with the low temperature data to obtain the preferred expression for  $k_1$ . We assume that  $k_2 \gg k_3$  as indicated by the low temperature branching ratios and combine the value of  $(k_2 + k_3)$  from Baldwin *et al.* with the low temperature IUPAC value of  $k_2$  to obtain the expression for  $k_2$ . The expression for  $k_1$  extrapolates reasonably well to the values obtained by Hidaka *et al.*<sup>20</sup> from their shock tube study of HCHO pyrolysis at temperatures of 1160–1890 K. For  $k_3$ , the 298 K value recommended by the IUPAC Panel is accepted.<sup>7</sup>

## References

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- <sup>2</sup>U. C. Sridharan, L. X. Qiu, and F. Kaufman, J. Phys. Chem. **86**, 4569 (1982).
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- <sup>5</sup>CEC, 1992; Supplement I, 1994 (see references in Introduction).
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#### Thermodynamic Data

$$\begin{aligned}\Delta H_{298}^{\circ} &= 60.96 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= 10.9 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 15.9 T^{1.52} \exp(-7510/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$5.2 \cdot 10^{-10} \exp(-11100/T)$	1160–1390	Madronich and Felder, 1984 <sup>1</sup>	(a)
$4.6 \cdot 10^{-10} \exp(-11558/T)$	1246–2297	Michael and Sutherland, 1988 <sup>2</sup>	(b)
$3.4 \cdot 10^{-10} \exp(-10750/T)$	1600–2500	Davidson <i>et al.</i> , 1988 <sup>3</sup>	(c)
<i>Reviews and Evaluations</i>			
$1.0 \cdot 10^{-16} T^{1.9} \exp(-9260/T)$	400–2400	Cohen and Westberg, 1983; <sup>4</sup> Tsang and Hampson, 1986 <sup>5</sup>	(d)
$7.5 \cdot 10^{-16} T^{1.6} \exp(-9270/T)$	300–2500	CEC, 1992; 1994 <sup>6</sup>	(e)

#### Comments

- (a) Flash photolysis of  $\text{H}_2\text{O}/\text{Ar}$  mixtures at a total pressure of 260 mbar.  $[\text{OH}]$  monitored by time resolved resonance fluorescence. Some experimental difficulties due to  $\text{H}$  atom diffusion.
- (b) Shock tube study in which  $\text{H}$  atoms were produced by flash photolysis of  $\text{H}_2\text{O}/\text{Ar}$  mixtures.  $[\text{H}]$  monitored by time resolved ARAS.
- (c) Shock tube study in which  $\text{H}$  and  $\text{OH}$  were produced by excimer laser photolysis at 193.3 nm of  $\text{H}_2\text{O}/\text{Ar}$  mixtures and  $[\text{OH}]$  was monitored by time resolved cw laser absorption.
- (d) Derived by Cohen and Wesberg<sup>4</sup> from the thermodynamic data and evaluation of the data for  $k_{-1}$ . This expression is also recommended by Tsang and Hampson.<sup>5</sup>
- (e) Based on data of Madronich and Felder,<sup>1</sup> Michael and Sutherland,<sup>2</sup> and the data for the reverse reaction.

#### Preferred Values

$k = 7.5 \cdot 10^{-16} T^{1.6} \exp(-9030/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 800–2500 K.

#### Reliability

$\Delta \log k = \pm 0.2$  over the range 800–2500 K.

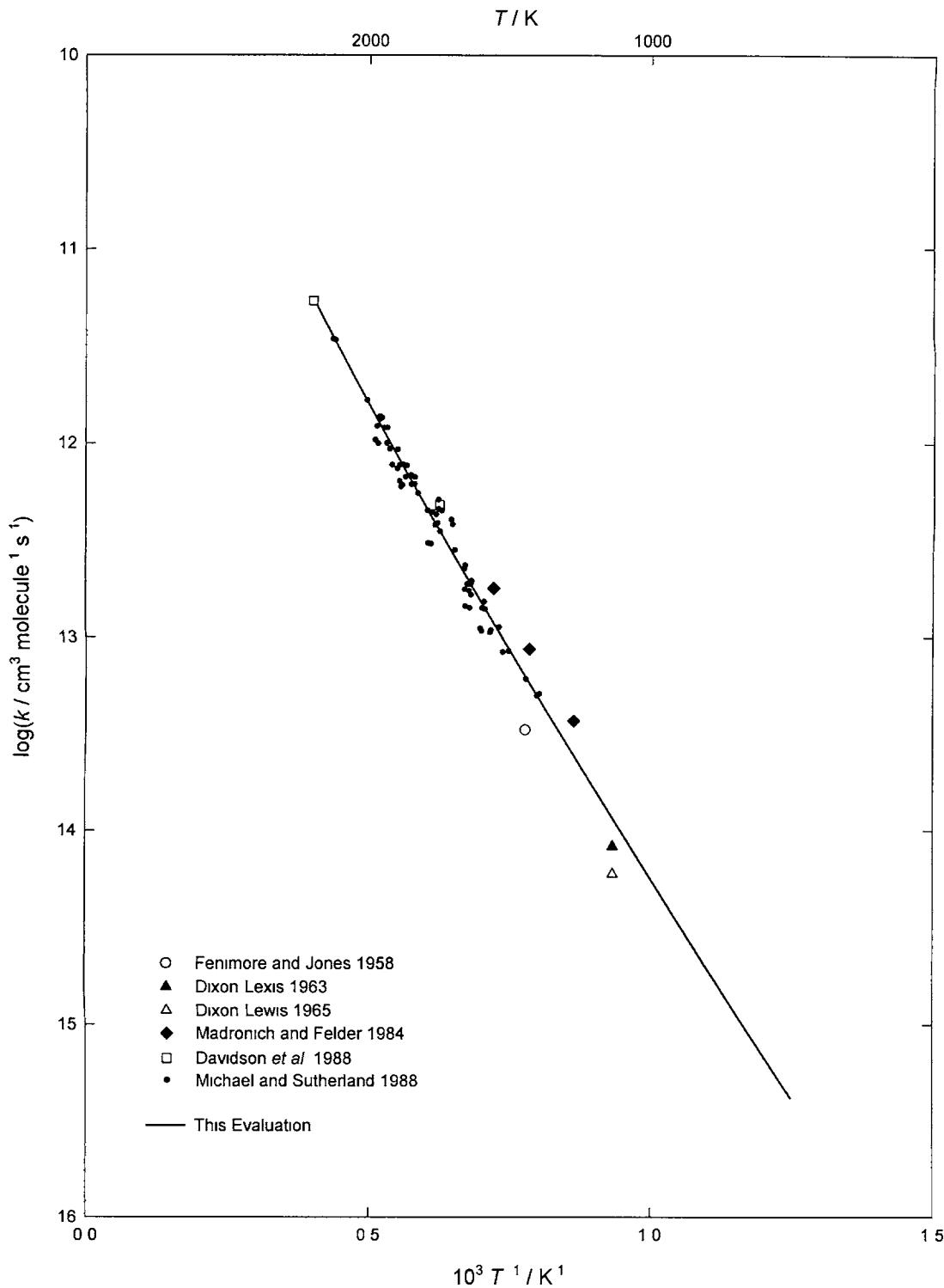
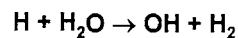
#### Comments on Preferred Values

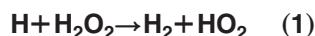
The direct rate constant measurements for this reaction, which are only available at high temperatures ( $> 1160 \text{ K}$ ),

are in good agreement. However the reverse reaction has been extensively studied over a wide temperature range and the preferred expression for  $k$  is therefore based on the expressions for the equilibrium constant and the rate constant  $k(\text{OH} + \text{H}_2)$ , from this evaluation. The expression so derived, which is changed slightly from our previous evaluations<sup>6</sup> due to changes in the thermodynamic data, is in excellent agreement with the studies cited in the Table and with the older studies of Fenimore and Jones,<sup>7</sup> Dixon-Lewis and Williams,<sup>8</sup> and Dixon-Lewis *et al.*<sup>9</sup> The expression derived by Michael<sup>10</sup> also gives values of  $k$  in excellent agreement over the whole temperature range, whereas the expression derived by Cohen and Westberg<sup>4</sup> is in excellent agreement at low temperatures, but at 2500 K give values  $\sim 50\%$  lower than our preferred expression.

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#### Thermodynamic Data

$$\begin{aligned}\Delta H^\circ_{298}(1) &= -67.1 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(1) &= 10.6 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 1.31 \cdot 10^2 T^{-0.508} \exp(+7850/T) \\ &\quad (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

$$\begin{aligned}\Delta H^\circ_{298}(2) &= -286.4 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(2) &= 23.4 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 2.64 \cdot 10^4 T^{-1.056} \exp(+34040/T) \\ &\quad (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2$ )

$\text{k/cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$5.2 \cdot 10^{-12} \exp(-1400/T)$	283–353	Klemm <i>et al.</i> , 1975 <sup>1</sup>	(a)
$k_1 = 1.04 \cdot 10^{-11} \exp(-2478/T)$	713–773	Baldwin and Walker, 1979 <sup>2</sup>	(b)
$k_2 = 1.33 \cdot 10^{-9} \exp(-4582/T)$			
<i>Reviews and Evaluations</i>			
$k_1 = 2.8 \cdot 10^{-12} \exp(-1890/T)$	300–800	Warnatz, 1984 <sup>3</sup>	(c)
$k_2 = 1.7 \cdot 10^{-11} \exp(-1805/T)$	300–1000		
$k_1 = 8.0 \cdot 10^{-11} \exp(-4005/T)$	300–2500	Tsang and Hampson, 1986 <sup>4</sup>	(d)
$k_2 = 4.0 \cdot 10^{-11} \exp(-2000/T)$	300–2500		
$k_1 = 2.8 \cdot 10^{-12} \exp(-1890/T)$	300–1000	CEC, 1992; 1994 <sup>5</sup>	(e)
$k_2 = 1.7 \cdot 10^{-11} \exp(-1800/T)$	300–1000		

#### Comments

- (a) Vacuum ultraviolet flash photolysis of  $\text{H}_2\text{O}_2/\text{He}$  mixtures at total pressures in the range 53–132 mbar.  $[\text{H}]$  monitored by time resolved resonance fluorescence. In the course of a later study<sup>6</sup> on the reaction of Cl with  $\text{H}_2\text{O}_2$  the rate constant for  $\text{H} + \text{H}_2\text{O}_2$  was measured at two temperatures to check the different methods of determining  $[\text{H}_2\text{O}_2]$  in the two studies. Values of  $4.5 \cdot 10^{-14}$  and  $9.9 \cdot 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  were obtained at 298 K and 359 K, respectively, in good agreement with the previous results.
- (b) Revision of the results of previous experimental studies from their laboratory<sup>7</sup> to allow for self heating and refinements in the reaction mechanism. Their own results at 773 K are combined with the low temperature results of Albers *et al.*<sup>12</sup> to give the cited expressions.
- (c) Accepts the expression derived by Baulch *et al.*<sup>8</sup> for  $k_1$ ,  $k_2$  based on data of Klemm *et al.*<sup>1</sup> and data in the 700 K region from the laboratory of Baldwin and Walker.<sup>2</sup>
- (d) Expression for  $k_2$  based on Klemm *et al.*<sup>1</sup> Expression for  $k_1$  chosen to fit data of Baldwin and Walker.<sup>2</sup>
- (e) Accepts findings of Warnatz.<sup>3</sup>

#### Reliability

$$\begin{aligned}\Delta \log k_1 &= \pm 0.5 \text{ over the range } 300\text{--}1000 \text{ K.} \\ \Delta \log k_2 &= \pm 0.3 \text{ over the range } 300\text{--}1000 \text{ K.}\end{aligned}$$

#### Comments on Preferred Values

At low temperatures the results of Klemm *et al.*<sup>1,6</sup> are the most direct and reliable. The overall rate constant was measured but they conclude that Channel (2) predominates throughout their temperature range. Their value at 298 K is supported by the value of Heicklen and Meagher.<sup>9</sup> There are a number of other studies<sup>10–12</sup> reporting values of  $k_1$  at low temperatures but none can be considered reliable.

At higher temperatures, Baldwin and Walker and their co-workers<sup>2</sup> have carried out a number of determinations of  $k_1/k_2$  and of both  $k_1$  and  $k_2$  in their studies on the  $\text{H}_2/\text{O}_2$  system at temperatures in the 700–800 K region.<sup>7</sup> The expressions that they have derived in their most recent evaluation of these studies are cited in the Table. The temperature range studied is small making the determination of accurate Arrhenius parameters difficult but the absolute values of the rate constants and  $k_1/k_2$  are likely to be reliable for this temperature region. Our preferred expressions for  $k_1$  and  $k_2$  give values which are compatible with the results of Baldwin and Walker<sup>2</sup> and also with the studies of Kijewski and Troe<sup>13</sup> at 870–1000 K and Forst and Giguere<sup>14</sup> within the error limits suggested.

The Arrhenius parameters of both channels are very uncertain but the studies from the Baldwin and Walker<sup>2</sup> group and a recent modeling study<sup>15</sup> suggest higher activation energies than given in our recommendations and higher than that found by Klemm *et al.*<sup>1</sup> at low temperatures. However

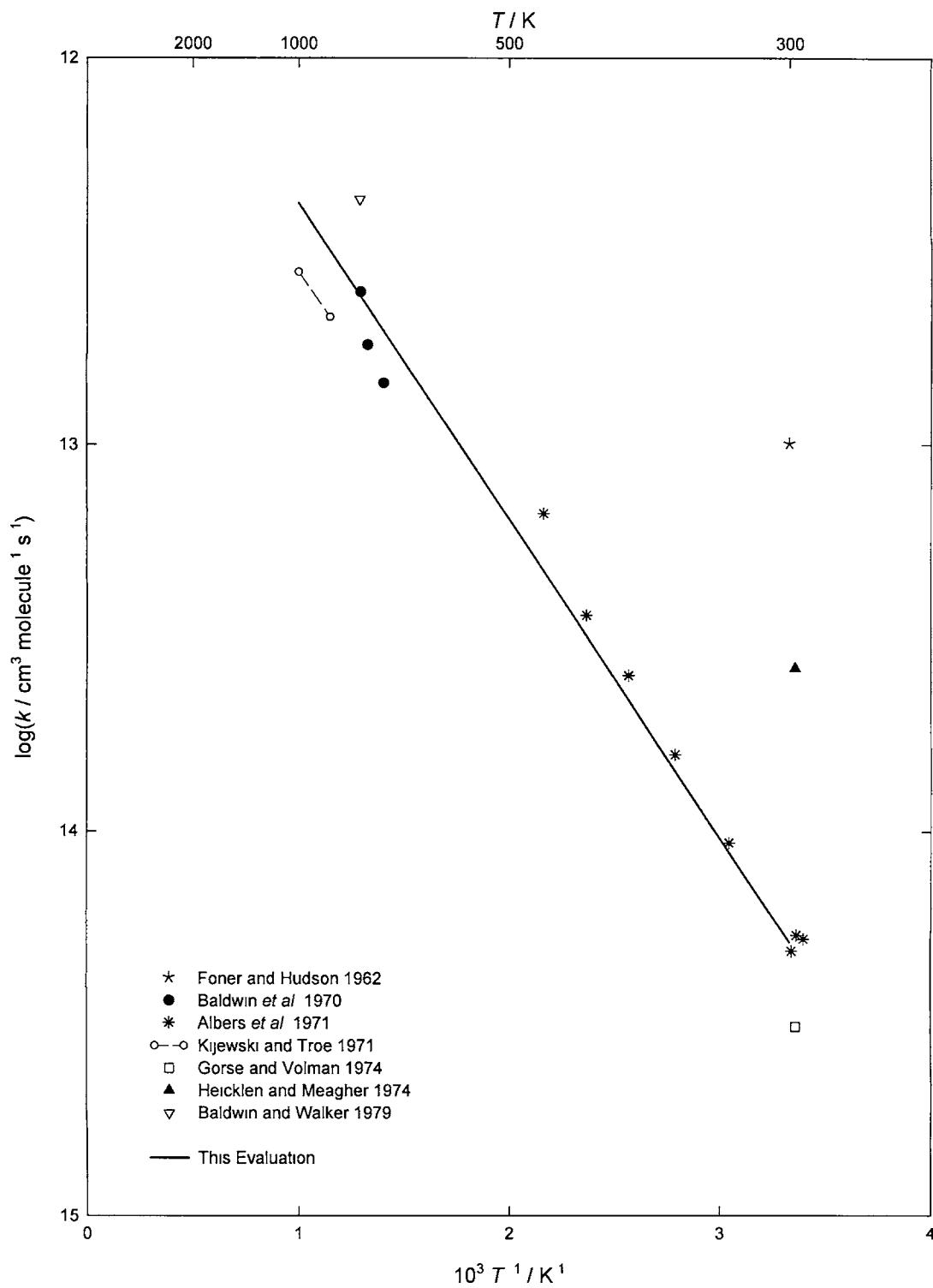
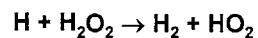
#### Preferred Values

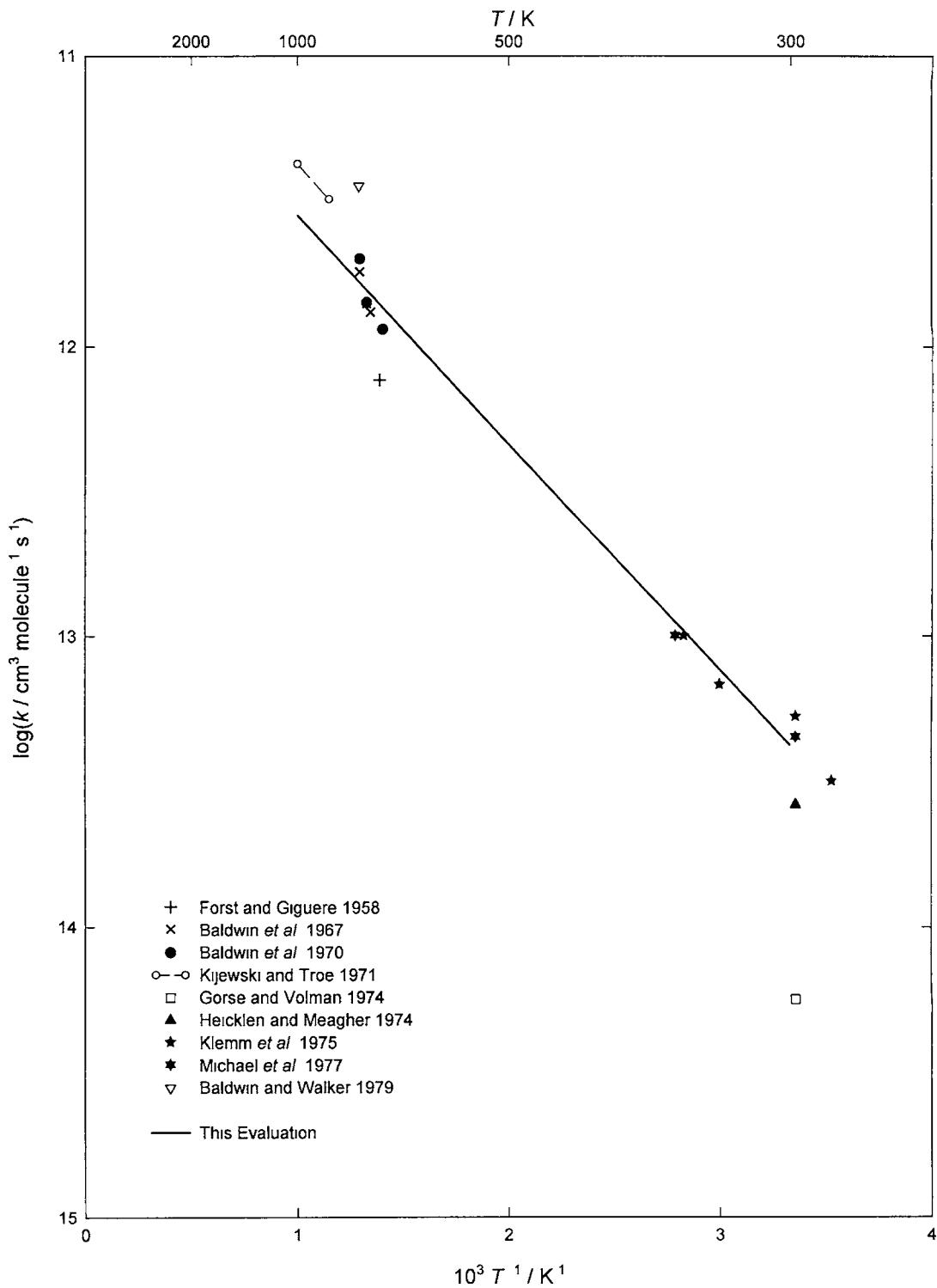
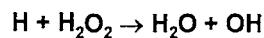
- $k_1 = 2.8 \cdot 10^{-12} \exp(-1890/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 300–1000 K.
- $k_2 = 1.7 \cdot 10^{-11} \exp(-1800/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 300–1000 K.

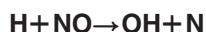
until more reliable experimental data become available our previous recommendations are retained with substantial error limits.

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- <sup>14</sup>W. Forst and P. A. Giguere, J. Phys. Chem. **62**, 340 (1958).
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#### Thermodynamic Data

$$\begin{aligned}\Delta H_{298}^{\circ} &= 201.6 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= 11.67 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 23.4 T^{-0.250} \exp(-24340/T) \\ &(300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$4.28 \cdot 10^{-10} \exp(-24560/T)$	2200–3250	Duxbury and Pratt, 1975 <sup>1</sup>	(a)
$3.71 \cdot 10^{-10} \exp(-25410/T)$	2400–4200	Flower <i>et al.</i> , 1977 <sup>2</sup>	(b)
$2.89 \cdot 10^{-10} \exp(-24760/T)$	1750–2040	McCullough <i>et al.</i> , 1977 <sup>3</sup>	(c)
$1.2 \cdot 10^{-9} \exp(-28500/T)$	2800–3570	Qin <i>et al.</i> , 1997 <sup>4</sup>	(d)
<i>Reviews and Evaluations</i>			
$2.8 \cdot 10^{-10} \exp(-24560/T)$	1750–4200	Hanson and Salimian, 1984 <sup>5</sup>	(e)
$3.6 \cdot 10^{-10} \exp(-24910/T)$	1500–4500	CEC, 1994 <sup>6</sup>	(f)

#### Comments

- (a) Shock tube study using highly diluted  $\text{H}_2/\text{NO}$  mixtures in Ar. [NO] and [OH] were monitored by time resolved UV absorption spectroscopy. Values of  $k$  obtained by detailed modeling of the [NO] and [OH] profiles. The rate expression was obtained by combining their own results with those of Campbell and Thrush<sup>7</sup> on the reverse reaction.
- (b) Shock tube study on NO/ $\text{H}_2/\text{inert gas}$  mixtures. Time resolved IR emission from NO and  $\text{H}_2\text{O}$  monitored. Values of  $k$  obtained by detailed modeling of the [NO] and [ $\text{H}_2\text{O}$ ] profiles.
- (c) Dilute NO/ $\text{H}_2/\text{Ar}$  mixtures were passed through an alumina packed flow reactor. The fractional decomposition of NO was measured as a function of flow rate using a chemiluminescence analyzer to monitor the [NO]. Values of  $k$  were obtained using a detailed flow and kinetic model.
- (d) Shock tube study using  $\text{H}_2/\text{NO}/\text{Ar}$  mixtures at total pressures of  $\sim 3$  bar. [OH] was monitored by time resolved laser absorption at 309.942 nm. Values of  $k$  were obtained by detailed modeling of the [OH] profiles.
- (e) Least squares analysis of the expressions of Duxbury and Pratt,<sup>1</sup> Flower *et al.*,<sup>2</sup> and McCullough *et al.*<sup>3</sup>
- (f) Based on the studies of Duxbury and Pratt,<sup>1</sup> Flower *et al.*,<sup>2</sup> and McCullough *et al.*<sup>3</sup>

#### Comments on Preferred Values

The data for the addition channel,  $\text{H} + \text{NO}(+\text{M}) \rightarrow \text{HNO}(+\text{M})$ , are evaluated on the data-sheet which follows the present one.

The preferred values for  $k$  are unchanged from our previous evaluations. They were derived by taking a mean value of the values of  $E/R$  obtained in the studies of Duxbury and Pratt,<sup>1</sup> Flower *et al.*,<sup>2</sup> and McCullough *et al.*<sup>3</sup> and a pre-exponential factor derived using this value of  $E/R$  and the mean value of  $k$  at 2500 K. Since our previous evaluations there have been two studies of the reaction, both at high temperatures, by Natarajan *et al.*<sup>8</sup> and Qin *et al.*<sup>4</sup> Qin *et al.*<sup>4</sup> obtain a slightly higher value of  $E/R$  over the fairly small temperature range covered but the individual data points are in excellent agreement with our preferred expression. There is considerable scatter on the data of Natarajan *et al.*<sup>8</sup> and the values of  $k$  obtained are slightly higher than our preferred values. The older study Bradley and Craggs<sup>9</sup> appears to give high values of  $k$  and those of Ando and Asaba<sup>10</sup> and Koshi *et al.*<sup>11</sup> values that are too low.

The preferred expression for the rate constant of the reverse reaction has been derived from measurements carried out at temperatures below 500 K (see data sheet), but when extrapolated to the higher temperature range covered here and combined with the preferred expression for  $k$ , it leads to values of the equilibrium constant within a factor of 2–3 of those given by the thermodynamic data. This is well within the error limits of all the quantities concerned.

#### Preferred Values

$k = 3.6 \cdot 10^{-10} \exp(-24910/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 1500–4500 K.

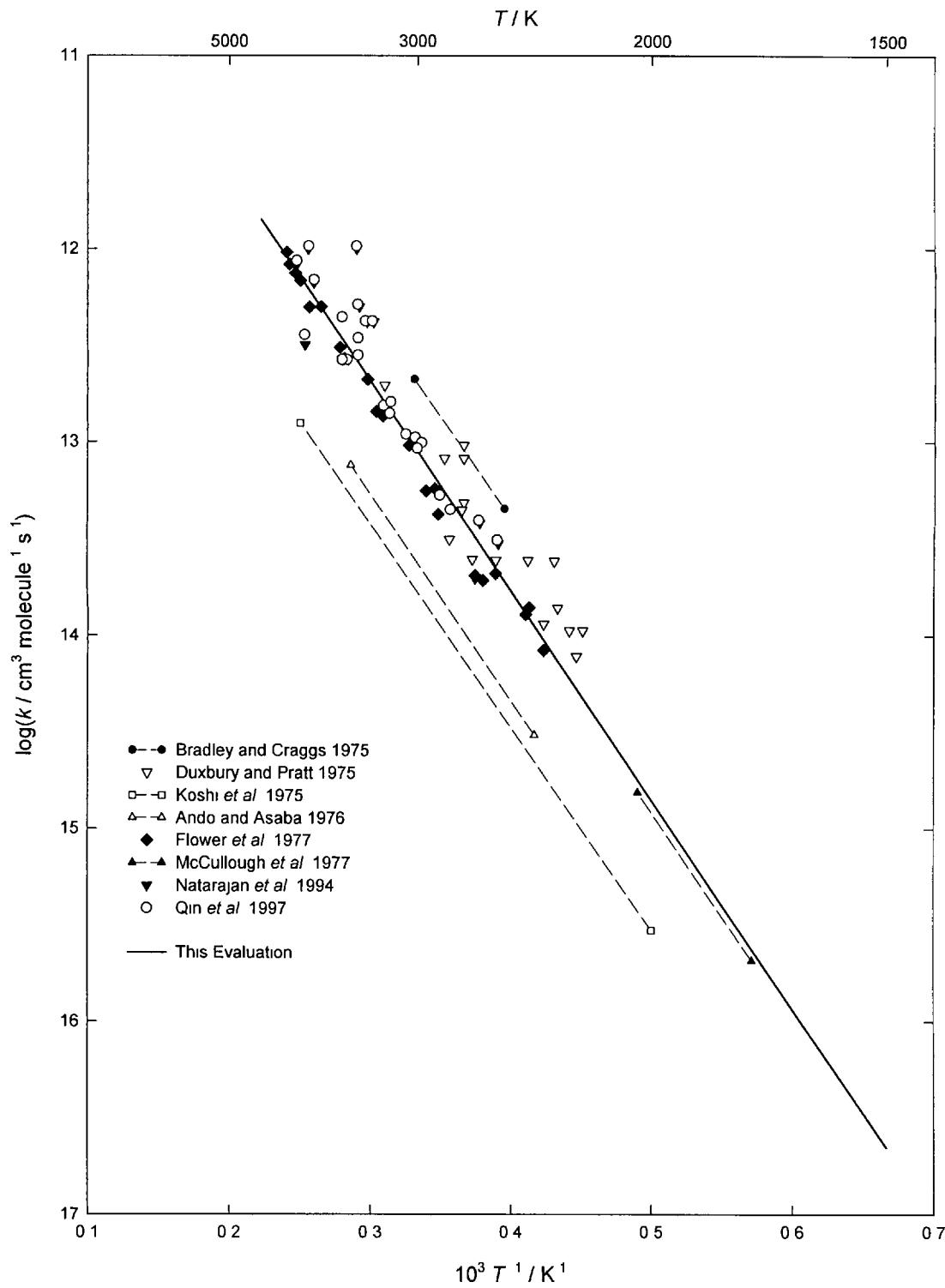
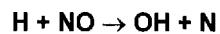
#### Reliability

$\Delta \log k = \pm 0.3$  over the range 1500–4500 K.

#### References

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## H+NO(+M)→HNO(+M)

### Thermodynamic Data

$$\begin{aligned}\Delta H_{298}^{\circ} &= -201.2 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= -104.6 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 3.65 \cdot 10^{-26} T^{0.262} \exp(+24180/T) \text{ cm}^3 \text{ molecule}^{-1} \\ &\quad (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

### Rate Coefficient Data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	[M]/molecule cm <sup>-3</sup>	Reference	Comments
<i>Rate Coefficient Measurements</i>				
<i>Low Pressure Range</i>				
$[\text{H}_2] 4.08 \cdot 10^{-32}$	294	$(1.09-13.2) \cdot 10^{16}$	Clyne and Thrush, 1961 <sup>1</sup>	(a)
$[\text{H}_2] 4.10 \cdot 10^{-32}$	340			
$[\text{H}_2] 3.23 \cdot 10^{-32}$	433			
$[\text{H}_2] 2.06 \cdot 10^{-32}$	704			
$[\text{H}_2] 5.62 \cdot 10^{-32}$	231	$(2.31-12.5) \cdot 10^{16}$	Clyne and Thrush, 1962 <sup>2</sup>	(b)
$[\text{H}_2] 4.00 \cdot 10^{-32}$	265			
$[\text{H}_2] 4.08 \cdot 10^{-32}$	293			
$[\text{Ar}] 2.40 \cdot 10^{-32}$	293			
$[\text{Ne}] 1.99 \cdot 10^{-32}$	293			
$[\text{He}] 1.82 \cdot 10^{-32}$	293			
$[\text{H}_2] 3.0 \cdot 10^{-32}$	298	$(6.5-12.9) \cdot 10^{16}$	Simonaitis, 1963 <sup>3</sup>	(c)
$[\text{Ar}] 3.03 \cdot 10^{-32}$	298	$(3.2-9.7) \cdot 10^{16}$	Hartley and Thrush, 1967 <sup>4</sup>	(d)
$[\text{H}_2] 5.71 \cdot 10^{-32}$	298			
$[\text{CO}_2] 6.23 \cdot 10^{-32}$	298			
$[\text{N}_2\text{O}] 6.75 \cdot 10^{-32}$	298			
$[\text{SF}_6] 10.9 \cdot 10^{-32}$	298			
$[\text{H}_2\text{O}] 18.8 \cdot 10^{-32}$	298			
$[\text{H}_2] 3.86 \cdot 10^{-32}$	298	$(3.2-48.6) \cdot 10^{18}$	Hikida, Eyre, and Dorfman, 1971 <sup>5</sup>	(e)
$[\text{H}_2] 6.3 \cdot 10^{-32}$	298	$(1.8-20) \cdot 10^{18}$	Ahumada, Michael, and Osborne, 1972 <sup>6</sup>	(f)
$[\text{He}] 4.3 \cdot 10^{-32}$	298			
$[\text{Ne}] 2.1 \cdot 10^{-32}$	298			
$[\text{Ar}] 3.9 \cdot 10^{-32}$	298			
$[\text{Kr}] 5.4 \cdot 10^{-32}$	298			
$[\text{H}_2] 2.49 \cdot 10^{-32} \exp(272/T)$	285-390	$(2.5-4.9) \cdot 10^{18}$	Atkinson and Cvetanovic, 1973 <sup>7</sup>	(g)
$[\text{Ar}] 2.32 \cdot 10^{-32}$	392	$7.4 \cdot 10^{16}$	Campbell and Handy, 1975 <sup>8</sup>	(h)
$[\text{N}_2] 3.98 \cdot 10^{-32}$				
$[\text{H}_2] 4.3 \cdot 10^{-32}$	298	$(1.6-10) \cdot 10^{18}$	Oka, Singleton, and Cvetanovic, 1977 <sup>9,10</sup>	(i)
$[\text{H}_2] 1.27 \cdot 10^{-32} \exp(364/T)$	298-477	$(8-100) \cdot 10^{18}$		
$[\text{NO}] 5.27 \cdot 10^{-32}$				
$[\text{H}_2] 4.65 \cdot 10^{-32}$	298	$(3.2-29.2) \cdot 10^{18}$	Ishikara, Sugawara, and Sato, 1979 <sup>11</sup>	(j)
$[\text{N}_2] 1.1 \cdot 10^{-27} T^{-1.75}$	1000-1170	$(7.5-8.9) \cdot 10^{18}$	Glarborg <i>et al.</i> , 1998 <sup>12</sup>	(k)
<i>High Pressure Range</i>				
$8.3 \cdot 10^{-10}$	300-313	$(3.2-2900) \cdot 10^{18} (\text{Ar}, \text{N}_2)$	Forte, 1981 <sup>13</sup>	(l)
<i>Reviews and Evaluations</i>				
$k_0[\text{H}_2] = [\text{H}_2] 1.5 \cdot 10^{-32} \exp(300/T)$	300-700		Baulch <i>et al.</i> , 1973 <sup>14</sup>	(m)
$k_0[\text{N}_2] = [\text{N}_2] 2.47 \cdot 10^{-28} T^{-1.32} \exp(-370/T)$	300-2500		Tsang and Herron, 1991 <sup>15</sup>	(n)
$k_0[\text{CO}_2] = [\text{CO}_2] 9.56 \cdot 10^{-29} T^{-1.17} \exp(-212/T)$				
$F_c(\text{N}_2) = 0.82$				
$F_c(\text{CO}_2) = 0.82$				
$k_\infty = 2.53 \cdot 10^{-9} T^{-0.41}$				

### Comments

- (a) Discharge flow system. H atoms produced by a radio frequency discharge in  $\text{H}_2$ . NO added downstream. Reaction progress monitored by detection of the HNO emission bands at 627.2 and 645.3 nm.

- (b) Technique as in (a) but Ar, Ne, and He used as carrier gases as well as  $\text{H}_2$ . HNO emissions monitored using the band at 762.5 nm.
- (c) Technique as in (a) but reaction progress monitored using H atom detection by isothermal calorimetry.

- (d) Technique as in (b); [H] determined by calorimetric probe and HNO emission monitored using the band at 760 nm.
- (e) Pulse radiolysis of H<sub>2</sub>/NO mixtures using a Febetron. [H] monitored by resonance fluorescence at 121.6 nm.
- (f) H atoms generated by mercury photosensitized photolysis of H<sub>2</sub> at 254 nm in large excess of bath gas (H<sub>2</sub>, He, Ne, Kr, or Ar) with varying amounts of NO. Decay of steady state concentration of H on termination of the irradiation monitored by resonance fluorescence at 121.6 nm.
- (g) Molecular modulation technique. H atoms generated by mercury photosensitized decomposition of H<sub>2</sub> at 253.7 nm in the presence of NO. HNO emission at  $\lambda \geq 600$  nm monitored.
- (h) Stirred flow reactor. O atoms generated by the N + NO reaction and mixed in the reactor with NO and H<sub>2</sub> in an N<sub>2</sub> or Ar carrier gas. Reaction progress monitored by detection of the NO<sub>2</sub> emission from the O + NO reaction.
- (i) Technique as in (g) but HNO emission over the range 720–800 nm monitored.
- (j) Pulse radiolysis of H<sub>2</sub>/NO mixtures. [H] monitored by resonance fluorescence at 121.6 nm.
- (k) Flow reactor study using flows of CO/O<sub>2</sub>/H<sub>2</sub>O/N<sub>2</sub> mixtures perturbed by additions of small amounts of NO. [CO], [CO<sub>2</sub>], [O<sub>2</sub>], and [NO] were monitored continuously at the reactor outlet by spectrophotometric and paramagnetic analyzers. Values of  $k$  were derived by fitting the [CO] profile using a detailed mechanism.
- (l) Photolysis at 254 nm of HI/NO mixtures in a bath gas of N<sub>2</sub> or Ar. [HI] or [I<sub>2</sub>] monitored by absorption spectroscopy. High pressure limit of  $k$  found at pressures >400 bar.
- (m) Based on the data of Clyne and Thrush.<sup>1,2</sup>
- (n) The expression of Baulch *et al.*<sup>14</sup> for  $k_0$  for M=H<sub>2</sub> and the data of Forte<sup>13</sup> are accepted and used to derive expressions for  $k_\infty$  and  $k_0$  for M=N<sub>2</sub> and M=CO<sub>2</sub>.

### Preferred Values

$k_0 = 4.23 \cdot 10^{-30} T^{-0.77}$  cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup> for M=H<sub>2</sub> over the range 230–750 K.

### Reliability

$\Delta \log k_0 = \pm 0.3$  for M=H<sub>2</sub> over the range 230–750 K.

### Comments on Preferred Values

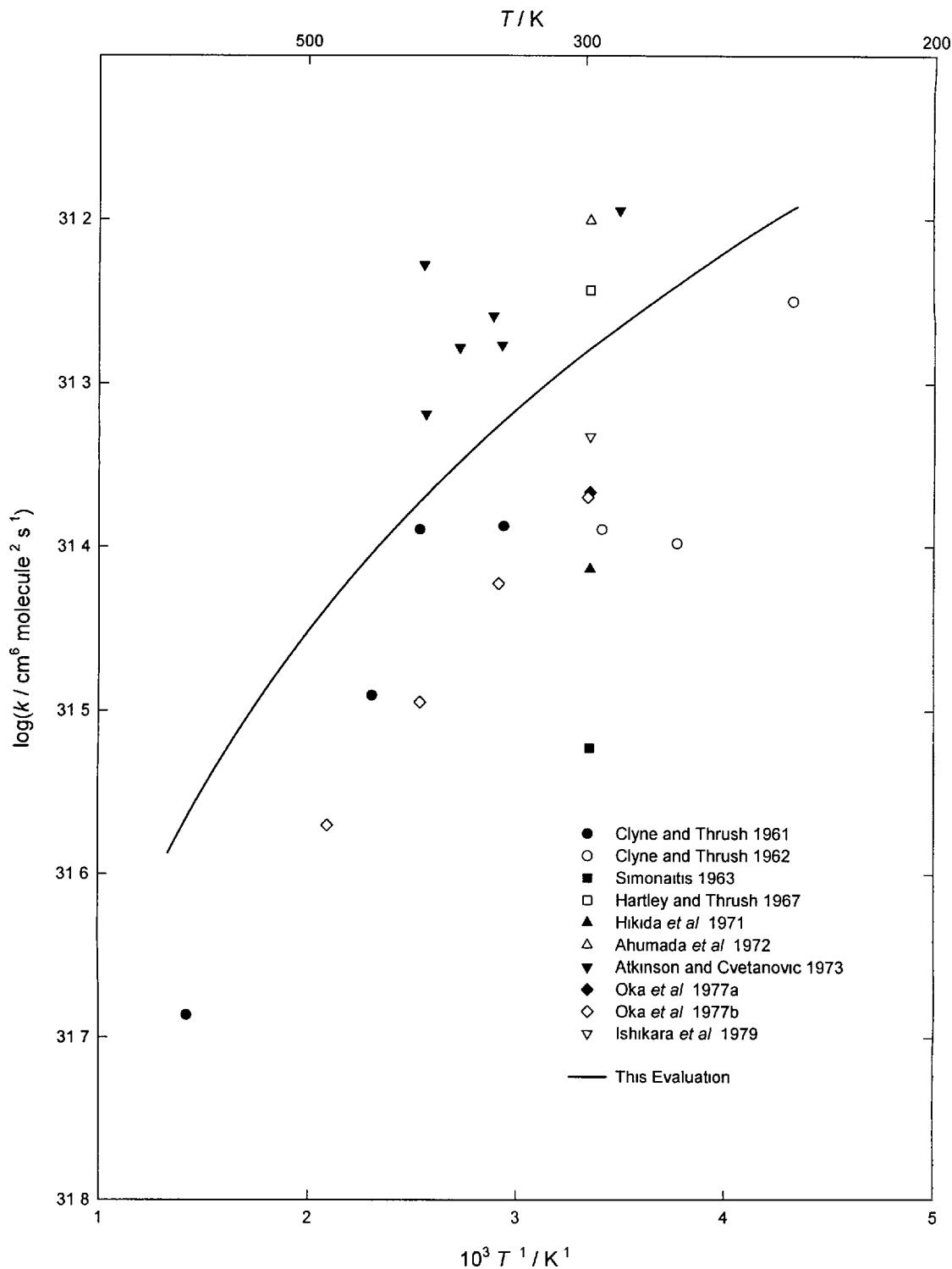
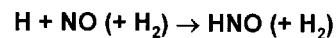
The data for the bimolecular channel, H+NO→OH+N, are evaluated on the preceding data sheet.

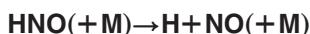
The combination reaction of H with NO will be in its low pressure (third order) region under the conditions pertaining in most combustion systems. Values of the rate constant have been measured for a number of bath gases at 298 K but only for H<sub>2</sub> as a collision partner are there sufficient data to derive an expression for  $k_0$  as a function of temperature. The preferred expression is obtained from a least squares fit to the data for  $k_0$  (M=H<sub>2</sub>) cited in the Table.<sup>1–7,9–11</sup>

For other collision partners values of  $k$  measured at 298 K give  $k_0(M=H_2) = k_0(M=N_2) = 1.7k_0(M=Ar)$  but at higher temperatures there are two recent flow reactor studies,<sup>12,16</sup> in which N<sub>2</sub> was the bath gas, which give values of  $k$  about a factor of 3–4 lower than expected from the expression for  $k(M=H_2)$ . No recommendations are made for collision partners other than H<sub>2</sub> at this stage.

### References

- <sup>1</sup>M. A. A. Clyne and B. A. Thrush, Trans. Faraday Soc. **57**, 1305 (1961).
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- <sup>13</sup>E. N. Forte, J. Photochem. **17**, 13 (1981).
- <sup>14</sup>D. L. Baulch, D. D. Drysdale, and D. G. Horne, *Evaluated Kinetic Data for High Temperature Reactions*, Vol. 2, Homogeneous Gas Phase Reactions of the H<sub>2</sub>-N<sub>2</sub>-O<sub>2</sub> System (Butterworths, London, 1973).
- <sup>15</sup>W. Tsang and J. T. Herron, J. Phys. Chem. Ref. Data **20**, 609 (1991).
- <sup>16</sup>M. T. Allen, R. A. Yetter, and F. L. Dryer, Combust. Flame **112**, 302 (1998).





#### Thermodynamic Data

$$\begin{aligned}\Delta H_{298}^{\circ} &= 201.2 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= 104.6 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 2.74 \cdot 10^{25} T^{-0.262} \exp(-24180/T) \text{ molecule cm}^{-3} \\ &(300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data

There are no experimental data on the rate constant of this reaction.

#### Preferred Values

$$k_0 = 3.8 \cdot 10^{-7} T^{-0.262} \exp(-23180/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ for M=H}_2 \text{ over the range 230--750 K.}$$

#### Reliability

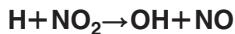
$$\Delta \log k_0 = \pm 0.4 \text{ for M=H}_2 \text{ over the range 230--750 K.}$$

#### Comments on Preferred Values

This reaction will be in its low pressure (second order)

region under conditions occurring in most combustion systems.

The preferred expression has been obtained by combining the expression for  $K_c$  with data on the rate constant of the reverse reaction (this evaluation). There are sufficient data to derive a temperature dependent expression for  $k_0$  only for  $\text{H}_2$  as a collision partner but approximate values of the relative efficiency for some other bath gases are given on the data sheet for the  $\text{H} + \text{NO(+M)}$  reaction.



#### Thermodynamic Data

$$\begin{aligned}\Delta H_{298}^{\circ} &= -123.7 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= 39.9 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 2.4 \cdot 10^4 T^{-0.751} \exp(+14570/T) \\ &(300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$7.1 \cdot 10^{-10} \exp(-505/T)$	240–460	Wagner, Welzbacher, and Zellner, 1976 <sup>1</sup>	(a)
$4.8 \cdot 10^{-10} \exp(-174/T)$	298–653	Bemand and Clyne, 1977; <sup>2</sup> Clyne and Monkhouse, 1977 <sup>3</sup>	(a)
$1.32 \cdot 10^{-10}$	230–400	Michael <i>et al.</i> , 1979 <sup>4</sup>	(b)
$1.50 \cdot 10^{-10}$	195–368		(a)
$2.2 \cdot 10^{-10} \exp(-182/T)$	297–760	Ko and Fontijn, 1990 <sup>5</sup>	(c)
<i>Reviews and Evaluations</i>			
$1.4 \cdot 10^{-10}$	195–650	Tsang and Herron, 1991 <sup>6</sup>	(d)
$4.0 \cdot 10^{-10} \exp(-340/T)$	200–300	NASA, 1997 <sup>7</sup>	(e)

#### Comments

- (a) Discharge flow study at pressures of a few mbar. [H] monitored by time resolved Lyman- $\alpha$  resonance fluorescence in the presence of a large excess of  $\text{NO}_2$ . Similar work from the same group<sup>8</sup> gives  $k = 6.0 \cdot 10^{-10} \exp(-505/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .
- (b) Flash photolysis of  $\text{NO}_2/\text{CH}_4/\text{Ar}$  mixtures at total pressures in the range 40–200 mbar. [H] monitored by time resolved Lyman- $\alpha$  resonance fluorescence.
- (c) Flash photolysis of  $\text{NO}_2/\text{CH}_4/\text{Ar}$  mixtures at pressures

in the range 123–413 mbar and a range of flow rates through the reaction cell. [H] monitored by time resolved Lyman- $\alpha$  resonance fluorescence.

- (d) The value of  $k$  at 298 K is based on the studies of Wagner *et al.*,<sup>1</sup> Bemand and Clyne,<sup>2</sup> Clyne and Monkhouse,<sup>3</sup> Michael *et al.*,<sup>4</sup> and Ko and Fontijn.<sup>5</sup> The temperature dependence is from the studies of Wagner *et al.*<sup>1</sup> and Ko and Fontijn.<sup>5</sup>
- (e) Based on the study of Michael *et al.*<sup>4</sup>

### Preferred Values

$k = 4.2 \cdot 10^{-10} \exp(-340/T)$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> over the range 230–800 K.

#### Reliability

$\Delta \log k = \pm 0.1$  at 230 K, rising to  $\pm 0.3$  at 800 K.

#### Comments on Preferred Values

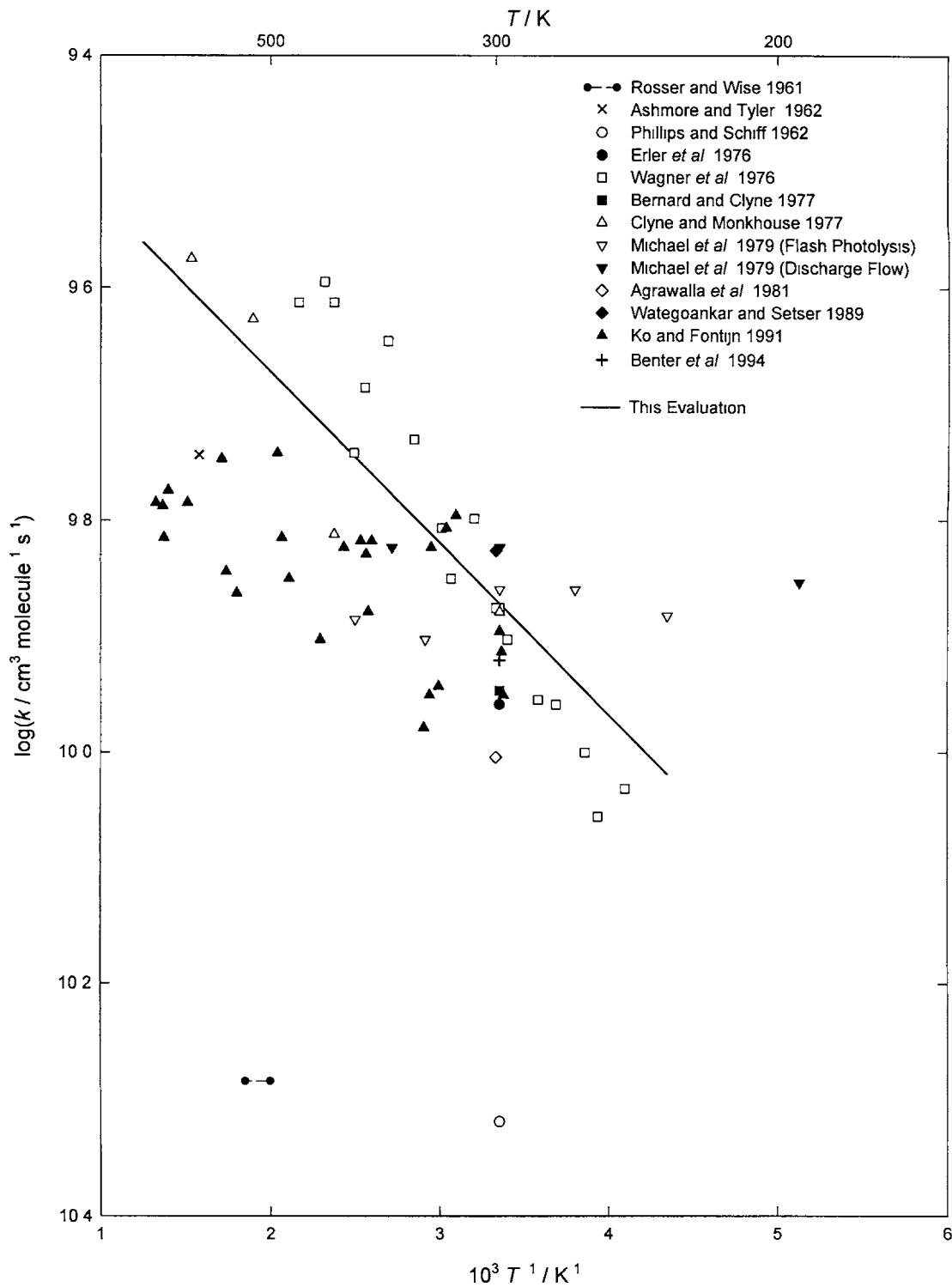
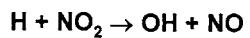
Early studies of this reaction gave rather low values of  $k$ .<sup>12–14</sup> Although the values obtained for the rate constant at 298 K are in fair agreement there is greater divergence at higher temperatures with values in the range 400–650 K differing by approximately a factor of 2. The preferred expression for  $k$  is a least squares fit to the data from the studies cited in the Table. There are also two relative rate measurements at 298 K<sup>9,10</sup> and another direct determination<sup>11</sup> which are in good agreement with the cited values.

Studies of the energy distribution in the reaction products indicate that it proceeds through a short lived HONO\* intermediate. However there is no evidence for a stabilization

channel under laboratory conditions and estimates<sup>5</sup> suggest that pressures in excess 100 bar might be required for significant HONO formation.

### References

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*Thermodynamic Data*

$$\Delta H^\circ_{298}(1) = -263.0 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = 40.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 7.1 \cdot 10^5 T^{-1.23} \exp(+31150/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(2) = 146.8 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = 57.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 1.52 \cdot 10^6 T^{-1.06} \exp(-18050/T) \\ (300 \leq T/\text{K} \leq 5000)$$

See Section 3 for the origin and quality of the Thermodynamic Data.

**Rate Coefficient Data ( $k = k_1 + k_2$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$5.8 \cdot 10^{-11} \exp(-6140/T)$	1210–1760	Fenimore and Jones, 1959 <sup>1</sup>	(a)
$7.1 \cdot 10^{-14}$	900	Dixon-Lewis, Sutton, and Williams, 1965 <sup>2</sup>	(b)
$4.8 \cdot 10^{-13}$	1360	Dixon-Lewis, Sutton, and Williams, 1965 <sup>3</sup>	
$6.6 \cdot 10^{-11} \exp(-6000/T)$	1700–2600	Henrici and Bauer, 1969 <sup>4</sup>	(c)
$6.6 \cdot 10^{-15}$	773	Baldwin, Gethin, and Walker, 1973 <sup>5</sup>	(d)
$3.7 \cdot 10^{-10} \exp(-8710/T)$	720–1120	Albers <i>et al.</i> , 1975 <sup>6</sup>	(e)
$1.0 \cdot 10^{-10} \exp(-6590/T)$	1000–1600	Balkhanine, Vandooren, and Van Tiggelen, 1977 <sup>7</sup>	(f)
$3.0 \cdot 10^{-9} \exp(-13600/T)$	2000–2850	Dean, Steiner, and Wang, 1978 <sup>8</sup>	(g)
$1.5 \cdot 10^{-9} \exp(-11100/T)$	1600–3000	Dean, Johnson, and Steiner, 1980 <sup>9</sup>	(h)
$2.5 \cdot 10^{-10} \exp(-7550/T)$	1450–2200	Hidaka, Takuma, and Suga, 1985 <sup>10</sup>	(i)
$4.2 \cdot 10^{-14} \exp(-2290/T) + 3.7 \cdot 10^{-10} \exp(-8430/T)$	414–1227	Marshall, Ko, and Fontijn, 1989 <sup>11</sup>	(j)
$9.2 \cdot 10^{-14} \exp(-2990/T)$	374–628	Arthur, Cooper, and Gershenson, 1997 <sup>12</sup>	(k)
<i>Reviews and Evaluations</i>			
$1.3 \cdot 10^{-10} \exp(-7600/T)$	700–2500	Baulch <i>et al.</i> , 1973, <sup>13</sup> Hanson and Salimian, 1985 <sup>14</sup>	(l)
$1.6 \cdot 10^{-10} \exp(-7600/T)$	700–2500	Tsang and Herron, 1991 <sup>15</sup>	(m)
$k_1 = 3.6 \cdot 10^{-10} \exp(-8430/T)$	1000–2000	Bozzelli, Chang, and Dean, 1994 <sup>16</sup>	(n)
$k_2 = 0.11 T^{-2.16} \exp(-18700/T)$			

**Comments**

- (a) Flame study on  $\text{H}_2/\text{N}_2\text{O}$  and  $\text{H}_2/\text{N}_2\text{O}/\text{air}$  mixtures at 80–550 mbar pressure. [H] determined using  $\text{H} + \text{D}_2\text{O}$  exchange reaction and mass spectrometric analysis. Values recalculated by Baulch *et al.*<sup>13</sup> and by Baldwin *et al.*<sup>5</sup> using more recent values of  $k(\text{H} + \text{D}_2\text{O})$ . Expression in Tables is that derived by Baldwin *et al.*<sup>5</sup>
- (b) Flame studies on  $\text{H}_2/\text{O}_2/\text{N}_2/\text{N}_2\text{O}$  and fuel rich  $\text{H}_2/\text{N}_2/\text{N}_2\text{O}$  mixtures at 1 bar pressure. [H] determined by Na chemiluminescence calibrated against  $\text{H} + \text{D}_2$  exchange. Analysis by mass spectrometric probe.
- (c) Shock-tube study using incident shocks in  $\text{H}_2/\text{N}_2\text{O}$  mixtures at  $\sim 1$  bar pressure. [OH] monitored by optical absorption at 309.4 nm.
- (d) Static system. Slowly reacting mixtures of  $\text{H}_2/\text{O}_2/\text{N}_2\text{O}/\text{He}$  at 330 and 660 mbar pressure. Reaction monitored by pressure changes. Yield of  $\text{N}_2$  determined by gas chromatography. Authors derive  $k/k(\text{H} + \text{O}_2) = (0.64 \pm 0.07)$ . Tabulated value of  $k$  obtained using  $k(\text{H} + \text{O}_2)$  from the present evaluation.
- (e) Discharge flow study. [H] monitored by ESR. Products determined by mass spectrometry in experiments with relatively high H and  $\text{H}_2$  concentrations. Kinetics studies used  $[\text{N}_2\text{O}] \gg [\text{H}]$ . No NO detected. Secondary chemistry is sufficiently significant to require measured rate coefficients to be corrected using measured stoichiometry factors.
- (f) Flame study using lean flat  $\text{N}_2\text{O}/\text{H}_2$  flame at 53 mbar pressure. Species ( $\text{N}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{H}_2$ ,  $\text{NO}$ ,  $\text{O}_2$ ,  $\text{H}$ ,  $\text{O}$ ,  $\text{OH}$ ,  $\text{H}_2\text{O}$ ) in flame sampled by supersonic molecular beam probe into mass spectrometer.  $\text{N}_2$  formation interpreted in terms of Channel (1) together with  $\text{O} + \text{N}_2\text{O}$  and  $\text{N}_2\text{O} + \text{M}$  reactions using their own values of  $k$  for these last two reactions.
- (g) Reflected shock waves in  $\text{H}_2/\text{CO}/\text{O}_2/\text{Ar}$  and  $\text{H}_2/\text{N}_2\text{O}/\text{CO}/\text{Ar}$  mixtures; emissions at 450 nm and 4.27  $\mu\text{m}$  from the  $\text{CO} + \text{O} \rightarrow \text{CO}_2 + h\nu$  reaction were monitored and used to derive [O] and [ $\text{CO}_2$ ] profiles. Expression for  $k$  derived by fitting assumed reaction mechanism to these profiles.
- (h) Technique as in (g) using  $\text{H}_2\text{CO}/\text{O}_2/\text{Ar}$ ,  $\text{H}_2\text{CO}/\text{N}_2\text{O}/\text{Ar}$ ,  $\text{H}_2\text{CO}/\text{O}_2/\text{CO}/\text{Ar}$ , and  $\text{H}_2\text{CO}/\text{N}_2\text{O}/\text{CO}/\text{Ar}$  mixtures.
- (i) Shock-tube study using incident and reflected shocks in  $\text{N}_2\text{O}/\text{H}_2/\text{Ar}$  mixtures. Emissions at 4.68  $\mu\text{m}$  were used to monitor  $[\text{N}_2\text{O}]$  and products ( $\text{N}_2\text{O}, \text{O}_2, \text{NO}$ ) were analyzed by mass spectrometry. Values of  $k$  were derived from fitting of the species profiles using an assumed reaction mechanism.
- (j) Flash photolysis of  $\text{NH}_3$  in a large excess of  $\text{N}_2\text{O}$ ; [H]

monitored by resonance fluorescence at 121.6 nm. Pressure of the bath gas, Ar, and other constituents varied over the range 72–632 mbar.  $k$  independent of pressure over this range. These results supersede earlier results<sup>17</sup> using similar technique.

- (k) Technique similar to (j) but with absorption at 121.6 nm to monitor [H]. Pressures of 395 mbar used with Ar as bath gas.
- (l) Hanson and Salimian<sup>14</sup> review the available data up to 1978 and accept earlier evaluation of Baulch *et al.*<sup>13</sup>
- (m) Expression of Hanson and Salimian<sup>14</sup> raised slightly to accommodate the more recent results of Hidaka *et al.*<sup>10</sup>
- (n) Review of experimental results combined with theoretical calculations.  $k_1$  is the high temperature component of the experimental expression of Marshall *et al.*<sup>11</sup>  $k_2$  is derived from theory. An expression is also derived from theory for the rate constant for formation of the adduct,  $\text{HN}_2\text{O}$ , which at a pressure of 1 bar  $\text{N}_2$  is  $k = 13.3 T^{-4.39} \exp(-5300/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

### Preferred Values

$$k = [5.5 \cdot 10^{-14} \exp(-2560/T) + 1.3 \cdot 10^{-9} \exp(-9750/T)] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the range } 350\text{--}2500 \text{ K.}$$

### Branching Ratios

No recommendation. See Comments on Preferred Values.

### Reliability

$\Delta \log k = \pm 0.3$  over the temperature range 350–2500 K.

### Comments on Preferred Values

As can be seen from the Arrhenius diagram there is reasonable agreement among the studies on the overall rate constant over a wide temperature range. A feature of the diagram is the pronounced change in slope in the 550–800 K region which, as discussed later, has been attributed to changes in the reaction mechanism. To accommodate this it is most convenient to express the overall rate constant as the sum of two Arrhenius expressions relating to the high and low temperature regimes.

The high temperature component of the preferred expression for  $k$  is based on the results from Refs. 1–10. Over the range 720–2000 K the data from these studies agree to within a factor of 2. The studies of Dean *et al.*<sup>8,9</sup> show greater divergence from the preferred expression at temperatures above 2000 K and give very high values of  $E/R$ . The results of Glass and Quy,<sup>18</sup> over the range 1473–2710 K, seem unacceptably low and are not used in the evaluation.

At temperatures below 650 K there are two recent studies<sup>11,12</sup> which used similar, but not identical, techniques under much the same conditions. They are in excellent agreement on the temperature dependence of  $k$  but give absolute values differing by a factor of approximately 2.5. It is not clear whether this is due to deficiencies in the techniques, which seem sound, or due to the sensitivity of  $k$  to pressure

at these temperatures. In one of the studies,<sup>11</sup> the pressure was varied by a factor of  $\sim 4$  in the low temperature regime but no effect on the value of  $k$  could be detected. The only other studies at low temperatures are those of Johnson and Simic<sup>19</sup> and of Schiavello and Volpi,<sup>20</sup> neither of which can be considered to give reliable values of  $k$ . The low temperature component of the preferred expression is based on the mean values from the studies of Marshall *et al.*<sup>11</sup> and Arthur *et al.*<sup>12</sup>

There have been a number of theoretical studies<sup>16,17,21</sup> to explain the way in which the rate constant changes with temperature and to characterize the branching ratios of the various possible reaction channels. The reaction is considered to proceed by direct H atom attack on the oxygen in the  $\text{N}_2\text{O}$ , leading to  $\text{OH} + \text{N}_2$ , or by H atom addition to form  $\text{HNNO}$  which, being energy rich, may decompose to form either  $\text{NH} + \text{NO}$  or, much less probably  $\text{OH} + \text{N}_2$ , or the adduct may rapidly isomerize to  $\text{NNOH}$  and decompose [Channel (1)]. Thus, the products  $\text{OH} + \text{N}_2$  [Channel (2)] may be formed by a direct or indirect path. The possibility also exists that at sufficiently high pressures the intermediate,  $\text{HNNO}$ , may be collisionally stabilized.

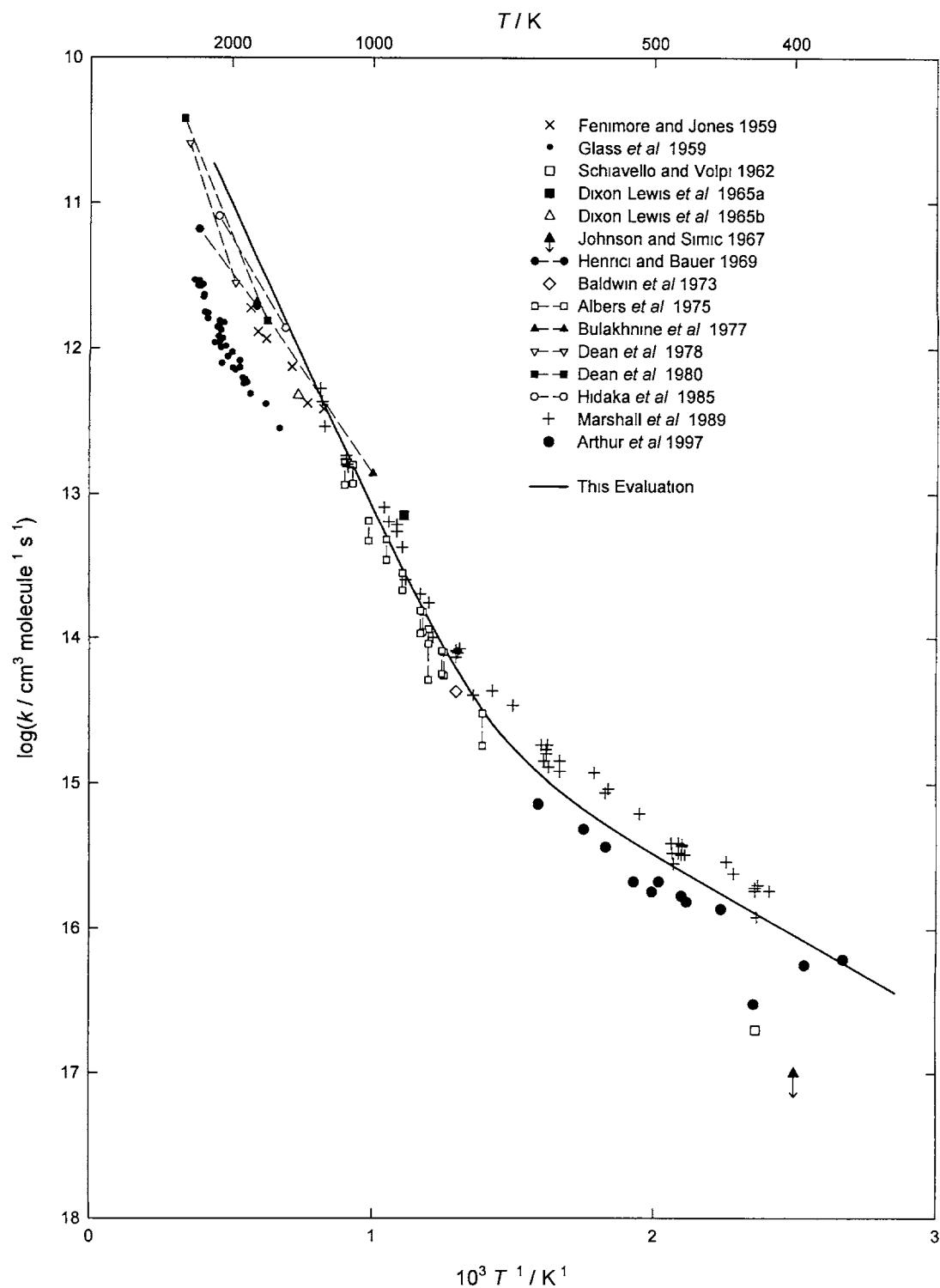
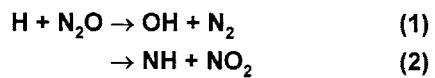
Theoretical and experimental studies are in agreement that the major reaction channel at high temperatures is Channel (1), producing  $\text{OH} + \text{N}_2$ . Theoretical treatments also suggest contributions from Channel (2) with  $k_2/k$  reaching values of  $\sim(0.07^{17}\text{--}0.12^{16})$  at 2000 K. Experimental results support the predominance of Channel (1) but provide very little information on contributions from other channels. Borisov *et al.*<sup>22</sup> obtained a value of  $k_2 = 1.0 \cdot 10^{-9} \exp(-14600/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  from a shock tube study, which gives  $k_2/k \approx 0.06$  at 2000 K in general support of the theoretical estimates. It should be possible, in principle, to derive information on the value of  $k_2$  from the thermodynamic data and values of  $k_{-2}$ . Unfortunately there is considerable uncertainty in  $k_{-2}$  at high temperatures. The available data have been reviewed by Bozzelli *et al.*<sup>16</sup> and by Hanson and Salimian.<sup>14</sup> The theoretical estimates<sup>16,17</sup> probably provide the best guide at this stage but it is clear that the formation of  $\text{OH} + \text{N}_2$  is the dominant path.

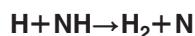
Two explanations for the change in slope of the Arrhenius plot in the 500–800 K region have been proposed. It has been suggested that quantum mechanical tunneling through the barrier to produce  $\text{HNNO}$  may lead to higher values of  $k$  than expected at low temperatures.<sup>17</sup> Alternatively, the low temperature behavior of  $k$  may be attributable to enhancement by collisional stabilization of  $\text{HNNO}$ ,<sup>16,21,12</sup> or both mechanisms may be contributing. Stabilization of  $\text{HNNO}$  requires that  $k$  is pressure dependent but there is no experimental support for this.

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*Thermodynamic Data*

$$\begin{aligned}\Delta H_{298}^{\circ} &= -101.8 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= -12.0 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 0.483 T^{-0.099} \exp(+12190/T) \\ (300 \leqslant T/\text{K} \leqslant 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$5 \cdot 10^{-11}$	1790–2000	Morley, 1981 <sup>1</sup>	(a)
$6 \cdot 10^{-11}$	2130		
$7.6 \cdot 10^{-11}$	2200		
<i>Reviews and Evaluations</i>			
$5 \cdot 10^{-11}$	1790–2200	Hanson and Salimian, 1985 <sup>2</sup>	(b)

**Comments**

- (a) Study on  $\text{H}_2/\text{O}_2/\text{Ar}$  flames doped with  $\text{CH}_3\text{CN}$ .  $[\text{NH}]$  monitored by LIF. Derivation of  $k$  based on an assumed mechanism for N atom formation. Results shown to be compatible with the data of Haynes.<sup>3</sup>
- (b) Accept Morley's results.<sup>1</sup>

**Preferred Values**

$k = 5 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 1500–2500 K.

*Reliability*

$\Delta \log k = \pm 0.3$  over the temperature range 1500–2500 K.

*Comments on Preferred Values*

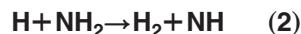
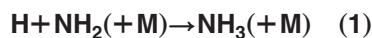
The results of Morley<sup>1</sup> are accepted, and the temperature range is extended since a substantial temperature dependence

of  $k$  is not expected. The interpretation of the experimental observations is difficult, hence the order of magnitude uncertainty limits. The value of  $k$  is compatible with the limited data on the reverse reaction.<sup>4,5</sup>

Zhang and Truong<sup>6</sup> have used *ab initio* molecular orbital calculations to derive an expression for  $k$  which is compatible with the limited high temperature data and extends to much lower temperatures.

**References**

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#### Thermodynamic Data

$$\begin{aligned}\Delta H_{298}^{\circ}(1) &= -453.4 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ}(1) &= -116.6 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 2.75 \cdot 10^{-27} T^{0.387} \exp(+54670/T) \text{ cm}^3 \text{ molecule}^{-1} \\ &(300 \leq T/\text{K} \leq 5000)\end{aligned}$$

$$\begin{aligned}\Delta H_{298}^{\circ}(2) &= -51.0 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ}(2) &= 2.54 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 8.35 T^{-0.218} \exp(+5940/T) \\ &(300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurement</i>			
$k_2 = 6.64 \cdot 10^{-11} \exp(-1836/T)$	2200–2800	Davidson <i>et al.</i> , 1990 <sup>1</sup>	(a)
$k_2 = 1.39 \cdot 10^{-9} T^{-0.218} \exp(-4160/T)$	1156–1680	Röhrig and Wagner, 1994 <sup>2</sup>	(b)
<i>Reviews and Evaluations</i>			
$k_2 = 1 \cdot 10^{-11}$	2000–3000	CEC, 1992; 1994 <sup>3</sup>	(c)

#### Comments

- (a) Shock tube study of  $\text{NH}_3$  decomposition in Ar bath gas. Temporal history of  $[\text{NH}_2]$  and  $[\text{NH}]$  were determined by narrow line laser absorption at 597.375 nm and 336.060 nm, respectively. Reactions were carried out in the pressure range 811–1115 mbar, with concentrations of ammonia ranging from 0.1% to 1.0%. Rate constants obtained by fitting of concentration profiles by computer simulation.
- (b) Shock tube study on  $\text{HN}_3/\text{H}_2/\text{Ar}$  mixtures.  $[\text{NH}]$  monitored in the presence of a large excess of  $\text{H}_2$  using time-resolved ring dye laser absorption at 336.1 nm. Values of  $k(\text{NH} + \text{H}_2)$  obtained have been converted to values of  $k$  using the thermodynamic data cited in the present evaluation.
- (c) Based on the scattered data of Roose,<sup>4</sup> Yumura and Asaba,<sup>5</sup> and Dove and Nip.<sup>6</sup>

#### Preferred Values

$k_1^{\circ} = 7.6 \cdot 10^{-35} T^{0.787} \exp(7840/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  for M=Ar over the range 2000–3000 K.

$k_1^{\infty} = 7.6 \cdot 10^{-10} \exp(-850/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 2000–3000 K.

$F_{c,1} = 0.58 \exp(-T/4581) + 0.42 \exp(-T/102)$  for M=Ar over the range 2000–3000 K.

$k_2 = 8.8 \cdot 10^{-11} \exp(-2515/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 1100–3000 K.

#### Reliability

$\Delta \log k_1^{\circ} = \pm 0.4$  over the range 2000–3000 K.

$\Delta \log k_1^{\infty} = \pm 0.5$  over the range 2000–3000 K.

$\Delta F_{c,1} = \pm 0.1$  for M=Ar over range 2000–3000 K.  
 $\Delta \log k_2 = \pm 0.2$  over the range 1100–3000 K.

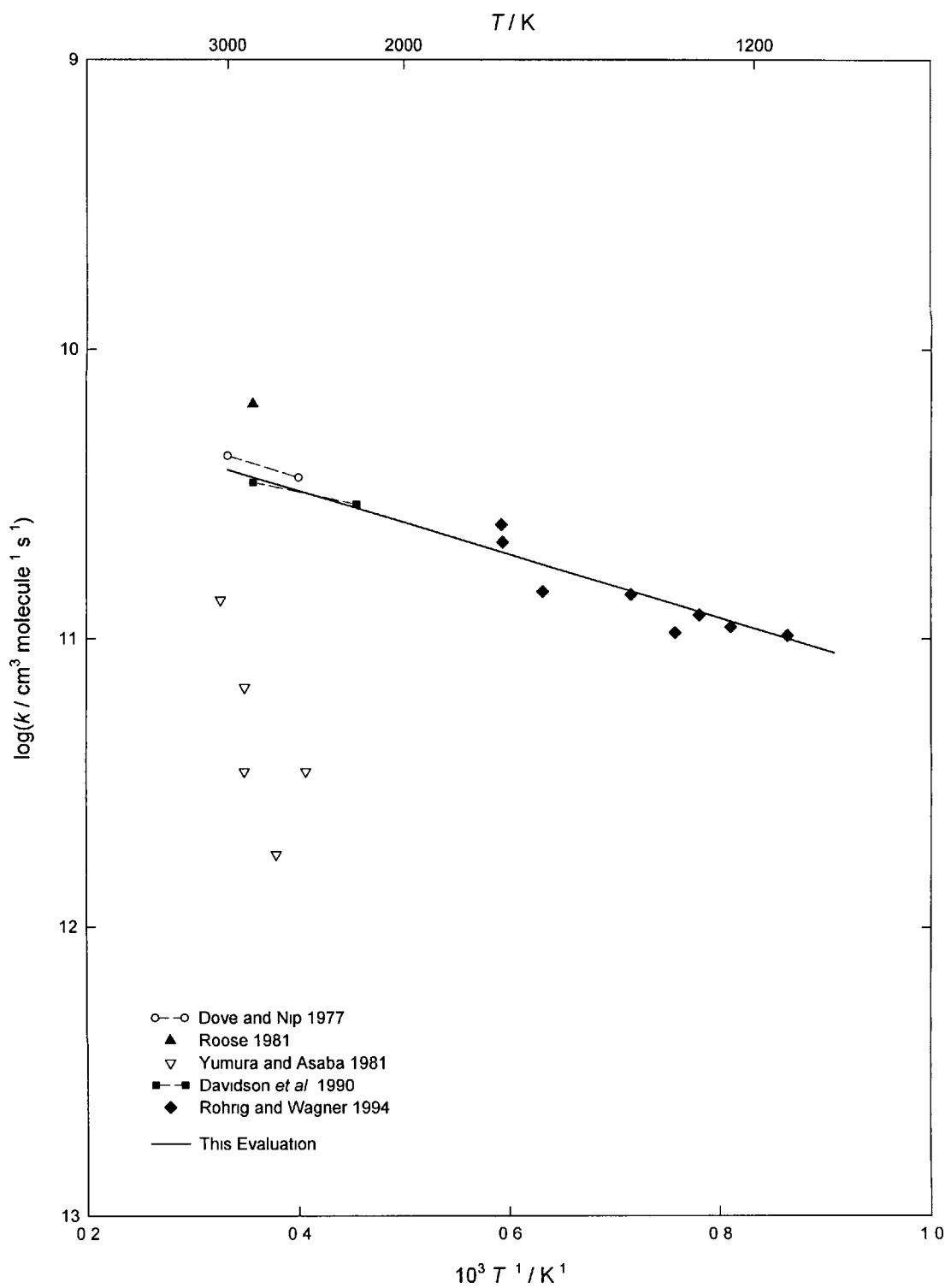
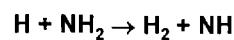
#### Comments on Preferred Values

The measurements on which our previous recommendations for  $k_2$  were based<sup>4–6</sup> were badly scattered. The present recommendations for  $k_2$  are based on the rate constant for the reverse reaction obtained in the study of Röhrig and Wagner<sup>2</sup> together with the values of Davidson *et al.*<sup>1</sup> since these experiments are much more reliable. We derive an expression weighing the results of Röhrig and Wagner<sup>2</sup> at twice those of Davidson *et al.*<sup>1</sup> The results can be seen in the accompanying Arrhenius plot. The preferred expression obtained is supported by the results of Dove and Nip<sup>6</sup> and of Roose<sup>4</sup> but those of Yumura and Asaba<sup>5</sup> are scattered and much lower.

An important problem in the treatment of the overall process is to know the conditions where the combination reaction becomes competitive with the abstraction process. For  $k_1$  our recommendations are based on the preferred values for the reverse reaction combined with the expression for the equilibrium constant, which can probably be used to make adequate estimates.

#### References

- <sup>1</sup> D. F. Davidson, K. Kohse-Höinghaus, A. Y. Chang, and R. K. Hanson, Int. J. Chem. Kinet., **22**, 513 (1990).
- <sup>2</sup> M. Röhrig and H. G. Wagner, 25th Symp. (Int.) Combustion, 1994, p. 975.
- <sup>3</sup> CEC, 1992; Supplement I, 1994 (see references in Introduction).
- <sup>4</sup> T. T. Roose, Ph.D thesis, Stanford University, reported in Ref. 7.
- <sup>5</sup> M. Yumura and T. Asaba, 18th Symp. (Int.) Combustion, 1981, p. 863.
- <sup>6</sup> J. E. Dove and W. S. Nip, Can. J. Chem., **57**, 689 (1977).
- <sup>7</sup> R. K. Hanson and S. Salimian, in *Combustion Chemistry*, edited by W. C. Gardiner (Springer, New York, 1984).





#### Thermodynamic Data

$$\begin{aligned}\Delta H^{\circ}_{298}(1) &= 402.4 \text{ kJ mol}^{-1} \\ \Delta S^{\circ}_{298}(1) &= 119.1 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 1.76 \cdot 10^{27} T^{-0.535} \exp(-48670/T) \text{ molecule cm}^{-3} \\ &(300 \leq T/\text{K} \leq 5000)\end{aligned}$$

$$\begin{aligned}\Delta H^{\circ}_{298}(2) &= 453.4 \text{ kJ mol}^{-1} \\ \Delta S^{\circ}_{298}(2) &= 116.6 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 3.64 \cdot 10^{26} T^{-0.387} \exp(-54670/T) \text{ molecule cm}^{-3} \\ &(300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{s}^{-1}$	T/K	[M]/molecule cm $^{-3}$	Reference	Comments
<i>Rate Coefficient Measurements</i>				
<i>Low Pressure Range</i>				
$[\text{Ar}]4.2 \cdot 10^{-8} \exp(-45800/T)$	2100–2900		Henrici, 1966 <sup>1</sup>	(a)
$[\text{Kr}]2.0 \cdot 10^{-8} \exp(-45790/T)$	2500–3000	$1.0 \cdot 10^{18}$	Dove and Nip, 1979 <sup>2</sup>	(b)
$[\text{Ar}]6.6 \cdot 10^{-8} \exp(-47270/T)$	2200–3300	$(7.5–880) \cdot 10^{17}$	Holzrichter and Wagner, 1981 <sup>3</sup>	(c)
$[\text{Ar}]3.7 \cdot 10^{-8} \exp(-47036/T)$	1740–3300	$(2.5–3.5) \cdot 10^{18}$	Davidson <i>et al.</i> , 1990 <sup>4</sup>	(d)
$[\text{Ar}]2.5 \cdot 10^{-8} \exp(-46860/T)$	1800–2500	$(6.9–27) \cdot 10^{18}$	Naumann, Braun-Unkhoff, and Frank, 1997 <sup>5</sup>	(e)
<i>High Pressure Range</i>				
$5.5 \cdot 10^{15} \exp(-54240/T)$	2200–3300	$(7.5–880) \cdot 10^{17}$	Holzrichter and Wagner, 1981 <sup>3</sup>	(c)
<i>Reviews and Evaluations</i>				
$k_0[\text{Ar}] = [\text{Ar}]7.4 \cdot 10^{-9} \exp(-41560/T)$	2000–3000		CEC, 1994 <sup>6</sup>	(f)
$k_\infty = 8.3 \cdot 10^{15} \exp(-55170/T)$	2000–3000			
$F_c(\text{Ar}) = 0.58 \exp(-T/4581) + 0.42 \exp(-T/102)$	2000–3000			
$k_0[\text{Ar}] = [\text{Ar}]4.2 \cdot 10^{-8} \exp(-47200/T)$	1740–3450		Dean and Bozzelli, 2000 <sup>7</sup>	(g)

#### Comments

- (a) Shock tube study. Decay of  $[\text{NH}_3]$  monitored by UV absorption at 230–250 nm. Results indicate that the decomposition of  $\text{NH}_3$  is unimolecular.
- (b) Pyrolysis of  $\text{NH}_3$  behind reflected shock waves.  $[\text{NH}_3]$ ,  $[\text{NH}_2]$ ,  $[\text{NH}]$ , and  $[\text{N}_2]$  profiles measured during the reaction by mass spectrometry. Rate coefficient extracted from a computer simulation with 10 reactions.
- (c) Study of  $\text{NH}_3$  decomposition behind incident and reflected shocks. The rate coefficients were obtained from the initial slope of the  $[\text{NH}_2]$  decay as monitored by UV absorption.
- (d) Data from the shock tube study of Roose,<sup>8</sup> reported by Hanson and Salimian,<sup>9</sup> reevaluated on the basis of improved data for the reaction  $\text{H} + \text{NH}_3 \rightarrow \text{H}_2 + \text{NH}_2$ .
- (e) Shock tube study on  $\text{NH}_3/\text{Ar}$  mixtures using  $\text{NH}_3$  concentrations between 12 ppm and 1.1%.  $[\text{NH}_3]$  was monitored by vacuum UV spectroscopy,  $[\text{H}]$  by ARAS, and  $[\text{NH}_2]$  by absorption at 597 nm. All of the concentration profiles were modeled satisfactorily using a detailed mechanism.
- (f) See Comments on Preferred Values.
- (g) Based on the analysis of Davidson *et al.*<sup>4</sup> and Hanson and Salimian.<sup>9</sup>

#### Preferred Values

$$\begin{aligned}k_0 &= 3.1 \cdot 10^{-8} \exp(-46860/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ for M = Ar over the range 2000–3000 K.} \\ k_\infty &= 2.8 \cdot 10^{17} T^{-0.39} \exp(-55525/T) \text{ s}^{-1} \text{ over the range 2000–3000 K.} \\ F_c &= 0.58 \exp(-T/4581) + 0.42 \exp(-T/102) \text{ for M = Ar over the range 2000–3000 K.}\end{aligned}$$

#### Reliability

$$\begin{aligned}\Delta \log k_0 &= \pm 0.3 \text{ for M = Ar over the range 2000–3000 K.} \\ \Delta \log k_\infty &= \pm 0.5 \text{ over the range 2000–3000 K.} \\ \Delta F_c &= \pm 0.1 \text{ for M = Ar over the range 2000–3000 K.}\end{aligned}$$

#### Comments on Preferred Values

Most of the experimental studies have been carried out close to the low pressure limit of the reaction. Only the results of Holzrichter and Wagner<sup>3</sup> allow extrapolation to the high pressure limit, but with considerable uncertainty. Since the measurements of Naumann *et al.*<sup>5</sup> covered the largest concentration range and in their study the concentrations of the key species in the reaction were monitored, their data are preferred here. However, their data are corrected for some fall-off, corresponding to  $k/k_0 = 0.81$  at 2.75 bar and 2300 K. These results are a factor of 0.75 lower than those of Davidson *et al.*,<sup>4</sup> a factor of 0.95 being due to the use of higher

pressures. Fall-off curves were constructed with  $F_c$  having the value 0.35 at 2300 K and  $N=1.33$ .

The rate constants for the spin forbidden channel, Channel (1), are estimated to be about a factor of 40 less than those of Channel (2).<sup>2,10</sup>

## References

- <sup>1</sup>H. Henrici, Ph.D. thesis, Göttingen, Germany, 1966.  
<sup>2</sup>J. E. Dove and W. S. Nip, Can. J. Chem. **57**, 689 (1979).

<sup>3</sup>K. Holzrichter and H. G. Wagner, 18th Symp. (Int.) Combustion, 1981, p. 769.

<sup>4</sup>D. F. Davidson, K. Kohse-Höninghaus, A. Y. Chang, and R. K. Hanson, Int. J. Chem. Kinet. **22**, 513 (1990).

<sup>5</sup>C. Naumann, M. Braun-Unkhoff, and P. Frank, Proc. 21st Symp. Shock Tubes and Waves, 1997, Paper 4260.

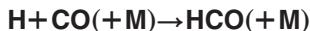
<sup>6</sup>CEC, Supplement 1, 1994 (see references in Introduction).

<sup>7</sup>A. M. Dean and J. W. Bozzelli, in *Combustion Chemistry II*, edited by W. C. Gardiner, Jr. (Springer, New York, 2000), p. 125.

<sup>8</sup>T. R. Roose, Ph.D. thesis, Stanford University, 1981.

<sup>9</sup>R. K. Hanson and S. Salimian, in *Combustion Chemistry*, edited by W. C. Gardiner, Jr. (Springer, New York, 1984), p. 361.

<sup>10</sup>J. Troe, J. Phys. Chem. **83**, 114 (1979).



### Thermodynamic Data

$$\Delta H_{298}^{\circ} = -64.3 \text{ kJ mol}^{-1}$$

$$\Delta S_{298}^{\circ} = -87.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c = 1.45 \cdot 10^{-25} T^{0.352} \exp(+7600/T) \text{ cm}^3 \text{ molecule}^{-1}$$

(300 ≤ T/K ≤ 5000)

See Section 3 for the source of the Thermodynamic Data.

### Rate Coefficient Data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	$[\text{M}]/\text{molecule cm}^{-3}$	Reference	Comments
<i>Rate Coefficient Measurements</i>				
<i>Low Pressure Range</i>				
$[\text{Ar}]7.2 \cdot 10^{-35}$	298	$(1.9-5.2) \cdot 10^{19}$	Hikida, Eyre, and Dorfman, 1971 <sup>1</sup>	(a)
$[\text{Ar}]5.3 \cdot 10^{-35}$	298	$(1.7-19) \cdot 10^{18}$	Ahumada, Michael, and Osbourne, 1972 <sup>2</sup>	(b)
$[\text{He}]4.7 \cdot 10^{-35}$	298	$(3.4-19) \cdot 10^{18}$		
<i>Reviews and Evaluations</i>				
$[\text{Ar}]5.3 \cdot 10^{-34} \exp(-370/T)$	300–2500		CEC, 1994 <sup>3</sup>	(c)

### Comments

- (a) H atoms generated by pulse radiolysis of  $\text{H}_2$  and monitored by Lyman- $\alpha$  absorption spectrophotometry.
- (b) H atoms generated by mercury photosensitized decomposition of  $\text{H}_2$  in the presence of an excess of CO. [H] was monitored by Lyman- $\alpha$  absorption spectrophotometry under steady state conditions and following the termination of the light pulse.
- (c) Value based on the recommendation for the reverse dissociation reaction,<sup>1</sup> converted to recombination using the equilibrium constant  $K_c = 2.07 \cdot 10^{-24} \times \exp(+7600/T) \text{ cm}^3 \text{ molecule}^{-1}$ . See Comments on Preferred Values.

### Comments on Preferred Values

The average of the results Hikida *et al.*<sup>1</sup> and Ahumada *et al.*<sup>2</sup> for  $\text{M}=\text{Ar}$  and the value from Ahumada *et al.*<sup>2</sup> for  $\text{M}=\text{He}$  are recommended for  $T=300 \text{ K}$ . Converting the results for HCO dissociation of Fredrichs *et al.*<sup>4</sup> for  $\text{M}=\text{Ar}$ , and of Krasnoperov *et al.*<sup>5</sup> for  $\text{M}=\text{He}$  near to 800 K, into values for the recombination rate constant, using the equilibrium constant, leads to the recommended temperature coefficients. A theoretical calculation of  $k_0$  by Qi and Bowman<sup>6</sup> is in good agreement with the results from Ahumada *et al.*<sup>2</sup>

### Preferred Values

$k_0 = 2.0 \cdot 10^{-35} T^{0.2} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  for  $\text{M}=\text{Ar}$  over the range 300–800 K.

$k_0 = 1.5 \cdot 10^{-36} T^{0.6} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  for  $\text{M}=\text{He}$  over the range 300–800 K.

### Reliability

$\Delta \log k_0 = \pm 0.3$  for  $\text{M}=\text{Ar}, \text{He}$  over the range 300–800 K.

### References

- <sup>1</sup>T. Hikida, J. A. Eyre, and L. M. Dorfman, J. Chem. Phys. **54**, 3422 (1971).
- <sup>2</sup>J. J. Ahumada, J. V. Michael, and D. T. Osborne, J. Chem. Phys. **57**, 3736 (1972).
- <sup>3</sup>CEC, Supplement I, 1994 (see references in Introduction).
- <sup>4</sup>G. Fredrichs, J. T. Herbon, D. F. Davidson, and R. K. Hanson, Phys. Chem. Chem. Phys. **4**, 5778 (2002).
- <sup>5</sup>L. N. Krasnoperov, E. N. Chesnekov, H. Stark, and A. R. Ravishankara (unpublished results), Presented at the 17th Int. Symp. on Gas Kinetics, Essen, 2002.
- <sup>6</sup>J. Qi and J. M. Bowman, J. Phys. Chem. **100**, 15165 (1996).

**HCO(+M)→H+CO(+M)***Thermodynamic Data*

$$\begin{aligned}\Delta H^\circ_{298} &= 64.3 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298} &= 87.8 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 6.87 \cdot 10^{24} T^{-0.352} \exp(-7600/T) \text{ molecule cm}^{-3} \\ &\quad (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{s}^{-1}$	T/K	[M]/molecule cm $^{-3}$	Reference	Comments
<i>Rate Coefficient Measurements</i>				
<i>Low Pressure Range</i>				
[Ar]2.6·10 $^{-10}$ exp(−7400/T)	1400–2200	(2.1–7.8)·10 $^{19}$	Schecker and Jost, 1969 <sup>1</sup>	(a)
[Ar]2.5·10 $^{-10}$ exp(−7340/T)	1700–2710	(2.4–4.5)·10 $^{18}$	Dean et al., 1979 <sup>2</sup>	(b)
[He]3.8·10 $^{-7}$ T $^{-1}$ exp(−8600/T)	637–832	(3.5–7.1)·10 $^{16}$	Timonen et al., 1987 <sup>3</sup>	(c)
[He]7.7·10 $^{-11}$ exp(−7820/T)	522–769	(1.0–1.5)·10 $^{19}$	Krasnoperov and Chesnekov, 2000 <sup>4</sup>	(d)
[He]3.7·10 $^{-11}$ exp(−7310/T)	522–583	1.0·10 $^{19}$	Krasnoperov et al., 2002 <sup>5</sup>	(e)
[Ar]6.6·10 $^{-11}$ exp(−7820/T)	835–1230	(0.2–1.5)·10 $^{19}$	Fredrichs et al., 2002 <sup>6</sup>	(f)
<i>Reviews and Evaluations</i>				
$k_0[\text{Ar}] = [\text{Ar}]2.6 \cdot 10^{-10} \exp(-7930/T)$	600–2500		CEC, 1992; 1994 <sup>7</sup>	(g)

**Comments**

- (a) Shock tube study of the thermal dissociation of HCHO. The reactant was monitored by UV absorption at 366 nm and by IR emission at 3.5  $\mu\text{m}$ .
- (b) Pyrolysis of 0.1%, 0.5%, and 1% mixtures of formaldehyde in Ar. HCHO monitored by IR emission at 3.5  $\mu\text{m}$  behind reflected shocks.
- (c) HCO radicals were generated by photodissociation of CH<sub>3</sub>CHO at 308 nm in a heatable tubular quartz reactor. The [HCO] decay was monitored using a photoionization mass spectrometer. The rates were measured from 637 to 832 K and extrapolated from 300 to 3000 K using an RRKM model adapted to treat the extremely sparse density of vibrational states of HCO.
- (d) Pulsed laser photolysis of acetaldehyde at 308 nm in a heatable high pressure flow reactor. [HCO] was monitored by absorption at 230 nm and 614.6 nm. Experiments with the He carrier gas at a density of 1.2 · 10 $^{21}$  molecule cm $^{-3}$  showed only minor deviations from the low pressure limit.
- (e) Technique as in (d) but cavity ring down spectroscopy used for detection. Rate data from this work were combined with those from Krasnoperov and Chesnekov<sup>4</sup> for  $T \geq 600$  K.
- (f) HCO generated by 308 nm photolysis of HCHO behind reflected shock waves in HCHO/Ar mixtures. [HCO] monitored by molecular modulation spectroscopy.
- (g) Based on the data of Schecker and Jost,<sup>1</sup> Dean et al.,<sup>2</sup> and Timonen et al.,<sup>3</sup> as analyzed by Troe.<sup>8</sup>

**Preferred Values**

$$k_0 = 6.6 \cdot 10^{-11} \exp(-7820/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ for M} = \text{Ar} \text{ over the range } 500\text{--}2500 \text{ K.}$$

**Reliability**

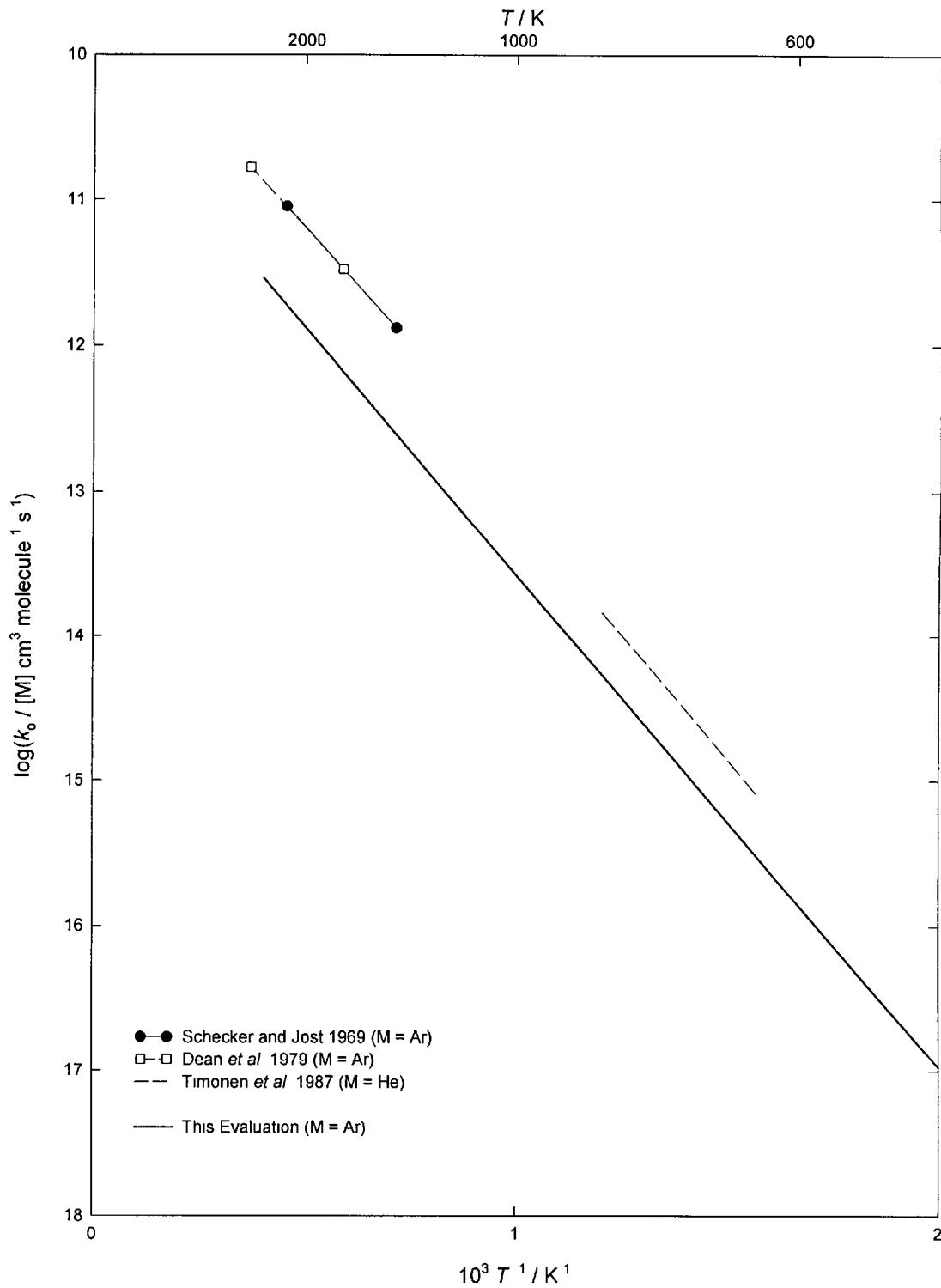
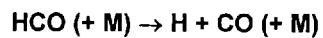
$$\Delta \log k_0 = \pm 0.3 \text{ for M} = \text{Ar} \text{ over the range } 500\text{--}2500 \text{ K.}$$

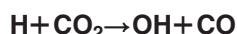
**Comments on Preferred Values**

The most sensitive measurements and the most directly obtained data are those of Fredrichs et al.,<sup>6</sup> which are preferred. They extrapolate to the lowest of the values derived at higher temperatures from more complicated reaction mechanisms. Even up to 100 bar the reaction is still close to the low pressure limit. The theoretical analysis by Troe<sup>8</sup> leads to collision efficiencies of 0.05 between 600 and 2500 K. The system may show unusual fall-off behavior because of its low density of vibrational states and its isolated resonances (see Wagner and Bowman<sup>9</sup>).

**References**

- <sup>1</sup>H. G. Schecker and W. Jost, Ber. Bunsenges. Phys. Chem. **73**, 521 (1969).
- <sup>2</sup>A. M. Dean, B. L. Craig, R. L. Johnson, M. C. Schultz, and E. E. Wang, 17th Symp. (Int.) Combustion, 1979, p. 577.
- <sup>3</sup>R. S. Timonen, E. Ratajczak, D. Gutman, and A. F. Wagner, J. Phys. Chem. **91**, 5325 (1987).
- <sup>4</sup>L. N. Krasnoperov and E. N. Chesnekov (unpublished results), Presented at the 16th Int. Symp. on Gas Kinetics, Cambridge, 2002.
- <sup>5</sup>L. N. Krasnoperov, E. N. Chesnekov, H. Stark, and A. R. Ravishankara (unpublished results), Presented at the 17th Int. Symp. on Gas Kinetics, Essen, 2002.
- <sup>6</sup>G. Fredrichs, J. T. Herbon, D. F. Davidson, and R. K. Hanson, Phys. Chem. Chem. Phys. **4**, 5778 (2002).
- <sup>7</sup>CEC, 1992; CEC, Supplement I, 1994 (see references in Introduction).
- <sup>8</sup>J. Troe, J. Chem. Phys. **66**, 4758 (1977).
- <sup>9</sup>A. F. Wagner and J. M. Bowman, J. Phys. Chem. **91**, 5314 (1987).



*Thermodynamic Data*

$$\begin{aligned}\Delta H_{298}^{\circ} &= 102.2 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= 52.9 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 2.12 \cdot 10^6 T^{-1.163} \exp(-12760/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
<i>Low Pressure Range</i>			
$5.0 \cdot 10^{-9} \exp(-16757/T)$	1217–1345	Fenimore and Jones, 1958 <sup>1</sup>	(a)
$1.4 \cdot 10^{-15}$	1072	Dixon-Lewis, Sutton, and Williams, 1965 <sup>2</sup>	(b)
$1.8 \cdot 10^{-10} \exp(-12530/T)$	2050–2920	Just and Stepanek, 1969 <sup>3</sup>	(c)
$1.7 \cdot 10^{-10} \exp(-12178/T)$	1023–1523	Kochubei and Moin, 1969 <sup>4</sup>	(d)
$2.1 \cdot 10^{-10} \exp(-13084/T)$	1173–1373	Shub, Apel'baum, and Temkin, 1970 <sup>5</sup>	(e)
$2.2 \cdot 10^{-15}$	1050	Eberius, Hoyermann, and Wagner, 1971 <sup>6</sup>	(f)
$1.7 \cdot 10^{-10} \exp(-12000/T)$	1450–1820	Wintergerst and Frank, 1993 <sup>7</sup>	(g)
$3.3 \cdot 10^{-10} \exp(-13500/T)$	2170–3150	Lissianski <i>et al.</i> , 1995 <sup>8</sup>	(h)
<i>Reviews and Evaluations</i>			
$2.5 \cdot 10^{-10} \exp(-13300/T)$	1000–3000	Baulch <i>et al.</i> , 1976 <sup>9</sup>	(i)
$2.7 \cdot 10^{-10} \exp(-13230/T)$	1000–3000	Warnatz, 1984 <sup>10</sup>	(j)
$2.5 \cdot 10^{-10} \exp(-13300/T)$	1000–3000	Tsang and Hampson, 1986 <sup>11</sup>	(k)

**Comments**

- (a) Flame study of  $\text{H}_2/\text{O}_2/\text{CO}_2$  mixtures at a total pressure of 1 bar Ar. [H] in the post-flame gases was determined by monitoring the formation of HD in the reaction  $\text{H} + \text{D}_2\text{O} \rightarrow \text{HD} + \text{OD}$  by mass spectrometry.
- (b) Flame study of  $\text{H}_2/\text{O}_2/\text{N}_2$  mixtures with trace amounts of  $\text{CO}_2$  at 1 bar. [H] determined in post-flame gases using the reaction  $\text{H} + \text{D}_2\text{O} \rightarrow \text{HD} + \text{OD}$  and mass spectrometric analysis of OD.
- (c) Shock tube study of  $\text{H}_2/\text{CO}_2/\text{Ar}$  mixtures. [ $\text{CO}_2$ ] decay monitored by IR emission at  $4.3 \mu\text{m}$  and interpreted with the mechanism  $\text{H} + \text{CO}_2 \rightarrow \text{OH} + \text{CO}$ ,  $\text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H}$ , and  $\text{H}_2(+\text{M}) \rightarrow \text{H} + \text{H}(+\text{M})$ .
- (d) Flow system study of  $\text{H}_2/\text{CO}_2$  mixtures at atmospheric pressure. Analysis of the reactants by gas chromatography and of the products by gravimetric methods. H atoms and  $\text{H}_2$  assumed to be in equilibrium via  $\text{H}_2(+\text{M}) \rightleftharpoons \text{H} + \text{H}(+\text{M})$ .
- (e) Flow system study of either  $\text{CO}/\text{H}_2\text{O}/\text{N}_2$  or  $\text{CO}_2/\text{H}_2/\text{N}_2$  mixtures at atmospheric pressure. H atoms assumed to be in equilibrium with  $\text{H}_2$ . Rate data extracted from the following reaction mechanism:  $\text{H} + \text{CO}_2 \rightleftharpoons \text{OH} + \text{CO}$  and  $\text{H}_2 + \text{OH} \rightleftharpoons \text{H}_2\text{O} + \text{H}$ .  $\text{H}_2\text{O}$  vapor determined by condensing and measuring volumetrically, the other gases were determined by gas chromatography.
- (f) Flame study of fuel rich  $\text{H}_2/\text{O}_2$  mixtures with added  $\text{CO}_2$ . [H] decay followed by electron spin resonance and the formation of OH by UV absorption spectroscopy.

- (g) Shock wave study. H atoms generated by thermal decomposition of  $\text{C}_2\text{H}_5\text{I}$  (0.2–3 ppm) in Ar. H and iodine atoms monitored by ARAS.
- (h) Shock wave study of  $\text{N}_2\text{O}/\text{H}_2/\text{CO}_2$  mixtures; [OH] was monitored by absorption at 309.4 nm. Additional experiments were carried out measuring the inhibiting effect of  $\text{CO}_2$  on the ignition of  $\text{CH}_4/\text{O}_2/\text{CO}_2$  mixtures by monitoring total light emission and pressure. Both methods lead to concordant results.
- (i) Based on the rate coefficient  $\log(k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = (-12.95 + 3.94 \cdot 10^{-4}T)$  for the reverse reaction  $\text{OH} + \text{CO} \rightarrow \text{H} + \text{CO}_2$  and the equilibrium constant. The recommended values are in good agreement with those of Just and Stepanek<sup>3</sup> and Shub, Apel'baum, and Temkin.<sup>5</sup>
- (j) Review of the literature data up to 1979.
- (k) Adopted the values recommended by Warnatz.<sup>10</sup>

**Preferred Values**

$$k = 4.7 \cdot 10^{-10} \exp(-13915/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad \text{over the range } 1000\text{--}3000 \text{ K.}$$

*Reliability*

$$\Delta \log k = \pm 0.2 \text{ over the range } 1000\text{--}3000 \text{ K.}$$

*Comments on Preferred Values*

The mechanism of this reaction is the reverse of that for the  $\text{OH} + \text{CO}$  reaction (see data sheet) and involves the initial formation of the energized intermediate ( $\text{HO}^{\bullet}\text{CO}$ ) which

may decompose back to reactants, decompose to give OH + CO, or may be collisionally stabilized. Because of the extensive measurements of the reverse reactions and their high internal consistency, we prefer to use the rate coefficients of the reverse reaction OH + CO → H + CO<sub>2</sub> in the low pressure range and convert them with the equilibrium constant above. Here we have chosen to use the results of Wooldridge *et al.*<sup>12</sup> The older<sup>1–6</sup> and the newer<sup>7,8</sup> direct measurements of *k* are fully consistent with these preferred values.

## References

- <sup>1</sup>C. P. Fenimore and G. W. Jones, J. Phys. Chem. **62**, 1578 (1958).  
<sup>2</sup>G. Dixon-Lewis, M. M. Sutton, and A. Williams, 10th Symp. (Int.) Combustion, 1965, p. 495.  
<sup>3</sup>Th. Just and S. Stepanek, 7th Symp. (Int.) Combustion, 1969, p. 626.

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<sup>5</sup>F. S. Shub, L. O. Apel'baum, and M. I. Temkin, Kinet. Catal. **11**, 462 (1970).

<sup>6</sup>K. H. Eberius, K. Hoyermann, and H. Gg. Wagner, 13th Symp. (Int.) Combustion, 1971, p. 713.

<sup>7</sup>K. Wintergerst and P. Frank, 19th Int. Symp. Shock Tubes and Waves, 1993.

<sup>8</sup>V. Lissianski, H. Yang, Z. Qin, M. R. Mueller, K. S. Shin, and W. C. Gardiner, Jr., Chem. Phys. Lett. **240**, 57 (1995).

<sup>9</sup>D. L. Baulch, D. D. Drysdale, J. Duxbury, and S. J. Grant, *Evaluated Kinetic Data for High Temperature Reactions*, Vol. 3, Homogeneous Gas Phase Reactions of the O<sub>2</sub>–O<sub>3</sub> System, the CO–O<sub>2</sub>–H<sub>2</sub> System and of Sulphur-containing Species (Butterworths, London, 1976).

<sup>10</sup>J. Warnatz, in *Combustion Chemistry*, edited by W. C. Gardiner, Jr. (Springer, New York, 1984).

<sup>11</sup>W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data **15**, 1087 (1986).

<sup>12</sup>M. S. Wooldridge, R. K. Hanson, and C. T. Bowman, Int. J. Chem. Kinet. **28**, 361 (1996).



### Thermodynamic Data

$$\Delta H^{\circ}_{298}(1) = -99.0 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298}(1) = 32.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 2.07 \cdot 10^5 T^{-1.223} \exp(+11480/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^{\circ}_{298}(2) = 39.3 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298}(2) = 16.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 1.32 \cdot 10^2 T^{-0.454} \exp(-4830/T) \\ (300 \leq T/\text{K} \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

### Rate Coefficient Data (*k*=*k*<sub>1</sub>+*k*<sub>2</sub>)

<i>k</i> /cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	<i>T</i> /K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
1.74 · 10 <sup>-10</sup> exp(-1000/ <i>T</i> )	1400–1500	Louge and Hanson, 1984 <sup>1</sup>	(a)
2.2 · 10 <sup>-11</sup>	295	Becker <i>et al.</i> , 2000 <sup>2</sup>	(b)
3.8 · 10 <sup>-11</sup>	548		
<i>Reviews and Evaluations</i>			
<i>k</i> <sub>1</sub> =8.9 · 10 <sup>-11</sup>	500–2500	Tsang, 1992 <sup>3</sup>	(c)
<i>k</i> <sub>2</sub> =1.1 · 10 <sup>-13</sup> <i>T</i> <sup>0.9</sup> exp(-6700/ <i>T</i> )			
<i>k</i> <sub>1</sub> =8.7 · 10 <sup>-11</sup>	1400–1500	CEC, 1992; 1994 <sup>4</sup>	(d)

### Comments

- (a) Shock tube study on C<sub>2</sub>N<sub>2</sub>/O<sub>2</sub>/N<sub>2</sub>O mixtures. [NCO] monitored by time resolved absorption at 440.5 nm. Rate constants deduced by kinetic modeling.
- (b) Pulsed laser photolysis at 248 nm of CINCO/Ar mixtures at a total pressure of 3.4 mbar in the presence of an excess of H atoms produced by a discharge in H<sub>2</sub>/Ar mixtures. [NCO] was monitored by time-resolved LIF at 438.6 nm.
- (c) The value for *k*<sub>1</sub> is derived from the expression of Louge and Hanson<sup>1</sup> and *k*<sub>2</sub> is obtained from data on the reverse reaction and thermodynamic data, which are superseded by more recent values.
- (d) Derived from the data of Louge and Hanson.<sup>1</sup>

### Preferred Values

*k*<sub>1</sub>=1.2 · 10<sup>-10</sup> exp(-500/*T*) cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> over the range 295–1500 K.

*k*<sub>2</sub>=4.4 · 10<sup>-14</sup> *T*<sup>1.02</sup> exp(-8630/*T*) cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> over the range 500–2500 K.

### Reliability

Δ log *k*<sub>1</sub>=±0.3 at 295 K, rising to ±0.5 at 1500 K.

Δ log *k*<sub>2</sub>=±0.7 over the range 500–2500 K.

### Comments on Preferred Values

The most direct determinations of *k* are given in the Table. The rate constant appears to be virtually independent of temperature as the values of *k* in the two studies cited<sup>1,2</sup> prob-

ably fall within their combined error limits. The preferred expression is a fit to the data from the two studies and is assigned to  $k_1$  (see below). Other values of  $k$  that have been quoted in the literature<sup>5–8</sup> are estimated, or come from the study of systems relatively insensitive to the value of  $k$ , and are not used in this evaluation.

Direct evidence for the occurrence of Channel (1) comes from the observation of  $\text{NH}(X^3\Sigma)$  formation in a molecular beam study.<sup>9</sup> Channel (2) is relatively unimportant except at the highest temperatures. Tsang<sup>2</sup> derived an expression for  $k_2$  from kinetic data on the reverse reaction and thermodynamic data. Since then there have been substantial corrections to the thermochemistry of the reaction and the expression given in this evaluation is derived from the expression for  $k(\text{O} + \text{HCN})$  from the present evaluation and the more recent

thermodynamic data. There is no evidence for the occurrence of the other exothermic channel giving  $\text{N} + \text{CO}_2$ .

<sup>1</sup> M. Y. Louge and R. K. Hanson, Combust. Flame **58**, 291 (1984).

<sup>2</sup> K. H. Becker, R. Kurtenbach, F. Schmidt and P. Wiesen, Combust. Flame **120**, 570 (2000).

<sup>3</sup> W. Tsang, J. Phys. Chem. Ref. Data **21**, 753 (1992).

<sup>4</sup> CEC, 1992; Supplement I, 1994 (see references in Introduction).

<sup>5</sup> J. N. Mulvihill and L. F. Phillips, 15th Symp. (Int.) Combustion, 1975, p. 113.

<sup>6</sup> W. M. Shaub and S. H. Bauer, Combust. Flame **32**, 35 (1978).

<sup>7</sup> P. Roth, R. Löhr, and H. D. Hermanns, Ber. Bunsenges. Phys. Chem. **84**, 835 (1980).

<sup>8</sup> J. M. Beer, M.-T. Jaques, W. Farmayan, and B. R. Taylor, 18th Symp. (Int.) Combustion, 1981, p. 101.

<sup>9</sup> E. Quinones, J. Chen, and P. J. Dagdigian, Chem. Phys. Lett. **174**, 65 (1990).



#### Thermodynamic Data

$$\Delta H_{298}^o(1) = -23.0 \text{ kJ mol}^{-1}$$

$$\Delta S_{298}^o(1) = 38.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 1.07 \cdot 10^6 T^{-1.355} \exp(+2320/T) \\ (300 \leq T/\text{K} \leq 4000)$$

$$\Delta H_{298}^o(2) = 25.0 \text{ kJ mol}^{-1}$$

$$\Delta S_{298}^o(2) = 9.39 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 24.0240 T^{-0.275} \exp(-3160/T) \\ (300 \leq T/\text{K} \leq 4000)$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$k_1 = 3.5 \cdot 10^{-10} \exp(-8500/T)$	2340–3270	Mertens <i>et al.</i> , 1991 <sup>1</sup>	(a)
$k_2 = 9.12 \cdot 10^{-10} \exp(-13700/T)$	2260–3250	Mertens and Hanson, 1996 <sup>2</sup>	(b)
<i>Reviews and Evaluations</i>			
$k_1 = 5 \cdot 10^{-11} \exp(-2300/T)$	1000	Tsang, 1992 <sup>3</sup>	(c)
$k_2 = 4.8 \cdot 10^{-17} T^{1.81} \exp(-8332/T)$	500–1000	CEC, 1992; 1994 <sup>4</sup>	(d)

#### Comments

- (a) Shock tube studies on the pyrolysis of 0.5%–2.0% HNCO in 274–780 mbar Argon.  $[\text{NH}_2]$  monitored by time-resolved narrow line laser absorption at 597 nm and  $[\text{HNCO}]$  by time resolved infrared emission near 5  $\mu\text{m}$ . Rate constants were obtained from computer simulation of the temporal profile of  $[\text{NH}_2]$ .
- (b) Studies using shock heated mixtures of 701–1186 mbar Argon containing 0.2000%–0.998% HNCO.  $[\text{NCO}]$  monitored by time-resolved cw laser absorption at 440 nm. The experimental results were combined with the lower temperature results from two previous studies for the reverse reaction<sup>5,6</sup> to derive the expression  $k_2 = 1.49 \cdot 10^{-16} T^{1.66} \exp(-7000/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .
- (c) The expression for  $k_2$  was based on the rate data of the reverse reaction and the thermodynamics. The expres-

sion reflects older, now superseded, thermodynamic data. The expression for  $k_1$ , for the addition-displacement reaction, was based on the lower temperature results of Le Bras and Combourieu<sup>7</sup> for hydrogen atom attack on  $\text{N}_3\text{H}$ .

- (d) Recommendation based on  $k(\text{H}_2 + \text{NCO})$  from Perry<sup>5</sup> and the thermodynamics. Since then there has been large changes in the accepted heat of formation of NCO.

#### Preferred Values

$k_1 = 5.96 \cdot 10^{-20} T^{2.49} \exp(-1180/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 500–3300 K.

$k_2 = 1.49 \cdot 10^{-16} T^{1.66} \exp(-7000/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 500–3300 K.

### Reliability

$\Delta \log k_1 = \pm 1$  at 500 K, decreasing to  $\pm 0.4$  over the range 2000–3300 K.

$\Delta \log k_2 = \pm 1$  at 500 K, decreasing to  $\pm 0.4$  over the range 2000–3300 K.

### Comments on Preferred Values

The only data available for our previous evaluations<sup>4</sup> had been obtained indirectly<sup>5,6–8</sup> and was widely scattered. Since then the measurements of Mertens *et al.*<sup>1</sup> and Mertens and Hanson<sup>2</sup> appear to have produced reliable high temperature results for both channels (1) and (2). At low temperatures, the only available values of  $k_1$  and  $k_2$  are derived from values of the rate constants for the reverse reactions<sup>5,8</sup> and the thermodynamic data. These values have also been plotted on the Arrhenius diagram.

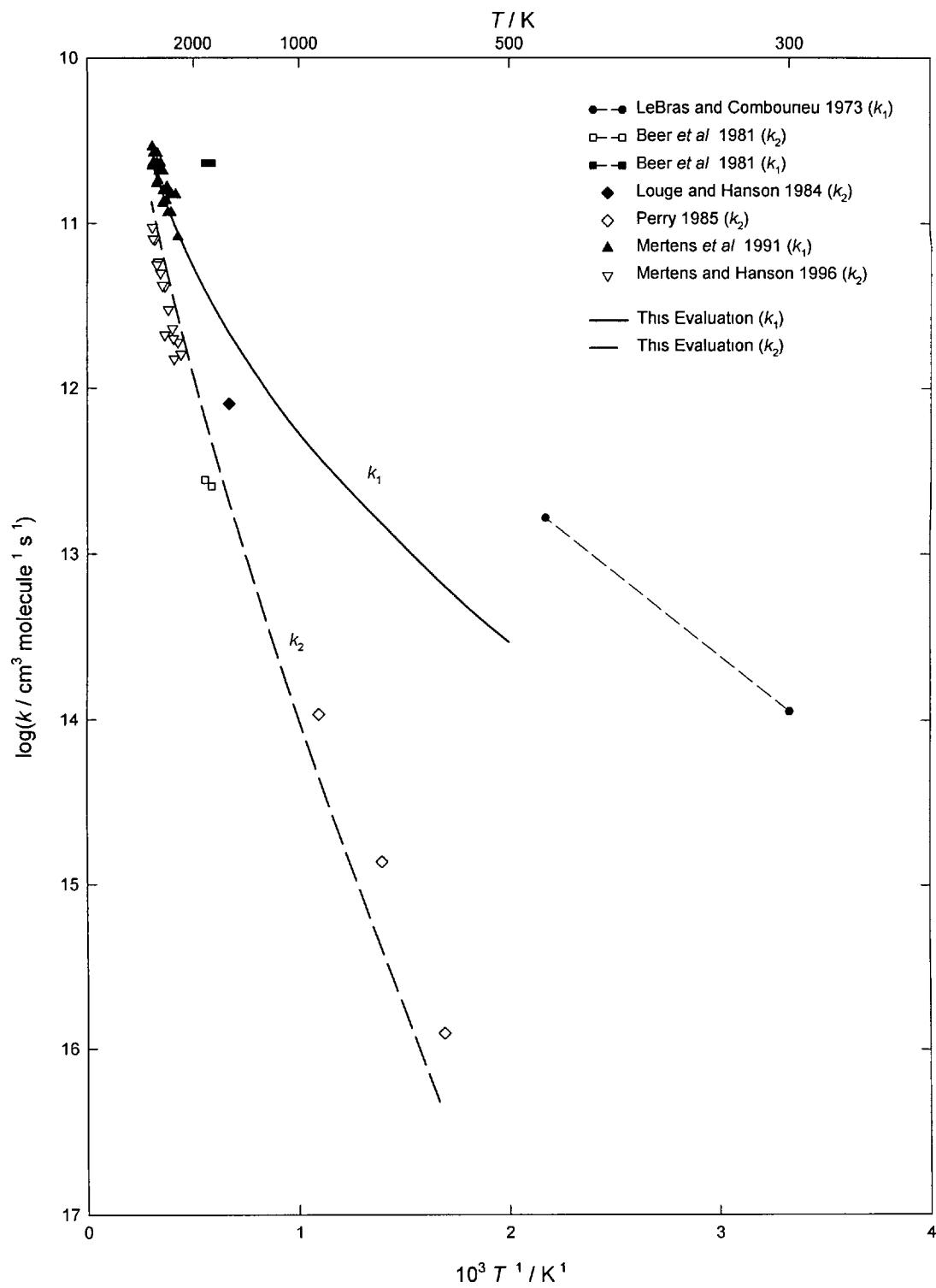
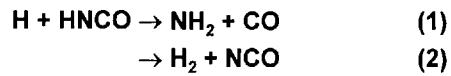
There has also been a recent theoretical study, by Nguyen *et al.*,<sup>9</sup> involving *ab initio* calculations based on Gaussian 92, which gives an expression for  $k_2$  which is very similar to the expression obtained by Mertens and Hanson<sup>2</sup> by combining their high temperature results with those of Perry<sup>5</sup> at lower temperatures. Our preferred expression for  $k_2$  is based on these two expressions.<sup>2,9</sup> The expression for  $k_1$  derived theo-

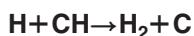
retically by Nguyen *et al.*<sup>9</sup> also reproduces the high temperature results of Mertens *et al.*<sup>1</sup> for  $k_1$  and, in the absence of reliable experimental data for the branching ratios over a wide temperature range, we use the expression derived by Nguyen *et al.*<sup>9</sup> as our preferred expression for  $k_1$ , but with substantial error limits.

A third channel, forming C(O)NH<sub>2</sub>, is also possible but it is clear that it cannot make an appreciable contribution under combustion conditions.

### References

- <sup>1</sup>J. D. Mertens, K. Kohse-Höinghaus, R. K. Hanson, and C. T. Bowman, Int. J. Chem. Kinet. **23**, 655 (1991).
- <sup>2</sup>J. D. Mertens and R. K. Hanson, 26th Symp. (Int.) Combustion, 1996, Vol. 26, p. 551.
- <sup>3</sup>W. Tsang, J. Phys. Chem. Ref. Data **21**, 753 (1992).
- <sup>4</sup>CEC, 1992; Supplement I, 1994 (see references in Introduction).
- <sup>5</sup>R. A. Perry, J. Chem. Phys. **82**, 12 (1985).
- <sup>6</sup>M. Y. Louge and R. K. Hanson, Combust. Flame **58**, 291 (1984).
- <sup>7</sup>G. Le Bras and J. Combourieu, Int. J. Chem. Kinet. **5**, 559 (1973).
- <sup>8</sup>J. M. Beer, M. T. Jacques, and B. R. Taylor, 8th Symp. (Int.) Combustion, 1981, p. 101.
- <sup>9</sup>M. T. Nguyen, D. Sengupta, L. Vereecken, J. Peeters, and L. G. Vanquickenborne, J. Phys. Chem. **100**, 1615 (1996).



*Thermodynamic Data*

$$\begin{aligned}\Delta H_{298}^{\circ} &= -97.7 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= -8.93 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 3.73 T^{-0.325} \exp(+11580/T) \\ (300 \leqslant T/\text{K} \leqslant 5000)\end{aligned}$$

See Section 3 for the origin source of the Thermodynamic Data

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$1.4 \cdot 10^{-11}$	297	Becker <i>et al.</i> , 1989 <sup>1</sup>	(a)

**Comments**

- (a) Excimer laser photolysis at 248 nm of  $\text{CH}_2\text{Br}_2$  or  $\text{CHClBr}_2$  in Ar/H<sub>2</sub> mixtures. [CH] monitored by LIF. Pseudo-first-order analysis of [CH] decay used, taking into account the contribution of the  $\text{CH} + \text{H}_2$  reaction.  $k$  found to be independent of total pressure over the range 2.6–16 mbar.

**Preferred Values**

$$k = 2.0 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the range } 1500\text{--}2500 \text{ K}$$

*Reliability*

$$\Delta \log k = \pm 0.6 \text{ over the range } 1500\text{--}2500 \text{ K.}$$

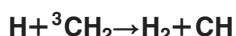
*Comments on Preferred Values*

The only direct measurement of  $k$  is that of Becker *et al.*<sup>1</sup>

at 297 K. They suggest that this reaction is a primary source of C atoms in flames. At higher temperatures, however, the rate constant of the reverse reaction has been measured in a shock-tube study by Dean *et al.*<sup>2</sup> They obtain the expression  $k(\text{C} + \text{H}_2) = 6.6 \cdot 10^{-10} \exp(-11700/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 1525–2540 K. When this is combined with the thermodynamic data for the reaction a value of  $k = 2 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  is obtained at 2000 K, which is taken as the preferred value but with substantial error limits.

**References**

- <sup>1</sup>K. H. Becker, B. Engelhardt, P. Wiesen, and K. D. Bayes, Chem. Phys. Lett. **154**, 342 (1989).  
<sup>2</sup>A. J. Dean, D. F. Davidson, and R. K. Hanson, J. Phys. Chem. **95**, 183 (1991).

*Thermodynamic Data*

$$\begin{aligned}\Delta H_{298}^{\circ} &= -11.96 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= 4.02 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 2.97 T^{-0.061} \exp(+1355/T) \\ (300 \leqslant T/\text{K} \leqslant 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$5.0 \cdot 10^{-11}$	1500–2570	Löhr and Roth, 1981 <sup>1</sup>	(a)
$2.7 \cdot 10^{-10}$	298	Böhland and Temps, 1984 <sup>2</sup>	(b)
$1.3 \cdot 10^{-11}$	2000–2800	Frank, Bhaskaran, and Just, 1986 <sup>3</sup>	(c)
$1.8 \cdot 10^{-10}$	298	Böhland, Temps, and Wagner, 1987 <sup>4</sup>	(d)
$2.7 \cdot 10^{-10}$	298	Boullart and Peeters, 1992 <sup>5</sup>	(e)
$3.8 \cdot 10^{-10} \exp(-1.3 \cdot 10^{-3}T)$	400–950	Devriendt <i>et al.</i> , 1995 <sup>6</sup>	(f)
$2.3 \cdot 10^{-10}$	2200–2600	Röhrig <i>et al.</i> , 1997 <sup>7</sup>	(g)
<i>Reviews and Evaluations</i>			
$1.0 \cdot 10^{-11} \exp(900/T)$	300–3000	CEC, 1992; 1994 <sup>8</sup>	(h)

### Comments

- (a) Analysis of H atom concentration profiles obtained using ARAS in shock heated  $\text{C}_2\text{H}_2/\text{O}_2/\text{Ar}$  mixtures.
- (b) Discharge flow study with LMR detection of  ${}^3\text{CH}_2$ . H produced from a discharge through  $\text{H}_2$ , and  ${}^3\text{CH}_2$  by a discharge through ketene.
- (c) Absorption spectroscopy study of [H] and [CO] following thermal dissociation of dilute ketene in argon behind reflected shocks.
- (d) Discharge flow study with LMR detection of  ${}^3\text{CH}_2$ . H produced from discharge through  $\text{H}_2$  and monitored by Lyman- $\alpha$  absorption.  ${}^3\text{CH}_2$  produced by pulsed laser photolysis of ketene at 193 nm.
- (e) Discharge flow study of the  $\text{O} + \text{C}_2\text{H}_2$  reaction with molecular beam mass-spectrometric analysis of products. The effect of varying the  $[\text{H}]/[\text{O}]$  ratio on  $[{}^3\text{CH}_2]$  in the steady state was determined leading to a value of  $k$  relative to  $k({}^3\text{CH}_2 + \text{O})$ . A value of  $k({}^3\text{CH}_2 + \text{O}) = 1.3 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was used, similar to the value obtained in the present evaluation.
- (f) As in note (e), except that  $\text{O} + \text{CH}_2\text{CO}$  was also used as a source of  ${}^3\text{CH}_2$ .
- (g) Shock tube study using reflected shocks in  $\text{C}_2\text{H}_6/\text{O}_2/\text{Ar}$  mixtures.  $[\text{CH}]$  was monitored by narrow linewidth laser absorption spectroscopy at 431.131 nm. Values of  $k$  were derived from simulation of the  $[\text{CH}]$  profiles using a detailed mechanism.  $k$  could only be determined to within a factor of 10 because of uncertainties in other rate coefficients in the mechanism.
- (h) Based on Refs. 3 and 4.

### Preferred Values

$k = 2.0 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 298–3000 K.

### Reliability

$\Delta \log k = \pm 0.3$  at 298 K, rising to 1.0 at 3000 K.

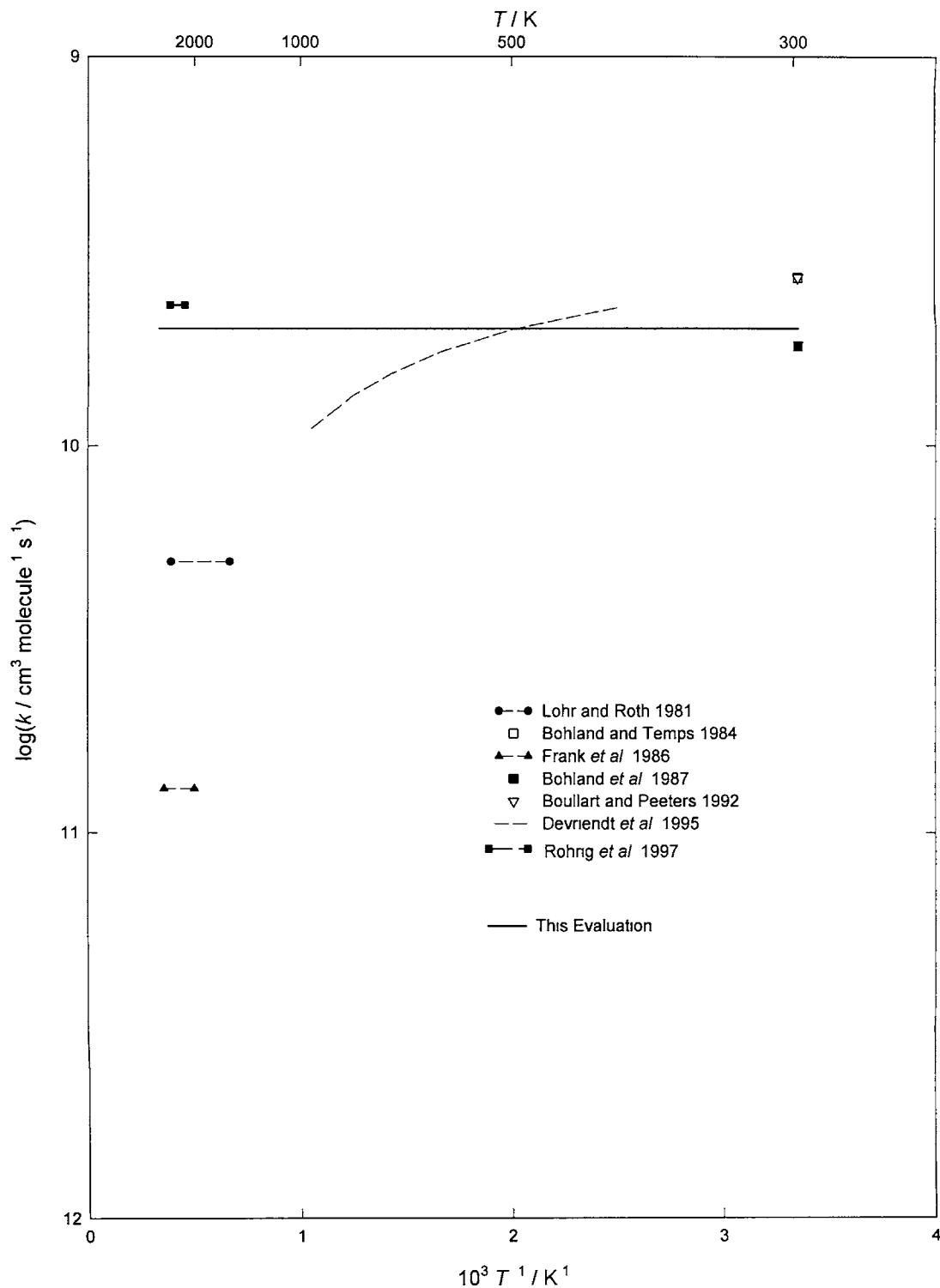
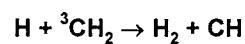
### Comments on Preferred Values

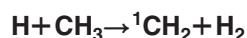
The data at low temperatures are in good agreement although it is not certain whether the rate constant has a small negative or a small positive temperature coefficient. In our previous evaluations, the 298 K value was based on the study of Böhland *et al.*<sup>4</sup> but Devriendt *et al.*<sup>6</sup> have suggested that the value of Böhland *et al.*<sup>4</sup> may be an underestimate because of the regeneration of  ${}^3\text{CH}_2$  from the reaction of  $\text{HCCO}$  with H atoms formed in the 193 nm photolysis of  $\text{CH}_2\text{CO}$ . Devriendt *et al.*<sup>6</sup> found a decrease in  $k$  with increase of temperature and proposed an abnormal  $T$  dependence (see Table). However, from their study of the reverse reaction, Fulle and Hippler<sup>9</sup> derive the expression,  $k = 3.5 \cdot 10^{-11} T^{0.32} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  in which  $k$  has a small positive temperature dependence.

At high temperatures the data range over an order of magnitude. For our preferred expression we have recommended a temperature independent value of  $k$ , which is compatible with the low and high temperature data within the substantial error limits proposed.

### References

- <sup>1</sup>R. Lohr and P. Roth, Ber. Bunsenges. Phys. Chem. **85**, 153 (1981).
- <sup>2</sup>T. Böhland and F. Temps, Ber. Bunsenges. Phys. Chem. **88**, 459 (1984).
- <sup>3</sup>P. Frank, K. A. Bhaskaran, and Th. Just, J. Phys. Chem. **90**, 2226 (1986).
- <sup>4</sup>T. Böhland, F. Temps, and H. Gg. Wagner, J. Phys. Chem. **91**, 1205 (1987).
- <sup>5</sup>W. Boullart and J. Peeters, J. Phys. Chem. **96**, 9810 (1992).
- <sup>6</sup>K. Devriendt, W. Van Poppel, W. Boullart, and J. Peeters, J. Phys. Chem. **99**, 16953 (1995).
- <sup>7</sup>M. Röhrig, E. L. Petersen, D. F. Davidson, R. K. Hanson, and C. T. Bowman, Int. J. Chem. Kinet. **29**, 781 (1997).
- <sup>8</sup>CEC, 1992; Supplement I, 1994 (see references in Introduction).
- <sup>9</sup>D. Fulle and H. Hippler, J. Chem. Phys. **106**, 8691 (1997).





#### Thermodynamic Data

$$\begin{aligned}\Delta H^\circ_{298} &= 63.93 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298} &= 10.74 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 2.38 \cdot 10^2 T^{-0.563} \exp(-7996/T) \\ &\quad (300 \leq T/\text{K} \leq 4000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$3.0 \cdot 10^{-10} \exp(-7580/T)$	1700–2300	Bhaskaran, Frank, and Just, 1980 <sup>1</sup>	(a)
$1.7 \cdot 10^{-11}$	1810	Langley and Burgess, 1989 <sup>2</sup>	(b)
$4.1 \cdot 10^{-10} \exp(-6884/T)$	1850–2100	Davidson <i>et al.</i> , 1995 <sup>3</sup>	(c)
<i>Reviews and Evaluations</i>			
$1.0 \cdot 10^{-10} \exp(-7600/T)$	300–2500	CEC, 1992; 1994 <sup>4</sup>	(d)

#### Comments

- (a) Shock tube study of methane decomposition using ARAS to monitor [H].
- (b) Studies on premixed, fuel rich methane/oxygen/argon flames with molecular beam sampling and mass spectrometric detection. Under the experimental conditions the  $\text{H} + \text{CH}_3$  reaction was the major removal reaction for  $\text{CH}_3$ .
- (c) Shock tube study on methyl iodide/argon and ethane/argon mixtures. Time resolved detection of  $\text{CH}_3$  by narrow line laser absorption at 216.615 nm. The methyl decay was dominated by recombination to form ethane, with some contributions from the  $\text{H} + \text{C}_2\text{H}_5$  channel. Over a limited range of  $T$ , deviations from  $\text{CH}_3$  second order kinetics could be ascribed to Channel (1). The fitted rate coefficient was that for the reverse reaction  ${}^1\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_3 + \text{H}$ , which was assumed independent of  $T$  over the range covered; the best fit value was  $2.2 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  which is to be compared with the value of  $9 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  recommended for rather lower temperatures in the present evaluation.
- (d) Based on the data for the reverse reaction and that of Bhaskaran *et al.*<sup>1</sup>

#### Preferred Values

$k = 2.1 \cdot 10^{-8} T^{-0.56} \exp(-8000/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 300–2500 K.

#### Reliability

$\Delta \log k = \pm 0.15$  over the range 300–1000 K,  $\pm 0.3$  over the range 1000–1700 K, and  $\pm 0.2$  over the range 1700–2500 K.

#### Comments on Preferred Values

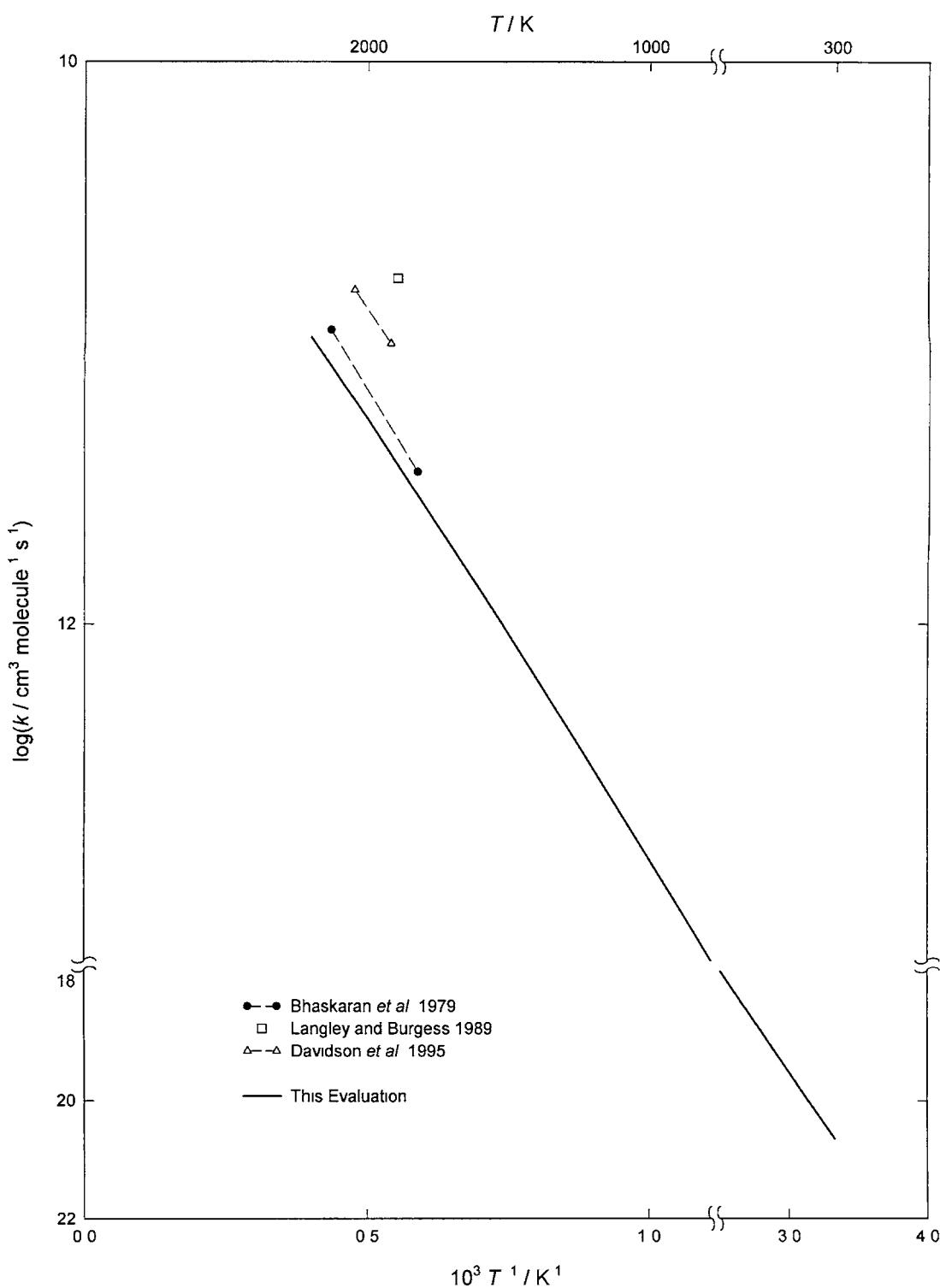
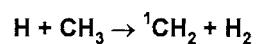
The values of  $k$  obtained in the shock tube studies of Bhaskaran *et al.*<sup>1</sup> and Davidson *et al.*<sup>3</sup> are in reasonable agreement and also agree to within a factor of  $\sim 3$  with the rate constants predicted by combining the thermodynamic data with the low temperature data on the reverse reaction, whereas the value of  $k$  obtained in the flame study of Langley and Burgess<sup>2</sup> seems unacceptably high.

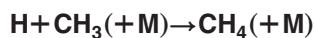
The preferred expression for  $k$  is obtained by combining the thermodynamic data with the data on the reverse reaction and assuming that  $k({}^1\text{CH}_2 + \text{H}_2)$  has a negligible temperature dependence.

The data for the addition channel,  $\text{H} + \text{CH}_3(+\text{M}) \rightarrow \text{CH}_4(+\text{M})$ , are evaluated separately on the data sheet which follows.

#### References

- <sup>1</sup> K. A. Bhaskaran, P. Frank, and Th. Just, 12th Int. Symp. on Shock Tubes and Waves, 1980, p. 503.
- <sup>2</sup> C. J. Langley and A. R. Burgess, Proc. R. Soc. London, Ser. A **351**, 33 (1976).
- <sup>3</sup> D. F. Davidson, M. D. Di Rosa, E. J. Chang, R. K. Hanson, and C. T. Bowman, Int. J. Chem. Kinet. **27**, 1179 (1995).
- <sup>4</sup> CEC, 1992; Supplement I, 1994 (see references in Introduction).



*Thermodynamic Data*

$$\Delta H_{298}^{\circ} = -439.3 \text{ kJ mol}^{-1}$$

$$\Delta S_{298}^{\circ} = -122.5 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c = 3.23 \cdot 10^{-27} T^{0.217} \exp(+53010/T) \text{ cm}^3 \text{ molecule}^{-1}$$

(300 ≤ T/K ≤ 5000)

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	[M]/molecule cm <sup>-3</sup>	Reference	Comments
<i>Rate Coefficient Measurements</i>				
<i>Low Pressure Range</i>				
$[\text{He}]3.2 \cdot 10^{-29}$	504	$(4.8-76.6) \cdot 10^{17}$	Brouard <i>et al.</i> , 1985 <sup>1</sup>	(a)
$[\text{He}]4.0 \cdot 10^{-29}$	300-600	$(4.8-163.5) \cdot 10^{17}$	Brouard, Macpherson, and Pilling, 1989 <sup>2</sup>	(b)
<i>Intermediate Fall-off Range</i>				
$5.3 \cdot 10^{-11}$	308	$9.4 \cdot 10^{17}(\text{C}_2\text{H}_6)$	Cheng and Yeh, 1977 <sup>3</sup>	(c)
$2.5 \cdot 10^{-10}$		$9.4 \cdot 10^{18}$		
$3.0 \cdot 10^{-10}$		$7.21 \cdot 10^{19}$		
$1.52 \cdot 10^{-11}$	504	$4.8 \cdot 10^{17}(\text{He})$	Brouard <i>et al.</i> , 1985 <sup>1</sup>	(a)
$3.44 \cdot 10^{-11}$		$1.93 \cdot 10^{18}$		
$7.75 \cdot 10^{-11}$		$7.67 \cdot 10^{18}$		
$2.26 \cdot 10^{-11}$	301	$8.1 \cdot 10^{17}(\text{He})$	Brouard, Macpherson, and Pilling, 1989 <sup>2</sup>	(b)
$6.36 \cdot 10^{-11}$		$3.3 \cdot 10^{18}$		
$1.82 \cdot 10^{-10}$		$1.63 \cdot 10^{19}$		
$1.35 \cdot 10^{-11}$	401	$6.1 \cdot 10^{17}$		
$4.44 \cdot 10^{-11}$		$2.4 \cdot 10^{18}$		
$1.44 \cdot 10^{-10}$		$1.47 \cdot 10^{19}$		
$2.11 \cdot 10^{-11}$	601	$1.7 \cdot 10^{18}$		
$3.78 \cdot 10^{-11}$		$4.9 \cdot 10^{18}$		
$6.18 \cdot 10^{-11}$		$1.14 \cdot 10^{19}$		
<i>High Pressure Range</i>				
$3.5 \cdot 10^{-10}$	504	$(4.8-76.7) \cdot 10^{17}(\text{He})$	Brouard <i>et al.</i> , 1985 <sup>1</sup>	(a)
$4.7 \cdot 10^{-10}$	300-600	$(8.1-16.4) \cdot 10^{18}(\text{He})$	Brouard, Macpherson, and Pilling, 1989 <sup>2</sup>	(b)
$3.5 \cdot 10^{-10}$	1290-1750	$(1.9-2.2) \cdot 10^{18}(\text{Kr})$	Su and Michael, 2002 <sup>4</sup>	(d)
<i>Reviews and Evaluations</i>				
$k_0[\text{He}] = [\text{He}]6.2 \cdot 10^{-29}(T/300)^{-1.8}$	300-1000		Cobos and Troe, 1990 <sup>5</sup>	(e)
$k_0[\text{C}_2\text{H}_6] = [\text{C}_2\text{H}_6]3.0 \cdot 10^{-28}(T/300)^{-1.8}$	300-1000			
$k_\infty = 3.5 \cdot 10^{-10}$	300-1000			
$F_c(\text{He}) = \exp(-0.45 - T/3230)$	300-1000			
$F_c(\text{C}_2\text{H}_6) = \exp(-0.34 - T/3039)$	300-1000			
$k_0[\text{He}] = [\text{He}]6.2 \cdot 10^{-29}(T/300)^{-1.8}$	300-1000		CEC, 1992; 1994 <sup>6</sup>	(f)
$k_0[\text{Ar}] = [\text{Ar}]6.0 \cdot 10^{-29}(T/300)^{-1.8}$	300-1000			
$k_0[\text{C}_2\text{H}_6] = [\text{C}_2\text{H}_6]3.0 \cdot 10^{-28}(T/300)^{-1.8}$	300-1000			
$k_\infty = 3.5 \cdot 10^{-10}$	300-1000			
$F_c(\text{He}) = 0.63 \exp(-T/3315) + 0.37 \exp(-T/61)$	300-1000			

**Comments**

- (a) 193 nm photolysis of acetone;  $[\text{CH}_3]$  and  $[\text{H}]$  monitored by time-resolved UV absorption and resonance fluorescence, respectively.  $[\text{CH}_3] \gg [\text{H}]$ .  $k_\infty$  obtained by RRKM/master equation fit.
- (b) Discharge flow study of  $\text{H} + \text{C}_2\text{H}_4$  system.  $\text{CH}_3$  generated by  $\text{H} + \text{C}_2\text{H}_5 \rightarrow 2\text{CH}_3$ . ESR detection of  $\text{H}$ .

- (c) Steady-state Hg photosensitization of  $\text{C}_2\text{H}_6$ . Products detected by mass spectrometry.  $k_\infty$  obtained by extrapolation of Lindemann plot.
- (d) Shock tube study of the thermal decomposition of  $\text{C}_2\text{D}_5\text{I}/\text{CH}_3\text{I}/\text{Kr}$  mixtures which generated D atoms and  $\text{CH}_3$  radicals.  $[\text{H}]$  and  $[\text{D}]$  were monitored by ARAS. A rate constant of  $2.20 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was measured for the reaction  $\text{CH}_3 + \text{D} \rightarrow \text{CH}_2\text{D} + \text{H}$ . This rate constant was converted to the high pressure limit

- for  $\text{CH}_3 + \text{H} \rightarrow \text{CH}_4$  using the theoretical ratio of 1.6 from Klippenstein, Georgieskii, and Harding.<sup>7</sup>
- (e) Theoretical calculation based on  $k_0$  calculations from Ref. 8, the representation of fall-off curves from Ref. 9, and the  $k_\infty$  treatment from Ref. 10. Collision efficiencies  $\beta_c$  at 300 K of 0.07 for M=He and of 0.15 for M=C<sub>2</sub>H<sub>6</sub> point to particularly inefficient energy transfer for which  $\langle \Delta E \rangle$  values may increase proportional to the temperature. Therefore, the temperature coefficient of  $k_0$  at  $T \leq 1000$  K was chosen as in the strong collision limit, i.e., assuming  $\beta_c$  to be temperature independent. The temperature coefficient of  $k_\infty$  was derived from SACM-modified PST calculations of Ref. 10, which also predicts the absolute value of  $k_\infty$  to be as recommended. The broadening factor contains a considerable weak collision contribution, strong collision broadening factors being given by  $F_c^{\text{SC}} = \exp(-0.09 - T/3320)$ .
- (f) See Comments on Preferred Values.

### Preferred Values

$k_0 = 1.8 \cdot 10^{-24} T^{-1.8} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  for M=He over the range 300–1000 K.

$k_0 = 1.7 \cdot 10^{-24} T^{-1.8} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  for M=Ar over the range 300–1000 K.

$k_0 = 8.6 \cdot 10^{-24} T^{-1.8} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  for M=C<sub>2</sub>H<sub>6</sub> over the range 300–1000 K.

$k_\infty = 3.5 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 300–2000 K.

$F_c = 0.63 \exp(-T/3315) + 0.37 \exp(-T/61)$  for M=He, Ar over the range 300–2000 K.

$F_c = 0.71 \exp(-T/3079) + 0.29 \exp(-T/54)$  for M=C<sub>2</sub>H<sub>6</sub> over the range 300–2000 K.

### Reliability

$\Delta \log k_0 = \pm 0.3$  for M=He over the range 300–1000 K.

$\Delta \log k_0 = \pm 0.5$  for M=Ar, C<sub>2</sub>H<sub>6</sub> over the range 300–1000 K.

$\Delta \log k_\infty = \pm 0.3$  over the range 300–2000 K.

$\Delta F_c = \pm 0.1$  for M=He, Ar, C<sub>2</sub>H<sub>6</sub> over the range 300–2000 K.

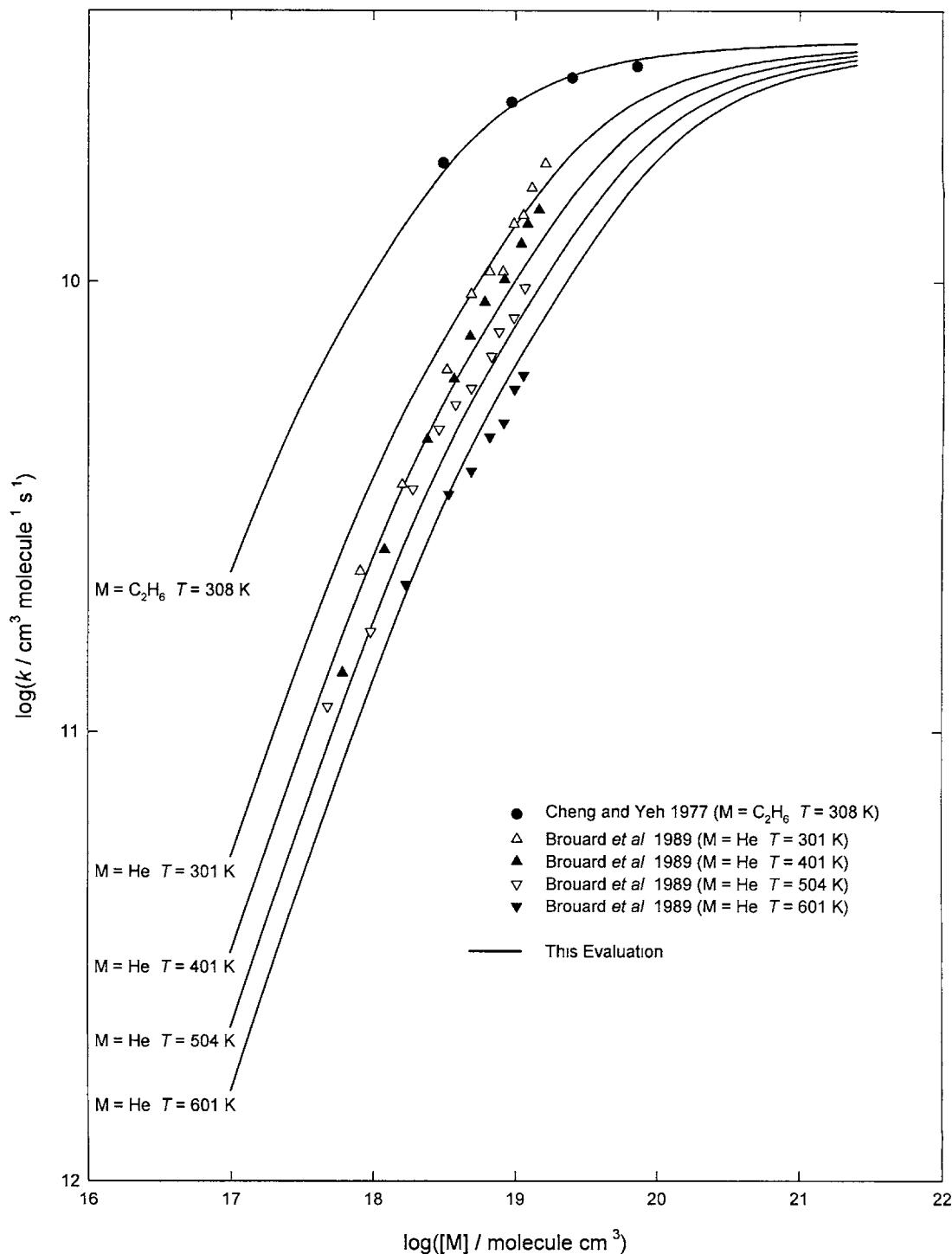
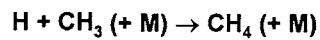
### Comments on Preferred Values

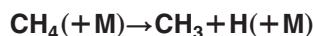
The preferred values are based on the modeling study by Cobos and Troe<sup>5</sup> of the experimental measurements of Brouard *et al.*,<sup>1,2</sup> with the high pressure limit based mainly on the data of Cheng and Yeh.<sup>3</sup> The results of the isotope exchange study of Su and Michael<sup>4</sup> are perfectly consistent with the derived value of  $k_\infty$ , extending the temperature range of validity of  $k_\infty$ . The Figure is a plot of representative fall-off curves and experimental data.

Data for the bimolecular reaction channel, H+CH<sub>3</sub>→H<sub>2</sub>+<sup>1</sup>CH<sub>2</sub>, are evaluated on the preceding data sheet.

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- J. Troe, Z. Phys. Chem. N.F. **161**, 209 (1989); J. Chem. Soc. Faraday Trans. **87**, 2299 (1991).



*Thermodynamic Data*

$$\Delta H_{298}^{\circ} = 439.3 \text{ kJ mol}^{-1}$$

$$\Delta S_{298}^{\circ} = 122.5 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c = 3.09 \cdot 10^{26} T^{-0.217} \exp(-53010/T) \text{ molecule cm}^{-3}$$

(300 ≤  $T/\text{K}$  ≤ 5000)

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{s}^{-1}$	$T/\text{K}$	[M]/molecule $\text{cm}^{-3}$	Reference	Comments
<i>Rate Coefficient Measurements</i>				
<i>Low Pressure Range</i>				
$[\text{Ar}]3.3 \cdot 10^{-7} \exp(-44800/T)$	1850–2500	$(3.3\text{--}90) \cdot 10^{19}$	Hartig, Troe, and Wagner, 1971 <sup>1</sup>	(a)
$[\text{Ar}]1.4 \cdot 10^{-7} \exp(-44030/T)$	1790–2325	$(1.8\text{--}15) \cdot 10^{18}$	Davidson <i>et al.</i> , 1992 <sup>2</sup>	(b)
$[\text{Ar},\text{Kr}]3.2 \cdot 10^{23} T^{-8.106} \exp(-59090/T)$	1600–4200	$(6.5\text{--}18) \cdot 10^{17}$	Kiefer and Kumaran, 1993 <sup>3</sup>	(c)
$[\text{Ar}]5.0 \cdot 10^{-8} \exp(-40760/T)$	1400–2500	$(2.2\text{--}5.5) \cdot 10^{18}$	Koike <i>et al.</i> , 2000 <sup>4</sup>	(d)
$[\text{Kr}]1.08 \cdot 10^{-7} \exp(-43610/T)$	1738–2069	$(3.2\text{--}3.4) \cdot 10^{18}$	Sutherland, Su, and Michael, 2001 <sup>5</sup>	(e)
<i>Intermediate Fall-off Range</i>				
$2.5 \cdot 10^{13} \exp(-48300/T)$	1850–2500	$3.3 \cdot 10^{19}(\text{Ar})$	Hartig, Troe, and Wagner, 1971 <sup>1</sup>	(a)
$4.7 \cdot 10^{12} \exp(-46900/T)$	1700–2300	$6.0 \cdot 10^{18}(\text{Ar})$	Roth and Just, 1975 <sup>6</sup>	(f)
$0.74 \cdot 10^{-8}$	995	$0.5 \cdot 10^{18}(\text{CH}_4)$	Chen <i>et al.</i> , 1975 <sup>7</sup>	(g)
$2.82 \cdot 10^{-8}$		$7.2 \cdot 10^{18}$		
$0.39 \cdot 10^{-7}$	1038	$0.3 \cdot 10^{17}$		
$2.57 \cdot 10^{-7}$		$6.9 \cdot 10^{18}$		
$0.98 \cdot 10^{-7}$	1068	$0.23 \cdot 10^{18}$		
$8.71 \cdot 10^{-7}$		$6.7 \cdot 10^{18}$		
$0.69 \cdot 10^{-6}$	1103	$0.43 \cdot 10^{18}$		
$3.86 \cdot 10^{-6}$		$6.5 \cdot 10^{18}$		
$2.82 \cdot 10^{12} \exp(-44500/T)$	1875–2240	$1.2 \cdot 10^{19}(\text{Ar})$	Bowman, 1975 <sup>8</sup>	(h)
$2.2 \cdot 10^{12} \exp(-45400/T)$	2000–2700	$6.0 \cdot 10^{18}(\text{Ar})$	Heffington <i>et al.</i> , 1977 <sup>9</sup>	(i)
$6.0 \cdot 10^{12} \exp(-45400/T)$		$1.7 \cdot 10^{19}$		
$2.3 \cdot 10^{11} \exp(-43200/T)$	1950–2770	$1.4 \cdot 10^{18}(\text{Ar})$	Tabayashi and Bauer, 1979 <sup>10</sup>	(j)
$9.1 \cdot 10^{11} \exp(-43200/T)$		$5.4 \cdot 10^{18}$		
$4.44 \cdot 10^{-6}$	1073	$1.0 \cdot 10^{20}(\text{Ar})$	Barnes, Pratt, and Wood, 1989 <sup>11</sup>	(k)
$5.28 \cdot 10^{-6}$		$3.4 \cdot 10^{20}$		
$9.80 \cdot 10^{-6}$	1098	$6.6 \cdot 10^{19}$		
$1.20 \cdot 10^{-5}$		$2.0 \cdot 10^{20}$		
$1.46 \cdot 10^{-5}$		$3.3 \cdot 10^{20}$		
$1.87 \cdot 10^{-5}$	1123	$3.2 \cdot 10^{19}$		
$2.31 \cdot 10^{-5}$		$6.5 \cdot 10^{19}$		
$3.19 \cdot 10^{-5}$		$1.9 \cdot 10^{20}$		
$4.32 \cdot 10^{-5}$	1148	$3.2 \cdot 10^{19}$		
$5.39 \cdot 10^{-5}$		$6.3 \cdot 10^{19}$		
$3.04 \cdot 10^{-6}$	1073	$3.4 \cdot 10^{19}(\text{CH}_4)$		
$5.11 \cdot 10^{-6}$		$1.4 \cdot 10^{20}$		
$4.93 \cdot 10^{-6}$		$3.4 \cdot 10^{20}$		
$8.25 \cdot 10^{-6}$	1098	$3.3 \cdot 10^{19}$		
$1.52 \cdot 10^{-5}$		$1.3 \cdot 10^{20}$		
$1.55 \cdot 10^{-5}$		$3.3 \cdot 10^{20}$		
$2.27 \cdot 10^{-5}$	1123	$3.2 \cdot 10^{19}$		
$3.63 \cdot 10^{-5}$		$1.3 \cdot 10^{20}$		
$4.20 \cdot 10^{-5}$		$3.2 \cdot 10^{20}$		
$6.03 \cdot 10^{-5}$	1148	$3.2 \cdot 10^{19}$		
$8.50 \cdot 10^{-5}$		$1.3 \cdot 10^{20}$		
$1.20 \cdot 10^{-4}$		$3.2 \cdot 10^{20}$		
<i>High Pressure Range</i>				
$1.3 \cdot 10^{15} \exp(-52300/T)$	1850–2500	$(3.3\text{--}90) \cdot 10^{19}(\text{Ar})$	Hartig, Troe, and Wagner, 1971 <sup>1</sup>	(a)
<i>Reviews and Evaluations</i>				
$k_0[\text{Ar}] = [\text{Ar}]7.5 \cdot 10^{-7} \exp(-45700/T)$	1000–3000		Cobos and Troe, 1990 <sup>12</sup>	(l)

$k/s^{-1}$	$T/K$	[M]/molecule cm $^{-3}$	Reference	Comments
$k_0[\text{Ar}] = [\text{CH}_4] 1.4 \cdot 10^{-6} \exp(-45700/T)$	1000–3000			
$k_\infty = 2.4 \cdot 10^{16} \exp(-52800/T)$	1000–3000			
$F_c(\text{Ar}) = \exp(-0.45 - T/3230)$	1000–3000			
$F_c(\text{CH}_4) = \exp(-0.37 - T/2210)$	1000–3000			
$k_0[\text{Ar}] = [\text{Ar}] 7.8 \cdot 10^{23} T^{-8.2} \exp(-59200/T)$	1700–5000		Cobos and Troe, 1992 <sup>13</sup>	(m)
$k_\infty = 2.46 \cdot 10^{16} \exp(-52800/T)$	1000–5000			
$F_c(\text{Ar}) = \exp(-T/1350) + \exp(-7834/T)$	1000–5000			
$k_0[\text{Ar}] = [\text{Ar}] 7.5 \cdot 10^{-7} \exp(-45700/T)$	1000–1700		CEC, 1992; 1994 <sup>14</sup>	(n)
$k_0[\text{Ar}] = [\text{Ar}] 7.8 \cdot 10^{23} T^{-8.2} \exp(-59200/T)$	1700–5000			
$k_0[\text{CH}_4] = [\text{CH}_4] 1.4 \cdot 10^{-6} \exp(-45700/T)$	1000–2000			
$K_\infty = 2.46 \cdot 10^{16} \exp(-52800/T)$	1000–3000			
$F_c(\text{Ar}) = \exp(-T/1350) + \exp(-7834/T)$	1000–5000			
$F_c(\text{CH}_4) = 0.31 \exp(-T/91) + 0.69 \exp(-T/2207)$	1000–2000			
$k_0[\text{Ar}] = [\text{Ar}] 1.7 \cdot 10^{-6} \exp(-48510/T)$	1785–2325	$(1.8-15) \cdot 10^{18}$	Davidson, Hanson, and Bowman, 1995 <sup>15</sup>	(o)

### Comments

- (a) Shock wave study of CH<sub>4</sub>/Ar mixtures. The reaction was followed by IR emission of CH<sub>4</sub> and by IR emission and UV absorption of the products.
- (b) Study of the decomposition of CH<sub>4</sub> in reflected shock waves. CH<sub>3</sub> concentrations monitored by narrow-linewidth laser absorption at 216 nm. CH<sub>3</sub> decay profiles were fitted with mechanism comprising 38 reactions.
- (c) Study of the pyrolysis of CH<sub>4</sub> in incident shock waves by the laser-Schlieren technique. Measurements carried out with mixtures of CH<sub>4</sub>(2%)/Kr, CH<sub>4</sub>(2%)/Ar, and CH<sub>4</sub>(0.5%)/Ar over the temperature range 2800–4300 K. Observed density gradient fitted with an extensive mechanism comprising 76 reactions. An RRKM analysis of the data yielded the above expression for  $k_0$  which, for  $T < 2000$  K, is in excellent agreement with the recommendation of Warnatz<sup>16</sup> [ $k = 3.3 \cdot 10^{-7} \exp(-44500/T) \text{ s}^{-1}$  over the range 1500–3000 K]. Kiefer and Kumaran,<sup>3</sup> therefore recommend the temperature limits 1600–4200 K.
- (d) Infrared emission at 3.4  $\mu\text{m}$  was used to monitor the pyrolysis of CH<sub>4</sub>/Ar mixtures in incident shock waves at pressures of 0.40–0.82 bar. Values of  $k$  were derived directly from the emission profiles and some modeling was carried out using a detailed mechanism.
- (e) Shock wave study in CH<sub>4</sub>/Kr mixtures. [H] was monitored by time-resolved ARAS at 121.6 nm behind reflected shocks. Values of  $k$  were derived by modeling a detailed mechanism to fit the measured [H] profiles.
- (f) Direct measurements of the time dependent H atom concentration by Lyman- $\alpha$  absorption during the pyrolysis of CH<sub>4</sub>/Ar mixtures in reflected shock waves.
- (g) Pyrolysis of CH<sub>4</sub> in a static system. Initial rates of methane decomposition and product formation determined based on gas chromatographic analysis of H<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, and C<sub>2</sub>H<sub>4</sub>.  $k_\infty$  values extrapolated with RRKM theory.
- (h) Study of the pyrolysis of CH<sub>4</sub>/O<sub>2</sub>/Ar mixtures in reflected shock waves. The reaction was followed by monitoring [OH] by UV absorption at 308 nm, [H<sub>2</sub>O]

and [CO] by IR emission at 6.3 and 4.8  $\mu\text{m}$ , respectively, and [O] by chemiluminescent emission following the reaction O+CO. The concentration profiles were fitted with a 23-reaction mechanism.

- (i) Shock wave study of CH<sub>4</sub> pyrolysis in Ar. The reaction was followed monitoring [CH<sub>4</sub>] by both emission and absorption at 3.392  $\mu\text{m}$ .
- (j) Shock wave measurements with CH<sub>4</sub>/Ar mixtures. Post shock-front density gradients measured optically (laser Schlieren technique) were fitted with a model comprising 12 reactions.
- (k) Pyrolysis of CH<sub>4</sub> in a flow reactor. Reactant and products (ethane, ethylene, acetylene, and propylene) detected by gas chromatography. Rate coefficients derived from an analysis of the very early stages of reaction (0.003%–0.05% conversion).
- (l) The experiments by Hartig *et al.*<sup>1</sup> have been re-evaluated taking into account the increasing amount of IR emission from species other than CH<sub>4</sub> as documented in Ref. 1. These corrections become most pronounced in the high pressure experiments. The theoretical calculations were carried out using the  $k_0$  formalism from Ref. 17, fall-off expression from Ref. 18, and SACM-modified PST calculations from Ref. 19 which leads to a nearly temperature independent value of  $k_\infty$  for the reverse recombination H+CH<sub>3</sub>→CH<sub>4</sub> of  $3.5 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .
- (m) Re-analysis of the kinetic data of Davidson *et al.*<sup>2</sup> and Kiefer and Kumaran<sup>3</sup> in terms of the theory of unimolecular reactions.<sup>17–19</sup> The analysis leads to an energy transferred per collision of  $50 \pm 20 \text{ cm}^{-1}$  for M=Ar over the temperature range 1000–5000 K.
- (n) See Comments on Preferred Value.
- (o) Re-analysis of the experiments of Davidson *et al.*<sup>2</sup> applying a re-evaluated absorption coefficient for CH<sub>3</sub> radicals<sup>20</sup> which is about half the value employed originally.<sup>2</sup>

### Preferred Values

$k_0 = 7.5 \cdot 10^{-7} \exp(-45700/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for M=Ar over the range 1000–1700 K.

$k_0 = 7.8 \cdot 10^{23} T^{-8.2} \exp(-59200/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$   
for M=Ar over the range 1700–5000 K.

$k_0 = 1.4 \cdot 10^{-6} \exp(-45700/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for M=CH<sub>4</sub> over the range 1000–2000 K.

$k_\infty = 2.4 \cdot 10^{16} \exp(-52800/T) \text{ s}^{-1}$  over the range 1000–3000 K.

$F_c = \exp(-T/1350) + \exp(-7834/T)$  for M=Ar over the range 1000–5000 K.

$F_c = 0.31 \exp(-T/91) + 0.69 \exp(-T/2207)$  for M=CH<sub>4</sub> over the range 1000–2000 K.

### Reliability

$\Delta \log k_0 = \pm 0.3$  for M=Ar over the range 1000–5000 K.

$\Delta \log k_0 = \pm 0.3$  for M=CH<sub>4</sub> over the range 1000–2000 K.

$\Delta \log k_\infty = \pm 0.3$  over the range 1000–3000 K.

$\Delta \log F_c = \pm 0.1$  for M=Ar over the range 1000–5000 K.

$\Delta \log F_c = \pm 0.1$  for M=CH<sub>4</sub> over the range 1000–2000 K.

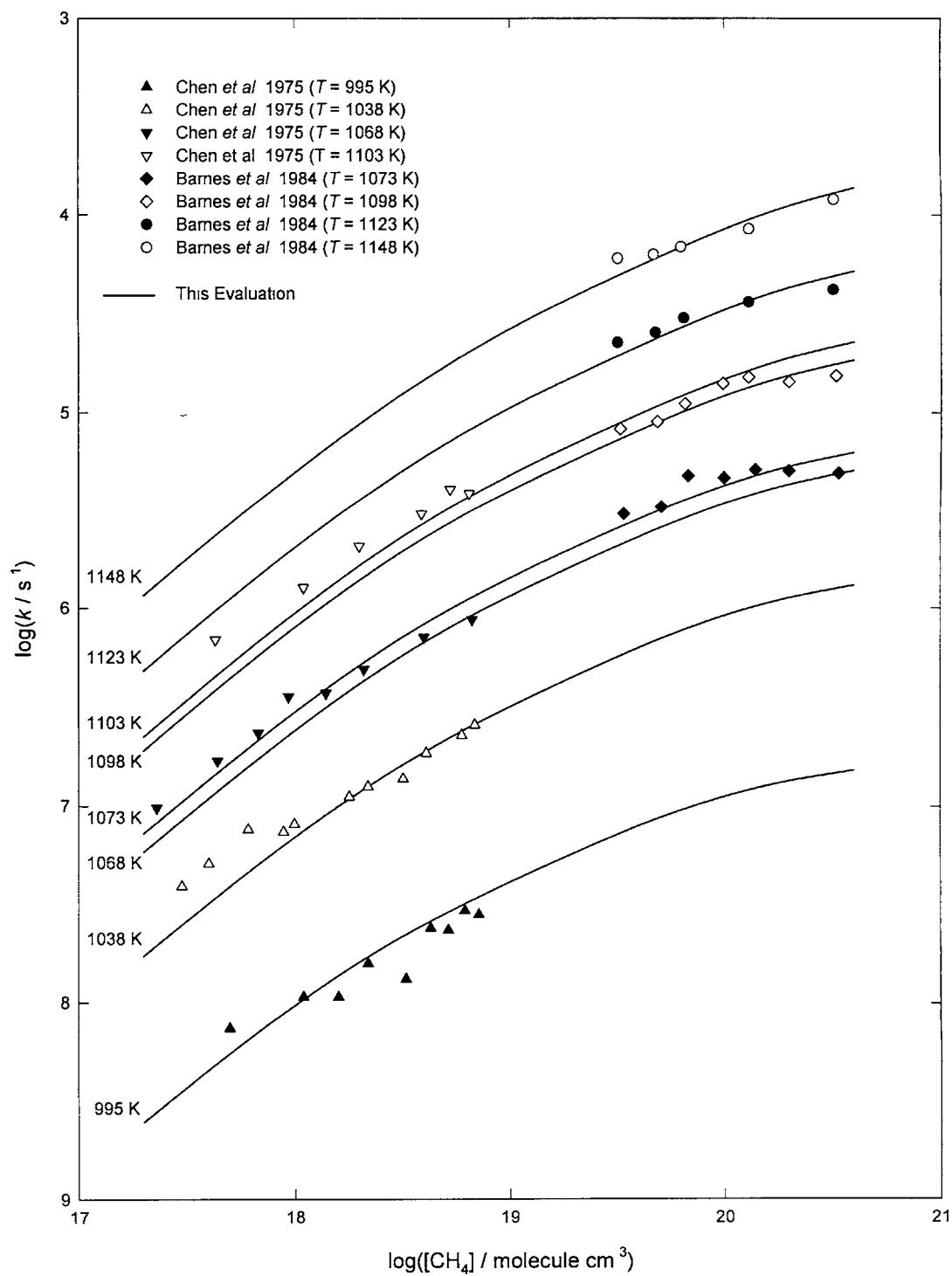
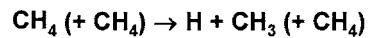
### Comments on Preferred Values

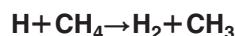
The recommended values remain unchanged from our previous evaluation.<sup>14</sup> The value for  $k_0$  follows from a detailed analysis of the experimental data of Hartig *et al.*,<sup>1</sup> Davidson *et al.*,<sup>2</sup> Kiefer and Kumaran,<sup>3</sup> Roth and Just,<sup>6</sup> Chen *et al.*,<sup>7</sup> Bowman,<sup>8</sup> Heffington *et al.*,<sup>9</sup> Tabayashi and Bauer,<sup>10</sup> Barnes *et al.*,<sup>11</sup> Cheng and Yeh,<sup>21</sup> and Brouard *et al.*<sup>22</sup> in terms of the theory of unimolecular reactions<sup>17–19</sup> as given in Refs. 12 and 13. From this evaluation  $\beta_c = 0.11$  was derived near 1000 K for M=CH<sub>4</sub><sup>12</sup> and  $\beta_c$  from 0.06 to 0.006 between 1000 and 5000 for M=Ar.<sup>13</sup> These values are consistent with an average energy transferred per collision of  $50 \pm 20 \text{ cm}^{-1}$ . The  $k_0$  values of Koike *et al.*<sup>3</sup> agree very well with those reported in Refs. 2, 3, and 15 and in a shock tube study of CH<sub>4</sub> pyrolysis and oxidation in the temperature range 1350–2500 K and pressure range 1.5–4.5 bar Hidaka *et al.*<sup>23</sup> found that the expression derived by Davidson *et al.*<sup>15</sup> provided the best fit to their results, which is consis-

tent with our preferred expressions. The recommended  $k_\infty$  values are consistent with a nearly temperature independent  $k_\infty$  of  $3.5 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the reverse association reaction. The Figure shows the dissociation fall-off curves for M=CH<sub>4</sub>. The  $F_c$  values calculated by RRKM theory may have to be revised (see Introduction, Sections 2.4, 2.5).

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*Thermodynamic Data*

$$\begin{aligned}\Delta H_{298}^0 &= 3.33 \text{ kJ mol}^{-1} \\ \Delta S_{298}^0 &= 23.89 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 5.07 \cdot 10^2 T^{-0.368} \exp(-815/T) \\ &\quad (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$5.3 \cdot 10^{-12}$	1600	Peeters and Mahnen, 1973 <sup>1</sup>	(a)
$3.55 \cdot 10^{-19} T^3 \exp(-8890/T)$	1300–1750	Biordi, Papp, and Lazzara, 1974 <sup>2</sup>	(b)
$2.7 \cdot 10^{-8} \exp(-13469/T)$	1325–1700	Biordi, Papp, and Lazzara, 1975 <sup>3</sup>	(c)
$1.2 \cdot 10^{-9} \exp(-7580/T)$	1700–2300	Roth and Just, 1975 <sup>4</sup>	(d)
$3.02 \cdot 10^{-10} \exp(-6627/T)$	640–818	Sephrad, Marshall, and Purnell, 1979 <sup>5</sup>	(e)
$1.78 \cdot 10^{-10} \exp(-6440/T)$	897–1729	Rabinowitz <i>et al.</i> , 1991 <sup>6</sup>	(f)
$4.2 \cdot 10^{-18}$	348	Marquaire <i>et al.</i> , 1994 <sup>7</sup>	(g)
$7.7 \cdot 10^{-18}$	363		
$9.6 \cdot 10^{-18}$	373		
$1.5 \cdot 10^{-17}$	390		
$3.3 \cdot 10^{-17}$	421		
$1.97 \cdot 10^{-20} T^{3.0} \exp(-4045/T)$	1350–2400	Hidaka <i>et al.</i> , 2000 <sup>8</sup>	(h)
$2.55 \cdot 10^{-10} \exp(-6874/T)$	748–1054	Bryukov, Slagle, and Knyazev, 2001 <sup>9</sup>	(i)
$2.935 \cdot 10^{-10} \exp(-6934/T)$	913–1697	Sutherland, Su, and Michael, 2001 <sup>10</sup>	(j)
<i>Reviews and Evaluations</i>			
$3.73 \cdot 10^{-10} T^3 \exp(-4045/T)$	300–1800	Clark and Dove, 1973; <sup>11</sup> Warnatz, 1984; <sup>12</sup> Tsang and Hampson, 1986 <sup>13</sup>	(k)
$1.51 \cdot 10^{-16} T^{1.9} \exp(-5420/T)$		Cohen, 1991 <sup>14</sup>	(l)
$2.18 \cdot 10^{-20} T^3 \exp(-4045/T)$	300–2000	CEC, 1992; 1994 <sup>15</sup>	(m)
$6.78 \cdot 10^{-21} T^{3.156} \exp(-4406/T)$	348–1950	Sutherland, Su, and Michael, 2001 <sup>10</sup>	(n)

**Comments**

- (a) Study of low pressure lean and stoichiometric CH<sub>4</sub>/O<sub>2</sub> flames. The concentrations of a number of species were monitored as a function of distance from the burner using a molecular beam sampling probe and mass spectrometric analysis. Species monitored included CH<sub>4</sub>, CO<sub>2</sub>, CO, O<sub>2</sub>, H<sub>2</sub>O, CH<sub>2</sub>O, CH<sub>3</sub>, CH<sub>3</sub>O<sub>2</sub>, CH<sub>3</sub>OH, O, H, H<sub>2</sub>, OH.
- (b) Study of low pressure lean CH<sub>4</sub>/O<sub>2</sub>/Ar flames. Concentration profiles of stable species and radicals were determined as a function of distance from the burner, sampling by means of a quartz cone into a quadrupole mass spectrometer. Only brief details of the data analysis are given and results are presented only on a graph.
- (c) Study of CF<sub>3</sub>Br inhibition of CH<sub>4</sub> flames; technique as in (f).
- (d) Shock tube study. [H] profiles were monitored by resonance absorption behind reflected shock waves in CH<sub>4</sub>/Ar mixtures.
- (e) Discharge flow study in which H atoms were added to a CH<sub>4</sub>/Ar mixture with CH<sub>4</sub> in excess. The C<sub>2</sub>H<sub>6</sub> yield, measured by gas chromatography, were determined as a function of the initial [CH<sub>4</sub>]/[H] and values of  $k$  derived by computer fitting of the C<sub>2</sub>H<sub>6</sub> profiles using a detailed mechanism.

- (f) Flash photolysis-shock tube technique used to study H reacting with CH<sub>4</sub> in large excess. H atoms were generated by vacuum-UV flash photolysis of CH<sub>4</sub>/Ar mixtures and the reaction progress followed in the reflected shock regime by monitoring [H] by ARAS. As well as the expression cited the results could equally well be represented by the expression  $k = 1.6 \cdot 10^{-19} T^{2.57} \exp(-3340/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Authors combine their own results with those of Kurylo *et al.*,<sup>18</sup> at lower temperatures, to derive the expression  $k = 6.6 \cdot 10^{-20} T^{2.24} \exp(-3220/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the range 426–1729 K. They point out that the extrapolation of this expression to lower temperatures gives much higher values than predicted by the data on the reverse reaction and the equilibrium constants.
- (g) Discharge flow study at total pressures in the range 6–40 mbar. H atoms were produced by a discharge in a H<sub>2</sub>/He mixture and CH<sub>4</sub> was added in large excess downstream. [H] was monitored by ESR. Ethane yields of ~0.015 were measured by GC indicating removal of CH<sub>3</sub> by reaction with H. The reaction was simulated using a detailed mechanism.
- (h) Shock tube study on the pyrolysis and oxidation of CH<sub>4</sub> using a range of CH<sub>4</sub>/O<sub>2</sub>/H<sub>2</sub>/Ar mixtures at pressures in the range 1.5–4.5 bar. Two shock tubes

were used. The first had facilities for time resolved and single pulse product analysis studies. IR emissions at 3.48  $\mu\text{m}$ , 4.24  $\mu\text{m}$ , and 2.56  $\mu\text{m}$  were monitored and reactants and products could be sampled and analyzed by GC. The second shock tube was equipped for laser absorption at 3.39  $\mu\text{m}$  and IR emission studies behind reflected shocks. The measured profiles were simulated using a detailed mechanism.

- (i) Discharge flow study with H atoms generated by a microwave discharge in  $\text{H}_2/\text{He}$  mixtures. [H] monitored in the presence of a large excess of  $\text{CH}_4$  by time-resolved resonance fluorescence at 121.6 nm.
- (j) Shock tube study on  $\text{CH}_4$  containing small amounts of  $\text{NH}_3$ . H atoms were produced by 193.3 nm photolysis of the  $\text{NH}_3$  and [H] was monitored behind reflected shocks by time-resolved ARAS at 121.6 nm. The effects of secondary reactions were checked using a detailed reaction mechanism.
- (k) Expression derived by Clark and Dove<sup>11</sup> using a BEBO calculation. Expression recommended by Warnatz<sup>12</sup> and by Tsang and Hampson.<sup>13</sup>
- (l) Based on a transition state treatment of H atom reactions with a number of alkanes and making use of a value of  $k(298 \text{ K})$  derived from the data on the reverse reaction and the equilibrium constant. Temperature range not specified.
- (m) Slightly modified form of the expression derived by Clark and Dove.<sup>11</sup>
- (n) Derived by combining the authors own results<sup>10</sup> with those of Rabinowitz *et al.*,<sup>6</sup> Wintergerst and Frank,<sup>16</sup> Marquaire *et al.*,<sup>7</sup> and Bryukov *et al.*<sup>9</sup>

### Preferred Values

$k = 1.02 \cdot 10^{-18} T^{2.50} \exp(-4825/T)$   $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$   
over the range 350–2500 K.

### Reliability

$\Delta \log k = \pm 0.2$  at 1000 K, rising to  $\pm 0.4$  at 350 K and 2500 K.

### Comments on Preferred Values

There is a substantial body of data on the rate constants for both the forward and reverse reaction. Hence, although the data for the rate constants of the forward and reverse steps have been evaluated largely independently, we have attempted to reconcile the expressions derived with the predictions of the thermodynamic data.

The rate constant of this reaction is quite well defined over the range 900–1700 K, particularly by the studies of Rabinowitz *et al.*,<sup>7</sup> and Sutherland *et al.*<sup>10</sup> At still higher temperatures our preferred expression is based on the studies of Peeters and Mahnen,<sup>1</sup> Roth and Just,<sup>4</sup> and Biordi *et al.*<sup>2,3</sup> The expression for  $k$  is compatible with the indirect measurements of Bush and Dyer<sup>17</sup> and the older study of Fenimore and Jones.<sup>18</sup>

At temperatures below 900 K there is considerable scatter in the data.<sup>5,7,9,19–30</sup> Between 600 K and 900 K the data of Sepehrad *et al.*,<sup>5</sup> Kurylo *et al.*,<sup>19</sup> and Panfilov and Voevodskii<sup>20</sup> are in good agreement but they differ significantly from values calculated from the data on the reverse reaction and the equilibrium constant and Cohen<sup>14</sup> has questioned the reliability of the studies of Sepehrad *et al.*,<sup>5</sup> and Kurylo *et al.*,<sup>19</sup> although both of these studies are in reasonable agreement with our preferred values. The other data in this region scatter over about a factor of 5. The data of Bryukov *et al.*<sup>9</sup> appear to be the most reliable and agree well with the higher temperature studies of Rabinowitz *et al.*,<sup>6</sup> and Sutherland *et al.*<sup>10</sup> in the temperature region where they overlap.

At temperatures approaching ambient the rate constant is small and difficult to measure under truly first order conditions. Only the study of Marquaire *et al.*<sup>7</sup> is in good agreement with values of  $k$  calculated from data on the reverse reaction and the equilibrium constant.

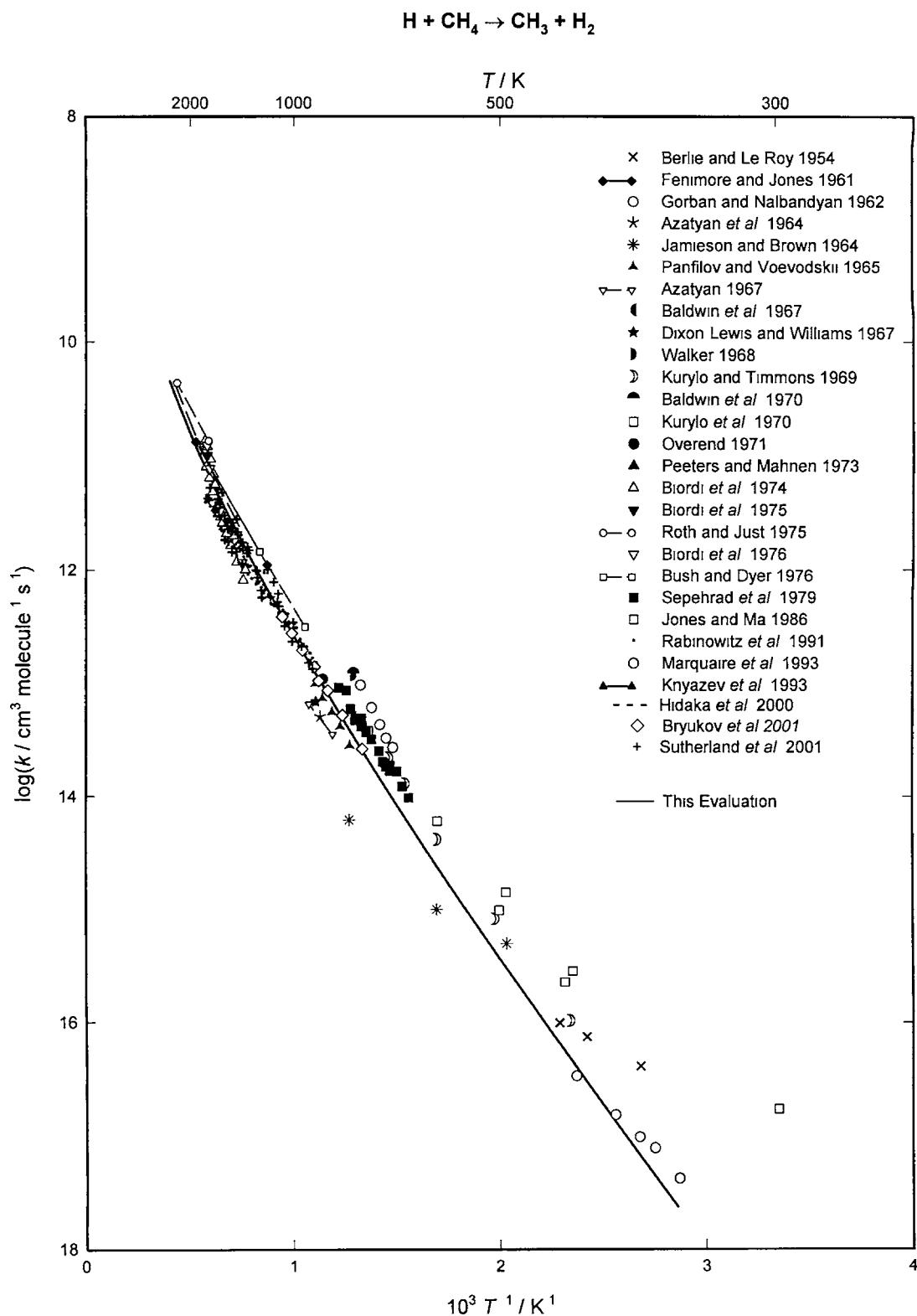
Cohen<sup>14</sup> has evaluated the data on a number of reactions between H atoms and alkanes and has fitted the data using a transition state treatment and Sutherland *et al.*<sup>10</sup> have also derived an expression which provides a good fit to the best of the data. Our preferred expression for  $k$  is in good agreement with the expressions of Cohen<sup>14</sup> and of Sutherland *et al.*<sup>11</sup> and is also chosen to be compatible with the data on the rate constant of the reverse reaction and the thermodynamic data.

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**H+HCO→H<sub>2</sub>+CO***Thermodynamic Data*

$$\Delta H^{\circ}_{298} = -371.61 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298} = -10.80 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c = 11.3 T^{-0.503} \exp(+44430/T)$$

(300 ≤ T/K ≤ 5000)

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

<i>k/cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup></i>	<i>T/K</i>	Reference	Comments
<i>Rate Coefficient Measurements</i>			
2.0·10 <sup>-10</sup>	298	Nadtochenko, Sarkisov, and Vedeneev, 1979 <sup>1</sup>	(a)
1.2·10 <sup>-10</sup>	298	Hochanadel, Sworsky, and Ogren, 1980 <sup>2</sup>	(b)
1.4·10 <sup>-10</sup>	298	Timonen, Ratajczak, and Gutman, 1987 <sup>3</sup>	(c)
1.3·10 <sup>-10</sup>	350		
9.6·10 <sup>-11</sup>	350		
3.58·10 <sup>-10</sup>	1200–2000	Hidaka <i>et al.</i> , 1993 <sup>4</sup>	(d)
<i>Reviews and Evaluations</i>			
1.5·10 <sup>-10</sup>	300–2500	CEC, 1992; 1994 <sup>5</sup>	(e)

**Comments**

- (a) Pulsed laser photolysis of CH<sub>3</sub>CHO/Ar mixtures at 13–250 mbar pressures; [CHO] monitored by intracavity dye laser absorption spectroscopy.
- (b) Flash photolysis of H<sub>2</sub>O/CH<sub>4</sub> or H<sub>2</sub>O/CO/CH<sub>4</sub> mixtures at 1–3 bar total pressures. [CHO] and [CH<sub>3</sub>] monitored in absorption at 230 nm and 213 nm, respectively. *k* derived by numerical modeling of the assumed mechanism.
- (c) Pulsed laser photolysis at 308 nm of CH<sub>3</sub>CHO/H/He mixtures with H atoms produced in a microwave discharge. Mass spectrometric detection of products.
- (d) Shock tube study using reflected shocks in HCHO/Ar mixtures; [HCHO] monitored by IR emission and absorption. Rate constant derived by modeling [HCHO] profiles using a 5-reaction mechanism. Total pressures were in the range 1.0–3.0 bar.
- (e) Based on the 298 K values of Nadtochenko *et al.*,<sup>1</sup> Hochanadel *et al.*,<sup>2</sup> and Timonen *et al.*<sup>3</sup> and an assumed, very small, temperature dependence.

**Preferred Values**

*k*=1.5·10<sup>-10</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> over the range 298–2500 K.

*Reliability*

Δ log *k*=±0.3 over the range 298–2500 K.

*Comments on Preferred Values*

The preferred value of *k* is based on the values at 298 K of Nadtochenko *et al.*,<sup>1</sup> Hochanadel *et al.*,<sup>2</sup> and Timonen *et al.*<sup>3</sup> The approximate *k* value of Reilly *et al.*<sup>6</sup> and the relative rate

measurements of Mack and Thrush,<sup>7</sup> Niki *et al.*,<sup>8</sup> and of Campbell and Handy,<sup>9</sup> are also compatible with this value of *k*.

The data of Timonen *et al.*<sup>3</sup> suggest a very small negative temperature dependence for *k*, which receives some support from the flame studies of Browne *et al.*<sup>10</sup> and Cherian *et al.*<sup>11</sup> However the interpretation of results from the shock tube studies of Cribb *et al.*<sup>12</sup> on methanol pyrolysis and of Hidaka *et al.*<sup>4</sup> on formaldehyde pyrolysis require very high values of *k*, implying that *k* increases slightly with temperature. Harding and Wagner<sup>13</sup> examined the reaction theoretically using *ab initio* calculations. Their results also suggest a weak positive temperature dependence for the rate constant but, for the moment, a value of *k* independent of temperature is recommended.

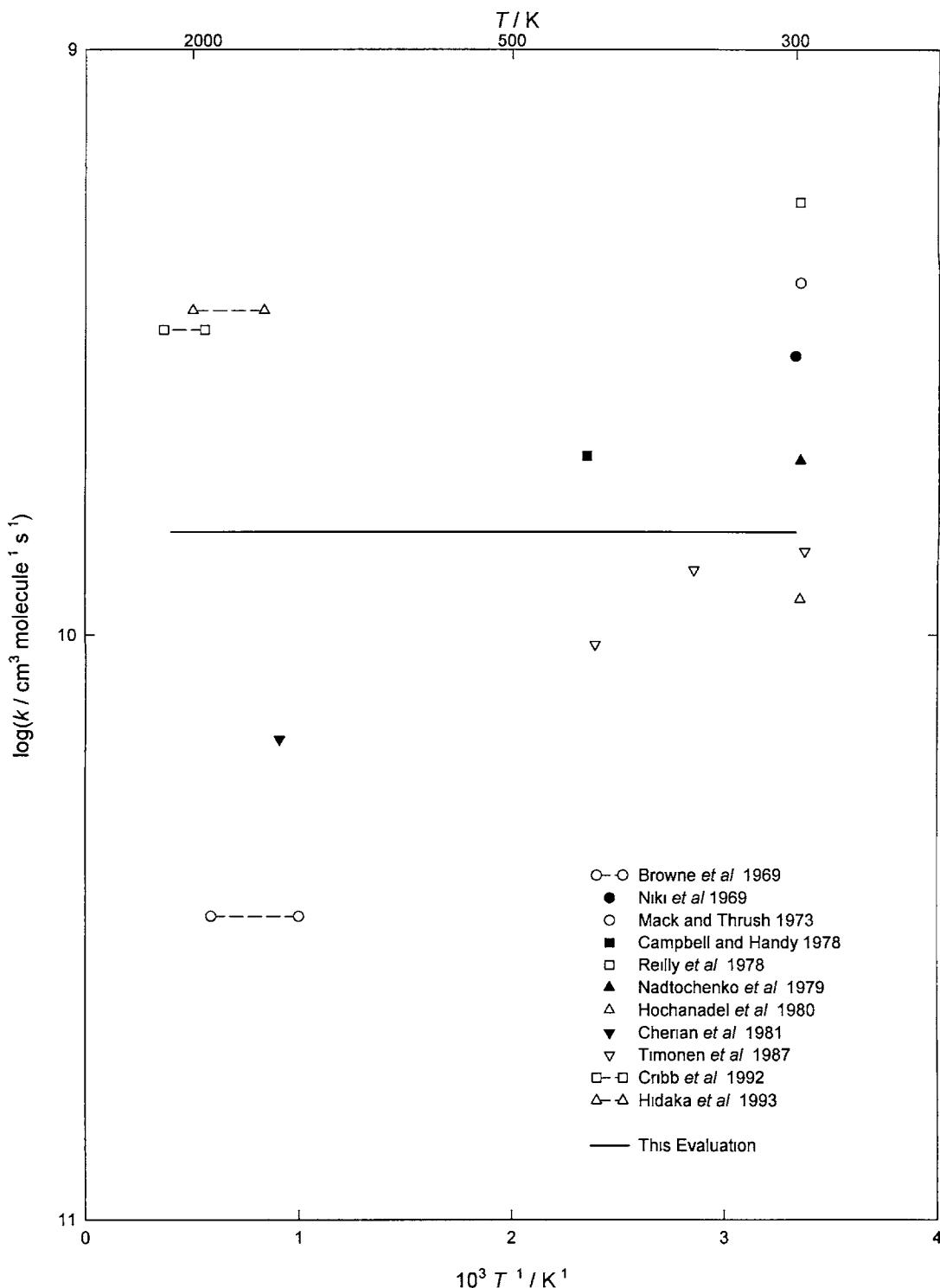
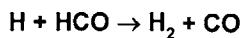
Harding and Wagner<sup>13</sup> concluded that at all temperatures the formation of H<sub>2</sub>+CO occurs predominantly by direct abstraction, rather than by adduct formation and subsequent elimination, and that pressure dependent stabilization of the adduct to form HCHO is unimportant even at 298 K, up to a pressure of 1 bar. Hochanadel *et al.*<sup>2</sup> also, in their experiments, could find no effect of pressure on *k* at 298 K for pressures in the range 1–3 bar of CO, H<sub>2</sub>, or CH<sub>4</sub>.

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<sup>9</sup>I. M. Campbell and B. J. Handy, J Chem. Soc. Faraday Trans. I **74**, 316 (1978).  
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- <sup>11</sup>M. A. Cherian, P. Rhodes, R. J. Simpson, and G. Dixon-Lewis, 18th Symp. (Int.) Combustion, 1981, p. 385.  
<sup>12</sup>P. H. Cribb, J. E. Dove, and S. Yamazaki, Combust. Flame **88**, 169 (1992); **88**, 186 (1992).  
<sup>13</sup>L. B. Harding and A. F. Wagner, 21st Symp. (Int.) Combustion, 1988, p. 721.



**H+HCHO→H<sub>2</sub>+HCO***Thermodynamic Data*

$$\begin{aligned}\Delta H_{298}^{\circ} &= -66.3 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= 21.6 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 6.42 \cdot 10^2 T^{-0.476} \exp(+7600/T) \\ &\quad (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

<i>k/cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup></i>	<i>T/K</i>	<i>Reference</i>	<i>Comments</i>
<i>Rate Coefficient Measurements</i>			
$3.7 \cdot 10^{-12}$	813	Baldwin and Cowe, 1962 <sup>1</sup>	(a)
$2.2 \cdot 10^{-11} \exp(-1892/T)$	297–652	Westenberg and de Haas, 1972 <sup>2</sup>	(b)
$5.4 \cdot 10^{-14}$	297	Ridley <i>et al.</i> , 1972 <sup>3</sup>	(c)
$3.3 \cdot 10^{-11} \exp(-1847/T)$	264–479	Klemm, 1979 <sup>4</sup>	(d)
$5.5 \cdot 10^{-10} \exp(-5280/T)$	1700–2500	Dean <i>et al.</i> , 1980 <sup>5</sup>	(e)
$4.8 \cdot 10^{-11} \exp(-1879/T)$	1180–1690	Choudhury and Lin, 1989 <sup>6</sup>	(f)
$6.6 \cdot 10^{-11} \exp(-2100/T)$	1900–2700	Cribb, Dove, and Yamazaki, 1992 <sup>7</sup>	(g)
$1.45 \cdot 10^{-11} \exp(-1744/T)$	296–603	Oehlers <i>et al.</i> , 2000 <sup>8</sup>	(h)
<i>Reviews and Evaluations</i>			
$2.1 \cdot 10^{-16} T^{1.62} \exp(-1090/T)$	300–1700	CEC, 1992; 1994 <sup>9</sup>	(i)

**Comments**

- (a) Inhibition of H<sub>2</sub>+O<sub>2</sub> reaction at the second ignition limit by added HCHO.
- (b) Discharge flow; H atoms monitored by ESR in presence of excess HCHO.
- (c) Pulsed vacuum UV photolysis of HCHO; H atom decay monitored by Lyman- $\alpha$  resonance fluorescence.
- (d) Flash photolysis; resonance fluorescence detection of H atoms.
- (e) HCHO/O<sub>2</sub>/Ar and HCHO/N<sub>2</sub>O/Ar mixtures investigated in reflected shock waves; HCHO monitored by IR emission.
- (f) Shock-wave pyrolysis of methyl nitrate/1,3,5 trioxane mixtures. CO production was monitored by time-resolved resonance absorption. *k* was determined by kinetic modeling and showed highest sensitivity to the values of  $k(\text{H}+\text{CHO}) = 1.2 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k(\text{CHO}+\text{M}) = 3.16 \cdot 10^{-10} \times \exp(-8566/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .
- (g) Shock-wave pyrolysis of CH<sub>3</sub>OH studied by laser Schlieren densitometry and dynamic mass spectrometry. *k* determined by computer simulation with rigorous sensitivity and error analysis for seven rate constants.
- (h) Discharge flow study with H atoms generated by a microwave discharge in H<sub>2</sub>/He mixtures. An excess of HCHO was used and [H] was monitored by EPR spectrometry and [HCO] by LIF. H atom concentrations were calibrated by titration with NO<sub>2</sub> and HCO concentrations using the F+HCHO reaction, with F atom concentrations determined from the H atom EPR signal from the F+H<sub>2</sub> reaction. Values of *k* were derived by fitting the [H] profile using a detailed mechanism and,

at one temperature, by fitting the [CHO] profile. Good agreement was obtained. The reaction D+HCHO was also studied.

- (i) Based on the analysis by Choudhury and Lin<sup>6</sup> of the data cited in Refs. 1–7.

**Preferred Values**

$$k = 6.8 \cdot 10^{-16} T^{1.47} \exp(-1230/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the range 290–2500 K.

See Note added in proof.

**Reliability**

$$\Delta \log k = \pm 0.1 \text{ at } 290 \text{ K, rising to } \pm 0.5 \text{ at } 2500 \text{ K.}$$

**Comments on Preferred Values**

The preferred value is a least squares 3 parameter fit to the low temperature data of Westenberg and de Haas,<sup>2</sup> Ridley *et al.*,<sup>3</sup> Klemm,<sup>4</sup> and Oehlers *et al.*<sup>8</sup> and the shock tube studies of Dean *et al.*,<sup>5</sup> Choudhury *et al.*,<sup>6</sup> and Cribb *et al.*<sup>7</sup> The temperature dependent studies were given equal weight using 2 data points each at the extremes of the temperature range studied. The earlier value of Baldwin and Cowe<sup>1</sup> at 813 K is well described by this expression, as are the room temperature data of Brennen *et al.*<sup>10</sup> and of Slemr and Warneck.<sup>11</sup> The values of *k* obtained by Vandooren *et al.*<sup>12</sup> seem unacceptably high and those of Nadtochenko *et al.*,<sup>13</sup> are too low.

From their studies of the D+HCHO reaction Oehlers *et al.*<sup>8</sup> have shown that the reaction mechanism involves addition as well as the commonly accepted abstraction process. Irdam *et al.*<sup>14</sup> have evaluated much of the experimental data and have modeled the abstraction reaction over a wide tem-

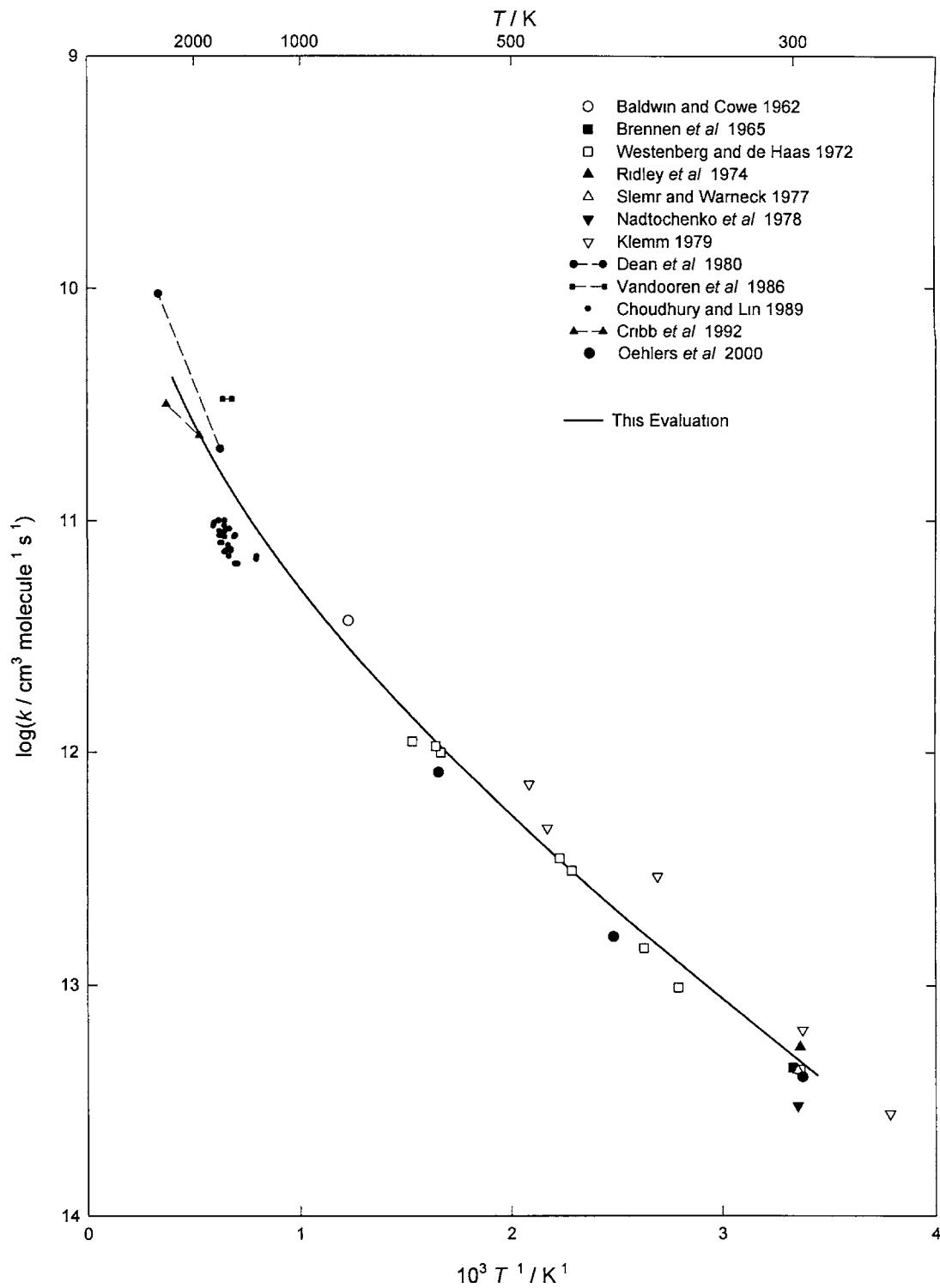
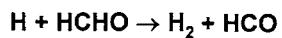
perature range using transition-state theory. The expression they derive is in excellent agreement with our preferred expression at low temperatures and within a factor of  $\sim 4$  at 2500 K.

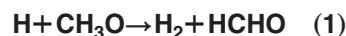
*Note added in proof.*

Since this data sheet was compiled, Friedrichs *et al.* [Int. J. Chem. Kinet. **34**, 374 (2002)] have studied in this reaction behind shock waves using  $C_2H_5I$  as the H atom source and detecting  $HCHO$  by VUV absorption. Over the range 1510–1960 K,  $k$  was given by  $k = 1.10 \cdot 10^{-9} \exp(-4880/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The results are significantly higher than given by our currently recommended expression. This new direct determination appears to be more reliable than the previously scattered results at these temperatures. We have therefore combined it with the lower temperature results of our currently recommended expression to give  $k = 3.34 \cdot 10^{-23} T^{3.81} \exp(-202/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 290–2500 K, which supersedes our previous recommendations. The error limits are unchanged.

## References

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- <sup>2</sup>A. A. Westenberg and N. de Haas, J. Phys. Chem. **76**, 2213 (1972).
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- <sup>9</sup>CEC, 1992; Supplement I, 1994 (see references in Introduction).
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- <sup>11</sup>F. Slemr and P. Warneck, Int. J. Chem. Kinet. **9**, 267 (1977).
- <sup>12</sup>J. Vandooren, L. Oldenhove de Guertechin, and P. J. Van Tiggelen, Combust. Flame **64**, 127 (1986).
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#### Thermodynamic Data

$$\begin{aligned}\Delta H^\circ_{298}(1) &= -342.8 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(1) &= -5.36 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 2.08 \cdot 10^3 T^{-0.994} \exp(+40940/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

$$\begin{aligned}\Delta H^\circ_{298}(2) &= -51.7 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(2) &= 33.7 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 2.73 \cdot 10^5 T^{-1.171} \exp(+5660/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$2.8 \cdot 10^{-11}$	300	Hoyermann <i>et al.</i> , 1981 <sup>1</sup>	(a)
$3.3 \cdot 10^{-11}$	1500	Zaslonko, Mukoseev, and Tyurin, 1988 <sup>2</sup>	(b)
$9.0 \cdot 10^{-11} \exp(-300/T)$	298–490	Dóbé, Bércecs, and Szilagyi, 1991 <sup>3</sup>	(c)
<i>Branching Ratios</i>			
$k_1/k = 0.81 \pm 0.12$	298	Dóbé, Bércecs, and Szilagyi, 1991 <sup>3</sup>	(d)
$k_2/k \geq 0.07 \pm 0.03$			
$k_2/k \approx 0.3$	298	Heinemann-Fiedler and Hoyermann, 1988 <sup>4</sup>	(e)
<i>Reviews and Evaluations</i>			
$3.0 \cdot 10^{-11}$	300–1000	CEC, 1992; 1994 <sup>5</sup>	(f)

#### Comments

- (a) Discharge flow study with mass spectrometric detection of reactants.  $k$  determined relative to  $k(\text{H} + \text{C}_2\text{H}_5) = 6 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (this evaluation).
- (b) Shock tube study using decomposition of Ar/methyl nitrite and Ar/methyl nitrate mixtures to generate  $\text{CH}_3\text{O}$  radicals. Chemiluminescence of  $\text{HCHO}$  monitored in the 480–580 nm region. Concentrations of  $\text{CH}_3\text{ONO}$  and  $\text{CH}_3\text{ONO}_2$  were measured in absorption at  $\sim 230$  nm.
- (c) Discharge flow study; laser induced fluorescence detection of  $\text{CH}_3\text{O}$  produced from 3 different sources, in the presence of an excess of H atoms.
- (d) Based on measured yields of  $\text{HCHO}$  and  $\text{OH}$ .  $\text{CH}_3\text{OH}$  also observed which is attributed to stabilization of an initially formed  $\text{CH}_3\text{OH}^*$  adduct.
- (e) Discharge flow study; time of flight mass spectrometric detection of  $\text{CH}_3$ .  $\text{F} + \text{CH}_4$  reaction used to calibrate the yield of  $\text{CH}_3$ .
- (f) Based on the results of Hoyermann *et al.*<sup>1</sup>

#### Preferred Values

$k = 9.0 \cdot 10^{-11} \exp(-300/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 298–1000 K.

$k_1/k = 0.7$ ;  $k_2/k = 0.3$  at 298 K.

#### Reliability

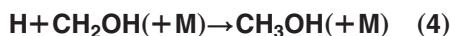
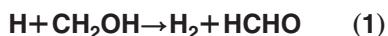
$\Delta \log k = \pm 0.1$  at 298 K, rising to  $\pm 0.3$  at 1000 K.  
 $\Delta(k_1/k) = {}^{+0.15}_{-0.20}$ ;  $(k_2/k) = \pm 0.2$  at 298 K.

#### Comments on Preferred Values

The preferred rate expression is that of Dóbé *et al.*<sup>3</sup> with which the value of  $k$  obtained by Hoyermann *et al.*<sup>1</sup> is in excellent agreement. The indirect estimate of  $k$  at  $\sim 1500$  K from the study of Zaslonko *et al.*<sup>2</sup> is in reasonable agreement when the substantial experimental uncertainties are taken into account. Branching ratios apply to low pressure only ( $< 15$  mbar). The increase in  $k$  with temperature may reflect an increasing component due to abstraction [Channel (1)].

#### References

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#### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = -308.8 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = -9.16 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 28.5 T^{-0.676} \exp(+36960/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(3) = -16.7 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = 19.18 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 2.77 \cdot 10^3 T^{-0.815} \exp(+1710/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(2) = 6.01 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = 12.38 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 6.95 \cdot 10^{17} \exp(-2860/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(4) = -401.7 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(4) = -118.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(4) = 8.6 \cdot 10^{-27} T^{0.131} \exp(+48480/T) \text{ cm}^3 \text{ molecule}^{-1} \\ (300 \leq T/\text{K} \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2 + k_3 + k_4$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$4.8 \cdot 10^{-11}$	290–300	Hoyermann <i>et al.</i> , 1981 <sup>1</sup>	(a)
$6.8 \cdot 10^{-11}$	296	Dóbé <i>et al.</i> , 1994 <sup>2</sup>	(b)
<i>Branching Ratios</i>			
$(k_1 + k_2)/k = 0.75$	290–300	Hoyermann <i>et al.</i> , 1981 <sup>1</sup>	(a)
$k_3/k = 0.3$	298	Heinemann-Fidler and Hoyermann, 1988 <sup>3</sup>	(c)
$k_3/k = 0.25$	296	Dóbé <i>et al.</i> , 1994 <sup>2</sup>	(b)
<i>Reviews and Evaluations</i>			
$k_1 = 1 \cdot 10^{-11}$	300–2500	Tsang, 1987 <sup>4</sup>	(d)
$k_3 = 1.6 \cdot 10^{-10}$			

#### Comments

- (a) Relative rate measurements made in a discharge flow study of the reaction of H and D atoms with deuterium labeled CH<sub>2</sub>OH species in He carrier gas at total pressures in the range 0.13–2.6 mbar. CH<sub>2</sub>OH and its isotopic variants were produced by the F+CH<sub>3</sub>OH reaction. Reactants and products were detected by molecular sampling into a mass spectrometer. Cited value of  $k$  obtained from the observed ratio  $k/k(\text{H} + \text{C}_2\text{H}_5) = 0.8$  using  $k(\text{H} + \text{C}_2\text{H}_5) = 6.0 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (this evaluation).
- (b) Discharge flow study with CH<sub>2</sub>OH radicals produced by the Cl+CH<sub>3</sub>OH reaction in a He carrier gas at a total pressure of 1.5 mbar. [CH<sub>2</sub>OH] and [OH] were monitored by time resolved LMR and [H] by ESR. The concentrations of CH<sub>2</sub>OH, H, and OH were established by gas titration reactions and the concentration profiles of these species were fitted by a substantial reaction mechanism. The corresponding reaction of CD<sub>2</sub>OD was also studied.
- (c) Technique similar to (a) but detection of species carried out using a time of flight mass spectrometer with a photoionization ion source.

(d)  $k_1$  estimated by analogy with H+C<sub>2</sub>H<sub>5</sub> reaction.  $k_3$  also estimated but source not given.

#### Preferred Values

$$k = 5.8 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.} \\ (k_1 + k_2)/k = 0.7 \text{ at } 298 \text{ K.}$$

#### Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta[(k_1 + k_2)/k] = \pm 0.1 \text{ at } 298 \text{ K.}$$

#### Comments on Preferred Values

The reaction of atomic H with CH<sub>2</sub>OH can occur by addition to form highly energized CH<sub>3</sub>OH\* or by direct abstraction [Channels (1) and (2)]. The energized CH<sub>3</sub>OH\* may be collisionally stabilized [Channel (4)] or may decompose to give a variety of products of which, in this case, CH<sub>3</sub>+OH are the most probable. The decomposition channels for CH<sub>3</sub>OH\* are discussed in more detail on the data sheet for the CH<sub>3</sub>+OH reaction which involves the same intermediate but with a slightly different degree of energization.

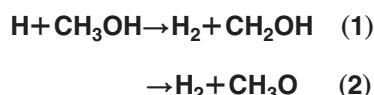
The preferred value for  $k$  is based on the two studies cited in the Table which are in reasonable agreement. Cribbs *et al.*<sup>5</sup> have also obtained a value of  $k = 1.7 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  from a study of methanol pyrolysis in shock waves at 1800–2740 K. The reaction was monitored by laser Schlieren densitometry and mass spectrometric detection of a number of species (CH<sub>3</sub>OH, CH<sub>2</sub>O, CO, C<sub>2</sub>H<sub>2</sub>, CH<sub>4</sub>, CH<sub>3</sub>, and H<sub>2</sub>O). Although the H + CH<sub>2</sub>OH reaction is a significant secondary reaction in the system the determination is rather indirect; modeling of a very substantial mechanism is required to extract the value of  $k$ . The temperature coefficient of  $k$  is expected to be small but until there are more direct studies no recommendation is made at elevated temperatures.

All of the studies of the branching ratios have been carried out at low pressures and give results in reasonable agreement. Studies with deuterium labeled species show that H<sub>2</sub> is formed with a yield of  $\sim 0.7$  in a direct process [Channels (1) and (2)] and since the CHOH is expected to isomerize rap-

idly to CH<sub>2</sub>O the two paths are indistinguishable. OH radicals have been detected with a yield of 25% in one study<sup>1</sup> and CH<sub>3</sub> radicals with a yield of 30% in another<sup>3</sup> establishing Channel (3) as the other pathway for the reaction under the low pressure conditions used. This is in accord with the estimates made by Tsang<sup>4</sup> using RRKM theory. At higher pressures increasing stabilization of the CH<sub>3</sub>OH [Channel (4)] is expected.

## References

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- <sup>5</sup>P. H. Cribbs, J. E. Dove, and S. Yamazaki, Combust. Flame **88**, 169 (1992).



### Thermodynamic Data

$$\begin{aligned} \Delta H^\circ_{298}(1) &= -34.27 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(1) &= 20.09 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 94.7 T^{-0.192} \exp(+3780/T) \\ (300 \leq T/\text{K} \leq 5000) \end{aligned}$$

$$\begin{aligned} \Delta H^\circ_{298}(2) &= 0.73 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(2) &= 5.57 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 1.32 T^{0.124} \exp(-200/T) \\ (300 \leq T/\text{K} \leq 5000) \end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

### Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$3.8 \cdot 10^{-11} \exp(-2669/T)$	295–653	Aders and Wagner, 1971 <sup>1</sup>	(a)
$5.7 \cdot 10^{-11} \exp(-1310/T)$	1000–2000	Vandooren and Van Tiggelen, 1981 <sup>2</sup>	(b)
$2.2 \cdot 10^{-11} \exp(-2650/T)$	500–680	Hoyermann, Sievert, and Wagner, 1981 <sup>3</sup>	(c)
$5.0 \cdot 10^{-10} \exp(-7120/T)$	1800–2740	Cribb, Dove, and Yamazaki, 1992 <sup>4</sup>	(d)
<i>Reviews and Evaluations</i>			
$3.52 \cdot 10^{-17} T^{2.1} \exp(-2450/T)$ $k_1/k_2 = 4$	600–2000	Tsang, 1987 <sup>5</sup>	(e)

### Comments

- (a) Fast-flow discharge system used. [H] monitored by ESR and concentration of stable species (CH<sub>3</sub>OH, O<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>) by mass spectrometry. CH<sub>3</sub>OH in large excess over H. The stoichiometry ( $\Delta H/\Delta \text{CH}_3\text{OH}$ ) was shown to approach one at  $[\text{CH}_3\text{OH}]/[\text{H}] > 50$ .  $k$  found to be independent of pressure over the range 1.8–46 mbar.
- (b) Molecular beam mass spectrometer used to sample fuel lean methanol/O<sub>2</sub>/H<sub>2</sub>/Ar flames burning at 53 mbar. Mole fractions of CO, CO<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>, CH<sub>3</sub>OH, HCHO,

Ar, H<sub>2</sub>O, H, O, OH, CH<sub>3</sub>, CH<sub>2</sub>OH (or CH<sub>3</sub>O) were determined as a function of distance from the burner. Steady state analysis used to obtain  $k$ .

- (c) Fast-flow discharge system used to study reaction of H/D atoms with normal and deuterated methanols. [H] monitored by molecular beam sampling into a mass spectrometer. Large excess of methanol over H used.  $k$  independent of pressure in the range 2.6–10.6 mbar.
- (d) Shock tube study of CH<sub>3</sub>OH decomposition with laser-Schlieren and time-of-flight (TOF) mass spectrometric detection systems. CH<sub>3</sub>OH/H<sub>2</sub>/Ar/He mixtures used. Concentration profiles of CH<sub>3</sub>OH, HCHO, CO, C<sub>2</sub>H<sub>2</sub>,

$\text{CH}_4$ ,  $\text{CH}_3$ , and  $\text{H}_2\text{O}$  were obtained.  $k$  obtained by modeling product profiles and fitting to assumed mechanism. Reaction written as occurring by Channel (1) but no distinction between the two channels was made in the experiments.

- (e) BEBO transition state calculation used to fit the results of Refs. 1–3 and those of Meagher *et al.*<sup>6</sup>  $k_1/k_4$  based on analogy of methyl radical reactions with methanol.

### Preferred Values

$$k = 5.7 \cdot 10^{-15} T^{1.24} \exp(-2260/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the range 295–2500 K.

### Reliability

$\Delta \log k = \pm 0.3$  at 295 K, rising to  $\pm 0.6$  at 2500 K.

### Comments on Preferred Values

There are three studies<sup>1,3,6</sup> at temperatures in the range 295–680 K which give very similar values for the temperature dependence of  $k$  but which differ by a factor of 4 with respect to the absolute values of  $k$ . The studies of Aders and Wagner<sup>1</sup> and of Hoyermann *et al.*<sup>3</sup> are in reasonable agreement but the values of  $k$  obtained by Meagher *et al.*<sup>6</sup> are much lower. The discrepancy may be due to uncertainties in

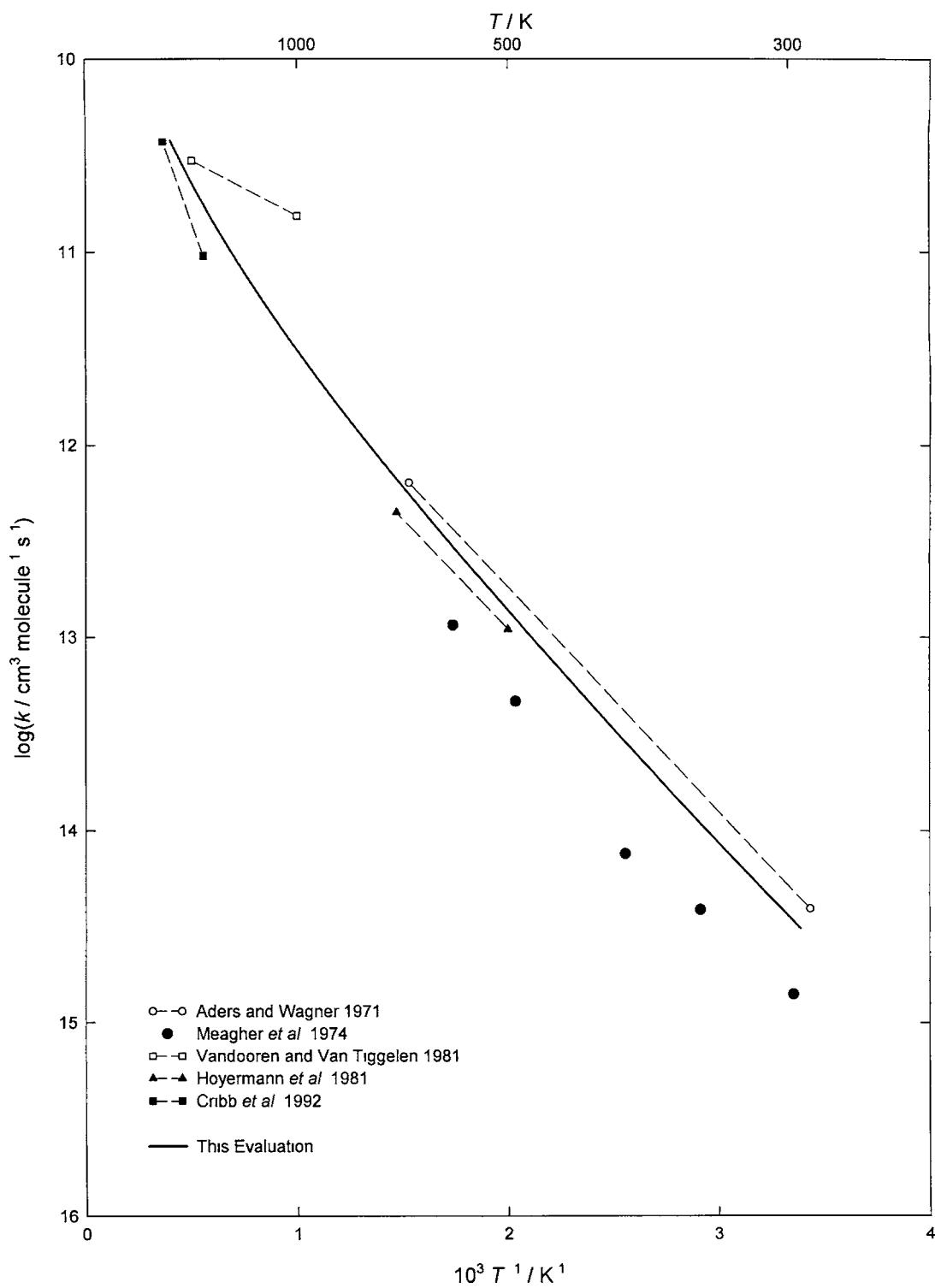
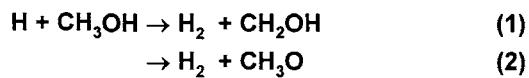
the stoichiometric factor which Meagher *et al.*<sup>6</sup> used to derive their values of  $k$  and for this reason the results of Aders and Wagner<sup>1</sup> and Hoyermann *et al.*<sup>3</sup> are preferred.

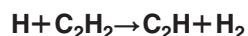
At higher temperatures there are two studies<sup>2,4</sup> giving similar values for  $k$  at 2000 K (within a factor of 2.5) but the values of the temperature dependence of  $k$  found differ widely and are also in disagreement with values obtained in the low temperature studies.<sup>1,3</sup>

The preferred expression for  $k$  is based on the low temperature results of Aders and Wagner<sup>1</sup> and Hoyermann *et al.*<sup>3</sup> and, at high temperatures, the mean value at 2000 K of the results of Vandooren *et al.*<sup>2</sup> and of Cribb *et al.*<sup>4</sup> There is no experimental information on the channel branching ratios but the thermochemistry of the reaction and the reaction path degeneracies would favor Channel (1).

### References

- <sup>1</sup> W. K. Aders and H. Gg. Wagner, Z. Phys. Chem. N.F. **74**, 224 (1971).
- <sup>2</sup> J. Vandooren and P. J. Van Tiggelen, 19th Symp. (Int.) Combustion, 1981, p. 473.
- <sup>3</sup> K. Hoyermann, R. Sievert, and H. Gg. Wagner, Ber Bunsenges. Phys. Chem. **85**, 169 (1981).
- <sup>4</sup> P. H. Cribb, J. E. Dove, and S. Yamazaki, Combust. Flame **88**, 169 (1992).
- <sup>5</sup> W. Tsang, J. Phys. Chem. Ref. Data **16**, 471 (1987).
- <sup>6</sup> J. F. Meagher, P. Kim, J. H. Lee, and R. B. Timmons, J. Phys. Chem. **78**, 2650 (1974).





#### Thermodynamic Data

$$\Delta H_{298}^{\circ} = 119.9 \text{ kJ mol}^{-1}$$

$$\Delta S_{298}^{\circ} = 28.37 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c = 4.83 \cdot 10^3 T^{-0.677} \exp(-14806/T) \\ (300 \leq T/\text{K} \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
See Comments on Preferred Values			
<i>Reviews and Evaluations</i>			
$1.0 \cdot 10^{-10} \exp(-11200/T)$	300–2500	Tsang and Hampson, 1986 <sup>1</sup>	(a)
$1.0 \cdot 10^{-10} \exp(-14000/T)$	1000–3000	CEC, 1992; 1994 <sup>2</sup>	(b)
$1.50 \cdot 10^{-13} T^{1.32} \exp(-15220/T)$		Peeters, Van Look, and Ceursters, 1996 <sup>3</sup>	(c)

#### Comments

- (a) Based on thermodynamic data and data on  $k(\text{C}_2\text{H} + \text{H}_2)$ , taking  $k(\text{C}_2\text{H} + \text{H}_2) = 1.9 \cdot 10^{-11} \exp(-1450/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .
- (b) Based on thermodynamic data and evaluation of the data for  $k(\text{C}_2\text{H} + \text{H}_2)$ .
- (c) Reverse reaction modeled using Transition State Theory and fitted to the low temperature data to derive an expression for  $k(\text{C}_2\text{H} + \text{H}_2)$  which was combined with thermodynamic data (evaluated by the authors) to obtain the expression for  $k$ .

#### Preferred Values

$$k = 1.67 \cdot 10^{-14} T^{1.64} \exp(-15250/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \\ \text{over the range 300–3000 K.}$$

#### Reliability

$$\Delta \log k = \pm 0.2 \text{ at 300 K, rising to } \pm 0.7 \text{ at 3000 K.}$$

#### Comments on Preferred Values

There are high temperature flame,<sup>4</sup> pyrolysis,<sup>5</sup> and shock tube<sup>6,7</sup> studies from which values of  $k$  have been derived. However they are all indirect, they involve complex systems, and the values of  $k$  obtained often depend on the particular thermodynamic data used. As in our previous evaluations we prefer to make use of the data on the reverse reaction for which fairly reliable values of the rate constant have been measured over the range 180–850 K. Our preferred expres-

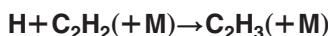
sion for  $k$  is therefore obtained by combining our expression for  $k(\text{C}_2\text{H} + \text{H}_2)$  (this evaluation) with the expression for  $K_c$  cited above. Since the most reliable high temperature experimental studies on  $k(\text{C}_2\text{H} + \text{H}_2)$  agree with our preferred expression for  $k(\text{C}_2\text{H} + \text{H}_2)$  to within a factor of  $\sim 3$ , the expression for  $k$  is recommended for use up to 3000 K with increasing error limits.

Peeters *et al.*<sup>3</sup> have used a transition state treatment of the reverse reaction to fit the low temperature data for  $k(\text{C}_2\text{H} + \text{H}_2)$  and have combined their expression for  $k(\text{C}_2\text{H} + \text{H}_2)$  with their thermodynamic data to obtain the expression cited in the Table. This expression agrees well with our preferred expression to within a factor of 2 over the range 300–3000 K.

The data for the addition channel,  $\text{H} + \text{C}_2\text{H}_2(+\text{M}) \rightarrow \text{C}_2\text{H}_3(+\text{M})$ , are evaluated separately on the data sheet which follows.

#### References

- <sup>1</sup> W. Tsang and R. F. Hampson, *J. Phys. Chem. Ref. Data* **15**, 1087 (1986).
- <sup>2</sup> CEC, 1992; Supplement I, 1994 (see references in Introduction).
- <sup>3</sup> J. Peeters, H. Van Look, and B. Ceursters, *J. Phys. Chem.* **100**, 15124 (1996).
- <sup>4</sup> W. G. Browne, R. P. Porter, J. D. Verlin, and A. H. Clarke, 12th Symp. (Int.) Combustion, 1969, p. 1035.
- <sup>5</sup> Yu. P. Yampolskii, K. P. Lavorskii, V. Maksimov, and V. M. Rybin, *Kinet. Katal.* **15**, 9 (1974).
- <sup>6</sup> W. Gardiner, T. Tanzawa, T. Koike, and K. Morinaga, *Bull. Chem. Soc. Jpn.* **58**, 1851 (1985).
- <sup>7</sup> J. H. Kiefer, S. Kapsalis, M. Z. Al-Alami, and K. A. Budach, *Combust. Flame* **51**, 71 (1983).

*Thermodynamic Data*

$$\begin{aligned}\Delta H_{298}^{\circ} &= -146.5 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= -81.6 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 2.42 \cdot 10^{-24} T^{0.020} \exp(+17600/T) \text{ cm}^3 \text{ molecule}^{-1} \\ &(300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	[M]/molecule cm $^{-3}$	Reference	Comments
<i>Rate Coefficient Measurements</i>				
<i>Intermediate Fall-off Range</i>				
$1.1 \cdot 10^{-14}$	193	$1.0 \cdot 10^{18}(\text{He})$	Payne and Stief, 1976 <sup>1</sup>	(a)
$1.4 \cdot 10^{-14}$		$6.0 \cdot 10^{18}$		
$1.9 \cdot 10^{-14}$	228	$4.2 \cdot 10^{17}$		
$3.7 \cdot 10^{-14}$		$4.2 \cdot 10^{18}$		
$5.1 \cdot 10^{-14}$		$2.1 \cdot 10^{19}$		
$3.2 \cdot 10^{-14}$	298	$3.2 \cdot 10^{17}$		
$1.1 \cdot 10^{-13}$		$3.2 \cdot 10^{18}$		
$1.6 \cdot 10^{-13}$		$2.3 \cdot 10^{19}$		
$5.0 \cdot 10^{-14}$	400	$2.4 \cdot 10^{17}$		
$2.3 \cdot 10^{-13}$		$2.4 \cdot 10^{18}$		
$4.2 \cdot 10^{-13}$		$1.7 \cdot 10^{19}$		
<i>High Pressure Range</i>				
$6.04 \cdot 10^{-14} T^{1.09} \exp(-1328/T)$	200–2000	$4.8 \cdot 10^{15}–4.8 \cdot 10^{19}(\text{He}, \text{N}_2)$	Knyazev and Slagle, 1996 <sup>2</sup>	(b)
<i>Reviews and Evaluations</i>				
$k_{\infty} = 1.4 \cdot 10^{-11} \exp(-1300/T)$	200–400		CEC, 1992;1994 <sup>3</sup>	(c)
$k_0[\text{He}] = [\text{He}] 3.3 \cdot 10^{-30} \exp(-740/T)$				
$F_c(\text{He}) \approx 0.44$				

**Comments**

- (a) Flash photolysis coupled with time resolved detection of H atoms via resonance fluorescence was employed in this study.
- (b) The unimolecular decomposition of C<sub>2</sub>H<sub>3</sub> was studied in a treated tubular flow reactor coupled to a photoionization mass spectrometer. C<sub>2</sub>H<sub>3</sub> was generated by the pulsed photolysis of vinyl bromide at 193 or 248 nm, or the photolysis of methyl vinyl ketone at 193 nm. Experiments were conducted with He, Ar, and N<sub>2</sub> pressures in the range  $(6–48) \cdot 10^{16}$  molecule cm $^{-3}$  and at temperatures between 879 and 1058 K. Fall-off behavior was reproduced using master equation modeling with tunneling effects included. Transition state properties were characterized by *ab initio* calculations. The rate coefficients were parameterized using the formalism of Ref. 4 and including the data for the reverse recombination reaction of Ref. 1. The resulting  $k_{\infty}$  for the recombination reaction agrees well with other experimental determinations.<sup>4–8</sup>

(c) Recommendation based on the experimental data of Payne and Stief<sup>1</sup> and a construction of the corresponding fall-off curve.

**Preferred Values**

$k_0 = 1.6 \cdot 10^{-20} T^{-3.47} \exp(-475/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  for M=He over the range 200–2000 K.

$k_0 = 1.0 \cdot 10^{-20} T^{-3.38} \exp(-426/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  for M=N<sub>2</sub> over the range 200–2000 K.

$k_{\infty} = 9.2 \cdot 10^{-16} T^{1.64} \exp(-1055/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 200–2000 K.

$F_c = 7.94 \cdot 10^{-4} T^{0.78}$  for M=He over the range 200–2000 K.

$F_c = 7.37 \cdot 10^{-4} T^{0.80}$  for M=N<sub>2</sub> over the range 200–2000 K.

**Reliability**

$\Delta \log k_0 = \pm 0.3$  for M=He, N<sub>2</sub> over the range 200–2000 K.

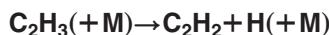
$\Delta \log k_\infty = \pm 0.3$  over the range 200–2000 K.  
 $\Delta F_c = \pm 0.1$  for M=He, N<sub>2</sub> over the range 200–2000 K.

### Comments on Preferred Values

The recent values of Knyazev and Slagle<sup>2</sup> for the reverse dissociation reaction of C<sub>2</sub>H<sub>3</sub> have been used to obtain the recommended  $k_\infty$  and  $k_0$  via the equilibrium constant above. These rate coefficients fit reasonably well with earlier recommendations.<sup>1,5–8</sup> The  $F_c$  values of Payne and Stief<sup>1</sup> have been adopted.

### References

- <sup>1</sup> W. A. Payne and L. J. Stief, J. Chem. Phys. **64**, 1150 (1976).
- <sup>2</sup> V. D. Knyazev and I. R. Slagle, J. Phys. Chem. **100**, 16899 (1996).
- <sup>3</sup> CEC, 1992; Supplement I, 1994 (see references in Introduction).
- <sup>4</sup> R. G. Gilbert, K. Luther, and J. Troe, Ber. Bunsenges. Phys. Chem. **87**, 169 (1983).
- <sup>5</sup> D. G. Keil, K. P. Lynch, J. A. Cowfer, and J. V. Michael, Int. J. Chem. Kinet. **8**, 825 (1976).
- <sup>6</sup> R. Ellul, P. Potzinger, R. Reimann, and P. Camilleri, Ber. Bunsenges. Phys. Chem. **85**, 407 (1981).
- <sup>7</sup> E. B. Gordon, A. P. Perminov, B. I. Ivanov, V. I. Matyushenko, A. N. Ponomarev, and V. L. Tal'roze, Sov. Phys. JETP **36**, 212 (1973).
- <sup>8</sup> E. B. Gordon, B. I. Ivanov, A. P. Perminov, and V. E. Balalaev, Chem. Phys. **35**, 79 (1978).



### Thermodynamic Data

$$\begin{aligned}\Delta H_{298}^0 &= 146.5 \text{ kJ mol}^{-1} \\ \Delta S_{298}^0 &= 81.6 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 4.13 \cdot 10^{23} T^{-0.020} \exp(-17600/T) \text{ molecule cm}^{-3} \\ &\quad (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

### Rate Coefficient Data

$k/\text{s}^{-1}$	T/K	[M]/molecule cm <sup>-3</sup>	Reference	Comments
<i>Rate Coefficient Measurements</i>				
<i>Low Pressure Range</i>				
[He] $6.58 \cdot 10^3 T^{-3.49} \exp(-18070/T)$	200–2000	$4.8 \cdot 10^{15}$ – $4.8 \cdot 10^{20}$	Knyazev and Slagle, 1996 <sup>1</sup>	(a)
[N <sub>2</sub> ] $4.26 \cdot 10^3 T^{-3.40} \exp(-18021/T)$	200–2000	$4.8 \cdot 10^{15}$ – $4.8 \cdot 10^{20}$		
<i>High Pressure Range</i>				
$3.86 \cdot 10^8 T^{1.62} \exp(-18650/T)$	200–2000	$4.8 \cdot 10^{15}$ – $4.8 \cdot 10^{20}$ (N <sub>2</sub> )	Knyazev and Slagle, 1996 <sup>1</sup>	(a)
<i>Reviews and Evaluations</i>				
$k_0[\text{Ar}, \text{N}_2] = [\text{Ar}, \text{N}_2] 6.9 \cdot 10^{17} T^{-7.5} \exp(-22900/T)$	500–2500		CEC, 1992; 1994 <sup>2</sup>	(b)
$k_\infty = 2 \cdot 10^{14} \exp(-20000/T)$	500–2500			
$F_c(\text{Ar}, \text{N}_2) = 0.35$	500–2500			

### Comments

- (a) Unimolecular decomposition of C<sub>2</sub>H<sub>3</sub> studied in a heated tubular flow reactor coupled to a photoionization mass spectrometer. C<sub>2</sub>H<sub>3</sub> formed by the pulsed photolysis of vinyl bromide at 193 or 248 nm, or the photolysis of methyl vinyl ketone at 193 nm. Experiments were conducted concentrations of He, Ar and N<sub>2</sub> in the range  $(6\text{--}48) \cdot 10^{18}$  molecule cm<sup>-3</sup> and at temperatures between 879 and 1058 K. Fall-off behavior was reproduced applying master equation modeling with tunneling effects included, transition state properties were characterized by *ab initio* calculations. The rate coefficients were parameterized using the formalism of Ref. 3 and including the data for the reverse recombination reaction of Refs. 4–8.
- (b) The preferred value for  $k_0$  is based on the RRKM fit of Tsang and Hampson<sup>9</sup> for the reverse reaction. The preferred value for  $k_\infty$  is from the evaluation of Warnatz<sup>10</sup> and based on the shock tube data of Skinner *et al.*<sup>11</sup>

### Preferred Values

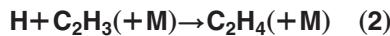
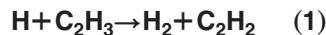
$$\begin{aligned}k_0 &= 6.6 \cdot 10^3 T^{-3.5} \exp(-18070/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ for M=He over the range 200–2000 K.} \\ k_0 &= 4.3 \cdot 10^3 T^{-3.4} \exp(-18020/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ for M=N}_2 \text{ over the range 200–2000 K.} \\ k_\infty &= 3.9 \cdot 10^8 T^{1.62} \exp(-18650/T) \text{ s}^{-1} \text{ over the range 200–2000 K.} \\ F_c &= 7.94 \cdot 10^{-4} T^{0.78} \text{ for M=He over the range 200–2000 K.} \\ F_c &= 7.37 \cdot 10^{-4} T^{0.80} \text{ for M=N}_2 \text{ over the range 200–2000 K.}\end{aligned}$$

### Reliability

$$\begin{aligned}\Delta \log k_0 &= \pm 0.3 \text{ for M=He over the range 200–2000 K.} \\ \Delta \log k_0 &= \pm 0.3 \text{ for M=N}_2 \text{ over the range 200–2000 K.} \\ \Delta \log k_\infty &= \pm 0.3 \text{ over the range 200–2000 K.} \\ \Delta F_c &= \pm 0.1 \text{ for M=He, N}_2 \text{ over the range 200–2000 K.}\end{aligned}$$

*Comments on Preferred Values*

The recent values of Knyazev and Slagle<sup>1</sup> are recommended and are consistent with the data of Payne and Stief,<sup>4</sup> Keil *et al.*,<sup>5</sup> Ellul *et al.*,<sup>6</sup> and Gordon *et al.*<sup>7,8</sup> for the reverse recombination reaction which were included in the analysis of Knyazev and Slagle<sup>1</sup> to derive the preferred rate coefficient. The present values for  $k_\infty$  are in close agreement with our previously recommended values.<sup>2</sup> On the other hand, the present  $k_0$  values are significantly higher than those preferred in our earlier evaluations.<sup>2</sup> The  $F_c$  values are from Ref. 1.

**References**<sup>1</sup>V. D. Knyazev and I. R. Slagle, J. Phys. Chem. **100**, 16899 (1996).<sup>2</sup>CEC, 1992; Supplement I, 1994 (see references in Introduction).<sup>3</sup>R. G. Gilbert, K. Luther, and J. Troe, Ber. Bunsenges. Phys. Chem. **87**, 169 (1983).<sup>4</sup>W. A. Payne and L. J. Stief, J. Chem. Phys. **64**, 1150 (1976).<sup>5</sup>D. G. Keil, K. P. Lynch, J. A. Cowfer, and J. V. Michael, Int. J. Chem. Kinet. **8**, 825 (1976).<sup>6</sup>R. Ellul, P. Potzinger, R. Reimann, and P. Camilleri, Ber. Bunsenges. Phys. Chem. **85**, 407 (1981).<sup>7</sup>E. B. Gordon, A. P. Perminov, B. I. Ivanov, V. I. Matyushenko, A. N. Ponomarev, and V. L. Tal'roze, Sov. Phys. JETP **36**, 212 (1973).<sup>8</sup>E. B. Gordon, B. I. Ivanov, A. P. Perminov, and V. E. Balalaev, Chem. Phys. **35**, 79 (1978).<sup>9</sup>W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data **15**, 1087 (1987).<sup>10</sup>J. Warnatz, in *Combustion Chemistry*, edited by W. C. Gardiner (Springer, New York, 1984).<sup>11</sup>G. B. Skinner, R. C. Sweet, and S. K. Davis, J. Phys. Chem. **75**, 1 (1971).*Thermodynamic Data*

$$\Delta H^\circ_{298}(1) = -289.5 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = -17.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 0.677 T^{-0.171} \exp(+34600/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(2) = -465.2 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = -129.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 1.60 \cdot 10^{-27} T^{0.221} \exp(+56080/T) \text{ cm}^3 \text{ molecule}^{-1} \\ (300 \leq T/\text{K} \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data ( $k = k_1 + k_2$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$2.0 \cdot 10^{-10}$	298	Fahr <i>et al.</i> , 1991 <sup>1</sup>	(a)
$1.80 \cdot 10^{-10}$	298	Fahr, 1995 <sup>2</sup>	(b)
$1.1 \cdot 10^{-10}$	213	Monks <i>et al.</i> , 1995 <sup>3</sup>	(c)
$1.0 \cdot 10^{-10}$	298		
<i>Reviews and Evaluations</i>			
$k_1 = 2 \cdot 10^{-11}$	300–2500	CEC, 1992; 1994 <sup>4</sup>	(d)

**Comments**

- (a) Photolysis of  $\text{C}_2\text{H}_3\text{I}$  at 193 nm was used to generate excited  $\text{C}_2\text{H}_3$  radicals which either dissociate to form  $\text{C}_2\text{H}_2$  and  $\text{H}$  or are collisionally stabilized leading to thermalized  $\text{C}_2\text{H}_3$  radicals. Product analysis by gas chromatography. By monitoring the  $\text{C}_4\text{H}_6$  formed at 210 nm and using a mechanism consisting of the reactions  $\text{C}_2\text{H}_3 + \text{C}_2\text{H}_3(+\text{M}) \rightarrow \text{C}_4\text{H}_6(+\text{M})$ ,  $\text{C}_2\text{H}_3 + \text{C}_2\text{H}_3 \rightarrow \text{C}_2\text{H}_2 + \text{C}_2\text{H}_4$ ,  $\text{H} + \text{C}_2\text{H}_3 \rightarrow \text{H}_2 + \text{C}_2\text{H}_2$ , and  $\text{H} + \text{C}_2\text{H}_3(+\text{M}) \rightarrow \text{C}_2\text{H}_4(+\text{M})$ , the rate coefficient for the reaction of  $\text{H}$  atoms with  $\text{C}_2\text{H}_3$  was determined. The experiments were conducted in 130 mbar He.
- (b) See comment (a).
- (c) Discharge flow technique coupled to mass spectrometric detection.  $\text{H}$  atoms and  $\text{C}_2\text{H}_3$  radicals generated by

the reaction of  $\text{F}$  atoms with  $\text{H}_2$  and  $\text{C}_2\text{H}_4$  which give  $\text{H}$  and  $\text{C}_2\text{H}_3$  respectively. The contribution of Channels (1) and (2) was determined by measuring the yields of  $\text{C}_2\text{D}_3\text{H}$  and  $\text{HD}$  in the reactions  $\text{H} + \text{C}_2\text{D}_3(+\text{M}) \rightarrow \text{C}_2\text{D}_3\text{H} (+\text{M})$  and  $\text{H} + \text{C}_2\text{D}_3 \rightarrow \text{C}_2\text{D}_2 + \text{HD}$ . The derived fractional products yields for Channels (1) and (2) were 0.76 and 0.24, respectively, at 213 K and 0.67 and 0.33, respectively, at 298 K. Fall-off extrapolations using the QRRKM model leads to the values:  $k_2^\circ[\text{He}] = [\text{He}]1.1 \cdot 10^{-27} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k_2^\infty = 8 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 213 K, and  $k_2^\circ[\text{He}] = [\text{He}]1.4 \cdot 10^{-27} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k_2^\infty = 1.7 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K. Extrapolations using the Troe formalism give the rate coefficients:  $k_2^\circ[\text{He}] = [\text{He}]5.4 \cdot 10^{-27} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k_2^\infty = 5 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 213 K, and  $k_2^\circ[\text{He}] = [\text{He}]3.5 \cdot 10^{-27} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k_2^\infty$

$=1.6 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K. The measurements were carried out at a pressure of 1.3 mbar of He.

- (d) Recommendation based on the indirect rate data of Skinner and Sokolski,<sup>5</sup> Benson and Haugen,<sup>6</sup> Skinner, Sweet, and Davis,<sup>7</sup> Keil, et al.,<sup>8</sup> Olson, Tanzawa, and Gardiner.<sup>9</sup>

### Preferred Values

$k_1 = 7 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 300 K.  
 $k_2^\circ = 3.5 \cdot 10^{-27} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  for M=He at 300 K.  
 $k_2^\infty = 1.6 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 300 K.  
 $F_{c,2} = 0.5$  for M=He at 300 K.

### Reliability

$\Delta \log k_1 = \pm 0.3$  at 300 K.  
 $\Delta \log k_2^\circ = \pm 0.3$  for M=He at 300 K.  
 $\Delta \log k_2^\infty = \pm 0.3$  at 300 K.  
 $\Delta F_{c,2} = \pm 0.1$  for M=He at 300 K.

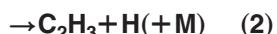
### Comments on Preferred Values

The recent measurements of Fahr<sup>1,2</sup> and Monks *et al.*<sup>3</sup> for the sum of the rate coefficients for Channels (1) and (2) are in reasonable agreement and form the basis for the present recommendation. The recommended  $k_1$  was derived from the branching ratio reported in Ref. 3. The value is substantially

larger than the only other room temperature value, that of Keil *et al.*<sup>8</sup> The measurements of Monks *et al.*<sup>3</sup> show that the Channel (1) has a small negative temperature dependence but Hidaka *et al.*<sup>10</sup> found that the modeling of their results from a shock tube study on ethylene pyrolysis and oxidation at 1100–2100 K required a value of  $1.6 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . A theoretical treatment of the reaction by Klippenstein and Harding<sup>11</sup> gives good agreement with the value of  $k_2^\infty$  but values of the branching ratio much smaller than the experimental values. More determinations are necessary to determine the relative role of both channels as a function of temperature and pressure.

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- P. S. Monks, F. L. Nesbitt, W. A. Wayne, M. Scanton, L. J. Stief, and D. E. Shallcross, J. Phys. Chem. **99**, 17151 (1995).
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### Thermodynamic Data

$$\begin{aligned}\Delta H^\circ_{298}(1) &= 175.7 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(1) &= 112.3 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 4.21 \cdot 10^{26} T^{-0.393} \exp(-21480/T) \text{ molecule cm}^{-3} \\ (300 \leqslant T/\text{K} \leqslant 5000) \end{aligned}$$

$$\begin{aligned}\Delta H^\circ_{298}(2) &= 465.2 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(2) &= 129.4 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 6.2 \cdot 10^{26} T^{-0.221} \exp(-56080/T) \text{ molecule cm}^{-3} \\ (300 \leqslant T/\text{K} \leqslant 5000) \end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

### Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{s}^{-1}$	T/K	[M]/molecule cm $^{-3}$	Reference	Comments
<i>Rate Coefficient Measurements</i>				
<i>Low Pressure Range</i>				
[Ar] $2.95 \cdot 10^{-7} \exp(-39000/T)$	1675–2210	$(2.5–32) \cdot 10^{18}$	Roth and Just, 1973 <sup>1</sup>	(a)
[Ar] $4.3 \cdot 10^{-7} \exp(-39900/T)$	1700–2200	$(6–16) \cdot 10^{18}$	Just, Roth, and Damm, 1976 <sup>2</sup>	(b)
[Ar] $4.9 \cdot 10^{-7} \exp(-40887/T)$	2000–2540	$(1.1–3.3) \cdot 10^{18}$	Tanzawa and Gardiner, 1980 <sup>3</sup>	(c)
[Ar] $1.5 \cdot 10^{-7} \exp(-37780/T)$	1600–2300	$4.7 \cdot 10^{18}$	Zelson, Davidson, and Hanson, 1994 <sup>4</sup>	(d)
<i>Reviews and Evaluations</i>				
$k_1^\circ [\text{Ar}, \text{Kr}] = [\text{Ar}, \text{Kr}] 5.8 \cdot 10^{-8} \exp(-36000/T)$	1500–3200		CEC, 1994 <sup>5</sup>	(e)
$k_2^\circ [\text{Ar}] = [\text{Ar}] 4.3 \cdot 10^{-7} \exp(-48600/T)$	1500–3200			

**Comments**

- (a) Shock tube study of  $\text{C}_2\text{H}_4$  (0.1%–1%)/Ar mixtures in reflected shocks.  $[\text{C}_2\text{H}_4]$  and  $[\text{C}_2\text{H}_2]$  followed simultaneously by IR emission at 3.0 and 3.35  $\mu\text{m}$ , respectively. Emission profiles corrected for interference between emission bands.  $\text{C}_2\text{H}_4$  decay found to proceed in two distinct phases; an initial phase of second order for which the rate coefficient was given as indicated above, and a latter phase for which the best interpretation was given by an order of 0.6 in [Ar] with rate coefficient  $k = 2.85 \cdot 10^{-2} \exp(-26570/T) \text{ cm}^{1.8} \text{ molecule}^{-0.6} \text{ s}^{-1}$ .
- (b) Shock tube study of  $\text{C}_2\text{H}_4$  (20–800 ppm)/Ar mixtures in reflected shocks.  $[\text{H}]$  followed by atomic resonance absorption at 121.5 nm calibrated by  $\text{H}_2$  dissociation in  $\text{H}_2/\text{Ar}$  mixtures.  $[\text{C}_2\text{H}_4]$  followed by absorption at 100.8 nm. H atom absorption corrected for  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_2$  contribution. The results of this work and those of Roth and Just<sup>1</sup> led the authors to conclude that there were two pathways for  $\text{C}_2\text{H}_4$  dissociation. Both sets of data were analyzed to give  $k_1$  (which was used in the analysis to obtain  $k_2$ ). The analysis of  $\text{C}_2\text{H}_4$  decomposition showed a strong influence of diluent on Channel (2) but only weak effects on Channel (1). The expression  $k_2 = 4.3 \cdot 10^{-7} \exp(-49400/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was obtained for Channel (2).
- (c) Pyrolysis of  $\text{C}_2\text{H}_4$  (2.5%, 5%, and 10%)/Ar mixtures behind incident shock waves. Analysis by laser Schlieren technique.  $k_1$  was obtained by optimization of a model comprising 14 reactions to fit initial deflection of laser beam.  $k_2$  was taken from Ref. 2, multiplied by 1.2 to improve fit to laser Schlieren data.
- (d) Pyrolysis of  $\text{C}_2\text{H}_4$  (189–444 ppm)/Ar mixtures in reflected shock waves.  $[\text{C}_2\text{H}_4]$  monitored by laser absorption spectroscopy and  $[\text{C}_2\text{H}_4]$  decay interpreted with a 32-reaction mechanism. Sensitivity analysis shows that the  $\text{C}_2\text{H}_4$  decomposition mechanism is only affected by the reaction (1). The measurements were carried out near the low pressure limit.
- (e) Recommended  $k_0$  value is based on the average of the values reported in Refs. 1–3 and Kiefer *et al.*<sup>6,7</sup>

**Preferred Values**

$k_1^0 = 3.4 \cdot 10^{-7} T \exp(-39390/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for M=Ar over the range 1500–3200 K.  
 $k_2^0 = 4.3 \cdot 10^{-7} \exp(-49400/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for M=Ar over the range 1500–3200 K.

*Reliability*

$\Delta \log k_1^0 = \pm 0.3$  for M=Ar over the range 1500–3200 K.  
 $\Delta \log k_2^0 = \pm 0.5$  for M=Ar over the range 1500–3200 K.

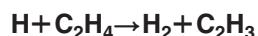
*Comments on Preferred Values*

The thermal decomposition of  $\text{C}_2\text{H}_4$  apparently is dominated by the 1,1 elimination channel to form singlet vinylidene ( $: \text{C}=\text{CH}_2$ ) which immediately isomerizes to acetylene. All experiments reported are in the fall-off region close to the low pressure limit. The agreement among the rate coefficients of Roth and Just,<sup>1</sup> Just *et al.*,<sup>2</sup> Tanzawa and Gardiner,<sup>3</sup> and the recent rate coefficients of Zelson *et al.*<sup>5</sup> is very good. Thus, we have chosen an average of the reported  $k_0$  values as the preferred value.

The experiments provide no information about the high pressure rate coefficient. The preferred value for  $k_2^0$  is unchanged from our previous evaluation and is based on the data of Just *et al.*<sup>2</sup> The rate constant of Channel (2) is expected to depend strongly on the bath gas.<sup>8</sup>

**References**

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*Thermodynamic Data*

$$\begin{aligned}\Delta H_{298}^{\circ} &= 29.3 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= 30.8 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 1.02 \cdot 10^3 T^{-0.373} \exp(-3890/T) \\ &\quad (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the origin source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$2.6 \cdot 10^{-10} \exp(-7000/T)$	1100–1500	Skinner, Sweet and Davis, 1971 <sup>1</sup>	(a)
$2.7 \cdot 10^{-13}$	1093	Yampol'skii, 1974 <sup>2</sup>	(b)
$4.4 \cdot 10^{-13}$	1213		
$2.5 \cdot 10^{-13}$	1073–1173	Nametkin, 1974 <sup>3</sup>	(c)
$8.3 \cdot 10^{-9} \exp(-11500/T)$	1700–2000	Just, Roth, and Damm, 1977 <sup>4</sup>	(d)
$1.25 \cdot 10^{-13}$	773	Baldwin <i>et al.</i> , 1984 <sup>5</sup>	(e)
$3.16 \cdot 10^{-14}$	900	Jayaweera and Pacey, 1988 <sup>6</sup>	(f)
$8.42 \cdot 10^{-17} T^{1.93} \exp(-6518/T)$	499–947	Knyazev <i>et al.</i> , 1996 <sup>7</sup>	(g)
<i>Reviews and Evaluations</i>			
$2.2 \cdot 10^{-18} T^{2.53} \exp(-6160/T)$	700–2000	Tsang and Hampson, 1986 <sup>8</sup>	(h)
$9 \cdot 10^{-10} \exp(-7500/T)$	700–2000	CEC, 1992; 1994 <sup>9</sup>	(i)

**Comments**

- (a) Shock tube study of H, D exchange in  $\text{C}_2\text{H}_4$  and its isotopomers. GC-MS analysis.
- (b) Thermal decomposition of  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{D}_4$ .  $\text{H}_2$  production monitored.  $k$  determined relative to rate coefficients for  $\text{H} + \text{D}_2$  and  $\text{H} + \text{CD}_4$  for which the values of Westenberg and de Haas<sup>10</sup> and McNesby and Gordon,<sup>11</sup> respectively, were used.
- (c) Radiochemical analysis of  $\text{C}_2\text{H}_4$  pyrolysis products.  $k$  based on  $\text{H}_2$  production.
- (d) Thermal decomposition of  $\text{C}_2\text{H}_4$  in reflected shock waves. H atom concentration monitored by time resolved atomic resonance absorption.
- (e) Addition of  $\text{C}_2\text{H}_4$  to slowly reacting  $\text{H}_2 + \text{O}_2$  mixtures.  $k$  measured relative to  $k(\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{OH})$  for which a value of  $1.03 \cdot 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 773 K (this evaluation) is used to calculate  $k$  from the ratio  $k(\text{H} + \text{C}_2\text{H}_4)/k_{\text{ref}} = 12 \pm 4$ .
- (f) Pyrolysis of  $\text{C}_2\text{H}_4$  in a flow system.  $\text{H}_2$  formation measured by gas chromatography. The value of  $k$  depends on the equilibrium constant for  $\text{H} + \text{C}_2\text{H}_4 \rightleftharpoons \text{C}_2\text{H}_5$  and the rate coefficient for  $\text{C}_2\text{H}_5 + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_6 + \text{C}_2\text{H}_3$ . The value given is a downward revision of the originally cited value ( $1.5 \cdot 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) proposed by Knyazev *et al.*<sup>7</sup>
- (g) Laser photolysis-photoionization mass spectrometric study of the reverse reaction,  $\text{C}_2\text{H}_3 + \text{H}_2 \rightarrow \text{H} + \text{C}_2\text{H}_4$ . Experimental results and those from *ab initio* calculations were combined to provide temperature dependent expressions for  $k$  for both forward and reverse reactions.
- (h) Based on a BEBO fit to the data in Ref. 4.

- (i) Based on the high temperature data in Ref. 4 and the low temperature data of Baldwin *et al.*<sup>5</sup> and Jayaweera and Pacey.<sup>6</sup>

**Preferred Values**

$$k = 3.9 \cdot 10^{-22} T^{3.62} \exp(-5670/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the range 400–2000 K.

*Reliability*

$$\Delta \log k = \pm 0.4 \text{ over the range 400–2000 K.}$$

*Comments on Preferred Values*

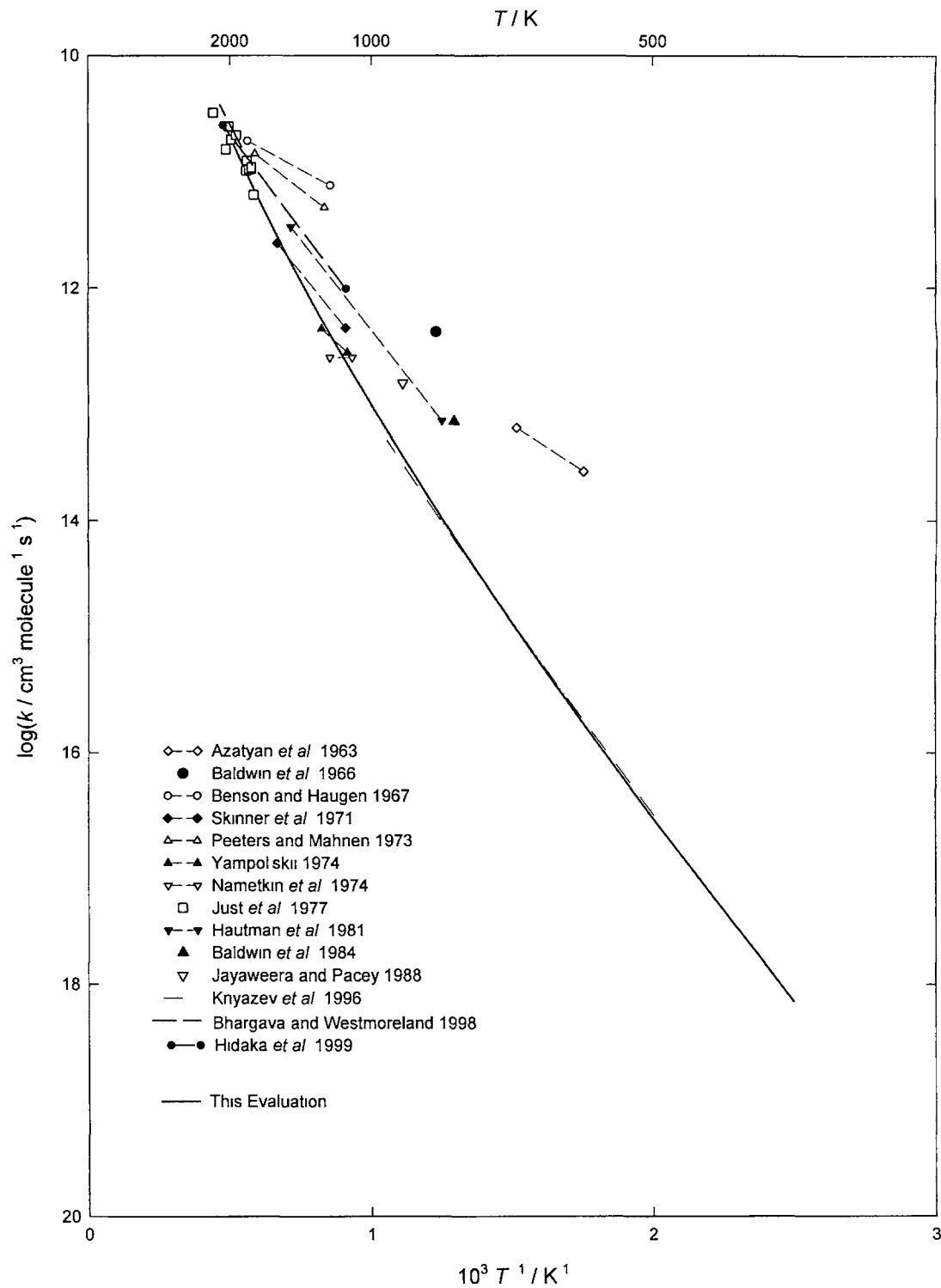
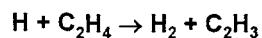
The preferred expression is a 3-parameter least squares fit to the data from the references cited in the Table which seem to give a consistent picture for the temperature dependence. The more recent data of Knyazev *et al.*<sup>7</sup> is preferred to earlier data at low temperatures<sup>12,13</sup> which may have been influenced by the addition reaction of H with  $\text{C}_2\text{H}_4$ . At high temperatures a flame study by Bhargava and Westmoreland<sup>14</sup> gives values in reasonable agreement over the range 1400–1800 K, and in a shock tube study on  $\text{C}_2\text{H}_4/\text{Ar}$  mixtures over the temperature range 1100–2100 K. Hidaka *et al.*<sup>15</sup> found that their results could be fitted using our previously recommended expression<sup>9</sup> which is in close agreement with the present recommendations at 2100 K but differs significantly at 1100 K. The data of Hautman *et al.*<sup>16</sup> and the older data of Benson and Haugen,<sup>17</sup> Peeters and Mahnan,<sup>18</sup> Baldwin *et al.*,<sup>12</sup> and Azatyan *et al.*<sup>13</sup> are considered less reliable and are not used in deriving the preferred values.

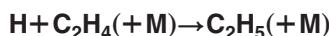
The data on the addition channel,  $\text{H} + \text{C}_2\text{H}_4 (+\text{M})$

$\rightarrow C_2H_5(+M)$ , are evaluated on the data sheet which follows the present one.

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- <sup>17</sup>S. W. Benson and G. R. Haugen, *J. Phys. Chem.* **71**, 1735 (1967).
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*Thermodynamic Data*

$$\Delta H_{298}^{\circ} = -149.5 \text{ kJ mol}^{-1}$$

$$\Delta S_{298}^{\circ} = -86.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c = 2.86 \cdot 10^{-25} T^{0.284} \exp(+17960/T) \text{ cm}^3 \text{ molecule}^{-1}$$

(300 ≤  $T/\text{K}$  ≤ 5000)

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	[M]/molecule cm <sup>-3</sup>	Reference	Comments
<i>Rate Coefficient Measurements</i>				
<i>Low Pressure Range</i>				
$[\text{He}]1.4 \cdot 10^{-29} \exp(-569/T)$	285–604	$(8-140) \cdot 10^{17}$	Lightfoot and Pilling, 1987 <sup>1</sup>	(a)
<i>Intermediate Fall-off Range</i>				
$3.2 \cdot 10^{-13}$	300	$1.6 \cdot 10^{17} (\text{N}_2)$	Braun and Lenzi, 1967 <sup>2</sup>	(b)
$4.3 \cdot 10^{-13}$		$3.2 \cdot 10^{17}$		
$6.7 \cdot 10^{-13}$		$9.3 \cdot 10^{17}$		
$1.9 \cdot 10^{-13}$		$1.6 \cdot 10^{17}$		
$4.0 \cdot 10^{-13}$		$4.8 \cdot 10^{17}$		
$8.0 \cdot 10^{-13}$		$24 \cdot 10^{17}$		
$3.3 \cdot 10^{-13}$	300	$1.6 \cdot 10^{17} (\text{He})$	Kurylo, Peterson, and Braun, 1970 <sup>3</sup>	(c)
$7.7 \cdot 10^{-13}$		$3.2 \cdot 10^{18}$		
$1.2 \cdot 10^{-12}$		$1.62 \cdot 10^{19}$		
$3.23 \cdot 10^{-12}$	775	$2.5 \cdot 10^{18} (\text{He})$	Brouard, Lightfoot, and Pilling, 1986 <sup>4</sup>	(d)
$2.97 \cdot 10^{-12}$	800	$2.4 \cdot 10^{18}$		
$2.79 \cdot 10^{-12}$	825	$2.3 \cdot 10^{18}$		
$2.0 \cdot 10^{-12}$	800	$1.2 \cdot 10^{18} (\text{He})$	Hanning-Lee <i>et al.</i> , 1993 <sup>5</sup>	(e)
$3.1 \cdot 10^{-12}$		$3.6 \cdot 10^{18}$		
$4.7 \cdot 10^{-12}$		$7.2 \cdot 10^{18}$		
$7.5 \cdot 10^{-13}$	298	$4.3 \cdot 10^{18} (\text{H}_2)$	Sillesen, Ratajczak, and Pagsberg, 1993 <sup>6</sup>	(f)
$6.51 \cdot 10^{-13}$	298	$5.8 \cdot 10^{17} (\text{N}_2)$	Clarke <i>et al.</i> , 2000 <sup>7</sup>	(g)
$7.40 \cdot 10^{-13}$		$1.1 \cdot 10^{18}$		
$8.48 \cdot 10^{-13}$		$1.9 \cdot 10^{18}$		
<i>High Pressure Range</i>				
$1.0 \cdot 10^{-12}$	300	$(1.6-29) \cdot 10^{17} (\text{N}_2)$	Braun and Lenzi, 1967 <sup>2</sup>	(b)
$1.36 \cdot 10^{-12}$	300	$(1.6-16) \cdot 10^{17} (\text{He})$	Kurylo, Peterson, and Braun, 1970 <sup>3</sup>	(c)
$9.1 \cdot 10^{-13}$	298	$(2.4-5.7) \cdot 10^{19} (\text{H}_2)$	Hikida, Eyre, and Dorfman, 1971 <sup>8</sup>	(h)
$1.3 \cdot 10^{-11} \exp(-755/T)$	303–478	$5.7 \cdot 10^{19} (\text{CO}_2)$	Penzhorn and Darwent, 1971 <sup>9</sup>	(i)
$1.6 \cdot 10^{-12}$	300	$(8.8-12900) \cdot 10^{15} (\text{He})$	Michael, Osborne, and Suess, 1973 <sup>10</sup>	(j)
$1.25 \cdot 10^{-12}$	300	$(2.6-5.3) \cdot 10^{19} (\text{He})$	Mihelcic <i>et al.</i> , 1975 <sup>11</sup>	(k)
$3.67 \cdot 10^{-11} \exp(-1042/T)$	198–300	$(1.5-2.3) \cdot 10^{19} (\text{Ar})$	Lee <i>et al.</i> , 1978 <sup>12</sup>	(l)
$1.1 \cdot 10^{-12}$	298	$(6.5-39) \cdot 10^{18} (\text{H}_2)$	Ishiwara <i>et al.</i> , 1978 <sup>13</sup>	(m)
$7.8 \cdot 10^{-19}$	298	$(6.6-32) \cdot 10^{17} (\text{H}_2)$	Oka and Cvetanovic, 1979 <sup>14</sup>	(n)
$4.7 \cdot 10^{-11} \exp(-1096/T)$	211–461		Sugawara, Okazaki, and Sato, 1981 <sup>15</sup>	(o)
$1.1 \cdot 10^{-12}$	300		Ellul <i>et al.</i> , 1981 <sup>16</sup>	(p)
$4.39 \cdot 10^{-11} \exp(-1087/T)$	285–604	$(8-140) \cdot 10^{17} (\text{He})$	Lightfoot and Pilling, 1987 <sup>1</sup>	(a)
<i>Reviews and Evaluations</i>				
$k_\infty = 6.6 \cdot 10^{-15} T^{1.28} \exp(-650/T)$	200–1100		CEC, 1992; 1994 <sup>17</sup>	(q)
$k_0 [\text{He}] = [\text{He}] 1.3 \cdot 10^{-29} \exp(-380/T)$	300–800			
$k_0 [\text{N}_2] = [\text{N}_2] 7.7 \cdot 10^{-30} \exp(-380/T)$	300–800			
$F_c(\text{N}_2) = 0.24 \exp(-T/40)$	300–800			
$+ 0.76 \exp(-T/1025)$				

**Comments**

- (a) Laser flash photolysis-resonance fluorescence study of the reaction  $\text{H} + \text{C}_2\text{H}_4$ . H atoms were generated by photolysis of  $\text{N}_2\text{O}$  at 193 nm in the presence of  $\text{H}_2$  and monitored by resonance fluorescence.

- (b) Flash photolysis of  $\text{C}_3\text{H}_6$  or  $\text{C}_2\text{H}_4$ , detection of H atoms by Lyman- $\alpha$  absorption. High pressure extrapolation to gas densities greater than  $2.4 \cdot 10^{18} \text{ molecule cm}^{-3}$ .
- (c) Vacuum UV flash photolysis of  $\text{C}_2\text{H}_4$ . Analysis of H atom concentration by resonance fluorescence and ab-

- sorption of Lyman- $\alpha$  radiation at 121.6 nm. Extrapolation to the high pressure limit via Lindemann plots.
- (d) ArF excimer laser flash photolysis of  $C_2H_4$  with detection of H atoms by Lyman- $\alpha$  resonance fluorescence. The approach to the  $H + C_2H_4 \rightleftharpoons C_2H_5$  equilibrium was directly observed.
- (e) Direct measurements of the approach to the  $H + C_2H_4 \rightleftharpoons C_2H_5$  equilibrium. H atoms generated by photolysis of  $C_2H_4$ -He mixtures at 193 nm and detected by time-resolved resonance fluorescence. Master equation analysis of data.
- (f) Pulsed radiolysis of  $H_2$  in the presence of  $C_2H_4 \cdot [CH_3]$  decay monitored by IR at  $606.12\text{ cm}^{-1}$ . Rate coefficients derived from a mechanism with 11 reactions.
- (g) High pressure flow technique with multiple resonance fluorescence detection of H atoms.
- (h) Pulse radiolysis of  $H_2$  with direct observation of H atoms by Lyman- $\alpha$  absorption spectroscopy. This study supersedes an earlier preliminary report<sup>18</sup> from the same laboratory.
- (i) Photolysis of HI in the presence of  $C_2H_4$ . Rate coefficients determined relative to the reaction  $H + HI \rightarrow H_2 + I$  for which a value of  $k = 2.0 \cdot 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  was employed.
- (j) Time-resolved Lyman- $\alpha$  absorption spectroscopy. H produced by Hg photosensitization of  $H_2$ .
- (k) Pulse radiolysis of  $H_2$  with Lyman- $\alpha$  detection of H atoms.
- (l) Flash photolysis-resonance fluorescence measurements. Photolysis of  $C_2H_4$  at  $\lambda \geq 110\text{ nm}$  and detection of H atoms by resonance fluorescence in Ar diluent.
- (m) Pulse radiolysis of  $H_2$  with detection of H atoms by Lyman- $\alpha$  absorption spectroscopy.
- (n) Irradiation of  $Hg/NO/H_2/C_2H_4$  mixtures with modulated light at  $253.7\text{ nm}$  in a flow system. Measurements of the luminescence of  $HNO(^1A'')$ .
- (o) Pulse radiolysis of  $H_2$ . Resonance absorption detection of H.
- (p) Pulsed Hg-sensitized photolysis of  $H_2$ . Resonance absorption detection of H.
- (q) See Comments on Preferred Values.

### Preferred Values

$k_0 = 1.3 \cdot 10^{-29} \exp(-380/T)\text{ cm}^6\text{ molecule}^{-2}\text{ s}^{-1}$  for M = He over the range 300–800 K.

$k_0 = 1.3 \cdot 10^{-29} \exp(-380/T)\text{ cm}^6\text{ molecule}^{-2}\text{ s}^{-1}$  for M = N<sub>2</sub> over the range 300–800 K.

$k_\infty = 6.6 \cdot 10^{-15} T^{1.28} \exp(-650/T)\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  over the range 200–1100 K.

$F_c = 0.24 \exp(-T/40) + 0.76 \exp(-T/1025)$  for M = He and N<sub>2</sub> over the range 300–800 K.

### Reliability

$\Delta \log k_0 = \pm 0.3$  for M = He, N<sub>2</sub> over the range 300–800 K.

$\Delta \log k_\infty = \pm 0.3$  over the range 200–1100 K.

$\Delta F_c = \pm 0.1$  for M = He, N<sub>2</sub> over the range 300–800 K.

### Comments on Preferred Values

This reaction has been extensively studied at low temperatures. The  $k_\infty$  value at 300 K is well established; the average of the experimental measurements of Lightfoot and Pilling,<sup>1</sup> Braun and Lenzi,<sup>2</sup> Hikida, Eyre, and Dorfman,<sup>7</sup> Eyre, Hikida, and Dorfman,<sup>18</sup> Penzhorn and Darwent,<sup>9</sup> Michael, Osborne, and Suess,<sup>10</sup> Mihelcic *et al.*,<sup>11</sup> Lee *et al.*,<sup>12</sup> Ishiwara *et al.*,<sup>13</sup> Oka and Cvetanovic,<sup>14</sup> Sugawara, Okazaki, and Sato,<sup>15</sup> and Ellul *et al.*<sup>16</sup> is  $(1.2 \pm 0.3) \cdot 10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ . The measurements in the fall-off region by Braun and Lenzi,<sup>2</sup> Clarke *et al.*,<sup>7</sup> Lightfoot and Pilling,<sup>1</sup> and Kurylo *et al.*,<sup>3</sup> indicate that there are no substantial differences in the values of  $k$  in the bath gases He and N<sub>2</sub>. The analysis of the reaction is based on a theoretical treatment of the measurements of Refs. 1, 3–5. Theoretical fall-off curves<sup>19</sup> and strong collision low pressure rate coefficients<sup>19,20</sup> were calculated using a reaction threshold of 154.78 kJ mol<sup>-1</sup>.<sup>21</sup> From this analysis the above recommended limiting rate coefficients were derived; the temperature dependence of  $k_\infty$  is depicted in Fig. 1. The collision efficiencies resulting from the theoretical analysis for M = He,  $\beta_c \approx 0.07$ , are approximately independent of temperature over the range 300–800 K. This finding is consistent with a temperature dependence of  $-\langle \Delta E \rangle$  of about  $T^{+0.8}$  in good agreement with recent results.<sup>21</sup> At atmospheric pressure and 300 K the reaction is close to the high pressure limit, i.e.,  $k/k_\infty \approx 0.9$ , while at 800 K it is in the fall-off regime, see Fig. 2. The expression for  $k_0$  for M = N<sub>2</sub> is based on the early work of Braun and Lenzi<sup>2</sup> which requires confirmation.

The data for the reaction channel,  $H + C_2H_4 \rightarrow H_2 + C_2H_3$ , are evaluated on the preceding data sheet.

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<sup>21</sup>Y. Feng, J. T. Niiranen, R. Benesura, V. D. Knyazev, D. Gutman, and W. Tsang, J. Phys. Chem. **97**, 871 (1993).

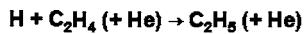
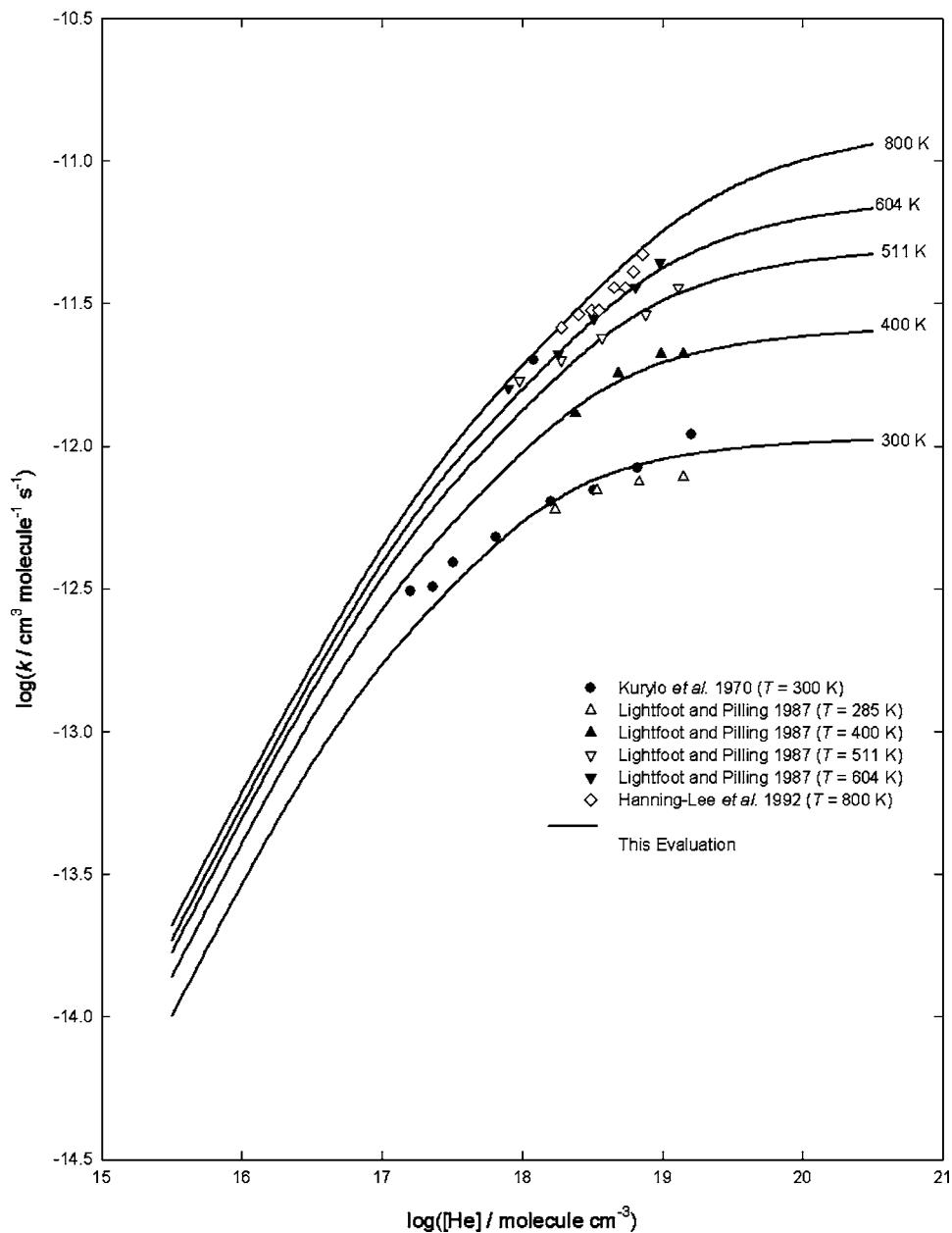


Fig. 1



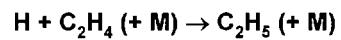
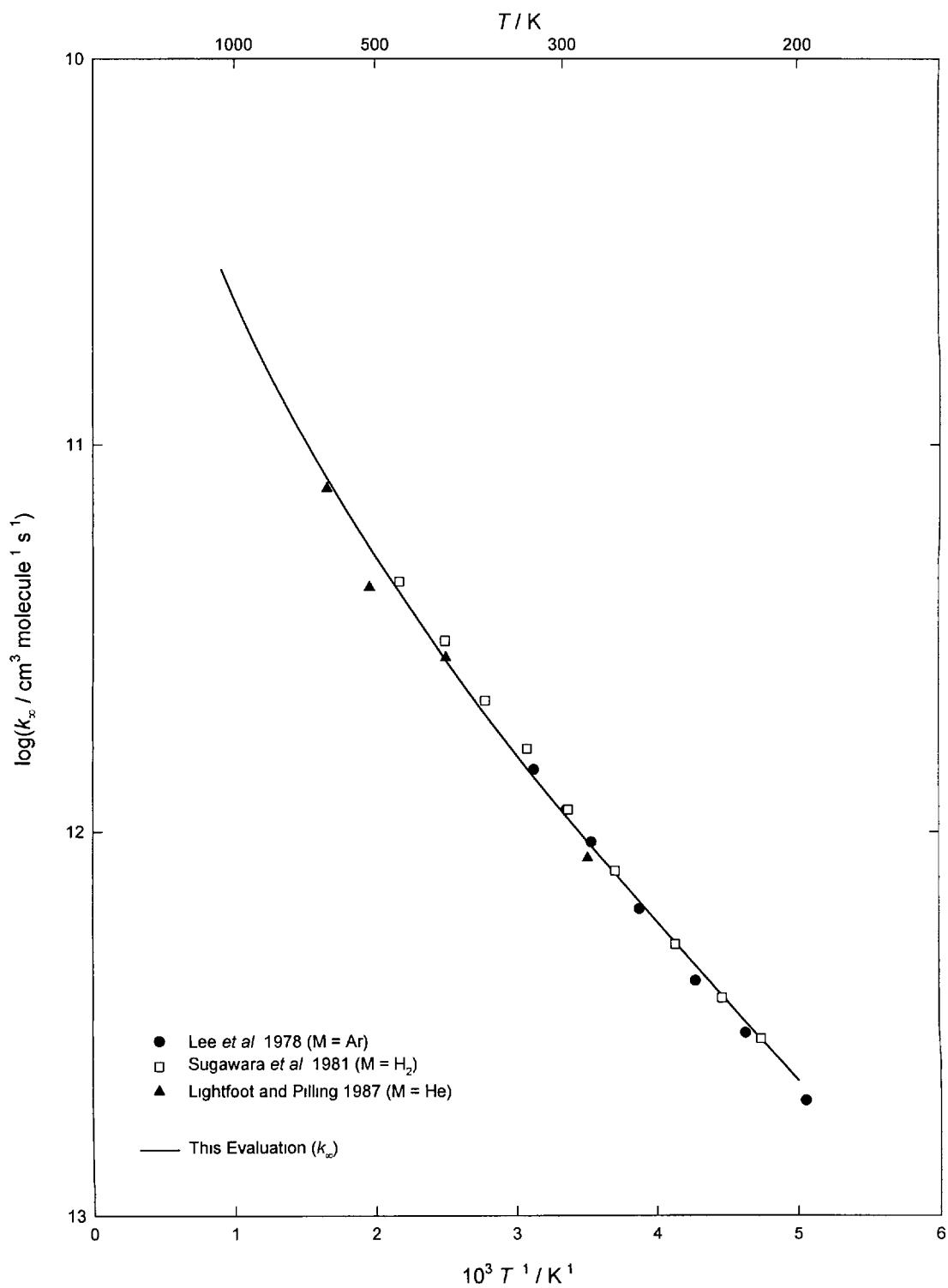
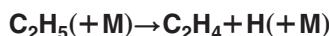


Fig. 2



*Thermodynamic Data*

$$\begin{aligned}\Delta H^\circ_{298} &= 149.5 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298} &= 86.7 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 3.49 \cdot 10^{24} T^{-0.824} \exp(-17962/T) \text{ molecule cm}^3 \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{s}^{-1}$	T/K	[M]/molecule cm $^{-3}$	Reference	Comments
<i>Rate Coefficient Measurements</i>				
<i>Low Pressure Range</i>				
$[\text{C}_2\text{H}_6] 1.1 \cdot 10^{-6} \exp(-16000/T)$	673–773	$(0.52\text{--}120) \cdot 10^{17}$	Loucks and Laidler, 1967 <sup>1</sup>	(a)
$[\text{C}_2\text{H}_6] 8.3 \cdot 10^{-15}$	902	$(1.1\text{--}27.2) \cdot 10^{17}$	Pacey and Wimalasena, 1984 <sup>2</sup>	(b)
$[\text{C}_2\text{H}_6] 3.3 \cdot 10^{-6} \exp(-17560/T)$	793–813	$(0.12\text{--}37) \cdot 10^{17}$	Simon, Foucaut, and Scacchi, 1988 <sup>3</sup>	(c)
<i>Intermediate Fall-off Range</i>				
1.3	673	$0.76 \cdot 10^{17} (\text{C}_2\text{H}_6)$	Loucks and Laidler, 1967 <sup>1</sup>	(a)
3.5		$5.6 \cdot 10^{17}$		
3.1	703	$0.55 \cdot 10^{17}$		
$2.4 \cdot 10^1$		$9.1 \cdot 10^{17}$		
$2.3 \cdot 10^1$	773	$0.44 \cdot 10^{17}$		
$2.7 \cdot 10^2$		$7.7 \cdot 10^{17}$		
$7.7 \cdot 10^2$	902	$1.1 \cdot 10^{17} (\text{C}_2\text{H}_6)$	Pacey and Wimalasena, 1984 <sup>2</sup>	(b)
$2.5 \cdot 10^3$		$6.6 \cdot 10^{17}$		
$5.6 \cdot 10^3$		$2.7 \cdot 10^{18}$		
$2.28 \cdot 10^1$	793	$0.37 \cdot 10^{17} (\text{C}_2\text{H}_6)$	Simon, Foucaut, and Scacchi, 1988 <sup>3</sup>	(c)
$2.72 \cdot 10^2$		$3.7 \cdot 10^{18}$		
$1.63 \cdot 10^1$	813	$1.2 \cdot 10^{18}$		
$5.54 \cdot 10^2$		$3.6 \cdot 10^{18}$		
$3.26 \cdot 10^2$	1094	$7.1 \cdot 10^{15}$	Feng <i>et al.</i> , 1993 <sup>4</sup>	(d)
$9.27 \cdot 10^1$	901	$4.22 \cdot 10^{16}$		
$4.49 \cdot 10^2$	927	$1.58 \cdot 10^{17}$		
<i>High Pressure Range</i>				
$2.7 \cdot 10^{14} \exp(-20580/T)$	673–773	$(0.52\text{--}120) \cdot 10^{17} (\text{C}_2\text{H}_6)$	Loucks and Laidler, 1967 <sup>1</sup>	(a)
$2.7 \cdot 10^4$	902	$(1.1\text{--}27.2) \cdot 10^{17} (\text{C}_2\text{H}_6)$	Pacey and Wimalasena, 1984 <sup>2</sup>	(b)
$1.6 \cdot 10^{13} \exp(-19120/T)$	793–813	$(0.12\text{--}37) \cdot 10^{17} (\text{C}_2\text{H}_6)$	Simon, Foucaut, and Scacchi, 1988 <sup>3</sup>	(c)
<i>Reviews and Evaluations</i>				
$k_\infty = 1.11 \cdot 10^{10} T^{+1.037}$	200–1100		Feng <i>et al.</i> , 1993 <sup>4</sup>	(d)
$k_\infty = 8.2 \cdot 10^{13} \exp(-20070/T)$	700–1100		CEC, 1994 <sup>5</sup>	(e)
$k_0 [\text{C}_2\text{H}_6] = [\text{C}_2\text{H}_6] 1.7 \cdot 10^{-6} \exp(-16800/T)$	700–900			
$F_c(\text{C}_2\text{H}_6) = 0.25 \exp(-T/97) + 0.75 \exp(-T/1379)$	700–1100			

**Comments**

- (a) The mercury-photosensitized decomposition of  $\text{C}_2\text{H}_6$  in a static system was used to generate  $\text{C}_2\text{H}_5$  radicals. Products measured by volumetry and gas chromatography. Rate coefficients were extracted from a mechanism with four reactions. Rate coefficients measured relative to  $\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5 \rightarrow \text{C}_4\text{H}_{10}$  for which a value of  $k = 3.3 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was taken.<sup>1</sup> Extrapolation towards the limiting rate coefficients from Lindemann plots.

- (b) Pyrolysis of  $\text{C}_2\text{H}_6$  in a flow system. The products,  $\text{CH}_4$  and  $\text{C}_2\text{H}_4$ , were measured by gas chromatography. Results interpreted with a 9-reaction mechanism, applying the steady-state approximation. Extrapolation to high and low pressure limits based on Ref. 6.
- (c) Pyrolysis of  $\text{C}_2\text{H}_6$  in a static system. The main products were  $\text{CH}_4$  and  $\text{C}_2\text{H}_4$  and were analyzed by gas chromatography. Analysis of literature values employing the RRKM and Troe's models.
- (d) Thermal decomposition of  $\text{C}_2\text{H}_5$  monitored by photoionization mass spectrometry.  $\text{C}_2\text{H}_5$  radicals were gen-

erated by 193 nm laser photolysis of 3-pentanone. Weak collision effects studied using modified strong collision and master equation analysis.

- (e) See Comments on Preferred Values.

### Preferred Values

$k_0 = 1.7 \cdot 10^{-6} \exp(-16800/T)$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for M = C<sub>2</sub>H<sub>6</sub> over the range 700–900 K.

$k_\infty = 8.2 \cdot 10^{13} \exp(-20070/T)$  s<sup>-1</sup> over the range 700–1100 K.

$F_c = 0.25 \exp(-T/97) + 0.75 \exp(-T/1379)$  for M = C<sub>2</sub>H<sub>6</sub> over the range 700–1100 K.

### Reliability

$\Delta \log k_0 = \pm 0.3$  for M = C<sub>2</sub>H<sub>6</sub> over the range 700–900 K.

$\Delta \log k_\infty = \pm 0.3$  over the range 700–1100 K.

$\Delta F_c = \pm 0.1$  for M = C<sub>2</sub>H<sub>6</sub> over the range 700–1100 K.

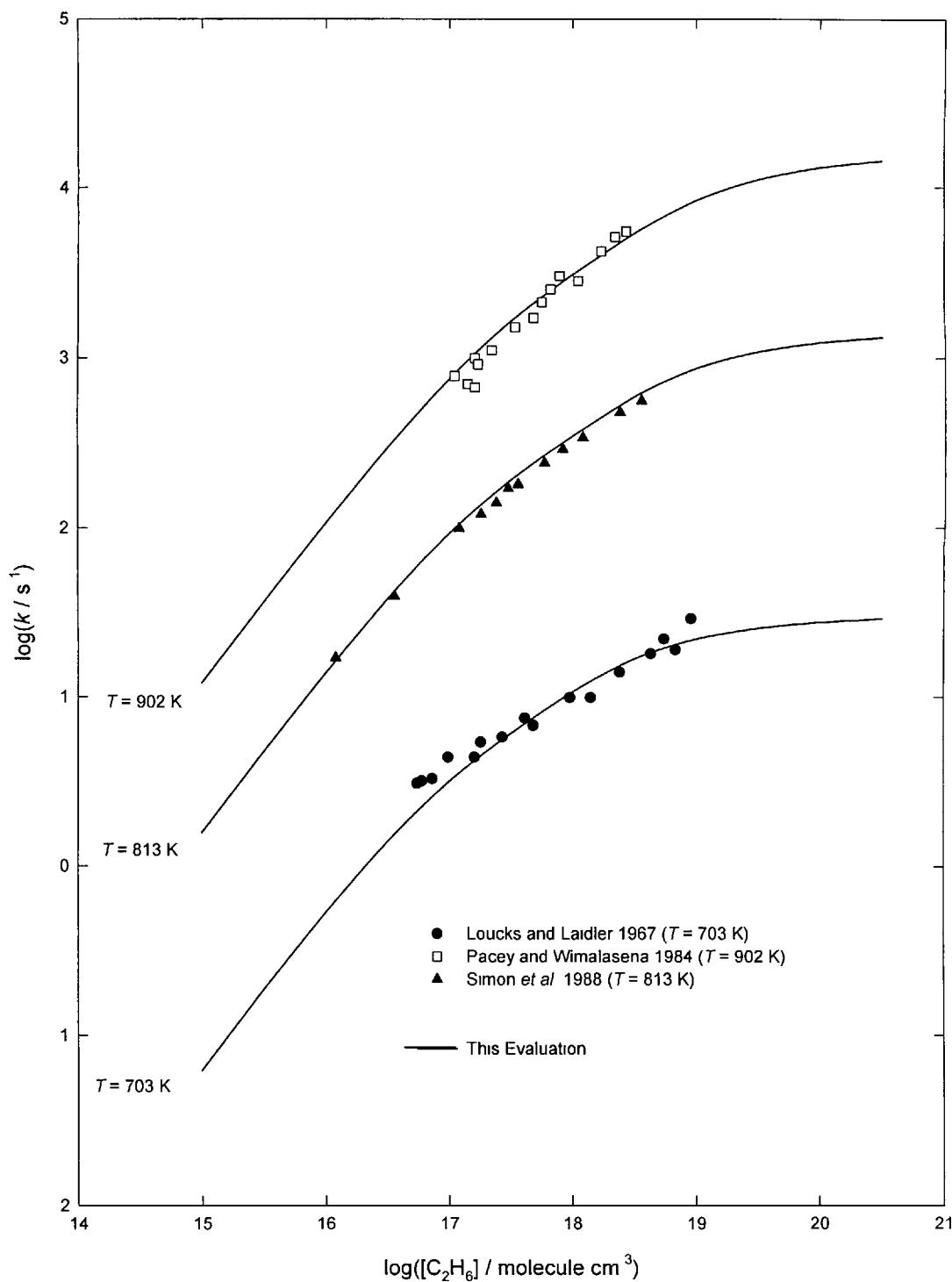
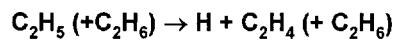
### Comments on Preferred Values

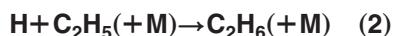
The present recommendation is unchanged from our previous evaluation<sup>5</sup> and is based on a theoretical analysis employing unimolecular rate theory<sup>6,7</sup> of the rate data of Loucks

and Laidler,<sup>1</sup> Pacey and Wimalasena,<sup>2</sup> Simon, Foucaut, and Scacchi,<sup>3</sup> and Feng *et al.*<sup>4</sup> Theoretical fall-off curves<sup>6</sup> were fitted to these data and the resulting  $k_0$  values were analyzed using the low pressure unimolecular rate theory from Refs. 6 and 7 employing a reaction threshold of 154.78 kJ mol<sup>-1</sup>.<sup>4</sup> Collisional efficiencies of about 0.14 for M = C<sub>2</sub>H<sub>6</sub> between 700 and 800 K were derived which are consistent with an average energy transferred per collision of  $-\langle \Delta E \rangle = 150\text{--}210$  cm<sup>-1</sup>. Similarly, from the experiments of Feng *et al.*<sup>4</sup> a value of  $-\langle \Delta E \rangle = 13$  cm<sup>-1</sup> for M = Ar was obtained. Selected fall-off curves and experimental data are shown in the Figure.

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#### Thermodynamic Data

$$\begin{aligned}\Delta H_{298}^{\circ}(1) &= -46.1 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ}(1) &= 26.2 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 7.01 \cdot 10^4 T^{-1.092} \exp(+4990/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

$$\begin{aligned}\Delta H_{298}^{\circ}(2) &= -422.7 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ}(2) &= -132.7 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 7.39 \cdot 10^{-28} T^{0.311} \exp(+50910/T) \text{ cm}^3 \text{ molecule}^{-1} \\ (300 \leq T/\text{K} \leq 4000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$6 \cdot 10^{-11}$	298	Kurylo, Peterson, and Braun, 1970 <sup>1</sup>	(a)
$k_1 = 6.0 \cdot 10^{-11}$	503–753	Camilleri, Marshall, and Purnell, 1974 <sup>2</sup>	(b)
$k_1 = 1.1 \cdot 10^{-10} \exp(-50/T)$	321–521	Pratt and Veltmann, 1976 <sup>3</sup>	(c)
$k_1 = 1.2 \cdot 10^{-11}$	1950–2770	Tabayashi and Bauer, 1979 <sup>4</sup>	(d)
$k_1 = 8.1 \cdot 10^{-11} \exp(-127/T)$	230–568	Pratt and Wood, 1984 <sup>5</sup>	(e)
$1.2 \cdot 10^{-10}$	963	Pacey and Wimalasena, 1984 <sup>6</sup>	(f)
<i>Reviews and Evaluations</i>			
$k_1 = 6.0 \cdot 10^{-11}$	300–1500	Tsang and Hampson, 1986 <sup>7</sup>	(g)
$k_1 = 6.0 \cdot 10^{-11}$	300–2000	CEC, 1992; 1994 <sup>8</sup>	(h)

#### Comments

- (a) Flash photolysis-resonance fluorescence study of the  $\text{H} + \text{C}_2\text{H}_4$  reaction. Computer simulation of the increase in H atom loss rate with  $[\text{H}]/[\text{C}_2\text{H}_4]$  allowed a determination of  $k$ , which was originally attributed to  $k_2$  but is more likely to be  $k_1$ .
- (b) Discharge flow study of  $\text{H} + \text{C}_2\text{H}_6$  reaction, with product analysis by gas chromatography. Numerical modeling used to extract value of  $k_1$ .
- (c) Discharge flow study of the  $\text{H} + \text{C}_2\text{H}_4$  reaction, with product analysis by mass spectrometry. Numerical modeling used to extract value of  $k_1$ .
- (d) Shock tube study of  $\text{CH}_4/\text{Ar}$  and  $\text{CH}_4/\text{O}_2/\text{Ar}$  mixtures. Reaction progress was followed by laser Schlieren.
- (e) Discharge flow study of the  $\text{CH}_3 + \text{O}_2$  reaction. The  $\text{CH}_3$  is formed by the  $\text{H} + \text{C}_2\text{H}_4$  reaction. Products were analyzed by GC and numerical analysis of a detailed mechanism was used to extract values of  $k$ .
- (f) Pyrolysis of  $\text{C}_2\text{H}_6$  in a flow system. The products,  $\text{CH}_4$  and  $\text{C}_2\text{H}_4$ , were measured by gas chromatography. Results interpreted with a 9-reaction mechanism, applying the steady-state approximation.
- (g) Based on results from Refs. 1, 2 and 10. A strong collision analysis of  $k_1/k_2$  is presented.
- (h) Evaluation based on Refs. 1–4.

#### Preferred Values

$k_1 = 7.0 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 298–2000 K.

#### Reliability

$\Delta \log k_1 = \pm 0.3$  at 298 K, rising to  $\pm 0.8$  at 2000 K.

#### Comments on Preferred Values

There are no direct measurements of the rate constant of this reaction which occurs as a secondary process in studies of the  $\text{H} + \text{C}_2\text{H}_4$  and  $\text{H} + \text{C}_2\text{H}_6$  reactions. The preferred value at 298 K is based on the results of Kurylo *et al.*,<sup>1</sup> Camilleri *et al.*,<sup>2</sup> Pratt and Veltmann,<sup>3</sup> and Pratt and Wood<sup>5</sup> which are cited in the table and give values covering the range  $(5 \pm 9) \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The less precise study of Teng and Jones<sup>9</sup> and the flow tube study of Halstead *et al.*<sup>10</sup> also give values in this range. The study of Michael *et al.*<sup>11</sup> gives a significantly lower value ( $2.5 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) and the more recent study of Sillesen *et al.*<sup>12</sup> gives a high value ( $\sim 3 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ).

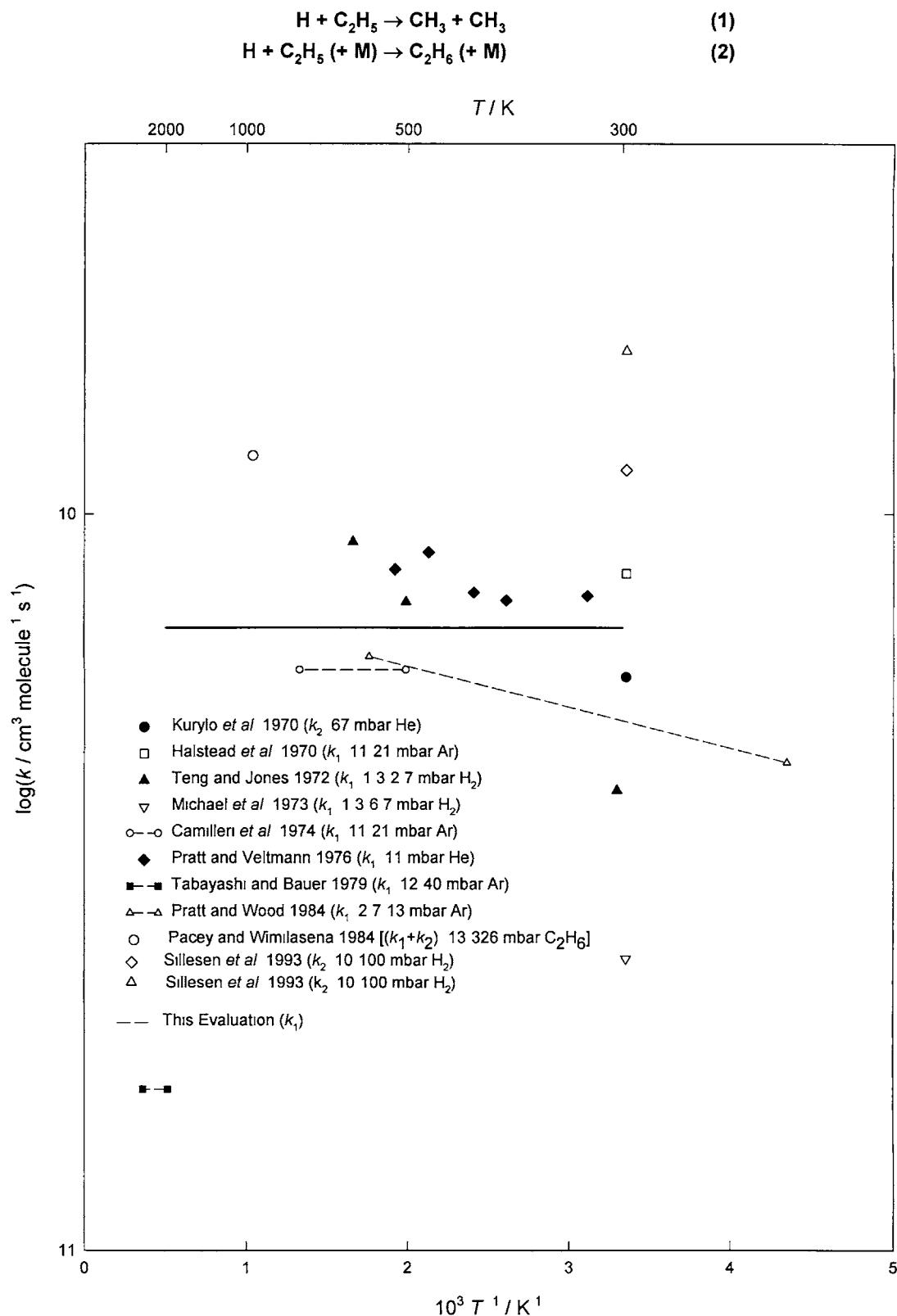
Information on the temperature dependence is very limited. A theoretical study by Harding and Klippenstein<sup>13</sup> finds that  $k$  increases by only a factor of 2 in going from 200 K to 1900 K. The precision of the Arrhenius parameters obtained in the studies of Teng and Jones,<sup>9</sup> Pratt and Veltmann,<sup>3</sup> and Pratt and Wood<sup>5</sup> is very uncertain because of the indirect nature of the studies and the relatively small temperature range covered. The value of  $(k_1 + k_2)$  found by Pacey and Wimalasena<sup>6</sup> at 963 K suggests a small increase with temperature while the shock tube study of Tabayashi and Bauer<sup>4</sup> implies a small negative temperature dependence. Provisionally a value of  $k$  independent of temperature is recommended with substantial error limits at high temperatures.

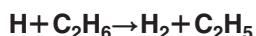
At the temperatures and pressures of most of the studies

cited in the Table, Channel (1) will dominate over Channel (2), but Channel (2) probably contributes at high pressures near room temperature. Theoretical<sup>13</sup> and experimental<sup>2</sup> studies confirm that addition is dominant over the alternative, abstraction channel,  $H + C_2H_5 \rightarrow H_2 + C_2H_4$ , but in a shock tube study of  $C_2H_6$  pyrolysis and oxidation Hidaka *et al.*<sup>14</sup> find that to fit their observations a value of  $7.5 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was required for the rate constant of the abstraction channel at temperatures of 950–1900 K.

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*Thermodynamic Data*

$$\begin{aligned}\Delta H^\circ_{298} &= -13.2 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298} &= 34.12 \text{ J K}^{-1} \text{ mol}^1 \\ K_c &= 3.99 \cdot 10^3 T^{-0.537} \exp(+1230/T) \\ &\quad (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$7.94 \cdot 10^{-11} \exp(-4310/T)$	990–1430	Fenimore and Jones, 1963 <sup>1</sup>	(a)
$1.3 \cdot 10^{-10} \exp(-4580/T)$	290–509	Azatyan <i>et al.</i> , 1969 <sup>2</sup>	(b)
$1.85 \cdot 10^{-10} \exp(-4680/T)$	290–579	Azatyan and Filippov, 1969 <sup>3</sup>	(b)
$1.04 \cdot 10^{-12}$	903	Azatyan, 1971 <sup>4</sup>	(c)
$3.2 \cdot 10^{-13}$	773	Baldwin and Walker, 1977 <sup>5,6</sup>	(d)
$1.8 \cdot 10^{-10} \exp(-4643/T)$	357–544	Jones, Morgan, and Purnell, 1977 <sup>7</sup>	(e)
$8.3 \cdot 10^{-11} \exp(-4580/T)$	281–347	Lede and Villiermaux, 1978 <sup>8</sup>	(f)
$8.7 \cdot 10^{-10} \exp(-6442/T)$	876–1016	Cao and Back, 1984 <sup>9</sup>	(g)
$2.3 \cdot 10^{-17}$	298	Jones and Ma, 1986 <sup>10</sup>	(h)
$1.9 \cdot 10^{-16} T^{1.9} \exp(-3790/T)$	950–1900	Hidaka <i>et al.</i> , 2000 <sup>11</sup>	(i)
$9.5 \cdot 10^{-11} \exp(-4316/T)$	467–826	Bryukov, Slagle, and Knyazev, 2001 <sup>12</sup>	(j)
<i>Reviews and Evaluations</i>			
$1.66 \cdot 10^{-10} \exp(-4831/T)$	300–2000	Cao and Back, 1984 <sup>13</sup>	(k)
$1.9 \cdot 10^{-16} T^{1.9} \exp(-3790/T)$	300–2000	Cohen, 1991 <sup>14</sup>	(l)
$2.35 \cdot 10^{-15} T^{1.5} \exp(-3725/T)$		CEC, 1992; 1994 <sup>15</sup>	(m)

**Comments**

- (a) Low pressure  $\text{H}_2/\text{O}_2/\text{C}_2\text{H}_6/\text{Ar}$  flames were studied; species analyzed using a mass spectrometric probe. Values of  $k$  were determined from measurements of  $[\text{O}_2]$  and  $[\text{C}_2\text{H}_6]$  as a function of distance above the burner.  $[\text{CO}]$  and  $[\text{CO}_2]$  were also monitored. Effectively values of  $k/k(\text{H}+\text{O}_2)$  were obtained and the values of  $k$  have been recalculated using  $k(\text{H}+\text{O}_2)$  from the present evaluation.
- (b) Discharge flow study using  $\text{H}/\text{C}_2\text{H}_6/\text{He}$  mixtures. The  $\text{C}_2\text{H}_6$  was in large excess and the  $[\text{H}]$  was monitored by ESR.
- (c) Study on the effect of  $\text{C}_2\text{H}_6$  on the first explosion limit of the  $\text{H}_2\text{-O}_2$  reaction. The ignition temperature was determined as a function of the partial pressures of  $\text{O}_2$  and  $\text{C}_2\text{H}_6$  in the mixtures. Values of  $k/k(\text{H}+\text{O}_2)$  were obtained;  $k(\text{H}+\text{O}_2)$  determined in the same study was used to calculate  $k$ .
- (d) Effect of small additions of ethane to a slowly reacting mixture of  $\text{H}_2$  and  $\text{O}_2$  was studied. Changes in pressure were measured and concentrations of reactants and products were determined as a function of time by gas chromatography. A value of  $k/k(\text{H}+\text{O}_2)=44.5$  was obtained which was combined with the value of  $k(\text{H}+\text{O}_2)$  from the present evaluation to give the cited value of  $k$ .
- (e) Discharge flow study on  $\text{H}/\text{C}_2\text{H}_6/\text{He}$  mixtures.  $[\text{H}]$ ,  $[\text{C}_2\text{H}_6]$ , and  $[\text{CH}_4]$  were monitored by quadrupole

mass spectrometry. Experiments were carried out with both an excess of  $\text{H}$  atoms and of  $\text{C}_2\text{H}_6$ . The stoichiometry of the reaction was determined as a function of temperature and used in deriving values of  $k$ .

- (f) Discharge flow study in which  $\text{H}$  atoms were generated by a corona discharge in  $\text{H}_2$  and introduced into a flow tube containing a flowing  $\text{C}_2\text{H}_6/\text{N}_2$  mixture. The flow tube was operated under conditions of both laminar and turbulent flow, at pressures up to 1 bar; several wall coatings were used.  $[\text{H}]$  was monitored by reaction of the  $\text{H}$  atoms with  $\text{HgO}$  and spectrophotometric measurement of the  $\text{Hg}$  vapor released.
- (g) Static system;  $\text{H}_2/\text{C}_2\text{H}_6$  mixtures were heated in a quartz bulb and concentrations of reactants and products were measured by gas chromatography. The  $\text{H}$  atom concentration is controlled by the rapid equilibrium between  $\text{H}_2$  and the  $\text{H}$  atoms. The main product is ethylene.
- (h) Discharge flow study in which the  $\text{H}$  atoms were generated by a microwave discharge in a  $\text{H}_2/\text{He}$  mixture and monitored by ESR. The initial  $[\text{H}]$  was determined by titration with  $\text{NO}_2$  and the reaction was carried out with  $\text{C}_2\text{H}_6$  in large excess.
- (i) Shock tube study on the pyrolysis and oxidation of  $\text{C}_2\text{H}_6$  using a range of  $\text{C}_2\text{H}_6/\text{O}_2/\text{H}_2/\text{Ar}$  mixtures at pressures in the range 1.2–4.0 bar. Two shock tubes were used. The first had facilities for time resolved and single pulse product analysis studies. IR emissions at 4.24  $\mu\text{m}$ , and 2.56  $\mu\text{m}$  were monitored, and reactants

and products could be sampled and analyzed by GC. The second shock tube was equipped for laser absorption at 3.39  $\mu\text{m}$  and IR emission studies behind reflected shocks. The measured profiles were simulated using a detailed mechanism. The absorption profile at 3.39  $\mu\text{m}$  and the yields of  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_2$  were sensitive to  $k$ . The best fit to them was obtained using the expression of Cohen.<sup>15</sup>

- (j) Discharge flow study with H atoms generated by a microwave discharge in  $\text{H}_2/\text{He}$  mixtures. [H] monitored in the presence of a large excess of  $\text{C}_2\text{H}_6$  by time-resolved resonance fluorescence at 121.6 nm.
- (k) Literature review to reconcile data on forward and reverse rates and hence decide the best value for the heat of formation of the ethyl radical.
- (l) Based on a Transition State Treatment together with a literature value of  $k(298 \text{ K}) = 2.82 \cdot 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Temperature range not specified.
- (m) Based on the data of Refs. 1, 8, 9, 10 and the studies of Berlie and LeRoy,<sup>16</sup> Parsamyan *et al.*,<sup>17</sup> Camilleri *et al.*,<sup>18</sup> and Baldwin and Walker.<sup>5</sup>

### Preferred Values

$$k = 1.63 \cdot 10^{-10} \exp(-4640/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad \text{over the range } 298\text{--}1500 \text{ K.}$$

### Reliability

$$\Delta \log k = \pm 0.4 \text{ at } 298 \text{ K, falling to } \pm 0.3 \text{ at } 1500 \text{ K.}$$

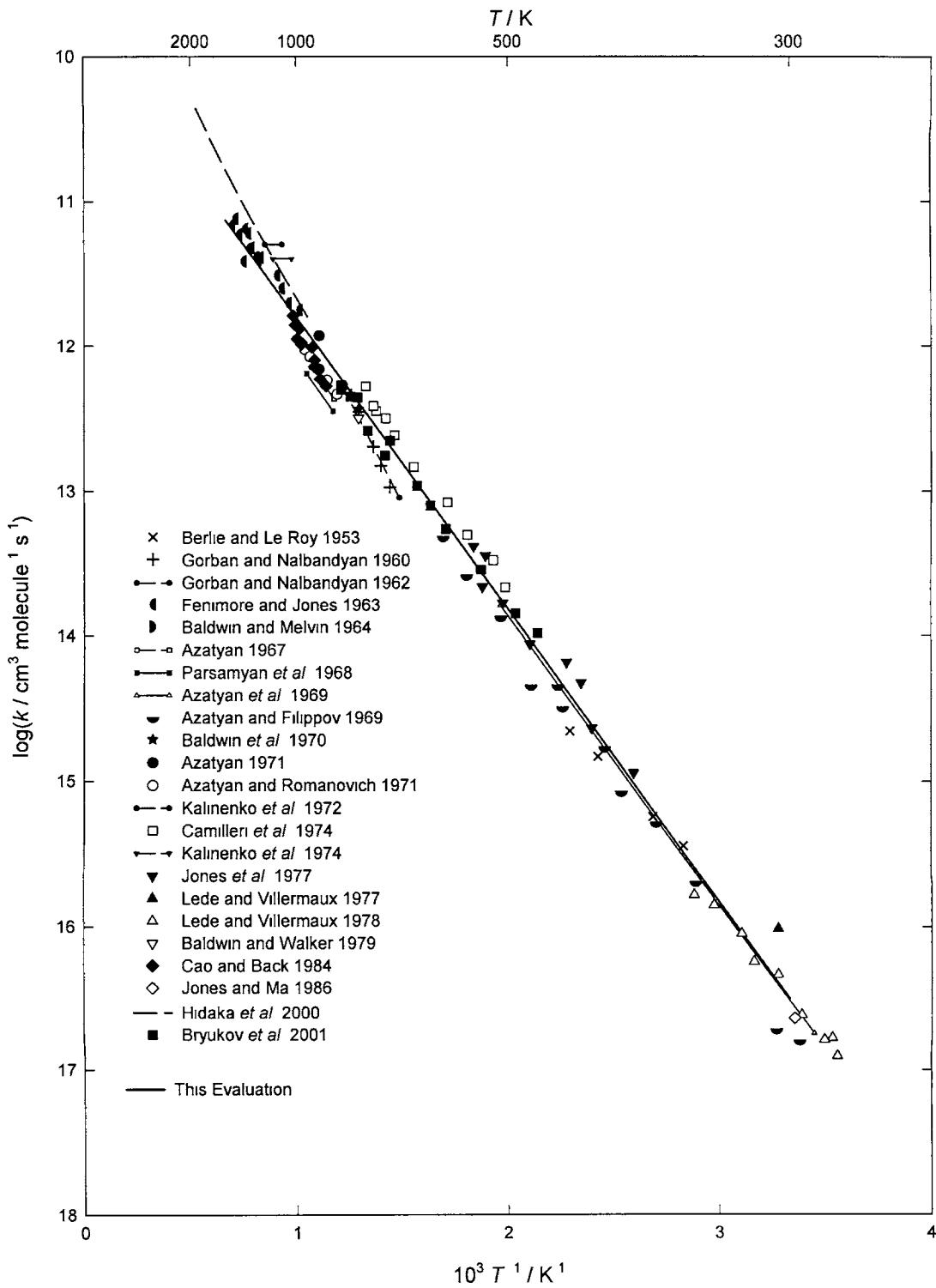
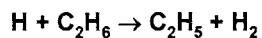
### Comments on Preferred Values

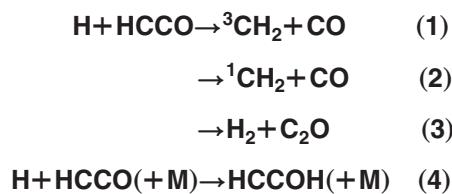
The rate constant is reasonably well defined over the range 280–1900 K but there are no measurements available at higher temperatures. The preferred expression is derived from the studies cited in the Table<sup>1–13</sup> with less weight being given to the low temperature studies of Azatyan *et al.*,<sup>2,3</sup> Lede and Villermaux,<sup>8</sup> and Jones and Ma.<sup>10</sup> In three of these studies<sup>2,3,8</sup> the rate constant values were based on assumed stoichiometries and in the other<sup>10</sup> secondary reactions may have been significant. Apart from the data in the cited studies, the other available data,<sup>16–24</sup> although more scattered, are compatible with the preferred expression.

The expression suggested by Clark and Dove,<sup>25</sup> which has been recommended by Warnatz<sup>26</sup> and by Tsang and Hampson,<sup>27</sup> gives a strongly curved Arrhenius plot and leads to high values of  $k$  at low and high temperatures.

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*Thermodynamic Data*

$$\Delta H^{\circ}_{298}(1) = -113.4 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298}(1) = 32.56 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 5.1 \cdot 10^5 T^{-1.382} \exp(+13250/T)$$

(300 ≤ T/K ≤ 5000)

$$\Delta H^{\circ}_{298}(3) = -106.7 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298}(3) = 3.69 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 6.7 T^{-0.20} \exp(+12730/T)$$

(300 ≤ T/K ≤ 5000)

$$\Delta H^{\circ}_{298}(2) = -75.5 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298}(2) = 26.37 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 2.64 \cdot 10^5 T^{-1.393} \exp(+8680/T)$$

(300 ≤ T/K ≤ 5000)

$$\Delta H^{\circ}_{298}(4) = -300.1 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298}(4) = -110.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(4) = 2.42 \cdot 10^{-27} T^{0.563} \exp(+36160/T) \text{ cm}^3 \text{ molecule}^{-1}$$

(300 ≤ T/K ≤ 5000)

See Section 3.1 for the origin and quality of the Thermodynamic Data.

**Rate Coefficient Data ( $k = k_1 + k_2 + k_3 + k_4$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$2.2 \cdot 10^{-10}$	285, 535	Vinckier, Schaekers, and Peeters, 1985 <sup>1</sup>	(a)
$2.5 \cdot 10^{-10}$	1500–1700	Frank, Bhaskaran, and Just, 1986 <sup>2</sup>	(b)
$2.0 \cdot 10^{-10}$	285	Van de Ven and Peeters, 1990 <sup>3</sup>	(c)
$2.3 \cdot 10^{-10}$	290–960	Peeters, Boullart, and Devriendt, 1995 <sup>4</sup>	(d)
$1.7 \cdot 10^{-10}$	297	Glass, Kumaran, and Michael, 2000 <sup>5</sup>	(e)
<i>Branching Ratios</i>			
$k_2/k = 0.92 \pm 0.15$	295	Boullart and Peeters, 1992 <sup>6</sup>	(f)
<i>Reviews and Evaluations</i>			
$2.5 \cdot 10^{-10}$	300–2500	CEC, 1992; 1994 <sup>7</sup>	(g)

**Comments**

- (a) Discharge-flow study of the O+C<sub>2</sub>H<sub>2</sub> reaction with radical concentrations being monitored by molecular beam mass spectrometry. Values of  $k/k(\text{O} + \text{CHCO}) = 1.3 \pm 0.2$  and  $1.4 \pm 0.4$  at 285 K and 535 K, respectively, were determined from the best fit to the [CHCO] time profile. The cited value of  $k$  is derived using  $k(\text{O} + \text{CHCO}) = 1.6 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (this evaluation).
- (b) Shock tube study on C<sub>2</sub>H<sub>2</sub>/N<sub>2</sub>O/Ar mixtures. [H], [O], and [CO] monitored simultaneously by atomic and molecular absorption spectroscopy. The H+CHCO reaction is important in the later stages of the O+C<sub>2</sub>H<sub>2</sub> reaction.  $k$  was determined from [O] and [H] profiles under optimized stoichiometry.
- (c) Discharge-flow study of the reaction of H atoms with C<sub>3</sub>O<sub>2</sub>/O<sub>2</sub> mixtures. Relative values of [CHCO] and absolute values of [H] were monitored by molecular beam mass spectrometry.  $k$  was obtained by modeling the [CHCO] and [H] profiles using a detailed reaction mechanism.
- (d) Discharge-flow study of the reaction of O atoms with C<sub>2</sub>H<sub>2</sub>/O<sub>2</sub> mixtures. [CO<sub>2</sub>], [O<sub>2</sub>], [C<sub>2</sub>H<sub>2</sub>], [H], and

[O] were monitored by molecular beam sampling mass spectrometry. A similar treatment of the data to that used in Ref. 1 gives values of  $k/k(\text{O} + \text{CHCO}) = 1.45 \pm 0.30$  with no significant temperature dependence over the range 290–960 K.

- (e) Pulsed laser photolysis at 193 nm of CH<sub>2</sub>CO/H<sub>2</sub> (or Ar) mixtures at total pressures in the range 2.6–250 mbar. [H] was monitored by time-resolved ARAS. Quantum yields for the dissociation channels of HCHO to <sup>3</sup>CH<sub>2</sub>+CO, <sup>1</sup>CH<sub>2</sub>+CO, H+HCCO, and C<sub>2</sub>O + H<sub>2</sub>, were determined.  $k$  values were obtained by modeling the [H] profiles using a detailed mechanism.

- (f) Discharge-flow study on C<sub>2</sub>H<sub>2</sub>/O/H/He mixtures. Molecular beam sampling mass spectrometry was used to monitor the [CH<sub>2</sub>] and the singlet and triplet methylene concentrations were distinguished by the change in the CH<sub>2</sub> signal on addition of CH<sub>4</sub>, which selectively scavenges CH<sub>2</sub>(<sup>1</sup>A<sub>1</sub>). Detailed modeling was used to check the derivation of the branching ratio.

- (g) Based on the data of Vinckier *et al.*<sup>1</sup> and Frank *et al.*<sup>2</sup>

**Referred Values**

$(k_1 + k_2) = 2.2 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 280–2000 K.

$k_1/k = 0.08$ ,  $k_2/k = 0.92$  at 298 K.

### Reliability

$\Delta \log(k_1+k_2) = \pm 0.2$  over the range 280–2000 K.  
 $\Delta k_1/k = {}^{+0.2}_{-0.08}$ ;  $\Delta k_2/k = {}^{+0.08}_{-0.2}$  at 298 K.

### Comments on Preferred Values

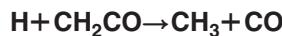
There are a number of studies from the same laboratory<sup>1,3,4</sup> which give consistent values of  $k$  over the temperature range 286–960 K. There is also a more recent study<sup>5</sup> based on ketene photolysis at 297 K which is in excellent agreement. The values obtained are high and show no significant change with temperature. The high temperature study of Frank *et al.*<sup>2</sup> gives a value in excellent agreement with the low temperature work and our preferred value is based on these studies,<sup>1–5</sup> which are cited in the Table. There are also two earlier studies which give low values of  $k$ .<sup>8,9</sup>

Studies on CH<sub>2</sub> formation in the C<sub>2</sub>H<sub>2</sub>/O/H system<sup>5,10</sup> indicate that the H+CHCO reaction proceeds by initial formation of a highly vibrationally excited adduct HCCOH which rapidly decomposes into CH<sub>2</sub>+CO. Both singlet and

triplet methylene formation are possible but singlet formation predominates<sup>5,10</sup> at low temperatures [Channel (2)] with  $k_2/k = 0.92 \pm 0.15$  at 295 K. This is supported by the photolysis study of Glass *et al.*<sup>5</sup> at 297 K. There is little evidence for C<sub>2</sub>O formation [Channel (3)] or stabilization of the adduct [Channel (4)] in any of the studies.

### References

- <sup>1</sup>C. Vinckier, M. Schaekers, and J. Peeters, *J. Phys. Chem.* **89**, 508 (1985).
- <sup>2</sup>P. Frank, K. A. Bhaskaran, and Th. Just, 21st Symp. (Int.) Combustion, 1988, p. 885.
- <sup>3</sup>P. Van de Ven and J. Peeters, *Bull. Soc. Chim. Belg.* **99**, 509 (1990).
- <sup>4</sup>J. Peeters, W. Boullart, and K. Devriendt, *J. Phys. Chem.* **99**, 3583 (1995).
- <sup>5</sup>G. P. Glass, S. S. Kumaran, and J. V. Michael, *J. Phys. Chem. A* **104**, 8360 (2000).
- <sup>6</sup>W. Boullart and J. Peeters, *J. Phys. Chem.* **96**, 9810 (1992).
- <sup>7</sup>CEC 1992; Supplement I, 1994 (see references in Introduction).
- <sup>8</sup>R. Löhr and P. Roth, *Ber. Bunsenges. Phys. Chem.* **85**, 153 (1981).
- <sup>9</sup>K. H. Homann and Ch. Wellman, *Ber. Bunsenges. Phys. Chem.* **87**, 609 (1983).
- <sup>10</sup>J. Peeters, S. Vanhaegelemeersch, J. Van Hoeymissen, R. Borms, and D. Vermeulen, *J. Phys. Chem.* **93**, 3892 (1989).



### Thermodynamic Data

$$\begin{aligned}\Delta H^\circ_{298} &= -134.6 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298} &= 35.01 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 9.87 \cdot 10^5 T^{-1.414} \exp(+15740/T) \\ &\quad (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

### Rate Coefficient Data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$1.88 \cdot 10^{-11} \exp(-1725/T)$	298–500	Michael <i>et al.</i> , 1979 <sup>1</sup>	(a)
$2.7 \cdot 10^{-11}$	1650–1850	Frank, Bhaskaran, and Just, 1986 <sup>2</sup>	(b)
$4.85 \cdot 10^{-11} \exp(-2328/T)$	863–1400	Hranislavljevic, Kumaran, and Michael, 1998 <sup>3</sup>	(c)
<i>Reviews and Evaluations</i>			
$1.12 \cdot 10^{-11} \exp(-1515/T)$	300–500	Warnatz, 1984 <sup>4</sup>	(d)
$3.0 \cdot 10^{-11} \exp(-1700/T)$	200–2000	CEC, 1992; 1994 <sup>5</sup>	(e)

### Comments

- (a) The reaction was studied by both flash photolysis and by the discharge flow technique. In both techniques an excess of CH<sub>2</sub>CO over H atoms was used and the [H] was monitored by resonance fluorescence at 121.6 nm. In the flash photolysis studies the H atoms were generated by photolysis of the ketene or of added CH<sub>4</sub> using wavelengths down to 105 nm and total pressures (bath gas Ar) in the range 26–130 mbar. The discharge flow study was limited to 298 K and carried out to check the results of the flash photolysis study. Values of

$k(298 \text{ K})$  obtained by the two techniques were  $6.9 \cdot 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $7.3 \cdot 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

- (b) Shock tube study of dilute ketene/argon mixtures using ARAS to detect H and CO. The rate constant was determined from simulations of the H atom profile using an 8-reaction scheme.
- (c) Shock tube study on Kr/CH<sub>2</sub>CO mixtures using pulsed laser photolysis of the CH<sub>2</sub>CO at 193.3 nm to produce H atoms. [H] was monitored by ARAS under conditions of pseudo first order decay of the [H] in the large excess of CH<sub>2</sub>CO.

- (d) Based on the studies of Carr *et al.*,<sup>6</sup> Slemr and Warneck,<sup>7</sup> and Michael *et al.*<sup>1</sup>
- (e) Mean value of  $k$ (298 K) from the studies of Carr *et al.*,<sup>6</sup> Slemr and Warneck,<sup>7</sup> and Michael *et al.*<sup>1</sup> combined with the temperature dependence of  $k$  obtained by Michael *et al.*<sup>1</sup>

### Preferred Values

$$k = 5.4 \cdot 10^{-14} T^{0.85} \exp(-1430/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the range 298–2000 K.

#### Reliability

$\Delta \log k = \pm 0.3$  at 298 K, rising to  $\pm 0.5$  at 2000 K.

#### Comments on Preferred Value

The reaction is fast and is believed to occur by addition followed by rapid decomposition of the adduct to form  $\text{CH}_3 + \text{CO}$  since, in the available studies,<sup>1–3,6–8</sup> there is no sign of any pressure dependence of  $k$ , and  $\text{CH}_3$  radicals have been detected directly in yields consistent with the reaction occurring exclusively to give  $\text{CH}_3 + \text{CO}$ .<sup>7</sup> Such a conclusion is consistent with the kinetics observed in the study of Carr *et al.*<sup>6</sup> and the estimated lifetime of the  $\text{CH}_3\text{CO}$  adduct.

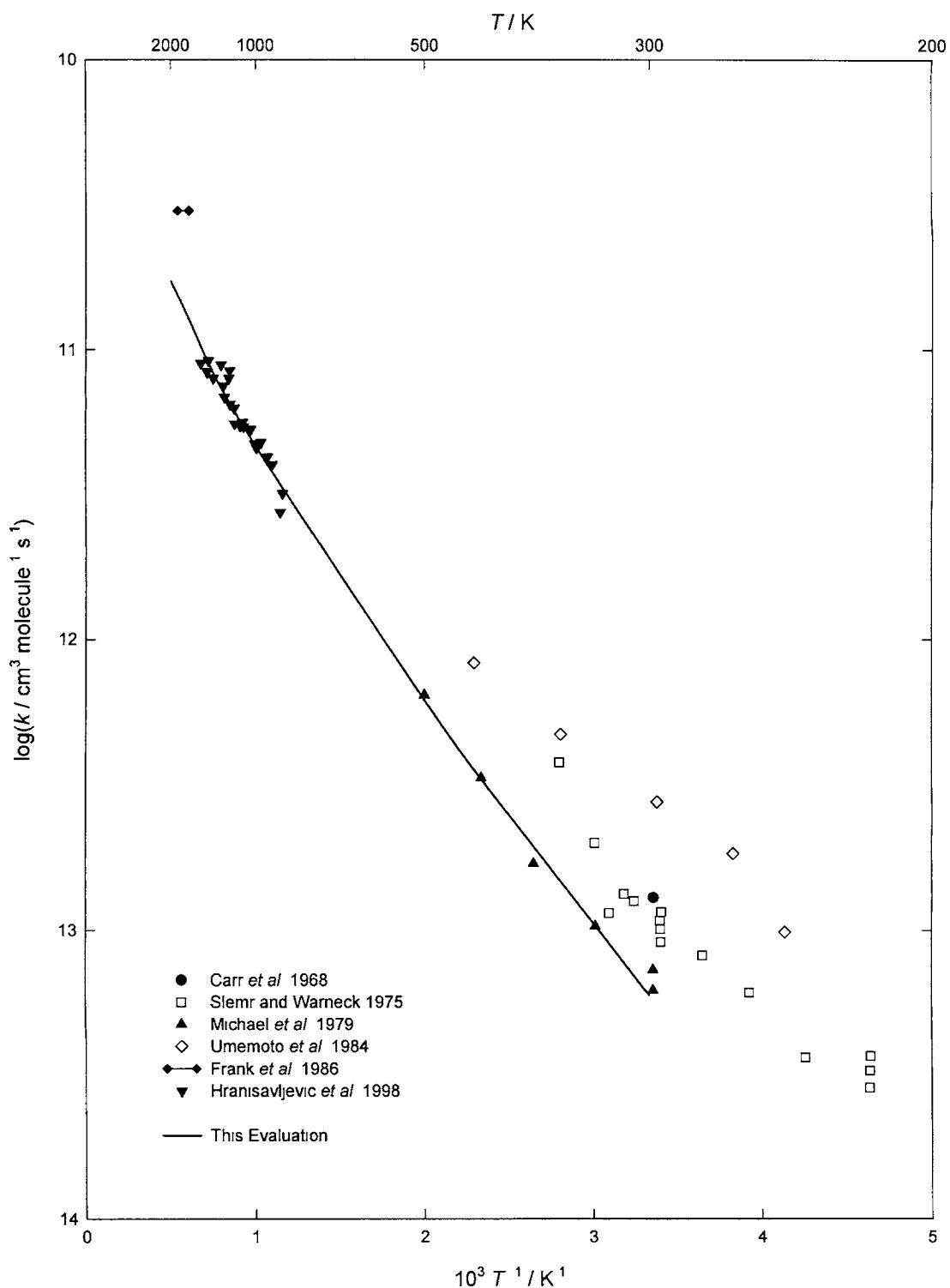
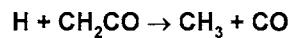
There are four low temperature studies,<sup>1,6–8</sup> three of which are in reasonable agreement,<sup>1,6,7</sup> but the pulse radiolysis

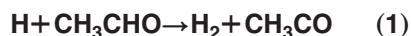
study of Umemoto *et al.*<sup>8</sup> gives much higher values, probably due to effects of secondary chemistry in their system. In the study of Michael *et al.*<sup>1</sup> two techniques were used, giving results in excellent agreement, which are preferred to the slightly higher results from the earlier studies of Carr *et al.*<sup>6</sup> and Slemr and Warneck.<sup>7</sup>

Hranisavljevic *et al.*<sup>3</sup> have combined their high temperature results with the low temperature results of Michael *et al.*<sup>1</sup> to derive the expression which we have adopted as our preferred expression for  $k$ . It extrapolates to give a value within a factor of 2 of the only other high temperature measurement of  $k$ , that of Frank *et al.*<sup>2</sup> at 2000 K.

### References

- <sup>1</sup>J. V. Michael, D. F. Nava, W. A. Payne, and L. J. Stief, *J. Chem. Phys.* **70**, 5222 (1979).
- <sup>2</sup>P. Frank, K. Bhaskaran, and Th. Just, *J. Phys. Chem.* **90**, 2226 (1986).
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- <sup>5</sup>CEC, 1992; Supplement I, 1994 (see references in Introduction).
- <sup>6</sup>R. W. Carr, I. D. Gay, G. P. Glass, and H. Nicki, *J. Chem. Phys.* **49**, 846 (1968).
- <sup>7</sup>F. Slemr and P. Warneck, *Ber. Bunsenges. Phys. Chem.* **79**, 152 (1975).
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#### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = -61.8 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = 19.5 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 3.76 \cdot 10^4 T^{-1.098} \exp(+6820/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(2) = -41.3 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = 20.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 0.37 T^{0.200} \exp(+5890/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(3) = 318.3 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = 29.6 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 5.41 \cdot 10^2 T^{-0.423} \exp(-38370/T) \\ (300 \leq T/\text{K} \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2 + k_3$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$2.2 \cdot 10^{-11} \exp(-1660/T)$	298–500	Whytock <i>et al.</i> , 1976 <sup>1</sup>	(a)
$1.4 \cdot 10^{-11} \exp(-3490/T)$	1550–1850	Beeley <i>et al.</i> , 1977 <sup>2</sup>	(b)
$9.8 \cdot 10^{-14}$	298	Michael and Lee, 1977 <sup>3</sup>	(c)
$1.1 \cdot 10^{-13}$	299	Ohmori <i>et al.</i> 1990 <sup>4</sup>	(d)
<i>Reviews and Evaluations</i>			
$6.8 \cdot 10^{-15} T^{1.16} \exp(-1210/T)$	300–2000	CEC 1992; 1994 <sup>5</sup>	(e)

#### Comments

- (a) Flash photolysis system with resonance fluorescence detection of H using Lyman  $\alpha$ .
- (b) Ignition of  $\text{CH}_3\text{CHO}/\text{O}_2/\text{Ar}$  mixtures behind incident shock waves. Stable and transient species monitored by UV and IR emission.  $k$  determined by numerical modeling of chemical scheme.
- (c) Discharge flow system with resonance fluorescence detection of H using Lyman  $\alpha$ .
- (d) Discharge flow system with mass spectrometric analysis at 3.36 mbar He total pressure.
- (e) See Comments on Preferred Values.

#### Preferred Values

$$k = 6.8 \cdot 10^{-15} T^{1.16} \exp(-1210/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \\ \text{over the range 298–2000 K.}$$

#### Reliability

$$\Delta \log k = \pm 0.1 \text{ at 298 K, rising to } \pm 0.4 \text{ at 2000 K.}$$

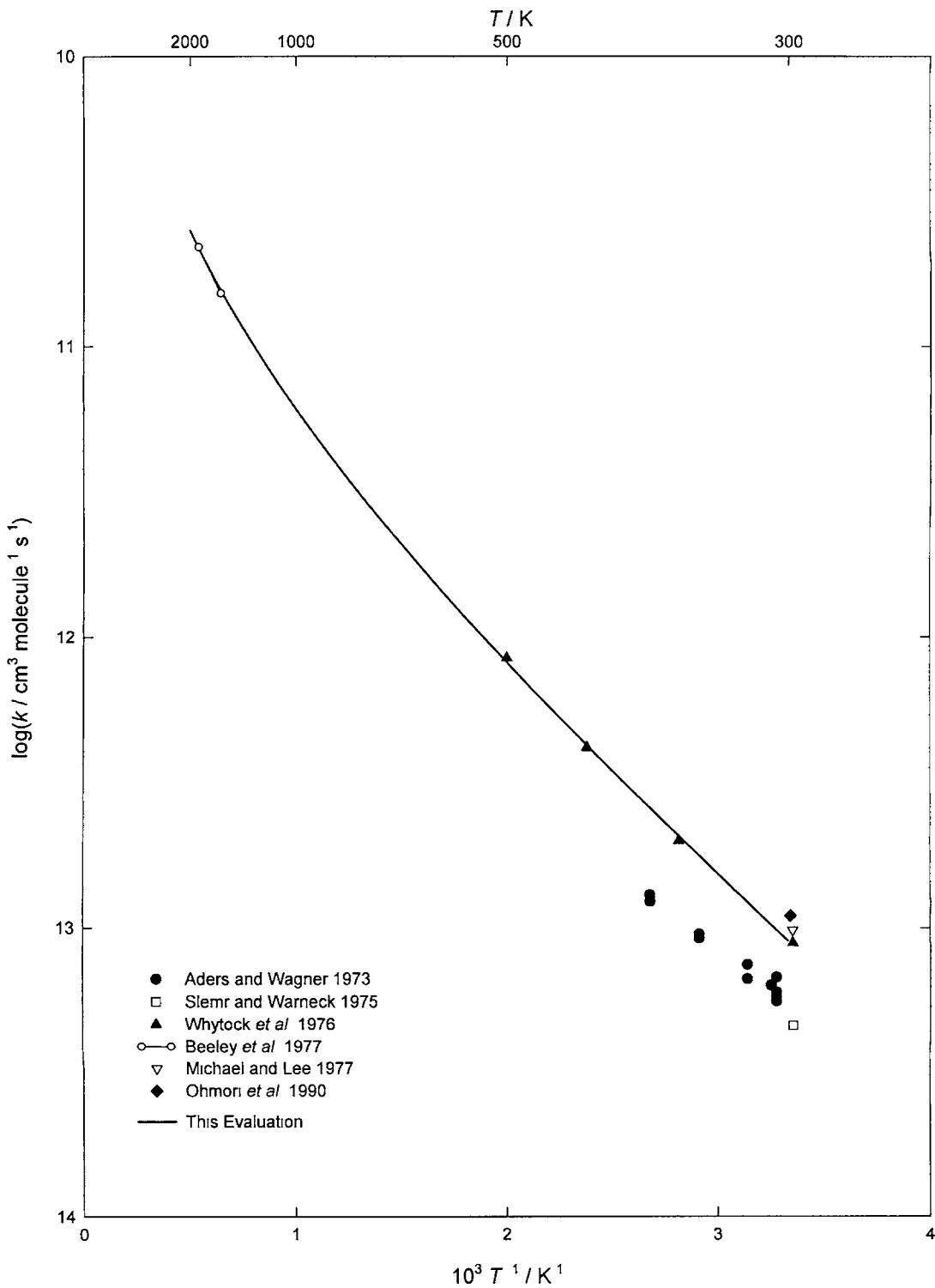
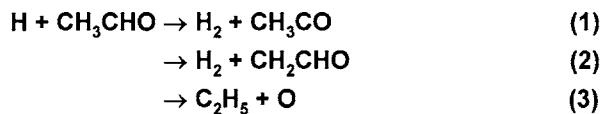
#### Comments on Preferred Values

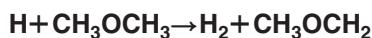
The preferred expression is a 3-parameter fit to the data of Whytock *et al.*,<sup>1</sup> Beeley *et al.*,<sup>2</sup> and Michael and Lee<sup>3</sup> which

cover the temperature range 298–1850 K. The recent room temperature data of Ohmori *et al.*<sup>4</sup> is consistent with this expression. Temperature dependence data of Whytock *et al.*<sup>1</sup> indicate curvature already in the 300–500 K range. Earlier data of Aders and Wagner<sup>6</sup> and Slemr and Warneck<sup>7</sup> at low temperature appear systematically low, probably due to less reliable measurement techniques. No experimental data are available on the contribution of the second and third channels. If it is assumed that  $k_2 = 0.5k(\text{H} + \text{C}_2\text{H}_6)$ ,  $k_2/k$  increases from 0.04 at 700 K to 0.5 at 1700 K. The contribution of the third channel is likely to be negligible at  $T < 1000$  K.

#### References

- <sup>1</sup> D. A. Whytock, J. V. Michael, W. A Payne, and L. J. Stief, *J. Chem. Phys.* **65**, 4871 (1976).
- <sup>2</sup> P. Beeley, J. F. Griffiths, B. A. Hunt, and A. Williams, 16th Symp. (Int.) Combustion, 1977, p. 1013.
- <sup>3</sup> J. V. Michael and J. H. Lee, *Chem. Phys. Lett.* **51**, 303 (1977).
- <sup>4</sup> K. Ohmori, A. Miyoshi, H. Matsui, and N. Washida, *J. Phys. Chem.* **94**, 3253 (1990).
- <sup>5</sup> CEC, 1992; Supplement I, 1994 (see references in Introduction).
- <sup>6</sup> W. K. Aders and H. Gg. Wagner, *Ber. Bunsenges. Phys. Chem.* **77**, 332 (1973).
- <sup>7</sup> F. Slemr and P. Warneck, *Ber. Bunsenges. Phys. Chem.* **79**, 152 (1975).



*Thermodynamic Data*

$$\begin{aligned}\Delta H_{298}^{\circ} &= -34.0 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= 30.6 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 2.25 \cdot 10^3 T^{-0.507} \exp(+3720/T) \\ &\quad (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$4.4 \cdot 10^{-12} \exp(-1960/T)$	273–426	Lee <i>et al.</i> , 1981 <sup>1</sup>	(a)
$5.3 \cdot 10^{-17} T^{1.9} \exp(-1860/T)$	900–1900	Hidaka, Sato, and Yamane, 2000 <sup>2</sup>	(b)
$1.84 \cdot 10^{-12}$	753	Tranter and Walker, 2001 <sup>3</sup>	(c)
<i>Reviews and Evaluations</i>			
$3.4 \cdot 10^{-20} T^3 \exp(-1451/T)$	270–1150	Tranter and Walker, 2001 <sup>2</sup>	(d)

**Comments**

- (a) Flash photolysis of  $\text{CH}_3\text{OCH}_3/\text{Ar}$  mixtures at total pressures in the range 40–260 mbar. [H] monitored by resonance fluorescence.
- (b) Shock tube study of pyrolysis of  $\text{CH}_3\text{OCH}_3/\text{H}_2/\text{Ar}$  mixtures. Three different shock tubes were used, one for time resolved and single pulse studies with provision for GC analysis of products, the other two for time resolved optical studies on reactants and products. The rate of change of  $[\text{CH}_3\text{OCH}_3]$ ,  $[\text{CH}_4]$ , and  $[\text{C}_2\text{H}_6]$  were shown to be sensitive to the value of  $k$ . Values of  $k$  were obtained by fitting the profiles of these quantities using a detailed mechanism.
- (c) Traces of  $\text{CH}_3\text{OCH}_3$  were added to slowly reacting  $\text{H}_2/\text{O}_2/\text{N}_2$  mixtures, over a wide range of compositions, at 753 K. Rate of consumption of  $\text{CH}_3\text{OCH}_3$  and  $\text{H}_2$  measured by GC. The data were analyzed using a detailed mechanism. Values of  $k/k(\text{H}+\text{O}_2)$  were determined and combined with the precisely known value of  $k(\text{H}+\text{C}_2\text{H}_6)/k(\text{H}+\text{O}_2)$  for this system and the value of  $k(\text{H}+\text{C}_2\text{H}_6)$  from the CEC, 1994 evaluation<sup>4</sup> to obtain  $k$ .
- (d) Based on the studies of Tranter and Walker,<sup>3</sup> Lee *et al.*<sup>1</sup> and a value of  $k = 1.8 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at  $\sim 1090$  K from the study of Faubel *et al.*<sup>6</sup>

**Preferred Values**

$$k = 5.3 \cdot 10^{-17} T^{1.9} \exp(-1860/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the range 270–2000 K.

*Reliability*

$$\Delta \log k = \pm 0.3 \text{ at } 270 \text{ K, rising to } \pm 0.5 \text{ at } 2000 \text{ K.}$$

*Comments on Preferred Values*

At low temperatures there have been a number of studies<sup>1,4–6</sup> of this reaction covering the temperature range

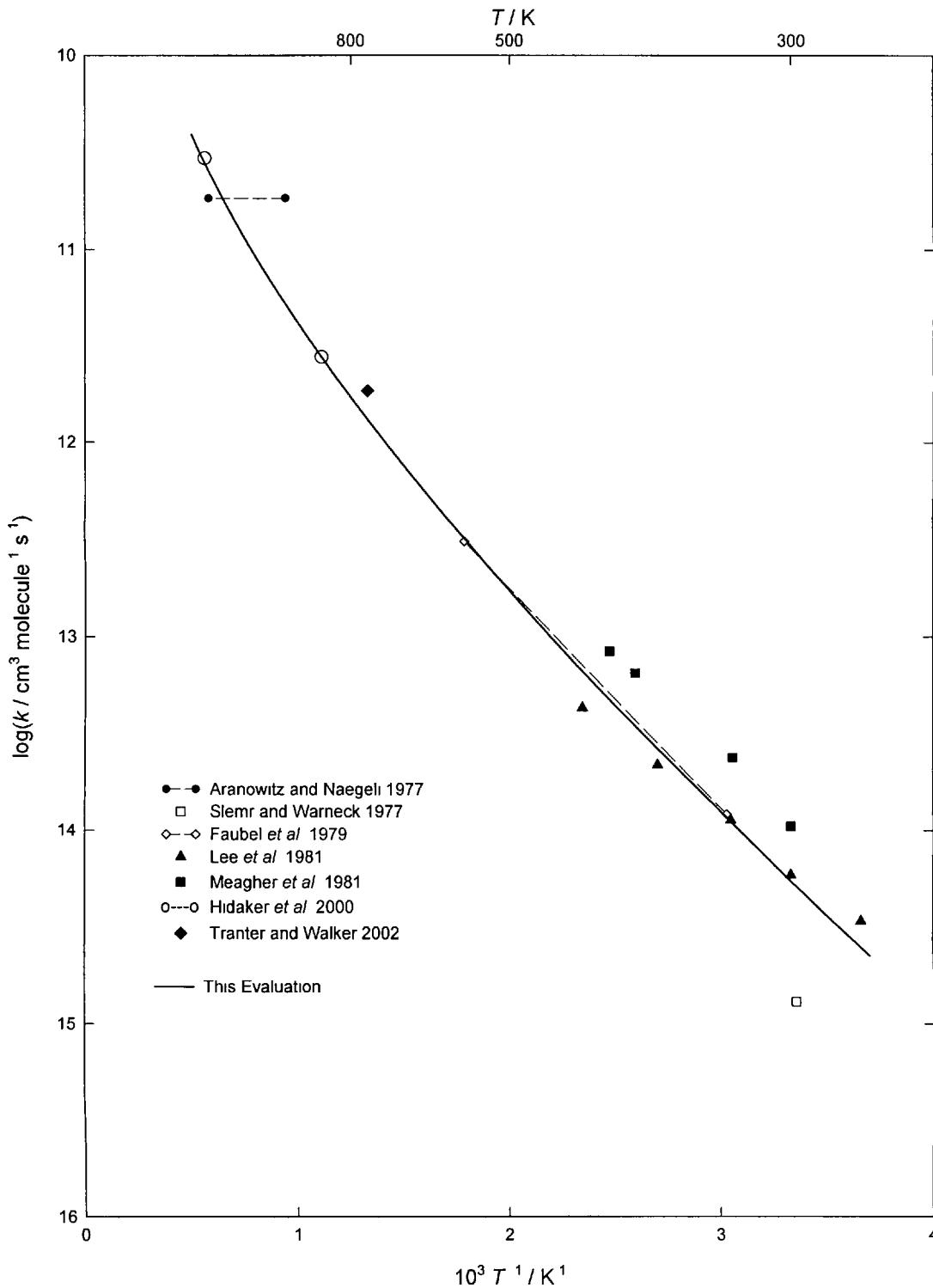
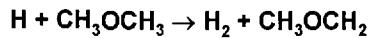
250–560 K, the results from which are shown on the Arrhenius plot. These studies have used discharge flow techniques<sup>4–6</sup> apart from that of Lee *et al.*<sup>1</sup> where flash photolysis was used. The studies differ significantly in the absolute values and temperature dependence found for  $k$ . It seems likely that in all of the discharge flow studies secondary reactions have affected the results. The effects of secondary chemistry have been recognized in some of the studies<sup>4,6</sup> and in one of them, Faubel *et al.*<sup>6</sup> measured the rate of consumption of both H and  $\text{CH}_3\text{OCH}_3$ , using the stoichiometry so derived to correct the apparent rate constant. However, there is substantial scatter on their results and their Arrhenius plot becomes very nonlinear at low temperatures. In their flash photolysis study Lee *et al.*<sup>1</sup> used very low  $[\text{H}]/[\text{CH}_3\text{OCH}_3]$  ratios ( $\sim 10^{-3}$ ) and because of this their work seems most likely to have achieved truly pseudo first order conditions. The preferred expression for  $k$  is therefore based on their results at low temperatures.

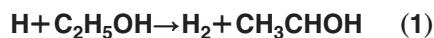
At higher temperatures there are data from the shock tube study of Hidaka *et al.*,<sup>2</sup> a pyrolysis study of Tranter and Walker,<sup>3</sup> and a less reliable pyrolysis study of Aronowitz and Naegeli<sup>7</sup> where the temperature is somewhat uncertain. The expression obtained by Hidaka *et al.*<sup>2</sup> has been adopted as our preferred expression since it extrapolates well to the low temperature data of Lee *et al.*<sup>1</sup> and agrees to within 10% of the value determined at 753 K by Tranter and Walker<sup>3</sup> when the value of  $k(\text{H}+\text{C}_2\text{H}_6)$  is used in conjunction with their relative rate data [Comment (c)].

**References**

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- <sup>3</sup>R. S. Tranter and R. W. Walker, Phys. Chem. Chem. Phys. **3**, 4722 (2001).  
<sup>4</sup>J. H. Meagher, P. Kim, J. H. Lee, and R. B. Timmons, J. Phys. Chem. **78**, 2650 (1981).  
<sup>5</sup>F. Slemr and P. Warneck, Int. J. Chem. Kinet. **9**, 267 (1977).  
<sup>6</sup>C. Faubel, K. Hoyermann, E. Strofer, and H. Gg. Wagner, Ber. Bunsenges. Phys. Chem. **83**, 532 (1979).  
<sup>7</sup>D. Aronowitz and D. Naegeli, Int. J. Chem. Kinet. **11**, 471 (1977).





#### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = -34.6 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = 16.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 2.0 \cdot 10^3 T^{-0.75} \exp(+3740/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(3) = 1.8 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = 9.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 17.0 T^{-0.20} \exp(-380/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(2) = -19.0 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = 10.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 0.16 T^{0.57} \exp(+2220/T) \\ (300 \leq T/\text{K} \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2 + k_3$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$7.0 \cdot 10^{-12} \exp(-2110/T)$	295–500	Aders and Wagner, 1973 <sup>1</sup>	(a)

#### Comments

- (a) Discharge-flow system used. [H] monitored by ESR spectroscopy. Other species monitored by mass spectrometry and stable products by gas chromatography. Derivation of the rate constant required determination of the stoichiometry factor ( $\Delta[\text{H}]/\Delta[\text{C}_2\text{H}_5\text{OH}]$ ). In another paper<sup>2</sup> Aders quotes the same expression, but a more limited temperature range (292–470 K), and states that the reaction took place under pseudo first order conditions ( $[\text{C}_2\text{H}_5\text{OH}] \gg [\text{H}]$ ).

#### Preferred Values

$k = 7.0 \cdot 10^{-12} \exp(-2110/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 295–700 K.

#### Reliability

$\Delta \log k = \pm 0.3$  over the temperature range 295–700 K.

#### Comments on Preferred Values

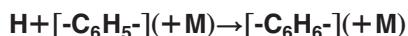
The expression for  $k$  obtained by Aders and Wagner<sup>1</sup> is accepted as our preferred expression. The only other measurement of  $k$  is that of Bansal and Freeman<sup>3</sup> derived from measurements of  $\text{H}_2$  yields in the radiolysis of  $\text{C}_2\text{H}_5\text{OH}/\text{C}_3\text{H}_6$  mixtures giving  $k = 4.2 \cdot 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 423 K, in reasonable agreement with the value of  $4.7 \cdot 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  pre-

dicted by the expression of Aders and Wagner.<sup>1</sup> However, until further confirmatory measurements are available substantial error limits are suggested.

There are no measurements of the channel branching ratios. By analogy with the reactions of  $\text{CH}_3$  and O with ethanol, Channel (1) would be expected to predominate. There is another exothermic channel, leading to  $\text{C}_2\text{H}_5 + \text{H}_2\text{O}$  ( $\Delta H^\circ_{298} = -103.9 \text{ kJ mol}^{-1}$ ), which has been invoked to explain product yields in some experiments,<sup>1</sup> but there is no direct evidence for its occurrence. Marinov<sup>4</sup> has estimated values for the branching ratios by comparison with previously determined branching ratios for model compounds having chemical structures and bonding features similar to ethanol (propane and methane were the chosen reference compounds). Marinov<sup>4</sup> uses as an overall  $k$  an expression derived by applying a  $T^{2.0}$  dependence to the low temperature data of Aders and Wagner<sup>1</sup> and combines this with the estimated branching ratios to derive expressions for  $k_1$ ,  $k_2$ , and  $k_3$  as a function of temperature. These expressions provide a useful guide to the branching ratios at higher temperatures.

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*Thermodynamic Data*

$$\Delta H_{298}^{\circ} = -473.4 \text{ kJ mol}^{-1}$$

$$\Delta S_{298}^{\circ} = -133.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c = 1.24 \cdot 10^{-28} T^{0.550} \exp(+57090/T) \text{ cm}^3 \text{ molecule}^{-1}$$

(300 ≤ T/K ≤ 5000)

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$1.3 \cdot 10^{-10}$	1380–1700	Braun-Unkhoff, Frank, and Just, 1988 <sup>1</sup>	(a)
$3.7 \cdot 10^{-10}$	300	Ackermann <i>et al.</i> , 1990 <sup>2</sup>	(b)
<i>Reviews and Evaluations</i>			
$1.3 \cdot 10^{-10}$	1400–1700	CEC, 1992; 1994 <sup>3</sup>	(c)

**Comments**

- (a) Dissociation of phenyl radicals behind reflected shock-waves. Phenyl radicals generated by pyrolysis of 1–100 ppm mixtures of nitrosobenzene in 1.5–6 bar total pressure Ar bath gas. H atoms monitored by ARAS. It was found that besides the dissociation reaction sequence of phenyl, the recombination step has the strongest influence on the measured [H].
- (b) Flash photolysis study. Phenyl radicals generated by pulsed photolysis of benzene at 193 nm. [H] determined by absorption of Lyman- $\alpha$  radiation at 121.6 nm, and benzene by absorption at 193 nm.
- (c) Preferred value based on the study of Braun-Unkhoff, Frank, and Just.<sup>1</sup>

**Preferred Values**

$k = 1.3 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 300–1700 K.

*Reliability*

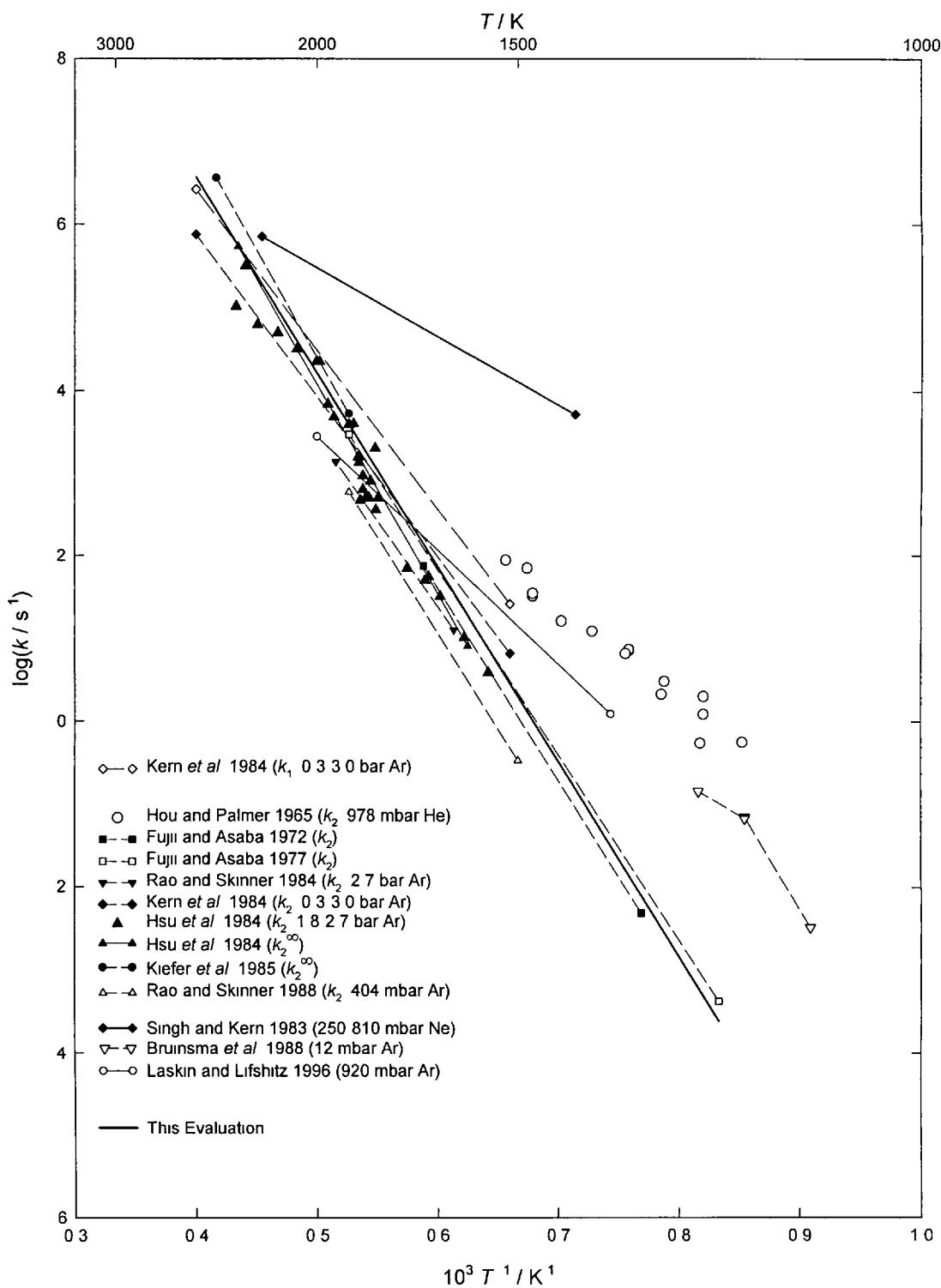
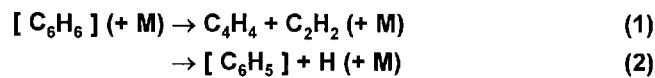
$\Delta \log k = \pm 0.5$  over the range 300–1700 K

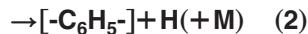
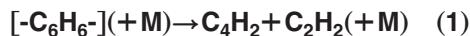
*Comments on Preferred Values*

The recommendation is unchanged from our previous evaluation<sup>3</sup> and is based on the experimental study of Braun-Unkhoff, Frank, and Just.<sup>1</sup> The reported value is dependent on the rate coefficient for phenyl radical recombination which is expected to be temperature independent. Within the recommended error limits the preferred value agrees with that of Ackermann *et al.*,<sup>2</sup> and we therefore recommend the preferred value over the temperature range 300–1700 K. Theoretical calculations by Mebel *et al.*<sup>4</sup> suggest that the formation of C<sub>6</sub>H<sub>6</sub> is the dominant channel up to ∼1500 K at 1 bar but at higher temperatures and lower pressures the formation of other products may become important.

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*Thermodynamic Data*

$$\Delta H^{\circ}_{298}(1) = 430.1 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298}(1) = 210.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 2.32 \cdot 10^{34} T^{-1.225} \exp(-52450/T) \text{ molecule cm}^{-3}$$

(300 ≤ T/K ≤ 5000)

$$\Delta H^{\circ}_{298}(2) = 473.4 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298}(2) = 133.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 8.11 \cdot 10^{27} T^{-0.550} \exp(-57090/T) \text{ molecule cm}^{-3}$$

(300 ≤ T/K ≤ 5000)

See Section 3 for the origin source of the Thermodynamic Data.

**Rate Coefficient Data ( $k = k_1 + k_2$ )**

$k/\text{s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$k_2 = 3.2 \cdot 10^{15} \exp(-53342/T)$	1300–1700	Fujii and Asaba, 1972 <sup>1</sup>	(a)
$k_2 = 1.6 \cdot 10^{15} \exp(-51329/T)$	1200–1900	Fujii and Asaba, 1977 <sup>2</sup>	(b)
$3.9 \cdot 10^9 \exp(-18935/T)$	1400–2200	Singh and Kern, 1983 <sup>3</sup>	(c)
$k_2 = 7.0 \cdot 10^{13} \exp(-47807/T)$	1630–1940	Rao and Skinner, 1984 <sup>4</sup>	(d)
$k_1 = 1.3 \cdot 10^{14} \exp(-44284/T)$	1515–2500	Kern <i>et al.</i> , 1984 <sup>5</sup>	(e)
$k_2 = 4.6 \cdot 10^{13} \exp(-44787/T)$	1515–2500		
$k_2 = 5.0 \cdot 10^{15} \exp(-54300/T)$	1600–2300	Hsu, Lin, and Lin, 1984 <sup>6</sup>	(f)
$k_2 = 2.0 \cdot 10^{17} \exp(-59381/T)$	1900–2400	Kiefer <i>et al.</i> , 1985 <sup>7</sup>	(g)
$k_2 = 9.3 \cdot 10^{14} \exp(-53342/T)$	1500–1900	Rao and Skinner, 1988 <sup>8</sup>	(h)
<i>Reviews and Evaluations</i>			
$k = 9.0 \cdot 10^{15} \exp(-54060/T)$	1200–2500	CEC, 1992; 1994 <sup>9</sup>	(i)

**Comments**

- (a) Rich mixtures of benzene and oxygen were pyrolyzed in a single-pulse shock tube behind incident shock waves. The formation of biphenyl was monitored by light absorption in the wavelength range 315–600 μm, and the formation of CO was monitored by IR emission in the wavelength range 3000–5000 μm. The products were also analyzed by gas chromatography. The experimental data from the initial stages of reaction were modeled by a simple reaction scheme.
- (b) The high temperature pyrolysis of benzene was studied in a single-pulse shock tube. Gas samples were heated by reflected shock waves and the products analyzed by gas chromatography. Benzene and biphenyl concentrations were also monitored by UV-vis absorption at  $\lambda = 200$ –600 nm. The experimental data were explained by a chain mechanism comprising 7 elementary reactions.
- (c) Pyrolysis of mixtures of 2.1%–5% benzene diluted in Ne was studied behind reflected shock waves. Products were analyzed by time-of-flight mass spectroscopy. The data could be reproduced with a 5-step reaction mechanism. The first-order rate expression given in the Table has been calculated for a density of  $1.6 \cdot 10^{18}$  molecule cm<sup>-3</sup> from the second-order rate coefficient evaluated by the authors.
- (d) Dilute mixtures of 3–20 ppm C<sub>6</sub>D<sub>6</sub> were pyrolyzed behind reflected shock waves at total pressures of 2–3 bar. The formation of D atoms was monitored by ARAS. A 6-step reaction mechanism was employed to

model the experimental data. The rate coefficient for H-atom production was determined by assuming approximate isotope effect calculations.

- (e) The rate coefficients for both channels were derived in a collaborative shock-tube study on C<sub>6</sub>H<sub>6</sub> and C<sub>6</sub>D<sub>6</sub> pyrolysis employing 3 independent analytical techniques: time-of-flight mass spectrometry, time resolved ARAS and laser schlieren density gradient profiles.
- (f) The oxidation of benzene under fuel lean conditions was studied behind reflected shock waves. CO formation was monitored with a stabilized cw CO laser. [CO] profiles were modeled with a 25-step mechanism, and a rate coefficient for Channel (2) was derived.
- (g) Pyrolysis of mixtures of 1 and 2 mol % benzene in a shock tube at total pressures in the range 0.2–1 bar Kr bath gas. Density gradient monitored by laser Schlieren technique. The observed density gradient and some time-of-flight mass spectra were modeled with a 26-step reaction mechanism. RRKM calculations are also presented. A high pressure limiting rate coefficient for channel (2) was derived.
- (h) Highly dilute mixtures of C<sub>6</sub>D<sub>6</sub>, C<sub>6</sub>H<sub>5</sub>Cl, C<sub>6</sub>H<sub>5</sub>Br, and C<sub>6</sub>H<sub>5</sub>I were pyrolyzed behind incident shock waves at a total pressure of 0.4 bar. Formation of H and D atoms was monitored by ARAS, and a rate coefficient for production of H atoms in Channel (2) was derived from approximate isotope effect calculations. RRKM calculation were carried out to account for unimolecular fall-off and to distinguish the rate coefficient for dissociation of C<sub>6</sub>H<sub>6</sub> and C<sub>6</sub>D<sub>6</sub>.

(i) See Comments on Preferred Value.

### Preferred Values

$k = 9.0 \cdot 10^{15} \exp(-54060/T)$  s<sup>-1</sup> over the range 1200–2500 K.

#### Reliability

$\Delta \log k = \pm 0.4$  at 1200 K, reducing to  $\pm 0.3$  at 2000 K.

#### Comments on Preferred Values

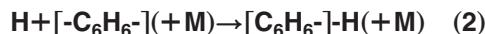
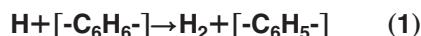
The preferred value remains unchanged from our previous evaluation<sup>9</sup> and is based on the work of Refs. 1–8 from which a first-order rate coefficient is derived. Almost all of the experimental work is interpreted by the authors as indicating that the H-atom producing reaction, Channel (2), is dominant. However, the diagnostic methods in many of the experiments do not allow distinction between the product channels to be made. Consequently a rate coefficient for the overall reaction is recommended.

Laskin and Lifshitz<sup>10</sup> have investigated product formation from benzene pyrolysis behind reflected shock waves employing gas chromatographic analysis in the temperature range 1450–2000 K. At temperatures around 1400 K biphenyl is the most abundant product [phenyl is produced in Channel (2)], but at higher temperatures C<sub>4</sub>H<sub>2</sub>+C<sub>2</sub>H<sub>4</sub> [from Channel (1)] become the dominant products. The overall rate coefficient reported by Laskin and Lifshitz<sup>10</sup> agrees with the

preferred value for  $T > 1700$  K; at lower temperatures biphenyl generation probably leads to an overestimate or the reaction rate. Bruinsma *et al.*<sup>11</sup> did not detect any products from the pyrolysis of benzene at  $T < 1170$  K, and only C<sub>2</sub>H<sub>2</sub> at higher temperatures. The rate coefficients reported by Bruinsma *et al.*<sup>11</sup> and Hou and Palmer<sup>12</sup> are most probably influenced by biphenyl production. A theoretical treatment of the reaction by Mebel *et al.*<sup>13</sup> also suggests that, as well as Channel (2), other channels should be considered in interpreting experiments on the decomposition of C<sub>6</sub>H<sub>6</sub>.

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*Thermodynamic Data*

$$\Delta H^\circ_{298}(1) = 37.4 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = 35.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 1.33 \cdot 10^4 T^{-0.701} \exp(-4900/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(2) = -91.8 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = -82.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 3.50 \cdot 10^{32} T^{-19.713} \exp(+7050/T) \text{ cm}^3 \text{ molecule}^{-1} \\ (300 \leq T/\text{K} \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data ( $k = k_1 + k_2$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$6.7 \cdot 10^{-11} \exp(-2170/T)$	298–1000	Nicovich and Ravishankara, 1984 <sup>1</sup>	(a)
$k_1 = 4.2 \cdot 10^{-11} \exp(-8052/T)$	1900–2200	Kiefer <i>et al.</i> , 1985 <sup>2</sup>	(b)
$k_1 = 8.8 \cdot 10^{-8} T^{-0.701} \exp(-8870/T)$	1050–1450	Heckmann, Hippler, and Troe, 1996 <sup>3</sup>	(c)
$k_1 = 1.27 \cdot 10^{-15} T^{1.729} \exp(-8058/T)$	500–1050	Park, Dyakov, and Lin, 1997 <sup>4</sup>	(d)
<i>Reviews and Evaluations</i>			
$k_2 = 6.6 \cdot 10^{-11} \exp(-2013/T)$	298–480	Kerr and Parsonage, 1972 <sup>5</sup>	(e)
$k_2 = 6.7 \cdot 10^{-11} \exp(-2170/T)$	298–1000	CEC, 1992; 1994 <sup>6</sup>	(f)

**Comments**

- (a) Flash photolysis-resonance fluorescence experiments at total pressures in the range 13–270 mbar Ar bath gas. H atoms generated by photolysis of benzene or  $\text{H}_2\text{O}$ .  $[\text{H}]$  monitored by resonance fluorescence at  $\lambda = 121.5 \text{ nm}$ . Authors estimated  $k_1 = 5 \cdot 10^{-12} \exp(-4076/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  which indicates contribution of Channel (1) to overall reaction is negligible for  $T < 1000 \text{ K}$ , and no pressure dependence was observed. Consequently a high pressure limiting rate coefficient for Channel (2) is derived for  $T < 1000 \text{ K}$ .
- (b) Shock tube study of the pyrolysis of benzene in Kr bath gas. Laser Schlieren analysis of the density gradient. Observed density gradient profiles were modeled by a 26-step mechanism.
- (c) Shock tube study using reflected shock waves. Phenyl radicals generated by nitrosobenzene pyrolysis. Formation of benzene and biphenyl monitored by UV absorption in the wavelength region 215–260 nm. A values for the reverse reaction was determined;  $k_{-1} = 6.7 \cdot 10^{-12} \exp(-3971/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .
- (d) Two experimental techniques were employed to study the reverse reaction. (i) Phenyl radicals generated by pyrolysis of dilute mixtures of nitrosobenzene in  $\text{H}_2$  at 1 bar total pressure over the temperature range 550–600 K. Formation of benzene monitored by rapid expansion into the absorption cell of a Fourier-transform infrared spectrometer. (ii) Phenyl radicals generated by the pulsed photolysis of phenylmethylketone at  $\lambda = 193 \text{ nm}$  in a flow reactor at 4 mbar total pressure over the temperature range 700–1020 K. Product formation monitored by mass spectrometry;  $k$  extracted from modeling  $[-\text{C}_6\text{H}_6^-]$  profiles.

- (e) Literature survey. Based on the data of Jennings and Cvetanovic<sup>23</sup> and Sauer and Ward.<sup>18</sup>
- (f) No recommendation is given for the abstraction reaction, Channel (1), because of the large scatter of the experimental data at high temperatures.<sup>2,7–11</sup> The preferred value for the adduct forming reaction, Channel (2), is based on the data of Nicovich and Ravishankara.<sup>1</sup>

**Preferred Values**

$$k_1 = 2.16 \cdot 10^{-7} T^{-0.70} \exp(-10070/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the range } 500–2200 \text{ K.}$$

$$k_2 = 6.7 \cdot 10^{-11} \exp(-2170/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the range } 298–500 \text{ K.}$$

**Reliability**

$$\Delta \log k_1 = \pm 0.15 \text{ over the range } 500–2200 \text{ K.}$$

$$\Delta \log k_2 = \pm 0.15 \text{ over the range } 298–500 \text{ K.}$$

**Comments on Preferred Values**

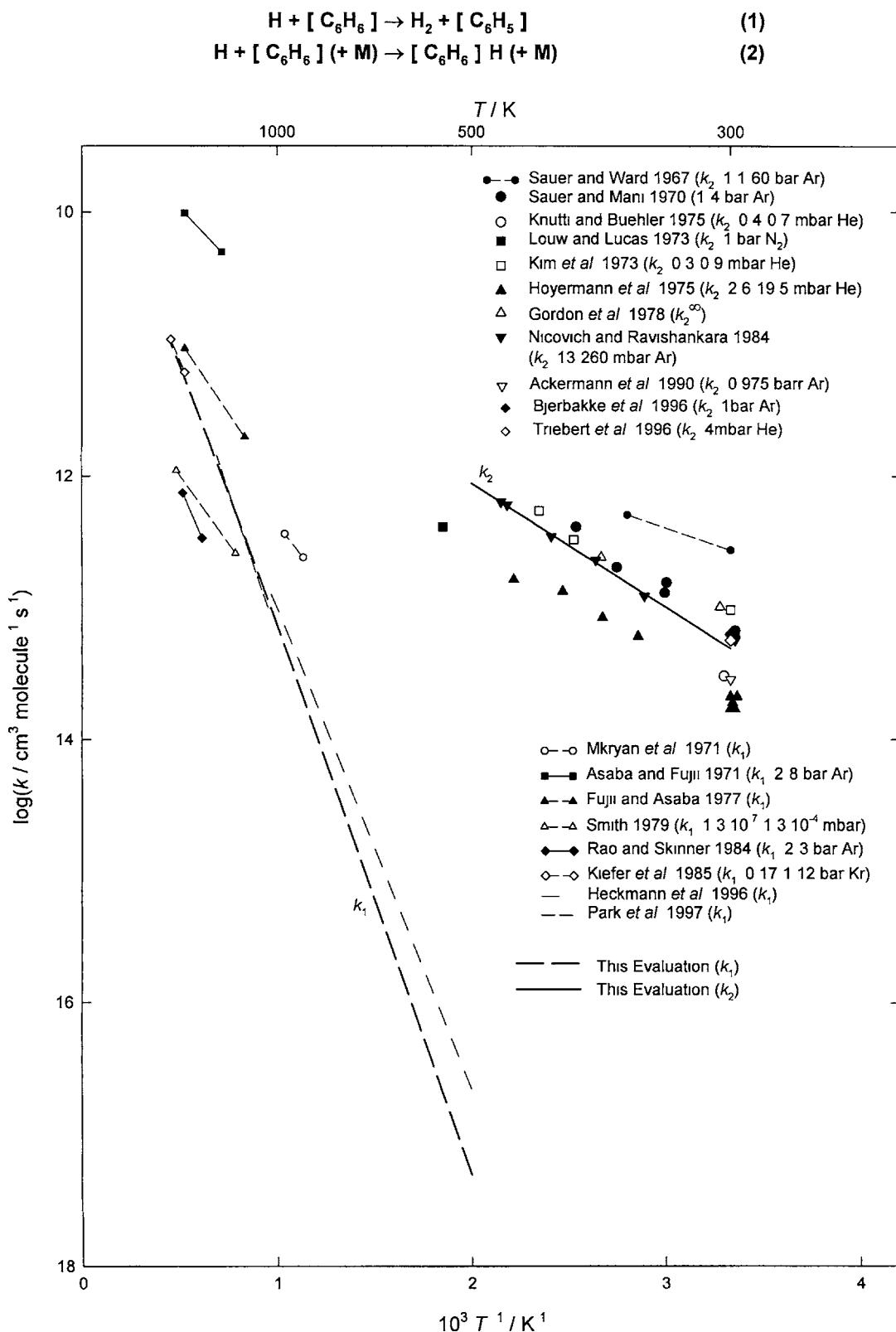
The preferred values for Channel (1) are based on recent measurements on the reverse reaction<sup>3,4</sup> in combination with the equilibrium constant given in this evaluation. A least squares fit to the data of Heckmann, Hippler, and Troe<sup>3</sup> and Park *et al.*<sup>4</sup> gives the expression  $k_{-1} = 1.6 \cdot 10^{-11} \exp(-5169/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The resulting expression for  $k_1$  agrees well with the determinations of  $k_1$  by Kiefer *et al.*<sup>2</sup> We therefore recommend the expression over the combined temperature range of Refs. 1–3. Mebel *et al.*<sup>12</sup> obtained the expression  $k_{-1} = 9.5 \cdot 10^{-20} T^{2.43} \exp(-3159/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the reverse reaction which, when combined with the equilibrium constant, is consistent with

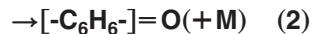
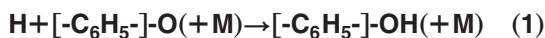
the experimental data of Heckmann, Hippler, and Troe<sup>3</sup> and of Park *et al.*<sup>4</sup>

Channel (2) has been studied by Nicovich and Ravishankara<sup>1</sup> under well defined conditions where  $k_2$  is close to its high pressure limit, and at sufficiently low temperatures to preclude a significant contribution from  $k_1$ . The expression of Nicovich and Ravishankara<sup>1</sup> is adopted as the preferred expression for  $k_2$ . There is considerable scatter on the values obtained for  $k_2$  at 298 K.<sup>13–22</sup> The values obtained by Triebert *et al.*,<sup>22</sup> and by Sauer and Mani,<sup>13</sup> are in good agreement with our preferred expression. Apart from that of Sauer and Mani,<sup>13</sup> most measurements of the temperature dependence of  $k_2$  give lower values of  $E/R$  than our preferred value but all cover a significantly smaller temperature range than the study of Nicovich and Ravishankara<sup>1</sup> on which our preferred expression is based. The preferred expression is very similar to that derived in the evaluation of Kerr and Parsonage.<sup>5</sup>

## References

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#### Thermodynamic Data

$$\Delta H^{\circ}_{298}(1) = -362.5 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298}(1) = -113.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 3.18 \cdot 10^{-25} T^{-0.204} \exp(+43370/T) \text{ cm}^3 \text{ molecule}^{-1}$$

(300 ≤ T/K ≤ 4000)

$$\Delta H^{\circ}_{298}(2) = -283.3 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298}(2) = -103.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 3.37 \cdot 10^{-15} T^{-3.266} \exp(+32530/T) \text{ cm}^3 \text{ molecule}^{-1}$$

(300 ≤ T/K ≤ 4000)

$$\Delta H^{\circ}_{298}(3) = -241.9 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298}(3) = 43.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 1.19 \cdot 10^8 T^{-2.037} \exp(+28600/T)$$

(300 ≤ T/K ≤ 4000)

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2 + k_3$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$3.3 \cdot 10^{-10}$	1000	He, Mallard, and Tsang, 1988 <sup>1</sup>	(a)
$6.7 \cdot 10^{-11}$	295	Buth, Hoyermann, and Seeba, 1994 <sup>2</sup>	(b)
<i>Reviews and Evaluations</i>			
$4.2 \cdot 10^{-10}$	1000	CEC, 1992; 1994 <sup>3</sup>	(c)

#### Comments

- (a) Study of the reaction of H atoms with phenol in single-pulse shock wave experiments at 2–5 bar total pressure. Product analysis by gas chromatography. Rate coefficient extracted by modeling with a 12-step mechanism.
- (b) Flow reactor study at 1–5 mbar total pressure. H atoms generated by discharge in dilute mixtures of  $\text{H}_2$  in Ar bath gas; phenoxy radicals generated by reaction of phenol with Cl. Mass spectrometric analysis of reaction products.  $k$  measured was relative to the reaction  $\text{H} + \text{C}_2\text{H}_5 \rightarrow 2\text{CH}_3$ . Value of  $k$  cited in the Table was calculated taking the value  $k(\text{H} + \text{C}_2\text{H}_5 \rightarrow 2\text{CH}_3)$  from the present evaluation.
- (c) Preferred value based on the data of He, Mallard, and Tsang.<sup>1</sup>

#### Preferred Values

$k = 2 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 295–1000 K.

#### Reliability

$\Delta \log k = \pm 0.4$  over the range 295–1000 K.

#### Comments on Preferred Values

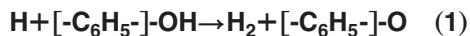
There are only two measurements of  $k$  and both studies are subject to uncertainties. The data of He, Mallard, and Tsang<sup>1</sup> may be subject to fall-off effects and there may be contribution from Channel (3), whereas although the data of Buth, Hoyermann, and Seeba<sup>2</sup> are likely to be close to the high pressure limit, they are limited by uncertainties in the

rate coefficient of the reference reaction. The rates of atom-radical reactions such as these are expected to be rapid and approximately temperature independent as appears to be the case here. We therefore recommend the average value of the two studies. The preferred value is consistent with the results of an RRKM calculation<sup>4</sup> which gave  $k_1^{\infty} = 4.2 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k(\text{H} + [-\text{C}_6\text{H}_5\text{-}] \text{-CH}_2 \rightarrow [-\text{C}_6\text{H}_5\text{-}] \text{-CH}_3) = 4.3 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (see Summary Table).

Product formation studies with D atoms have shown that Channel (2) is preferred as no  $[-\text{C}_6\text{H}_5\text{-}] \text{-OD}$  was observed;<sup>2</sup> the observed ion abundance ratio for the masses 95 and 67 was 2:1 rather than 16:1 which is expected for deuterated phenol. However, the mass spectrum of cyclohexa-1,4-diene-one is not sufficiently well known to allow positive identification of this product. Since Channel (2) is less exothermic it is plausible that the combination produces cyclohexa-1,4-diene-one preferentially. In a flow reactor study of the thermolysis of anisole in the temperature range 790–1020 K, Arends, Louw, and Mulder<sup>5</sup> showed qualitatively that at elevated temperatures occurrence of Channel (3) may be necessary to explain their observed [CO] profiles.

#### References

- <sup>1</sup> Y. Z. He, W. G. Mallard, and W. Tsang, *J. Phys. Chem.* **92**, 2196 (1988).
- <sup>2</sup> R. Buth, K. H. Hoyermann, and J. Seeba, 25th Symp. (Int.) Combustion, 1994, p. 841.
- <sup>3</sup> CEC, 1992; Supplement I, 1994 (see references in Introduction).
- <sup>4</sup> S. G. Davis, H. Wang, K. Brezinsky and C. K. Law, 26th Symp. (Int.) Combustion, 1996, p. 1025.
- <sup>5</sup> I. W. C. E. Arends, R. Louw, and P. Mulder, *J. Phys. Chem.* **97**, 7914 (1993).

*Thermodynamic Data*

$$\begin{aligned}\Delta H^\circ_{298}(1) &= -73.9 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(1) &= 14.5 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 9.24 T^{-0.023} \exp(+8770/T) \\ &(300 \leq T/\text{K} \leq 4000)\end{aligned}$$

$$\begin{aligned}\Delta H^\circ_{298}(2) &= -1.89 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(2) &= 23.3 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 3.21 \cdot 10^4 T^{-1.188} \exp(+10/T) \\ &(300 \leq T/\text{K} \leq 4000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data ( $k = k_1 + k_2$ )**

$k/\text{s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$k_1 = 1.9 \cdot 10^{-10} \exp(-6240/T)$	1000–1150	He, Mallard, and Tsang, 1988 <sup>1</sup>	(a)
$k_2 = 3.7 \cdot 10^{-11} \exp(-3990/T)$	1000–1150	Horn, Frank, and Just, 1998 <sup>2</sup>	(b)
$k = 8.1 \cdot 10^{-11} \exp(-4190/T)$	1100–1300		
<i>Reviews and Evaluations</i>			
$k_1 = 1.9 \cdot 10^{-10} \exp(-6240/T)$	1000–1150	CEC, 1992; 1994 <sup>3</sup>	(c)
$k_2 = 3.7 \cdot 10^{-11} \exp(-3990/T)$	1000–1150		

**Comments**

- (a) Single-pulse shock tube experiments at total pressures of 2.5–5 bar Ar. H atoms generated by the fast decomposition of C<sub>8</sub>H<sub>18</sub> to H + *iso*-C<sub>4</sub>H<sub>8</sub>. Phenol is in large excess over C<sub>8</sub>H<sub>18</sub> and is thus the main H atom sink. Benzene produced through Channel (2) together with isobutene yields were measured by GC analysis, to establish the branching ratio for Channels (1) and (2). Absolute rate data were obtained using CH<sub>4</sub> + H as an internal standard, i.e., by observing the change in benzene yield with addition of several percent of CH<sub>4</sub>. Kinetic complications were investigated by varying the stoichiometry and by computer simulation.
- (b) Measurements behind reflected shock waves at ~2.5 bar. H atoms generated from decomposition of ethyliodide in mixtures containing 30 ppm phenol with 0.5 ppm ethyliodide in Ar bath gas. [H] decay monitored by ARAS.
- (c) Preferred value based on the study of He *et al.*<sup>1</sup>

**Preferred Values**

$$\begin{aligned}k_1 &= 1.9 \cdot 10^{-10} \exp(-6240/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad \text{over} \\ &\text{the range } 1000\text{--}1500 \text{ K.} \\ k_2 &= 3.7 \cdot 10^{-11} \exp(-3990/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad \text{over} \\ &\text{the range } 1000\text{--}1500 \text{ K.}\end{aligned}$$

$$\begin{aligned}k_1/k &= 0.892 - 540/T \text{ over the range } 1000\text{--}1500 \text{ K.} \\ k_2/k &= 0.108 + 540/T \text{ over the range } 1000\text{--}1500 \text{ K.}\end{aligned}$$

**Reliability**

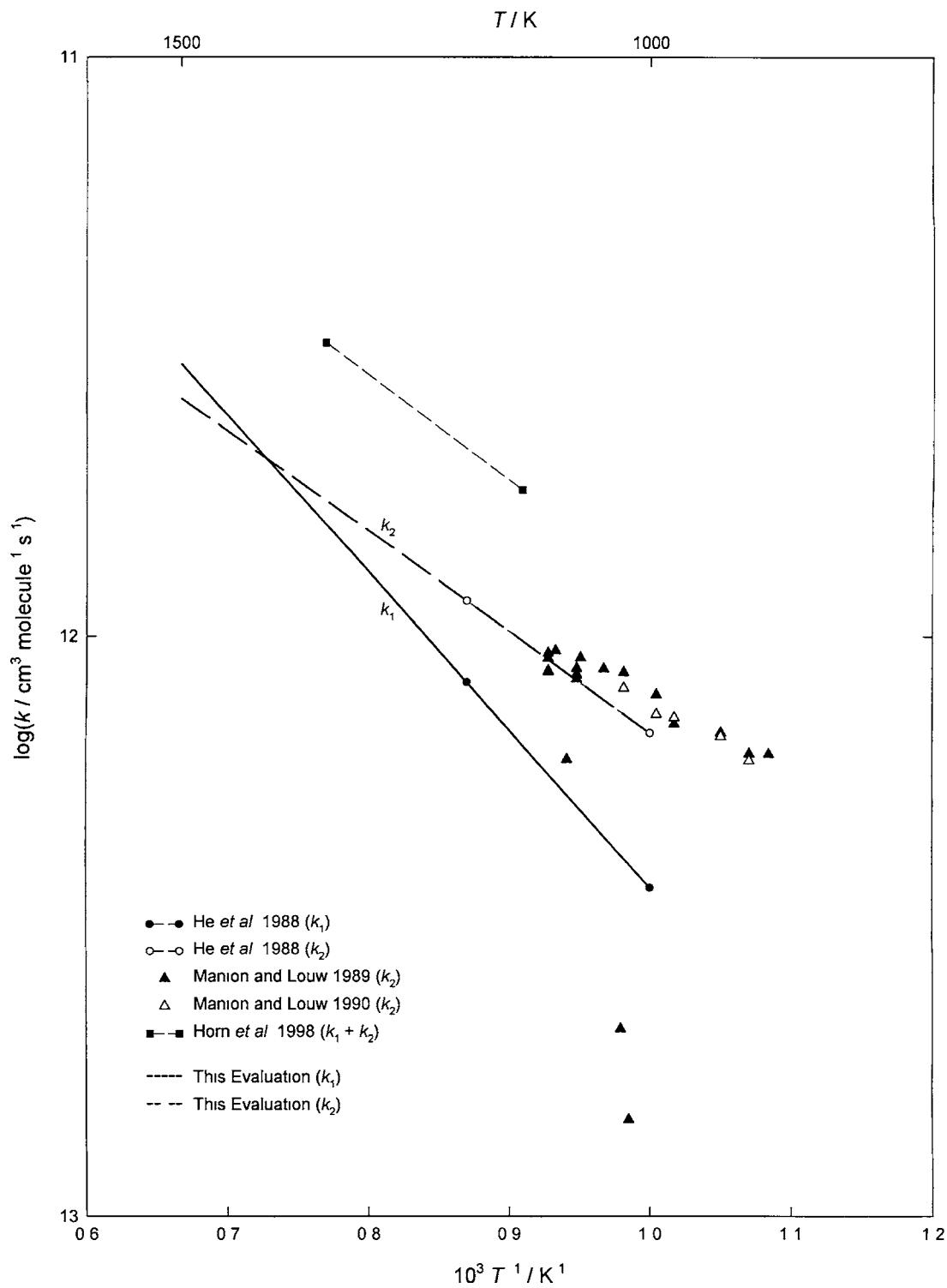
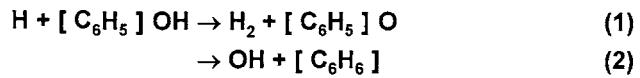
$$\begin{aligned}\Delta \log k_1 &= \Delta \log k_2 = \pm 0.2 \text{ over the range } 1000\text{--}1500 \text{ K.} \\ \Delta(k_1/k) &= \Delta(k_2/k) = \pm 0.2 \text{ over the range } 1000\text{--}1500 \text{ K.}\end{aligned}$$

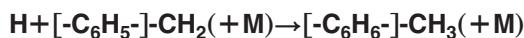
**Comments on Preferred Values**

The data of Horn *et al.*<sup>2</sup> are in excellent agreement with the sum of the rate coefficients determined by He *et al.*<sup>1</sup>. Manion and Louw<sup>4,5</sup> have also studied this reaction by phenol thermolysis in a heated flow reactor. Reaction products, including benzene, were determined by gas chromatography with flame ionization or mass spectrographic detection. The more direct studies of He *et al.*<sup>1</sup> and Horn *et al.*<sup>2</sup> are preferred but the results of Manion and Louw<sup>4,5</sup> for  $k_2$  are in agreement with the recommendations.

**References**

- <sup>1</sup> Y. Z. He, W. G. Mallard, and W. Tsang, J. Phys. Chem. **92**, 2196 (1988).
- <sup>2</sup> Ch. Horn, P. Frank, and Th. Just, 27th Symp. (Int.) Combustion, 1998, p. 321.
- <sup>3</sup> CEC, 1992; CEC, Supplement I, 1994 (see references in Introduction).
- <sup>4</sup> J. A. Manion and R. Louw, J. Phys. Chem. **93**, 3563 (1989).
- <sup>5</sup> J. A. Manion and R. Louw, J. Phys. Chem. **94**, 4124 (1990).



*Thermodynamic Data*

$$\Delta H_{298}^{\circ} = -375.4 \text{ kJ mol}^{-1}$$

$$\Delta S_{298}^{\circ} = -113.5 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c = 8.40 \cdot 10^{-25} T^{-0.482} \exp(+45190/T) \text{ cm}^3 \text{ molecule}^{-1}$$

(300 ≤ T/K ≤ 5000)

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

<i>k/cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup></i>	<i>T/K</i>	<i>Reference</i>	<i>Comments</i>
<i>Rate Coefficient Measurements</i>			
4.3 · 10 <sup>-10</sup>	298	Ackermann <i>et al.</i> , 1990 <sup>1</sup>	(a)
4.3 · 10 <sup>-10</sup>	1300–1650		
<i>Reviews and Evaluations</i>			
4.3 · 10 <sup>-10</sup>	300–2000	CEC, 1992; 1994 <sup>2</sup>	(b)

**Comments**

- (a) Three independent studies, two at room temperature (pulse radiolysis and laser flash photolysis) and one at higher temperatures (1300–1650 K shock wave). (i) Benzyl radicals were generated by pulsed radiolysis or toluene in 1 bar Ar total pressure and monitored by absorption at 305.3 nm, applying correction for methylcyclohexadienyl radical absorption. (ii) Flash photolysis of toluene in Ar with 193 nm radiation, determination of [H] by absorption of Lyman  $\alpha$  radiation at 121.6 nm. (iii) Dissociation of benzyl iodide (to generate benzyl radicals), and dissociation of ethyl iodide (to generate H atoms), behind reflected shock waves. Benzyl radical concentration monitored by absorption at 260 nm.
- (b) Preferred value based on the data of Bartels, Edelbüttel-Einhaus, and Hoyermann.<sup>3</sup>

**Preferred Values**

$k = 4.3 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 300–1650 K.

**Reliability**

$\Delta \log k = \pm 0.3$  over the range 300–1650 K.

**Comments on Preferred Values**

The data of Ackermann *et al.*<sup>1</sup> are in good agreement with the room temperature value of Bartels, Edelbüttel-Einhaus, and Hoyermann<sup>3</sup> and the SACM calculations of Brand *et al.*<sup>4</sup> which give  $k_{\infty} = 3.3 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 1100 K based on pressure dependent pulsed photolysis experiments. The SACM calculations show that the preferred value is close to the limiting high pressure rate coefficient.

**References**

- <sup>1</sup>L. Ackermann, H. Hippler, P. Pagsberg, C. Reihs, and J. Troe, *J. Phys. Chem.* **94**, 5247 (1990).
- <sup>2</sup>CEC, 1992; Supplement I, 1994 (see references in Introduction).
- <sup>3</sup>M. Bartels, J. Edelbüttel-Einhaus, and K. Hoyermann, 22nd Symp. (Int.) Combustion, 1989, p. 1041.
- <sup>4</sup>U. Brand, H. Hippler, L. Lindemann, and J. Troe, *J. Phys. Chem.* **94**, 6305 (1990).



#### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = 375.4 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = 113.5 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 1.19 \cdot 10^{24} T^{0.482} \exp(-45190/T) \text{ molecule cm}^{-3} \\ (300 \leqslant T/\text{K} \leqslant 5000)$$

$$\Delta H^\circ_{298}(2) = 433.9 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = 162.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 1.81 \cdot 10^{33} T^{-1.833} \exp(-52830/T) \text{ molecule cm}^{-3} \\ (300 \leqslant T/\text{K} \leqslant 5000)$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$k_1 = 2.0 \cdot 10^{13} \exp(-38900/T)$	1011–1137	Szwarc, 1948 <sup>1</sup>	(a)
$k_1 = 2.5 \cdot 10^{12} \exp(-37091/T)$	1011–1122	Takahashi, 1960 <sup>2</sup>	(b)
$k_1 = 1.3 \cdot 10^{18} \exp(-52340/T)$	1185–1206		
$k_1 = 6.3 \cdot 10^{14} \exp(-42778/T)$	913–1143	Price, 1962 <sup>3</sup>	(c)
$k_1 = 9.2 \cdot 10^{15} \exp(-44737/T)$	920–970	Brooks, Cummings, and Peacock, 1971 <sup>4</sup>	(d)
$k_1 = 2.0 \cdot 10^{15} \exp(-44383/T)$	1500–1900	Müller-Markgraf and Troe, 1986 <sup>5</sup>	(e)
$k_1 = 8.1 \cdot 10^{12} \exp(-36354/T)$	1300–1800	Mizerka and Kiefer, 1986 <sup>6</sup>	(f)
$k_2 = 4.0 \cdot 10^{11} \exp(-45291/T)$	1300–1800		
$k_2 = 8.9 \cdot 10^{12} \exp(-36534/T)$	1600–2100	Pamidimukkala <i>et al.</i> , 1987 <sup>7</sup>	(g)
$k_1 = 2.8 \cdot 10^{15} \exp(-44730/T)$	1450–1900	Brouwer, Müller-Markgraf and Troe, 1988 <sup>8</sup>	(h)
$k_1 = 3.6 \cdot 10^{15} \exp(-45000/T)$	1380–1700	Braun-Unkhoff, Frank, and Just, 1989 <sup>9</sup>	(i)
$k_1 = 2.5 \cdot 10^{14} \exp(-43180/T)$	1450–1790	Rao and Skinner, 1989 <sup>10</sup>	(j)
$k_2 = 1.5 \cdot 10^{15} \exp(-47408/T)$	1450–1790		
$k_1 = 1.8 \cdot 10^{16} \exp(-46187/T)$	300–1200	Brand <i>et al.</i> , 1990 <sup>11</sup>	(k)
$k_1 = 1 \cdot 10^{15} \exp(-43300/T)$	1100–1900	Hippler, Reihs, and Troe, 1990 <sup>12</sup>	(l)
$k_1^\infty = 6.3 \cdot 10^{15} \exp(-45465/T)$	1100–1900		
<i>Reviews and Evaluations</i>			
$3.1 \cdot 10^{15} \exp(-44890/T)$	920–2200	CEC, 1992; 1994 <sup>13</sup>	(m)

#### Comments

- (a) Pyrolysis of toluene and xylene in a flow system at pressures between 3 and 20 mbar.
- (b) Flow system with mass spectrometric analysis. It was concluded that the curvature of the Arrhenius plot found for Channel (1) was caused mainly by competitive reactions.
- (c) Pyrolysis of toluene in a flow system at pressures in the range 8–28 mbar. Products measured by gas chromatography. Toluene decay strongly influenced by surface reactions at  $T < 1000$  K. Reported Arrhenius parameters for Channel (1) derived from isolated homogeneous reaction.
- (d) Pyrolysis of toluene in a static reactor at total pressures below 300 mbar of the N<sub>2</sub> bath gas ( $P_{\text{toluene}} \leq 30$  mbar). Stable compounds analyzed by gas chromatography.
- (e) Supersedes an earlier shock tube study<sup>14</sup> on toluene decomposition in which the reaction was monitored by UV absorption of toluene and benzyl radicals in the wavelength region 200–350 nm. Rate parameters were derived with an assumed stability for benzyl radicals. Müller-Markgraf and Troe<sup>5</sup> found benzyl radicals were less stable and reinterpreted the results of Astholz, Durant, and Troe<sup>14</sup> accordingly to give rate coefficients for Channel (1) for the pressure range 1–8 bar.

- (f) Shock tube study of the pyrolysis of ethylbenzene with laser Schlieren analysis. Rate expressions for Channels (1) and (2) have been included in the reaction mechanism by the authors and originate from their unpublished laser Schlieren measurements of toluene pyrolysis.
- (g) Shock tube studies of toluene pyrolysis. In separate experiments, time-of-flight mass spectrometry (Kr bath gas) and laser Schlieren densitometry (Ne bath gas) were employed to monitor the reaction. A rate coefficient for the formation of methyl and phenyl radicals [Channel (2)] was deduced at total pressures of around 0.5 bar by fitting to a 26 step mechanism. A high pressure limiting rate coefficient of  $1.2 \cdot 10^{16} \exp(-47505/T) \text{ s}^{-1}$  has also been calculated for Channel (2).
- (h) Thermal decomposition of toluene has been reinvestigated in shock waves detecting toluene, benzyl, and benzyl fragment concentrations by UV absorption spectrometry. Evidence for the predominance of Channel (1) is presented. The thermally averaged rate coefficient for Channel (1) is consistent with specific rate coefficients  $k(E,J)$  from laser excitation experiments.
- (i) Shock tube study of toluene pyrolysis in Ar bath gas behind reflected shock waves. H atom production monitored by ARAS. In separate experiments phenyl radical decomposition was also studied behind re-

- flected shock waves. (Phenyl radicals were generated from pyrolysis of nitrosobenzene and production of H atoms monitored by ARAS.) Results for phenyl dissociation indicate that the main product channel is H atom production [Channel (1)] and that  $k_2 \leq 0.2k_1$ .
- (j) Shock tube study of deuterated and nondeuterated toluene pyrolysis behind incident shock waves at 0.4 bar total pressure. [H] and [D] monitored by ARAS. Rate coefficients deduced by fitting with a 7-reaction mechanism. RRKM analysis of fall-off behavior shows that the experimental data are close to the high pressure limit. Results supersede those of an earlier study.<sup>15</sup>
- (k) Pressure dependent study of the photosensitized decomposition of toluene with pulsed 193 nm radiation. Reactant decay and benzyl radical formation monitored by UV absorption measurements in the 220–320 nm wavelength region. Pressure range 0.024–0.15 mbar. Reported rate coefficients derived from SACM calculations.
- (l) Thermal dissociation of high concentrations of toluene studied in reflected shock waves over the temperature range 1250–1500 K. Reaction monitored by absorption at  $\lambda = 260$  nm (see also Ref. 8). At this wavelength the absorption coefficient of the benzyl radical exceeds that of toluene by 2 orders of magnitude and very small conversions of toluene to benzyl can be detected. No dependence of the measured rate coefficient on pressure in the range 0.3–25 bar was detected. From an evaluation of their data and those of Braun-Unkhoff, Frank, and Just,<sup>9</sup> the authors report a value for  $k_1^\infty$ .
- (m) Recommended rate coefficient for Channel (1); see Comments on Preferred Values.

### Preferred Values

$k_1 = 3.1 \cdot 10^{15} \exp(-44890/T)$  s<sup>-1</sup> over the range 920–2200 K.

$k_2 = 1.2 \cdot 10^{14} \exp(-41972/T)$  s<sup>-1</sup> over the range 1000–2100 K.

### Reliability

$\Delta \log k_1 = \pm 0.3$  at 920 K rising to  $\pm 0.5$  at 2200 K.

$\Delta \log k_2 = \pm 0.7$  at 1000 K falling to  $\pm 0.5$  at 2100 K.

### Comments on Preferred Values

The preferred values for Channel (1) remains unchanged from our previous evaluation.<sup>13</sup> A large variety of studies on toluene pyrolysis exist in the lower temperature range, up to approximately 1000 K, but most of these studies were conducted under experimental conditions in which bimolecular reactions of toluene, leading to dibenzyl and other compounds, dominate. The investigation of unimolecular decomposition of toluene becomes less difficult at temperatures above 900 K. Most of the available data give evidence for the product channel being Channel (1), leading to benzyl radicals and H atoms. From some of the experiments, in

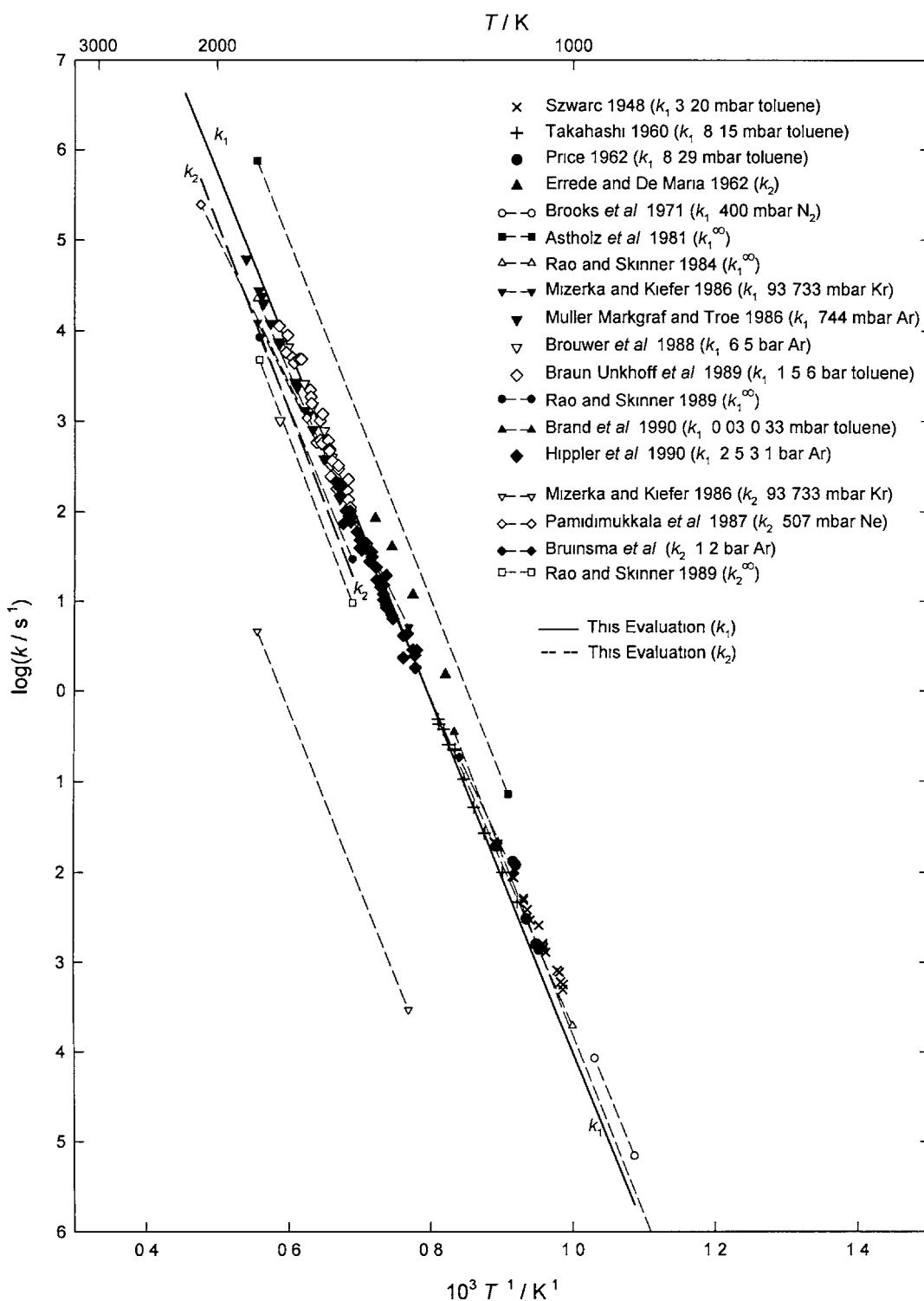
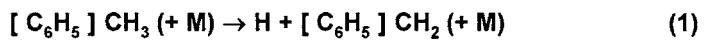
conjunction with the calculated limiting high pressure rate coefficient, it can be deduced that the recommended Arrhenius expression, covering a density range of about (0.6–1.8)  $\cdot 10^{19}$  molecule cm<sup>-3</sup>, is close to the high pressure limit.

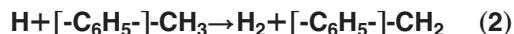
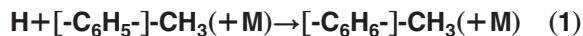
The recommended expression for Channel (2) is based on the data of Pamidimukkala *et al.*<sup>7</sup> and Rao and Skinner<sup>10</sup> which are in reasonable agreement. Thermochemical arguments, together with the findings of some of the authors,<sup>9</sup> give evidence that the rate for Channel (2) should not exceed 10%–20% of the rate for Channel (1) for  $T \leq 2000$  K. The preferred expression for  $k_2$  is based on the mean of the activation energies of Pamidimukkala *et al.*<sup>7</sup> and Rao and Skinner<sup>10</sup> and an A factor fitted to both sets of experimental data. The preferred value gives  $k_2/k_1 = 0.28$  at 2000 K, and 0.08 at 1000 K. Flow tube studies with end product analysis by Bruinsma *et al.*<sup>16</sup> and Errede and DeMaria<sup>17</sup> report values of  $k_2$  that are similar to, or greater than  $k_1$ . The study of Errede and DeMaria<sup>17</sup> has been criticized by Benson and O'Neal<sup>18</sup> as being indirect and yielding improbable values for the pre-exponential factor and activation energy.

Luther *et al.*<sup>19</sup> have measured the branching ratio of the two channels by laser excitation. A theoretical analysis, modeling the  $k(E,J)$  for the two channels, was performed. Thermal averaging for conditions of the high pressure limit resulted in  $k_2/k_1 = 0.89$  at 2000 K, and 0.147 at 1000 K. These data cannot easily be compared with the experimental data obtained by shock tube experiments, since the data were obtained in the fall-off regime, and pressure effects on the branching ratio become important.

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#### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = -97.6 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = -100.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 6.21 \cdot 10^{-28} T^{0.948} \exp(+11950/T) \text{ cm}^3 \text{ molecule}^{-1}$$

(300 ≤ T/K ≤ 5000)

$$\Delta H^\circ_{298}(3) = -39.5 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = 28.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 2.23 \cdot 10^5 T^{-1.283} \exp(+4260/T)$$

(300 ≤ T/K ≤ 5000)

$$\Delta H^\circ_{298}(2) = -60.5 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = 14.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 1.96 T^{0.331} \exp(+7000/T)$$

(300 ≤ T/K ≤ 5000)

$$\Delta H^\circ_{298}(4) = 37.4 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(4) = 24.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(4) = 2.63 \cdot 10^3 T^{-0.665} \exp(-4870/T)$$

(300 ≤ T/K ≤ 5000)

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2 + k_3 + k_4$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$k_1 = 1.7 \cdot 10^{-13}$	298	Sauer and Ward, 1967 <sup>1</sup>	(a)
$k_2 = 8.3 \cdot 10^{-11} \exp(-1864/T)$	1500–1800	Astholtz, Durant, and Troe 1981 <sup>2</sup>	(b)
$k_2 = 1.3 \cdot 10^{-20} T^{5.5} \exp(-171/T)$	600–1700	Rao and Skinner, 1984 <sup>3</sup>	(c)
$k_2 = 1.8 \cdot 10^{-20} T^{3.0} \exp(-1183/T)$	950–1100	Robaugh and Tsang, 1986 <sup>4</sup>	(d)
$k_3 = 1.1 \cdot 10^{-21} T^{3.0} \exp(+377/T)$	950–1100		
$k_1 = 7.3 \cdot 10^{-24} T^{4.0} \exp(-1057/T)$	1300–1800	Mizerka and Kiefer, 1986 <sup>5</sup>	(e)
$9.7 \cdot 10^{-13}$	773	Baldwin, Scott, and Walker, 1986 <sup>6</sup>	(f)
$k_3 = 5.0 \cdot 10^{-13}$	773		
$k_2 = 8.3 \cdot 10^{-10} \exp(-6290/T)$	1380–1700	Braun-Unkhoff, Frank, and Just, 1988 <sup>7</sup>	(g)
$k_2 = 2.1 \cdot 10^{-9} \exp(-7460/T)$	1300–1700	Hippler, Reihls, and Troe, 1990 <sup>8</sup>	(h)
$k_1 = 1.8 \cdot 10^{-13}$	300	Ackermann <i>et al.</i> , 1990 <sup>9</sup>	(i)
$k_3 = 2.6 \cdot 10^{-11} \exp(-2914/T)$	898–1100	Manion and Louw, 1990 <sup>10</sup>	(j)
$k_1 = 2.0 \cdot 10^{-13}$	338	Markert and Pagsberg, 1993 <sup>11</sup>	(k)
$k_1 = 2.0 \cdot 10^{-13}$	298	Triebert <i>et al.</i> , 1998 <sup>12</sup>	(l)
<i>Reviews and Evaluations</i>			
$k_1 = 1.7 \cdot 10^{-13}$	298	Kerr and Parsonage, 1972 <sup>13</sup>	(m)
$k_1 = 1.2 \cdot 10^{-13}$	298	CEC, 1992; 1994 <sup>14</sup>	(n)
$k_2 = 6.6 \cdot 10^{-22} T^{3.44} \exp(-1570/T)$	600–2500		
$k_3 = 9.6 \cdot 10^{-11} \exp(-4070/T)$	770–1100		

#### Comments

- (a) Pulse radiolysis with end product analysis by gas chromatography. Transient species monitored as a function of time by absorption in the wavelength range 260–340 nm.
- (b) Shock tube study of toluene pyrolysis in Ar bath gas. Toluene and benzyl radicals monitored by absorption in the wavelength range 200–350 nm. A rate expression for Channel (2) was derived with an assumed benzyl radical stability.
- (c) Shock tube study with initial mixtures of toluene-d<sub>8</sub> and neopentane and toluene-d<sub>8</sub> in Ar bath gas. D and H atoms were monitored as a function of time by ARAS. Investigation covered the temperature ranges 1200–1460 K for neopentane and toluene mixtures and 1410–1730 K for the toluene experiments. Results were combined with unpublished data of Ravishankara and Nicovich to deduce a non-Arrhenius expression for Channel (2).

- (d) Single-pulse shock-tube study. H atoms generated by thermolysis of 2,2,3,3-tetramethyl butane. Stable product analysis by gas chromatography. Rate coefficients have been derived relative to the rate coefficient  $k(\text{H} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2) = 2.2 \cdot 10^{-20} T^{3.0} \exp(-4045/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (this evaluation). Rate expressions for the formation of benzene and methyl radicals [Channel (3)] and of benzyl radicals and hydrogen [Channel (2)] were obtained.
- (e) Shock tube study of ethylbenzene pyrolysis in Kr bath gas. Laser Schlieren density gradients fitted with a 23-step mechanism.
- (f) Small amounts of toluene (0.05%–0.5%) were added to slowly reacting mixtures of hydrogen and oxygen at 773 K. Under the experimental conditions the  $\text{H}_2 + \text{O}_2$  reaction provides a reproducible source of H, O, and OH radicals. Measurements of the relative consumption of  $\text{H}_2$  and the additive by gas chromatogra-

- phy permits the evaluation of the rate coefficients for the reaction of H, O, and OH with toluene.
- (g) Shock tube study of the pyrolysis of very low concentrations of toluene in Ar bath gas. H atom formation monitored by ARAS. [H] profiles were sensitive to  $k_2$  in the latter stages of the experiment.
- (h) Shock tube study behind reflected shock waves. H atoms generated by the pyrolysis of ethyliodide. Reaction monitored by absorption at  $\lambda = 260$  nm. At this wavelength the absorption coefficient of benzyl radicals is 2 orders of magnitude greater than that of toluene allowing very small conversions of toluene to be detected. The data were combined with that of Robaugh and Tsang<sup>4</sup> and the unpublished results of Ravishankara and Nicovich to derive a rate expression for  $k_2 = 2.1 \cdot 10^{-10} \exp(-4210/T)$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for the temperature range 600–1800 K.
- (i) Flash photolysis study. Phenyl radicals generated by pulsed photolysis of benzene at 193 nm. [H] determined by absorption of Lyman- $\alpha$  radiation at 121.6 nm, and benzene by absorption at 193 nm.
- (j) Thermolysis of  $[-C_6D_5]-CH_3$  in H<sub>2</sub> bath gas in a flow reactor at 1 bar total pressure. Mass spectroscopic analysis of product formation. Rate coefficients reported relative to the value  $k(H+[-C_6D_6^-] \rightarrow [-C_6D_5H^-] + D) = 8.1 \cdot 10^{-11} \exp(-2350/T)$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.<sup>10</sup>
- (k) H atoms generated from the pulsed radiolysis of H<sub>2</sub>. Reaction monitored by time-resolved UV absorption spectroscopy in the wavelength region 200–400 nm.
- (l) Discharge flow study in which toluene reacted with an excess of H atoms ( $[H]/[C_6H_5CH_3] = 2–20$ ) in He carrier gas at 4 mbar pressure. [C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>] was monitored by quadrupole mass-spectrometry and the value of  $k$  was derived by modeling the [C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>] profile using a simple mechanism.
- (m) Based on the study of Sauer Jr. and Ward<sup>1</sup> which is supported by the results of Allen *et al.*<sup>15</sup>
- (n) See Comments on Preferred Values.

### Preferred Values

$k_1 = 1.8 \cdot 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> over the range 298–350 K.

$k_2 = 6.6 \cdot 10^{-22} T^{3.44} \exp(-1570/T)$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> over the range 600–2500 K.

$k_3 = 9.6 \cdot 10^{-11} \exp(-4070/T)$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> over the range 770–1100 K.

### Reliability

$\Delta \log k_1 = \pm 0.2$  over the range 298–350 K.

$\Delta \log k_2 = \pm 0.3$  over the range 600–2500 K.

$\Delta \log k_3 = \pm 0.3$  over the range 770–1100 K.

### Comments on Preferred Values

The recommended rate coefficients for Channels (2) and (3) remain unchanged from our previous evaluation.<sup>14</sup> The

expression for Channel (2) is based on the data of Astholz, Durant, and Troe,<sup>2</sup> Rao and Skinner,<sup>3</sup> Robaugh and Tsang,<sup>4</sup> Mizerka and Kiefer,<sup>5</sup> Baldwin, Scott, and Walker,<sup>6</sup> Braun-Unkhoff, Frank, and Just,<sup>7</sup> and Hippler, Reihs, and Troe.<sup>8</sup> The value for Channel (3) is based on the data of Robaugh and Tsang,<sup>4</sup> Baldwin, Scott, and Walker,<sup>6</sup> and Manion and Louw.<sup>10</sup> On the plot the data of Rao and Skinner<sup>3</sup> overlie those of Mizerka and Kiefer.<sup>5</sup> The value for Channel (1) is based on the data of Sauer and Ward,<sup>1</sup> Ackermann *et al.*,<sup>9</sup> Markert and Pagsberg,<sup>11</sup> and Triebert *et al.*<sup>12</sup> The data for Channel (1) of Knutti and Buehler,<sup>16</sup> for Channel (2) of Mkyran, Oganesyan, and Nalbandyan,<sup>17</sup> and for Channel (3) of Benson and Shaw,<sup>18</sup> have not been included in deriving the preferred values. There are insufficient data to recommend an expression for Channel (4); the only data are those of Pamidimukkala *et al.*<sup>19</sup> Furthermore, there are insufficient data to justify recommending a rate expression for the overall H-consuming reaction over the whole temperature range.

Most of the experimental measurements provide evidence for the formation of benzyl radicals [Channel (2)]. Only a few of the experiments permit discrimination between the channels at elevated temperatures. Therefore, for the majority of the studies, the different product pathways have been inferred by modeling with the aid of plausible reaction mechanisms rather than by direct measurement. To reconcile the measurements of the rate coefficient around room temperature with values at elevated temperatures it has to be assumed that a change in the reaction mechanism occurs, possibly from Channel (1) being dominant at room temperature to Channel (2) at  $T > 1000$  K.<sup>20</sup> In the range between room temperature and 1000 K Channel (3) appears to be significant.<sup>4</sup> There is insufficient information to recommend a value for  $k_4$  which is not expected to be important at  $T < 2500$  K according to the available data.<sup>19</sup>

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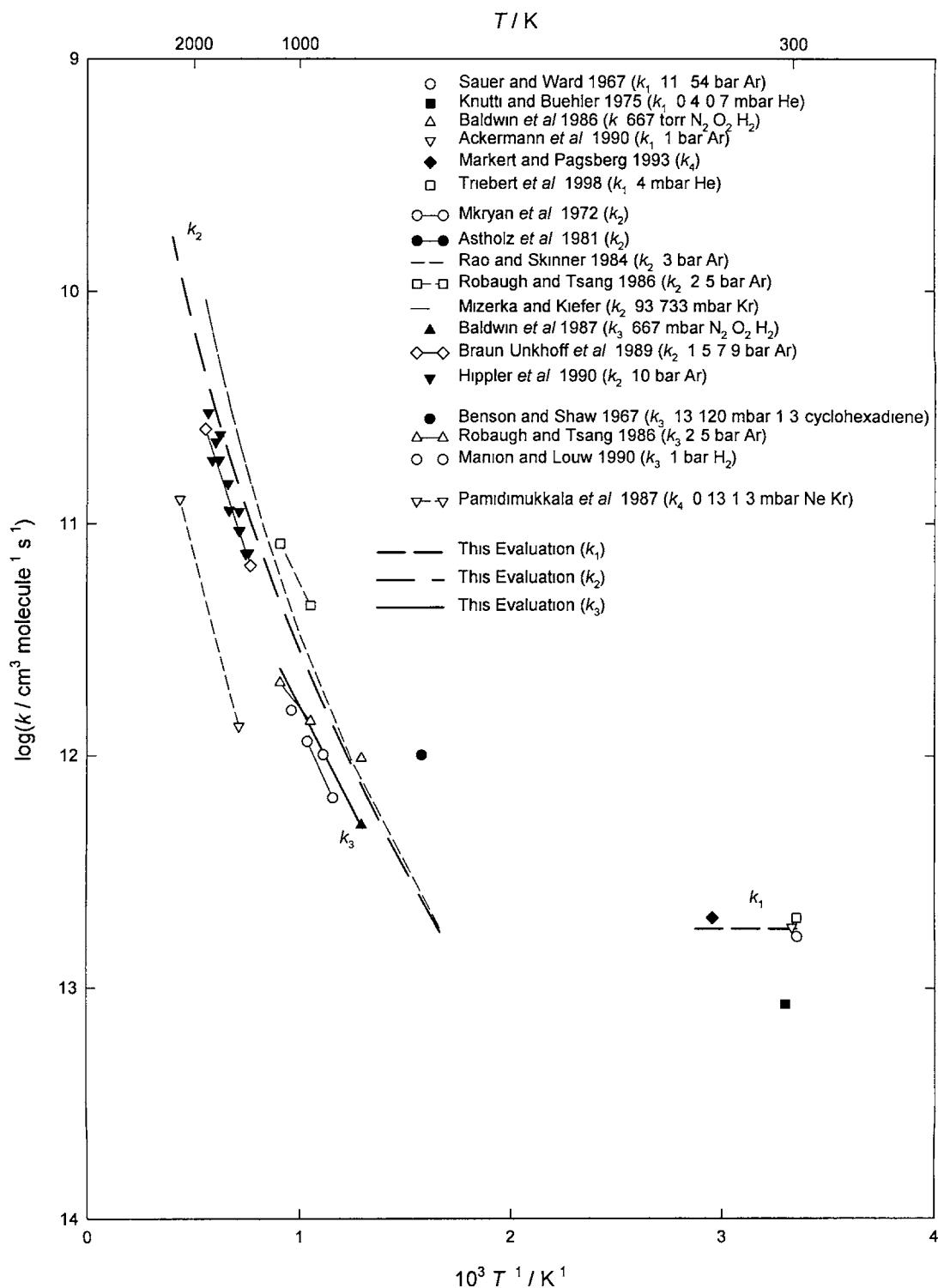
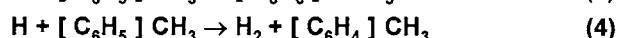
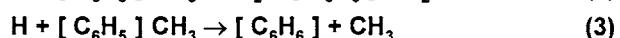
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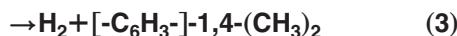
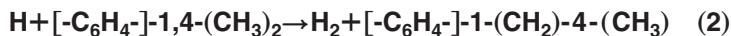
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#### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = -98.2 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = -96.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 5.60 \cdot 10^{-28} T^{1.051} \exp(+12010/T) \text{ cm}^3 \text{ molecule}^{-1}$$

(300 ≤ T/K ≤ 5000)

$$\Delta H^\circ_{298}(2) = -60.2 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = 5.24 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 2.18 \cdot 10^{-2} T^{0.697} \exp(+7980/T)$$

(300 ≤ T/K ≤ 5000)

$$\Delta H^\circ_{298}(3) = 37.6 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = 143.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 2.81 \cdot 10^7 T^{0.001} \exp(-4480/T)$$

(300 ≤ T/K ≤ 5000)

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2 + k_3$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$k_1 = 5.8 \cdot 10^{-13}$	298	Sauer and Mani, 1970 <sup>1</sup>	(a)
$k_1 = 1.8 \cdot 10^{-13}$	300	Ackermann <i>et al.</i> , 1990 <sup>2</sup>	(b)
$k_2 = 6.6 \cdot 10^{-10} \exp(-4210/T)$	1200–1800	Hippler, Seisel, and Troe, 1994 <sup>3</sup>	(c)
<i>Reviews and Evaluations</i>			
$5.8 \cdot 10^{-13}$	298	CEC, 1992; 1994 <sup>4</sup>	(d)

#### Comments

- (a) Pulse-radiolysis study at pressures around 75 bar. Analysis from transient spectra, with  $\lambda_{\max} = 310 \text{ nm}$ , assumed to be the adduct  $[-\text{C}_6\text{H}_5-]\text{-1,4-(CH}_3)_2$ .
- (b) Flash photolysis study at 1 bar. Phenyl radicals generated by pulsed photolysis of benzene at 193 nm.  $[\text{H}]$  determined by absorption of Lyman- $\alpha$  radiation at 121.6 nm, and benzene by absorption at 193 nm.
- (c) Shock tube study of the thermolysis of *p*-xylene in Ar bath gas behind reflected shock waves. The concentrations of *p*-xylene and the 4-methylbenzyl radical were determined by UV absorption in the spectral region 210–350 nm.
- (d) Preferred value based on the data of Sauer and Mani.<sup>1</sup>

#### Preferred Values

$$k_1 = 3.8 \cdot 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_2 = 6.6 \cdot 10^{-10} \exp(-4210/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the range } 1200\text{--}1800 \text{ K.}$$

#### Reliability

$$\Delta \log k_1 = \pm 0.4 \text{ at } 298 \text{ K.}$$

$$\Delta \log k_2 = \pm 0.5 \text{ over the range } 1200\text{--}1800 \text{ K.}$$

#### Comments on Preferred Values

Experimental data are limited. We assume the low temperature data of Sauer and Mani<sup>1</sup> and Ackermann *et al.*,<sup>2</sup> refer to the adduct formation channel. The preferred value is an average of the values reported by the two studies. The shock tube data of Hippler, Seisel, and Troe<sup>3</sup> refer to the abstraction reaction, Channel (2), leading to 4-methylbenzyl formation.

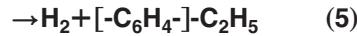
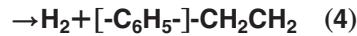
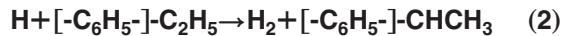
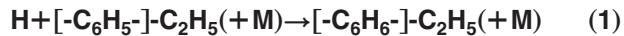
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<sup>3</sup> H. Hippler, S. Seisel, and J. Troe, 25th Symp. (Int.) Combustion, 1994, p. 875.

<sup>4</sup> CEC, 1992; Supplement I, 1994 (see references in Introduction).



#### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = -98.1 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = -100.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 2.16 \cdot 10^{-27} T^{0.765} \exp(+11930/T) \text{ cm}^3 \text{ molecule}^{-1}$$

(300 ≤ T/K ≤ 3000)

$$\Delta H^\circ_{298}(3) = -45.8 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = 57.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 4.46 \cdot 10^{10} T^{-2.615} \exp(4686/T)$$

(300 ≤ T/K ≤ 3000)

$$\Delta H^\circ_{298}(5) = 37.4 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(5) = 52.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(5) = 2.89 \cdot 10^4 T^{-0.517} \exp(-4810/T)$$

(300 ≤ T/K ≤ 3000)

$$\Delta H^\circ_{298}(2) = -76.5 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = -5.16 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 6.4 \cdot 10^{-1} T^{0.049} \exp(+9050/T)$$

(300 ≤ T/K ≤ 3000)

$$\Delta H^\circ_{298}(4) = -12.9 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(4) = 31.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(4) = 1.7 \cdot 10^3 T^{-0.492} \exp(+1270/T)$$

(300 ≤ T/K ≤ 3000)

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2 + k_3 + k_4 + k_5$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$k_1 = 3.3 \cdot 10^{-13}$	298	Sauer and Mani, 1970 <sup>1</sup>	(a)
$k_1 = 2.5 \cdot 10^{-13}$	298	Triebert <i>et al.</i> , 1998 <sup>2</sup>	(b)
$k = 1.36 \cdot 10^{-12}$	773	Ellis, Scott, and Walker, 2003 <sup>3</sup>	(c)
$k_2 = 7.8 \cdot 10^{-13}$			
$k_3 = 3.9 \cdot 10^{-13}$			
<i>Reviews and Evaluations</i>			
$3.3 \cdot 10^{-13}$	298	CEC, 1991; 1994 <sup>4</sup>	(d)
$k_2 = 5.5 \cdot 10^{-17} T^2 \exp(-2690/T)$	600–1200	Ellis, Scott, and Walker, 2002 <sup>3</sup>	(e)
$k_3 = 1.65 \cdot 10^{-18} T^2 \exp(-475/T)$	600–1200		
$k_4 = 1.2 \cdot 10^{-15} T^{1.5} \exp(-3730/T)$	600–1200		
$k_5 = 3.2 \cdot 10^{-17} T^2 \exp(-4880/T)$	600–1200		
$(k_2 + k_3 + k_4 + k_5) = 2.5 \cdot 10^{-20} T^3 \exp(-1580/T)$	600–1200		

#### Comments

- (a) Pulse-radiolysis study at pressures around 75 bar. Analysis of transient spectra, with  $\lambda_{\max} = 309 \text{ nm}$ , assumed to be that of the adduct  $[-\text{C}_6\text{H}_5\text{-}] \cdot \text{C}_2\text{H}_5$ .
- (b) Discharge flow study in which ethylbenzene was reacted with an excess of H atoms ( $[\text{H}]/[\text{C}_6\text{H}_5\text{C}_2\text{H}_5] = 2–20$ ) in He carrier gas at 4 mbar pressure.  $[\text{C}_6\text{H}_5\text{C}_2\text{H}_5]$  was monitored by quadrupole mass spectrometry and the value of  $k$  was derived by modeling the  $[\text{C}_6\text{H}_5\text{C}_2\text{H}_5]$  profile using a simple mechanism.
- (c) Study of the relative rates of consumption of  $\text{H}_2$  and  $[-\text{C}_6\text{H}_5\text{-}] \cdot \text{C}_2\text{H}_5$  when traces of  $[-\text{C}_6\text{H}_5\text{-}] \cdot \text{C}_2\text{H}_5$  were added to  $\text{H}_2/\text{O}_2/\text{N}_2$  mixtures over a very wide range of mixture composition.  $k$  obtained by combining the experimentally determined ratio  $k/k(\text{H}+\text{O}_2)$  with the

precisely known  $k(\text{H}+\text{C}_2\text{H}_6)/k(\text{H}+\text{O}_2)$  and  $k(\text{H}+\text{C}_2\text{H}_6)$  from the present evaluation. Value of  $k_3$  obtained from the ratio  $k_3/k(\text{H}+\text{O}_2)$  by computer fit of the initial benzene and  $\text{C}_2\text{H}_4$  yields across a wide range of mixture composition. The yields of benzene and ethene were equal, as expected, because 99% of the  $\text{C}_2\text{H}_5$  radicals give ethene.

(d) Value of Sauer and Mani<sup>1</sup> accepted.

(e) Based on the single values of  $k$ ,  $k_2$ , and  $k_3$  obtained at 773 K by Ellis *et al.*<sup>3</sup> and on the non-Arrhenius expressions given by these authors for the analogous  $\text{H}+\text{toluene}$  reaction pathways.  $k_4$  was taken to be 50% of  $k(\text{H}+\text{C}_2\text{H}_6)$  to allow for path degeneracy. The parameters given for  $k_5$  are considered by the authors to be too low, but they emphasize that abstraction from

the ring is more important than hitherto suggested. Channel (5), comprising H abstraction from all possible ring positions, contributes to the total abstraction less than 10% at temperatures below 2000 K. The expression for the sum of  $k_2-k_5$  was obtained by adding the individual rate coefficients followed by interpolation.

### Preferred Values

$$k_1 = 2.9 \cdot 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_2 = 4.4 \cdot 10^{-22} T^{3.44} \exp(-505/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the range 600–1200 K.

$$k_3 = 9.6 \cdot 10^{-11} \exp(-4070/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the range } 700\text{--}1100 \text{ K.}$$

$$k_4 = 3.9 \cdot 10^{-22} T^{1.90} \exp(-3340/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the range } 500\text{--}2000 \text{ K.}$$

$$k_5 = 1.3 \cdot 10^{-17} T^2 \exp(-4880/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the range } 600\text{--}1200 \text{ K.}$$

### Reliability

$$\Delta \log k_1 = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta \log k_2 = \pm 0.3 \text{ over the range } 600\text{--}800 \text{ K, rising to } \pm 0.5 \text{ at } 1200 \text{ K.}$$

$$\Delta \log k_3 = \pm 0.3 \text{ over the range } 700\text{--}900 \text{ K, rising to } \pm 0.5 \text{ at } 1100 \text{ K.}$$

$$\Delta \log k_4 = \pm 0.3 \text{ over the range } 500\text{--}1000 \text{ K, rising to } \pm 0.5 \text{ at } 2000 \text{ K.}$$

$$\Delta \log k_5 = \pm 0.3 \text{ over the range } 600\text{--}800 \text{ K, rising to } \pm 0.5 \text{ at } 1200 \text{ K.}$$

### Comments on Preferred Values

In the absence of other experimental data we recommend

for the addition channel, (1), a mean of the values of Sauer and Mani,<sup>1</sup> and Triebert *et al.*,<sup>2</sup> with substantial error limits. The value is in reasonable agreement with the values  $1.8 \cdot 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $3.8 \cdot 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the addition of H atoms to toluene and p-xylene, respectively at 298 K, from the present evaluation. The experimental value of  $k_2$  at 773 K is in excellent agreement with  $k(\text{H} + \text{toluene} \rightarrow \text{benzyl} + \text{H}_2) = 2.8 \cdot 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  in terms of path degeneracy and the difference of about 16 kJ mol<sup>-1</sup> in the enthalpies of the reaction. The preferred expression for  $k_2$  is based on that for  $\text{H} + \text{toluene} \rightarrow \text{benzyl} + \text{H}_2$  as both reactions involve the formation of radicals with a resonance structure. The pre-exponential factor was adjusted for path degeneracy, the same  $T$  exponent adopted, and the exponential term obtained from a fit to the data point at 773 K. The studies of Ellis *et al.*<sup>3</sup> show that  $k_3$  is within experimental error the same as  $k(\text{H} + \text{toluene} \rightarrow \text{benzene} + \text{CH}_3)$  at 773 K. Given this fact, and the similar nature of the two reactions, the preferred expression for the latter rate coefficient is adopted here for  $k_3$ . See comment (e) for discussion on the rate coefficients  $k_4$  and  $k_5$ .

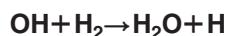
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<sup>4</sup> CEC, 1992; Supplement I, 1994 (see References in Introduction).

*Thermodynamic Data*

$$\begin{aligned}\Delta H^\circ_{298} &= -60.94 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298} &= -10.90 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 6.29 \cdot 10^{-2} T^{0.161} \exp(+7510/T) \\ &\quad (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$5.79 \cdot 10^{-15}$	300	Overend, Paraskevopoulos, and Cvjetanovic, 1975 <sup>1</sup>	(a)
$5.9 \cdot 10^{-12} \exp(-2008/T)$	298–425	Atkinson, Hansen, and Pitts, 1975 <sup>2</sup>	(b)
$4.12 \cdot 10^{-19} T^{2.44} \exp(-1281/T)$	298–992	Tully and Ravishankara, 1980 <sup>3</sup>	(b)
$6.1 \cdot 10^{-15}$	298	Zellner and Steinert, 1981 <sup>4</sup>	(c)
$4.9 \cdot 10^{-12} \exp(-1990/T)$	250–400	Ravishankara <i>et al.</i> , 1981 <sup>5</sup>	(b)
$7.9 \cdot 10^{-11} \exp(-3067/T)$	1700–2500	Frank and Just, 1985 <sup>6</sup>	(d)
$4.48 \cdot 10^{-12}$	1212	Bott and Cohen, <sup>7</sup>	(e)
$3.56 \cdot 10^{-16} T^{1.52} \exp(-1736/T)$	800–1550	Oldenborg <i>et al.</i> , 1992 <sup>8</sup>	(f)
$7.2 \cdot 10^{-20} T^{2.69} \exp(-1150/T)$	230–420	Talukdar <i>et al.</i> , 1996 <sup>9</sup>	(g)
<i>Reviews and Evaluations</i>			
$1.05 \cdot 10^{-17} T^2 \exp(-1490/T)$	240–2400	Cohen and Westberg, 1983 <sup>10</sup>	(h)
$1.7 \cdot 10^{-16} T^{1.6} \exp(-1660/T)$	300–2500	CEC, 1992; 1994 <sup>11</sup>	(i)
$3.56 \cdot 10^{-16} T^{1.52} \exp(-1736/T)$	250–2581	Oldenborg <i>et al.</i> , 1988 <sup>8</sup>	(j)
$5.5 \cdot 10^{-12} \exp(-2000/T)$	200–450	NASA, 1997 <sup>12</sup>	(k)
$7.7 \cdot 10^{-12} \exp(-2100/T)$	250–450	IUPAC, 1997 <sup>13</sup>	(l)

**Comments**

- (a) Flash photolysis of  $\text{H}_2\text{O}/\text{H}_2/\text{He}$  or  $\text{N}_2\text{O}/\text{H}_2/\text{He}$  mixtures at total pressures in the range 0.053–1 bar. [OH] monitored by time-resolved resonance absorption.
- (b) Pulsed vacuum UV photolysis of  $\text{H}_2\text{O}/\text{H}_2/\text{Ar}$  mixtures at total pressures in the range 20–33 mbar. [OH] monitored by time-resolved resonance fluorescence at 306.4 nm.
- (c) Discharge-flow study with OH production by the  $\text{H} + \text{NO}_2$  reaction and [OH] monitored by resonance fluorescence.
- (d) Shock tube study using reflected shocks in  $\text{N}_2\text{O}/\text{H}_2/\text{O}_2/\text{Ar}$  mixtures. [H] and [O] monitored by time-resolved ARAS.
- (e) Shock tube study using reflected shock waves in *t*-butyl peroxide/ $\text{H}_2/\text{Ar}$  mixtures. [OH] detected by time-resolved absorption using a resonance lamp. Pressures were in the range 1.1–1.3 bar.
- (f) Pulsed laser photolysis of  $\text{H}_2\text{O}/\text{H}_2/\text{Ar}$  mixtures at 193 nm and a total pressure of 0.26 bar. [OH] monitored by time-resolved LIF at 310.85 nm under conditions of pseudo-first-order OH decay. Reported expression is a fit to multiple data sets—see Comment (j)
- (g) Pulsed laser photolysis of  $\text{H}_2\text{O}_2$  at 248 nm or 193 nm used to generate OH radicals in the presence of a large excess of  $\text{H}_2$ . [OH] monitored by time-resolved pulsed LIF and, in some experiments, [H] was monitored by time-resolved resonance fluorescence. Total pressures were in the range 65–499 mbar.

- (h) Evaluation of the available data with heavy weight given to the data of Ravishankara *et al.*<sup>5</sup> and Gardiner *et al.*<sup>14</sup> in deriving the preferred expression for  $k$ .
- (i) Adopted the expression recommended by Zellner<sup>15</sup> in his review of the non-Arrhenius behavior of the bimolecular reactions of OH radicals.
- (j) Fit to the data of Oldenborg *et al.*,<sup>8</sup> Tully and Ravishankara,<sup>3</sup> Ravishankara *et al.*,<sup>5</sup> Frank and Just,<sup>6</sup> and the data on the reverse reaction of Michael and Sutherland,<sup>16</sup> and Davidson *et al.*<sup>17</sup>
- (k) Fit to the data of Greiner,<sup>18</sup> Stuhl and Niki,<sup>19</sup> Westenberg and De Haas,<sup>20</sup> Smith and Zellner,<sup>21</sup> Atkinson *et al.*,<sup>2</sup> Overend *et al.*,<sup>1</sup> Tully and Ravishankara,<sup>3</sup> Zellner and Steinert,<sup>4</sup> and Ravishankara *et al.*<sup>5</sup>
- (l) Fit to the data of the nine studies cited in (k) together with the data of Talukdar *et al.*<sup>9</sup>

**Preferred Values**

$$k = 3.6 \cdot 10^{-16} T^{1.52} \exp(-1740/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the range 250–2500 K.

*Reliability*

$$\Delta \log k = \pm 0.1 \text{ at } 250 \text{ K, rising to } \pm 0.3 \text{ at } 2500 \text{ K.}$$

*Comments on Preferred Values*

There have been numerous studies of this reaction and the rate constant is now well defined over a wide temperature range. Only the more recent data<sup>1–9,14,18–21,23–33</sup> are shown

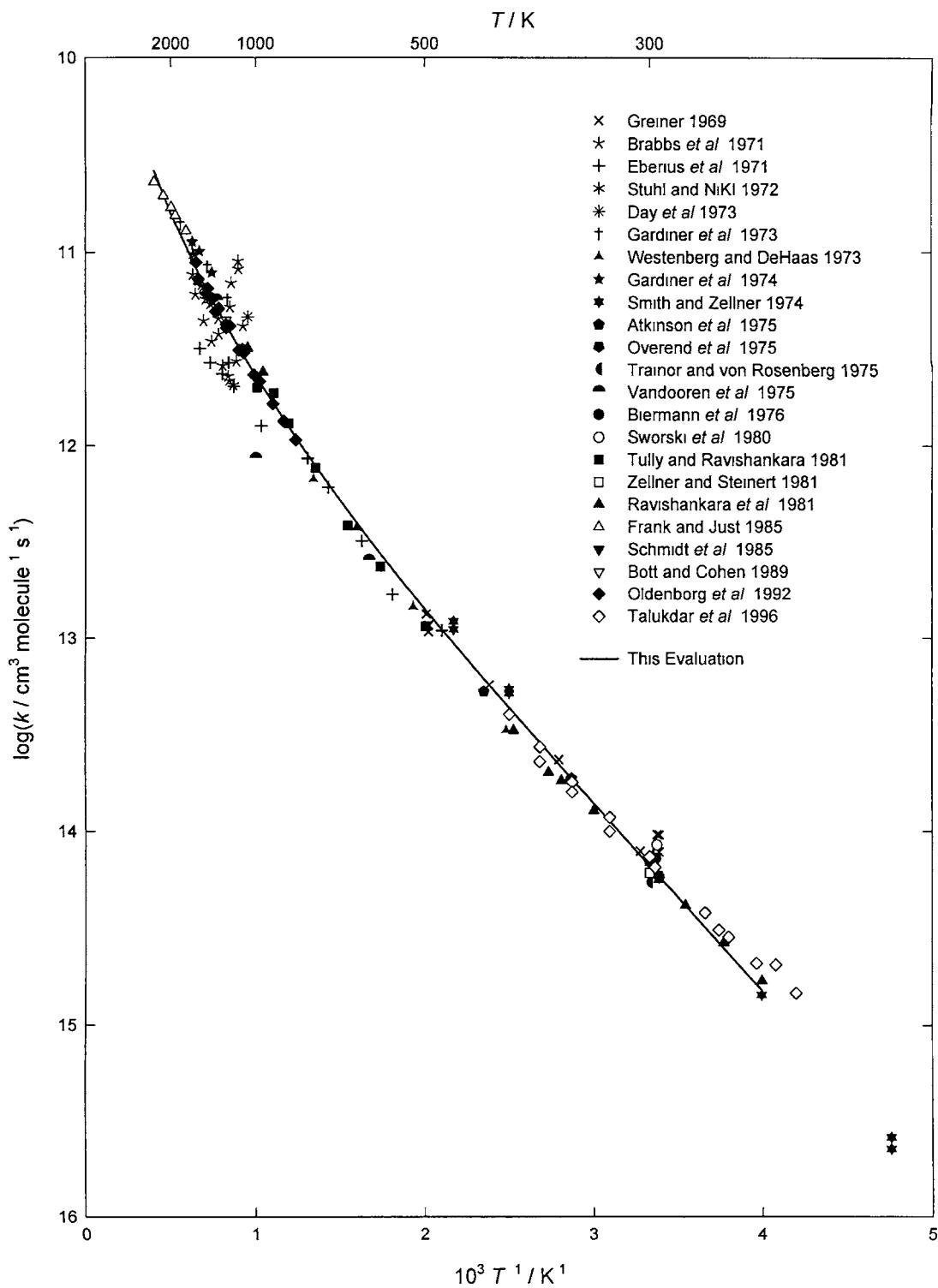
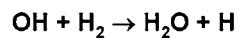
on the Arrhenius diagram. The early data have been evaluated by Baulch *et al.*<sup>22</sup> and by Cohen and Westberg.<sup>10</sup>

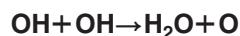
The low temperature data, which are relevant to atmospheric modeling, have been evaluated by the IUPAC and NASA Panels who both base their recommendations on nine studies<sup>1–5,18–21</sup> and, in the case of the IUPAC Panel, the work of Talukdar *et al.*<sup>9</sup> The more recent studies of this group give slightly lower values of  $k$  and at low temperature our preferred values are based on these studies,<sup>1–5,9</sup> which are cited in the Table. Among them is the study of Tully and Ravishankara<sup>3</sup> which extends up to 992 K and overlaps with the pulsed photolysis study of Oldenborg *et al.*<sup>8</sup> covering the range 800–1550 K. These two studies are in excellent agreement and span the range between the low temperature data and the shock tube studies at higher temperatures.

At higher temperatures there have been a number of shock tube studies in good agreement covering the temperature range 1200–2500 K and two recent studies of  $k(H + H_2O)$ <sup>16,17</sup> which when combined with the equilibrium constant give excellent agreement with the direct studies. Oldenborg *et al.*<sup>8</sup> have combined their own data with that from the studies of Tully and Ravishankara,<sup>3</sup> Frank and Just,<sup>6</sup> Ravishankara *et al.*,<sup>5</sup> Michael and Sutherland,<sup>16</sup> and Davidson *et al.*<sup>17</sup> to derive an expression for  $k$  which we adopt as our preferred expression. It is very similar to that derived earlier by Michael and Sutherland<sup>16</sup> based on the same data, apart from that of Oldenborg *et al.*<sup>8</sup> It can be seen from the Arrhenius diagram that, although this expression is based on a relatively small number of the studies, it is supported by most of the available data.

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- <sup>12</sup>NASA Evaluation No 12, 1997 (see references in Introduction).
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#### Thermodynamic Data

$$\begin{aligned}\Delta H_{298}^{\circ} &= -66.8 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= -17.6 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 3.36 \cdot 10^{-2} T^{0.139} \exp(+8200/T) \\ &(300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data

$\text{k}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$2.3 \cdot 10^{-12}$	350	Westenberg and de Haas, 1973 <sup>1</sup>	(a)
$2.1 \cdot 10^{-12}$	298	McKenzie, Mulcahy, and Steven, 1973 <sup>2</sup>	(a)
$2.1 \cdot 10^{-12}$	300	Trainor and von Rosenberg, 1974 <sup>3</sup>	(b)
$1.7 \cdot 10^{-12}$	298	Farquharson and Smith, 1980 <sup>4</sup>	(c)
$3.2 \cdot 10^{-12} \exp(-242/T)$	250–580	Wagner and Zellner, 1981 <sup>5</sup>	(d)
$1.56 \cdot 10^{-28} T^{4.77} \exp(4570/T)$	1050–2380	Wooldridge, Hanson, and Bowman, 1994 <sup>6</sup>	(e)
$7.1 \cdot 10^{-13} \exp(210/T)$	233–360	Bedjanian, Le Bras, and Poulet, 1999 <sup>7</sup>	(f)
<i>Reviews and Evaluations</i>			
$2.5 \cdot 10^{-15} T^{1.14} \exp(-50/T)$	250–2500	CEC, 1992; 1994 <sup>8</sup>	(g)
$4.2 \cdot 10^{-12} \exp(-240/T)$	200–500	NASA, 1997 <sup>9</sup>	(h)
$5.93 \cdot 10^{-20} T^{2.40} \exp(1063/T)$	298–2380	Wooldridge, Hanson, and Bowman, 1994 <sup>6</sup>	(i)
$2.8 \cdot 10^{-20} T^{2.6} \exp(945/T)$	200–500	IUPAC, 2001 <sup>10</sup>	(j)

#### Comments

- (a) Discharge flow study; OH generated by titration of H atoms with  $\text{NO}_2$ . [OH] monitored by ESR spectroscopy.
- (b) Flash photolysis of  $\text{H}_2\text{O}$ . [OH] monitored by resonance absorption spectroscopy.
- (c) Discharge flow study; OH generated by titration of H atoms with  $\text{NO}_2$ . [OH] monitored by resonance fluorescence.
- (d) Flash photolysis of  $\text{H}_2\text{O}/\text{N}_2$  mixtures. [OH] monitored by resonance absorption.
- (e) Shock tube using incident shocks in  $\text{HNO}_3/\text{Ar}$  mixtures at total pressures in the range 0.2–0.6 bar. [OH] monitored by time-resolved cw laser absorption.  $k$  derived by fitting [OH] profiles by numerical simulations of a 17-reaction mechanism.
- (f) Discharge flow study in which OH radicals were produced in a flow of He carrier gas at a total pressure of 1.3 mbar by the reaction  $\text{H} + \text{NO}_2$ . HO was detected by mass spectrometry as  $\text{HOBr}$ , formed by addition of excess of  $\text{Br}_2$  downstream of the reaction zone. The absolute concentration of OH was deduced by measurement of the depletion of  $[\text{Br}_2]$ . The  $\text{OH} + \text{OD}$ , and  $\text{OD} + \text{OD}$  reactions were also studied.
- (g) Adopts the recommendation of Ernst, Wagner, and Zellner.<sup>11</sup>
- (h) Based on the data in Refs. 1–5.
- (i) Fit to the data of Wooldridge *et al.*,<sup>6</sup> Wagner and Zellner,<sup>5</sup> and the NASA value of  $k$  (298 K).<sup>9</sup>
- (j) Based on a value of  $1.5 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at

298 K and the temperature coefficient is from an *ab initio* modeling study of Harding and Wagner.<sup>12</sup>

#### Preferred Values

$k = 5.56 \cdot 10^{-20} T^{2.42} \exp(970/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 250–2400 K.

#### Reliability

$\Delta \log k = \pm 0.15$  over the range 250–2400 K.

#### Comments on Preferred Values

The low temperature data have been thoroughly evaluated by the NASA and IUPAC Panels and their recommended value of  $k$  at 298 K is adopted. This value is based on the data from Refs. 1–5, and apart from the low value of Breen and Glass,<sup>13</sup> there are a number of other older studies<sup>14–18</sup> supporting it as well as the more recent study of Bedjanian *et al.*<sup>7</sup> Two studies of the temperature dependence of  $k$  in the low temperature region<sup>5,7</sup> give overlapping values of  $k$  but in one case a small negative temperature dependence is found<sup>7</sup> and in the other a small positive value.<sup>5</sup> The recommended expression fits both within the suggested error limits.

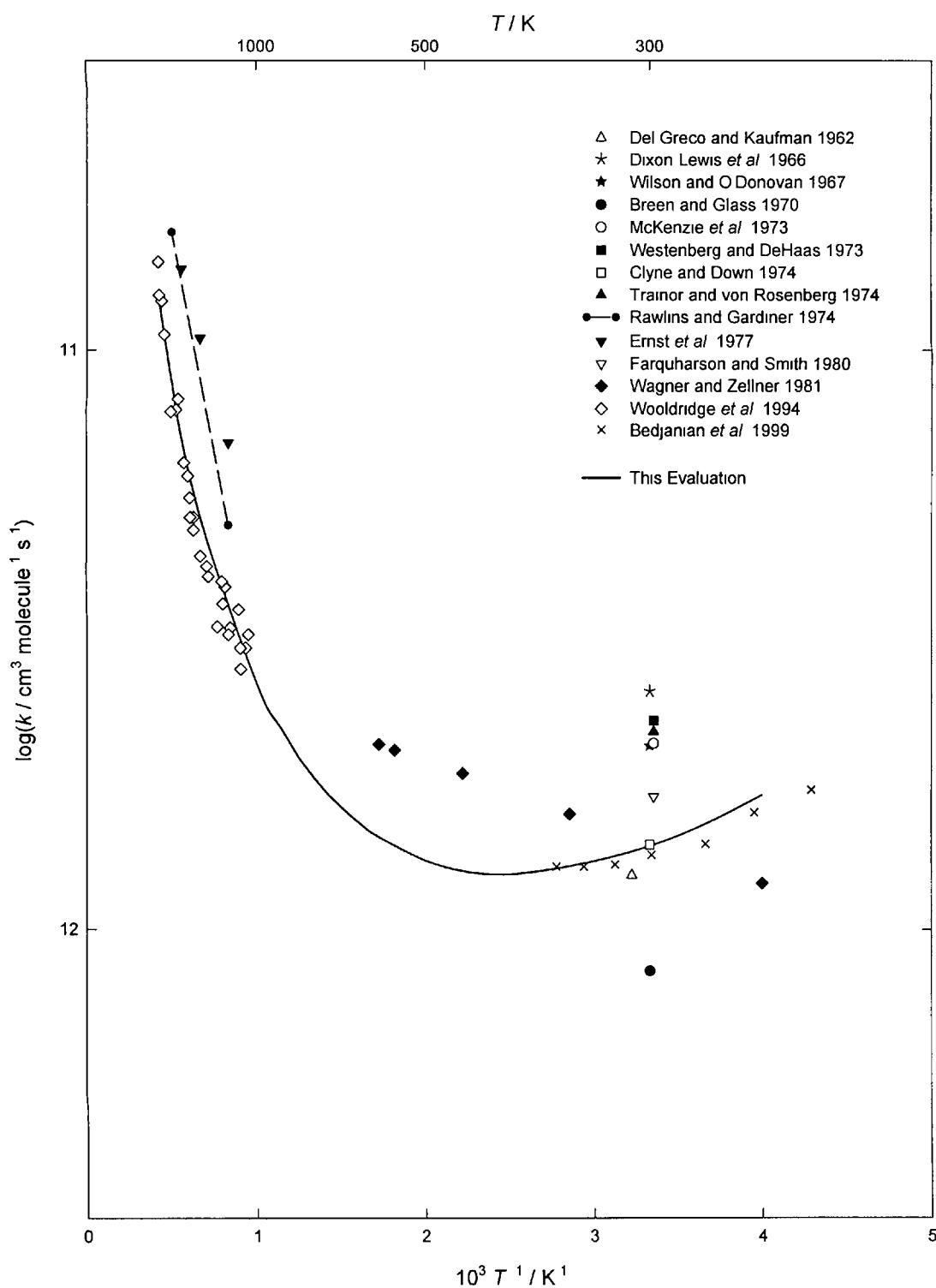
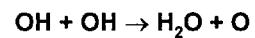
At higher temperatures, a recent shock-tube study by Wooldridge *et al.*,<sup>6</sup> over the temperature range 1050–2380 K, gives values of the rate constant approximately a factor of 2 lower than the older data of Gardiner *et al.*,<sup>19</sup> Rawlins and Gardiner,<sup>20</sup> and Ernst *et al.*<sup>11</sup> The results of Wooldridge *et al.*<sup>6</sup> are supported by two recent studies of the reverse reaction by Lifshitz and Michael<sup>21</sup> and Sutherland *et al.*<sup>22</sup> over much the same temperature range. There is considerable

scatter in the results of both of these studies<sup>21,22</sup> but when combined with the thermodynamic data for the reaction they give values of  $k$  which are in good agreement with those of Wooldridge *et al.*<sup>6</sup> Wooldridge *et al.*<sup>6</sup> derived an expression for  $k$  over an extended temperature range (298–2380 K) by combining their own results with those of Wagner and Zellner<sup>5</sup> and the consensus value at 298 K.<sup>9,10</sup> Our preferred expression is a fit to the high temperature data of Wooldridge *et al.*<sup>6</sup> and the lower temperature data of Bedjanian *et al.*<sup>7</sup>

There are two other exothermic channels for the reaction between OH radicals, leading to the products  $H_2 + O_2$ , or  $H + HO_2$ . Both are much less favorable than the channel giving  $O + H_2O$ . The data for the addition channel,  $OH + OH(+M) \rightarrow H_2O_2(+M)$ , are evaluated on the data sheet which follows the present one.

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*Thermodynamic Data*

$$\begin{aligned}\Delta H_{298}^{\circ} &= -210.5 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= -132.9 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 3.91 \cdot 10^{-30} T^{1.066} \exp(+25660/T) \text{ cm}^3 \text{ molecule}^{-1} \\ (300 \leqslant T/\text{K} \leqslant 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	[M]/molecule cm $^{-3}$	Reference	Comments
<i>Rate Coefficient Measurements</i>				
<i>Low Pressure Range</i>				
$[\text{N}_2] 2.5 \cdot 10^{-31}$	300	$6.5 \cdot 10^{17}$	Trainor and von Rosenberg, 1974 <sup>1</sup>	(a)
$[\text{N}_2] 6.9 \cdot 10^{-31} (T/300)^{-0.8}$	253–353	$(0.6–27) \cdot 10^{18}$	Zellner <i>et al.</i> , 1988 <sup>2</sup>	(b)
$[\text{H}_2\text{O}] 4.0 \cdot 10^{-30}$	298			
$[\text{H}_2\text{O}] 4.1 \cdot 10^{-30}$	353			
$[\text{He}] 3.7 \cdot 10^{-31}$	298	$(3.9–340) \cdot 10^{19}$	Forster <i>et al.</i> , 1995 <sup>3</sup>	(c)
<i>High Pressure Range</i>				
$1.5 \cdot 10^{-11}$	253–353		Zellner <i>et al.</i> , 1988 <sup>2</sup>	(b)
$2.2 \cdot 10^{-11}$	298		Forster <i>et al.</i> , 1995 <sup>3</sup>	(c)
$2.6 \cdot 10^{-11}$	200–400	$(3.5–16) \cdot 10^{20}$	Fulle <i>et al.</i> , 1996 <sup>4</sup>	(d)
<i>Reviews and Evaluations</i>				
$k_0 [\text{N}_2] = [\text{N}_2] 6.1 \cdot 10^{-29} T^{-0.76}$	250–1400		Brouwer <i>et al.</i> , 1987 <sup>5</sup>	(e)
$k_\infty = 1.2 \cdot 10^{-10} T^{-0.37}$	200–1500			
$F_c(\text{N}_2) = 0.5$	200–1500			
$k_0 [\text{N}_2] = [\text{N}_2] 6.1 \cdot 10^{-29} T^{-0.76}$	250–1400		CEC, 1992; 1994 <sup>6</sup>	(f)
$k_0 [\text{H}_2\text{O}] = [\text{H}_2\text{O}] 4 \cdot 10^{-30}$	300–400			
$k_\infty = 1.2 \cdot 10^{-10} T^{-0.37}$	200–1500			
$F_c(\text{N}_2) = 0.5$	200–1500			
$k_0 [\text{air}] = [\text{air}] 6.2 \cdot 10^{-31} (T/300)^{-1.0}$	200–350		NASA, 1997 <sup>7</sup>	(g)
$k_\infty = 2.6 \cdot 10^{-11}$	200–350			
$F_c(\text{air}) = 0.6$	200–300			
$k_0 [\text{N}_2] = [\text{N}_2] 6.9 \cdot 10^{-31} (T/300)^{-0.8}$	200–400		IUPAC, 1999 <sup>8</sup>	(h)
$k_\infty = 2.6 \cdot 10^{-11}$	200–300			
$F_c(\text{N}_2) = 0.5$	200–400			

**Comments**

- (a) Flash photolysis of  $\text{H}_2\text{O}$ . OH radicals detected by absorption spectroscopy at 306.4 nm.
- (b) Flash photolysis of  $\text{H}_2\text{O}$  vapor in  $\text{N}_2$ . Detection of OH by laser induced fluorescence. Comparison with earlier data of Trainor and von Rosenberg,<sup>1</sup> Black and Porter,<sup>9</sup> and Cadwell and Back.<sup>10</sup>
- (c) OH radicals generated by laser photolysis of  $\text{N}_2\text{O}$  at 193 nm in the presence of  $\text{H}_2\text{O}$ . OH measurements were carried out with saturated laser induced fluorescence. The pressure range of the experiments covers the major part of the fall-off curve. The apparent discrepancy between the results of Trainor and von Rosenberg<sup>1</sup> and Zellner *et al.*<sup>2</sup> disappears when the contribution of the reaction  $\text{HO} + \text{HO} \rightarrow \text{H}_2\text{O} + \text{O}$  is separated by means of the fall-off plot.
- (d) See comment (c). Measurements were carried out over the temperature range 200–700 K. A negative temperature coefficient of  $k_\infty$  was observed above 400 K, the

magnitude of which depends on the precise contribution from the reaction  $\text{HO} + \text{HO} \rightarrow \text{H}_2\text{O} + \text{O}$ .

- (e) Theoretical construction of fall-off curves for the forward and reverse reaction based on the experimental results of Zellner *et al.*<sup>2</sup> and consistent with  $\text{H}_2\text{O}_2$  photolysis lifetime measurements.
- (f) Based on the experiments of Zellner *et al.*<sup>2</sup> and the theoretical modeling of Ref. 5.
- (g) Based on the data of Zellner *et al.*<sup>2</sup> and Forster *et al.*<sup>3</sup>
- (h) Based on the results of Forster *et al.*<sup>3</sup> which are consistent with previous measurements of Trainor and von Rosenberg<sup>1</sup> and Zellner *et al.*<sup>2</sup>

**Preferred Values**

$k_0 = 6.6 \cdot 10^{-29} T^{-0.8} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  for  $\text{M} = \text{N}_2$  over the range 200–400 K.

$k_0 = 4.0 \cdot 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  for  $\text{M} = \text{H}_2\text{O}$  over the range 200–400 K.

$k_\infty = 2.6 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 200–400 K.

$F_c = 0.5$  for M=N<sub>2</sub>, H<sub>2</sub>O over the range 200–400 K.

#### Reliability

$\Delta \log k_0 = \pm 0.2$  for M=N<sub>2</sub>, H<sub>2</sub>O over the range 200–400 K.

$\Delta \log k_\infty = \pm 0.2$  over the range 200–400 K.

$\Delta F_c = \pm 0.1$  for M=N<sub>2</sub>, H<sub>2</sub>O over the range 200–400 K.

#### Comments on Preferred Values

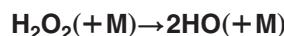
The discrepancies between the results of Trainor and von Rosenberg<sup>1</sup> and Zellner *et al.*<sup>2</sup> noted in Ref. 7 disappear when the pressure dependence of the reaction is analyzed over the wide range applied by Fulle, Hamann, and Hippler.<sup>4</sup> By this treatment, the kinetics of the reactions OH+OH (+M)→H<sub>2</sub>O<sub>2</sub>(+M) and OH+OH→H<sub>2</sub>O+O can be conveniently separated. The preferred values are an average of the results of Trainor and von Rosenberg,<sup>1</sup> Zellner *et al.*,<sup>2</sup> and Fulle, Hamann, and Hippler,<sup>4</sup> based on a fall-off curve

employing  $F_c = 0.5$  at 298 K. The temperature dependence of  $k_0$  is from the theoretical analysis of Brouwer *et al.*<sup>5</sup>

Data for the other reaction channel, OH+OH→H<sub>2</sub>O + O, are evaluated on the preceding data sheet.

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#### Thermodynamic Data

$$\Delta H^\circ_{298} = 210.5 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298} = 132.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c = 2.55 \cdot 10^{29} T^{-1.066} \exp(-25660/T) \text{ molecule cm}^{-3}$$

(300 ≤ T/K ≤ 5000)

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data

$k/\text{s}^{-1}$	T/K	[M]/molecule cm <sup>-3</sup>	Reference	Comments
<i>Rate Coefficient Measurements</i>				
<i>Low Pressure Range</i>				
$[\text{Ar}] 3.0 \cdot 10^{-8} \exp(-21600/T)$	450–1450	$(0.5\text{--}5) \cdot 10^{19}$	Kijewski and Troe, 1972 <sup>1</sup>	(a)
$[\text{Ar}] 3.8 \cdot 10^{-8} \exp(-21960/T)$	950–1250	$(0.7\text{--}10) \cdot 10^{19}$	Kappel, Luther, and Troe, 2002 <sup>2</sup>	(b)
<i>Reviews and Evaluations</i>				
$k_0[\text{N}_2] = [\text{N}_2] 2.0 \cdot 10^{-7} \exp(-22900/T)$	700–1500		Baulch <i>et al.</i> , 1972 <sup>3</sup>	(c)
$k_0[\text{Ar}] = [\text{Ar}] 3.2 \cdot 10^{-8} \exp(-21640/T)$	1000–1400		Brouwer <i>et al.</i> , 1987 <sup>4</sup>	(d)
$k_\infty = 3.0 \cdot 10^{14} \exp(-24374/T)$	1000–1500			
$F_c(\text{Ar}) = 0.5$	500–1500			
$k_0[\text{Ar}] = [\text{Ar}] 3.0 \cdot 10^{-8} \exp(-21600/T)$	1000–1500		CEC, 1992; 1994 <sup>5</sup>	(e)
$k_0[\text{N}_2] = [\text{N}_2] 2.0 \cdot 10^{-7} \exp(-22900/T)$	700–1500			
$k_\infty = 3.0 \cdot 10^{14} \exp(-24400/T)$	1000–1500			
$F_c(\text{Ar}) = 0.5$	700–1500			

#### Comments

- (a) Shock wave experiments on H<sub>2</sub>O<sub>2</sub> decomposition monitoring UV absorption by H<sub>2</sub>O<sub>2</sub> and HO<sub>2</sub>. Minor correction of earlier results of Meyer *et al.*<sup>6</sup> and Troe<sup>7</sup> by taking into account the water content of the shock heated H<sub>2</sub>O<sub>2</sub>/Ar mixtures.
- (b) See Comment (a). Corrections applied in Ref. 1 were

shown to be unjustified. Deviations from low pressure behavior were observed at unexpectedly low bath gas concentrations.

- (c) Comprehensive review of data published up to 1972. Recommendation based on the low pressure results from static reactor,<sup>8</sup> and flow system<sup>9–12</sup> experiments which are in good agreement over the limited temperature range studied, (719–941) K. The results are also in

agreement with data from shock wave experiments<sup>6,7</sup> extending the temperature range to 1500 K.

- (d) Theoretical evaluation of low pressure, high pressure, and fall-off data for dissociation and recombination in comparison to energy-resolved dissociation lifetime measurements after laser excitation.
- (e) See Comments on Preferred Values.

### Preferred Values

$k_0 = 3.8 \cdot 10^{-8} \exp(-21960/T)$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for M = Ar over the range 1000–1500 K.

$k_0 = 2.0 \cdot 10^{-7} \exp(-22900/T)$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for M = N<sub>2</sub> over the range 700–1500 K.

$k_\infty = 3.0 \cdot 10^{14} \exp(-24400/T)$  s<sup>-1</sup> over the range 1000–1500 K.

$F_c = 0.5$  for M = Ar over the range 1000–1500 K.

### Reliability

$\Delta \log k_0 = \pm 0.2$  for M = Ar over the range 1000–1500 K.

$\Delta \log k_0 = \pm 0.2$  for M = N<sub>2</sub> over the range 700–1500 K.

$\Delta \log k_\infty = \pm 0.5$  over the range 700–1500 K.

$\Delta \log F_c = \pm 0.1$  for M = Ar over the range 700–1500 K.

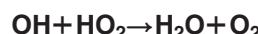
### Comments on Preferred Values

The preferred values are slightly changed from our previ-

ous evaluations<sup>5</sup> and are based on the low pressure experimental results reviewed in Ref. 3 and from Ref. 2, together with theoretical modeling.<sup>4</sup> The  $k_\infty$  values are consistent with the recombination rate coefficient<sup>6</sup> for the reverse process measured by Fulle *et al.*<sup>13</sup> at temperatures up to 700 K.

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### Thermodynamic Data

$$\Delta H^\circ_{298} = -294.6 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298} = -18.86 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c = 0.374 T^{-0.204} \exp(+35390/T) \\ (300 \leq T/\text{K} \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

### Rate Coefficient Data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$8.3 \cdot 10^{-11}$	1400–1800	Peeters and Mahnen, 1973 <sup>1</sup>	(a)
$4.8 \cdot 10^{-11} \exp(250/T)$	254–382	Keyser, 1988 <sup>2</sup>	(b)
$1.0 \cdot 10^{-10}$	1810–2550	Goodings and Hayhurst, 1988 <sup>3</sup>	(c)
$3.3 \cdot 10^{-11}$	950–1250	Hippler and Troe, 1992 <sup>4</sup>	(d)
See figure	1118–1566	Hippler, Neunaber, and Troe, 1995 <sup>5</sup>	(e)
<i>Reviews and Evaluations</i>			
$4.8 \cdot 10^{-11} \exp(250/T)$	300–2000	CEC, 1992; 1994 <sup>6</sup>	(f)
$4.8 \cdot 10^{-11} \exp(250/T)$	250–400	NASA, 1997 <sup>7</sup>	(f)
$4.8 \cdot 10^{-11} \exp(250/T)$	250–400	IUPAC, 1997 <sup>8</sup>	(f)

### Comments

- (a) Study on lean and stoichiometric CH<sub>4</sub>/O<sub>2</sub> flat flames at 53 mbar total pressure. Molecular beam sampling and mass spectrometric analysis of the flame species.
- (b) Discharge flow study. [OH] monitored by LIF and [HO<sub>2</sub>] by reaction with NO<sub>2</sub> and LIF detection of the

OH produced. NO<sub>2</sub> added to remove O and H atoms. The value of  $k$  obtained agrees with studies at higher pressures leading the author to conclude that there is little or no pressure dependence of  $k$  over the range 1 mbar–1 bar. Modeling of the system suggests that previous low-pressure studies were subject to error due to the presence of small amounts of H and O.

- (c) Atmospheric-pressure, lean, one-dimensional, premixed,  $\text{H}_2/\text{O}_2/\text{N}_2$  flames; axial temperature profile measured by sodium line reversal. Rate inferred from a detailed kinetic analysis of the recombination rate in the post flame gases using a 14-reaction mechanism.
- (d) Shock tube study on  $\text{H}_2\text{O}_2/\text{Ar}$  mixtures.  $[\text{H}_2\text{O}_2]$ ,  $[\text{HO}_2]$ , and  $[\text{OH}]$  monitored by UV absorption.  $[\text{HO}_2]$  profiles analyzed to obtain relative rate of reaction of OH with  $\text{HO}_2$  and  $\text{H}_2\text{O}_2$ .
- (e) Shock tube study using incident and reflected shocks in  $\text{H}_2\text{O}_2/\text{Ar}$  mixtures.  $[\text{HO}]$  monitored by cw laser absorption. Fitting of the  $[\text{OH}]$  profile by computer simulation used to obtain  $k$ .
- (f) Expression of Keyser<sup>2</sup> adopted.

### Preferred Values

$k = 4.8 \cdot 10^{-11} \exp(250/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 250–400 K.

$k = 1.54 \cdot 10^{-8} \exp(-8810/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 1300–2000 K.

### Reliability

$\Delta \log k = \pm 0.2$  over the range 250–400 K and  $\pm 0.5$  over the range 1300–2000 K.

### Comments on Preferred Values

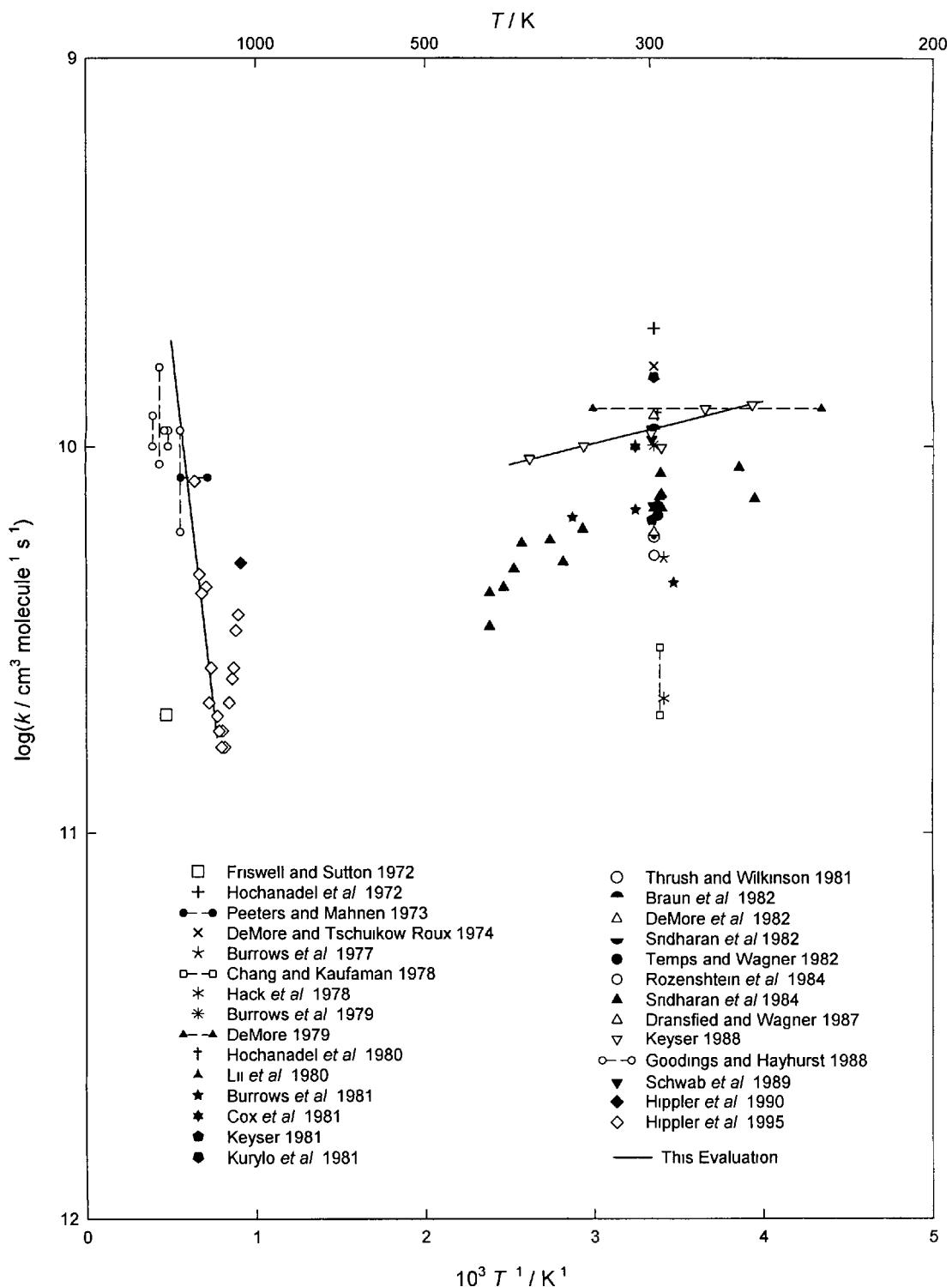
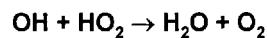
The low temperature data on this reaction have been reviewed by the NASA and IUPAC Panels whose findings are accepted. Their recommendations are based on the results of Keyser,<sup>2</sup> which is the only low temperature study cited in the Table. Disregarding the very low values obtained by Hack *et al.*<sup>9</sup> and Chang and Kaufman,<sup>10</sup> the remaining data at low temperature fall into two groups, a set of values<sup>9–22</sup> at  $k \sim 7 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  obtained from studies at low pressures and a group of higher values<sup>2,23–31</sup> ( $\sim 1 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) obtained at pressures close to 1 bar. Keyser's work<sup>2</sup> suggested that the discrepancy between them was due to secondary chemistry arising from the presence of small amounts of H and O atoms in the low-pressure work, rather than being due to  $k$  being pressure dependent. The temperature dependence of  $k$  found by Keyser<sup>2</sup> is also adopted. The only other determination of the temperature dependence of  $k$  by Sridharan *et al.*<sup>20</sup> supports the small negative dependence found by Keyser<sup>2</sup> even though the absolute values of  $k$  obtained by Sridharan *et al.*<sup>20</sup> appear to be systematically low.

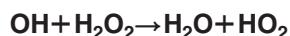
However, extrapolation of the low temperature expression for  $k$  does not reproduce the few available high temperature data.<sup>1,3–5,32–34</sup> Hippler *et al.*<sup>5</sup> have carried out a shock tube study of the reaction over the temperature range 1118–1566 K and find a complex temperature dependence of  $k$ . The rate constant initially declines in value as the temperature in-

creases reaching a minimum at  $\sim 1250$  K and rises again at temperatures beyond (see Arrhenius diagram). This behavior is similar to that of the  $\text{HO}_2 + \text{HO}_2$  reaction and is suggestive of formation and decomposition of an intermediate complex, with the implication that  $k$  is possibly pressure dependent. The preferred expression at high temperatures is based on the high temperature studies cited in the Table but substantial error limits are suggested until confirmatory studies of both the temperature and pressure dependence of  $k$  are carried out.

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*Thermodynamic Data*

$$\begin{aligned}\Delta H_{298}^{\circ} &= -127.0 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= -0.33 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 8.25 T^{-0.347} \exp(+15240/T) \\ &(300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$2.96 \cdot 10^{-12} \exp(-164/T)$	250–459	Sridharan, Reimann, and Kaufman, 1980 <sup>1</sup>	(a)
$2.51 \cdot 10^{-12} \exp(-126/T)$	245–423	Keyser, 1980 <sup>2</sup>	(b)
$3.7 \cdot 10^{-12} \exp(-260/T)$	273–410	Wine, Semmes, and Ravishankara, 1981 <sup>3</sup>	(c)
$1.6 \cdot 10^{-12}$	295	Nelson, Marinelli, and Johnston, 1981 <sup>4</sup>	(d)
$1.67 \cdot 10^{-12}$	296	Temps and Wagner, 1982 <sup>5</sup>	(e)
$1.81 \cdot 10^{-12}$	298	Marinelli and Johnston, 1982 <sup>6</sup>	(f)
$2.93 \cdot 10^{-12} \exp(-158/T)$	250–370	Kurylo <i>et al.</i> , 1982 <sup>7</sup>	(g)
$7.0 \cdot 10^{-20} T^{2.5} \exp(838/T)$	241–413	Lamb <i>et al.</i> , 1983 <sup>8</sup>	(h)
$2.62 \cdot 10^{-12}$	713	Baldwin <i>et al.</i> , 1984 <sup>9</sup>	(i)
$2.76 \cdot 10^{-12} \exp(-110/T)$	273–410	Vaghjiani, Ravishankara, and Cohen, 1989 <sup>10</sup>	(j)
$1.99 \cdot 10^{-12}$	298	Vaghjiani and Ravishankara, 1990 <sup>11</sup>	(k)
$1.99 \cdot 10^{-12}, 1.93 \cdot 10^{-12}$	249, 299	Lovejoy <i>et al.</i> , 1990 <sup>12</sup>	(l)
$5.0 \cdot 10^{-12}$	1100	Hippler, Troe, and Willner, 1990 <sup>13</sup>	(m)
$1.53 \cdot 10^{-12}$	298	Turnipseed <i>et al.</i> , 1991 <sup>14</sup>	(n)
$8.4 \cdot 10^{-12}$	1000	Hippler and Troe, 1992 <sup>15</sup>	(o)
$1.3 \cdot 10^{-11}$	1100		
$3.2 \cdot 10^{-11}$	1200		
$1.75 \cdot 10^{-12}$	298	Mellouki <i>et al.</i> , 1994 <sup>16</sup>	(p)
$2.72 \cdot 10^{-6} \exp(-14800/T) + 3.2 \cdot 10^{-12} \exp(-215/T)$	930–1680	Hippler, Neunaber, and Troe, 1995 <sup>17</sup>	(q)
<i>Reviews and Evaluations</i>			
$1.3 \cdot 10^{-11} \exp(-670/T)$	300–1000	CEC 1992; 1994 <sup>18</sup>	(r)
$2.72 \cdot 10^{-6} \exp(-14800/T) + 3.2 \cdot 10^{-12} \exp(-215/T)$	240–1700	Hippler, Neunaber, and Troe, 1995 <sup>17</sup>	(s)
$2.9 \cdot 10^{-12} \exp(-160/T)$	240–460	NASA, 1997 <sup>19</sup>	(t)
$2.9 \cdot 10^{-12} \exp(-160/T)$	240–460	IUPAC, 1997 <sup>20</sup>	(u)

**Comments**

- (a) Discharge flow study with OH production by H + NO<sub>2</sub> reaction. [OH] monitored by LIF and [H] and [O] by resonance fluorescence. [H<sub>2</sub>O<sub>2</sub>] determined by absorption at 213.9 nm.
- (b) Discharge flow study with OH production by the H + NO<sub>2</sub> reaction. [OH] monitored by LIF and [H<sub>2</sub>O<sub>2</sub>] determined photometrically at 199.5 nm.  $k$  found to be independent of pressure between 1.3 and 5 mbar.
- (c) Pulsed laser photolysis of H<sub>2</sub>O<sub>2</sub> at 266 nm. [OH] monitored by rf and [H<sub>2</sub>O<sub>2</sub>] determined photometrically at 228.8 nm. Total pressures, 134 mbar He or 53 mbar SF<sub>6</sub>.
- (d) Pulsed laser photolysis of HNO<sub>3</sub>. [OH] monitored by rf and [H<sub>2</sub>O<sub>2</sub>] determined photometrically at 200 nm. Total pressure, 13 mbar Ar.
- (e) Discharge flow study with OH production by F + H<sub>2</sub>O reaction. [OH] and [HO<sub>2</sub>] monitored by LMR.
- (f) Pulsed laser photolysis of H<sub>2</sub>O<sub>2</sub>. [OH] monitored by RF and [H<sub>2</sub>O<sub>2</sub>] determined photometrically at 200 nm. Total pressure, 13 mbar Ar.

- (g) Flash photolysis of H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O/Ar mixtures. [OH] monitored by resonance fluorescence and [H<sub>2</sub>O<sub>2</sub>] determined photometrically at 213.9 nm. Total pressures, 26–40 mbar.
- (h) Flash photolysis of H<sub>2</sub>O<sub>2</sub>. [OH] monitored by resonance fluorescence and [H<sub>2</sub>O<sub>2</sub>] determined photometrically in the 205–220 nm range and by FTIR. Total pressure, 1 bar.
- (i) Thermal decomposition of tetramethylbutane/O<sub>2</sub> mixtures; yields of H<sub>2</sub> and *i*-butane measured using a permanent gas analyzer and GC, respectively. Computer simulation gave  $k/k(\text{OH} + \text{H}_2) = 3.9 \pm 0.5$  from the variation of the initial rate with [H<sub>2</sub>]. Value of  $k$  in Table calculated using  $k(\text{OH} + \text{H}_2)$  from this evaluation. The result is in good agreement with earlier, similar work in the same laboratory on the CO and H<sub>2</sub> sensitized decomposition of H<sub>2</sub>O<sub>2</sub> which gave, respectively,  $k/k(\text{OH} + \text{H}_2) = (21 \pm 2)^{24}$  at 713 K and  $(5.0 \pm 1.0)^{25}$  over the range 713–773 K.
- (j) Low-pressure flow reactor with OH production by excimer laser photolysis of H<sub>2</sub>O<sub>2</sub> or O<sub>3</sub> and H<sub>2</sub>O or H<sub>2</sub>.

- [OH] monitored by pulsed LIF; [H<sub>2</sub>O<sub>2</sub>] determined by UV absorption. Total pressure, 1.3–130 mbar.
- (k) Flow reactor with OH production by excimer laser photolysis of H<sub>2</sub>O<sub>2</sub> or CH<sub>3</sub>OOH. [OH] monitored by pulsed LIF; [H<sub>2</sub>O<sub>2</sub>] determined by UV absorption. Total pressure, 0.4–0.6 bar.
- (l) Flow reactor with production of OH by pulsed laser photolysis of H<sub>2</sub>O<sub>2</sub>. [OH] monitored by pulsed LIF. Total pressure, 65 mbar.
- (m) Shock tube study using incident shock waves in H<sub>2</sub>O<sub>2</sub>/Ar mixtures. [OH] monitored by cw laser absorption. Total pressure, 1 bar.
- (n) Flow reactor with OH production by excimer laser photolysis of H<sub>2</sub>O<sub>2</sub>. [OH] monitored by pulsed LIF. Total pressure, 0.4 bar.
- (o) Shock tube study using incident shock waves in H<sub>2</sub>O<sub>2</sub>/Ar mixtures. [HO<sub>2</sub>], [H<sub>2</sub>O<sub>2</sub>], and [OH] monitored by UV absorption. Rate determined from a quasi-steady state analysis of the HO<sub>2</sub> yield.
- (p) Pulsed laser photolysis of H<sub>2</sub>O<sub>2</sub>. [OH] monitored by LIF and [H<sub>2</sub>O<sub>2</sub>] determined by UV absorption. Total pressure, 0.15 bar.
- (q) Shock tube using incident and reflected shocks in H<sub>2</sub>O<sub>2</sub>/Ar mixtures. OH concentration-time profiles were determined by cw laser absorption and the profiles fitted by numerical simulations using a 4-reaction mechanism. Total pressure, 0.2–1.1 bar. The expression given for *k* was derived using low temperature data from some other studies.
- (r) Accepts *E/R* from CODATA, 1980 with a higher A factor to agree with *k* at 298 K.
- (s) Fit to authors' data over the range 980–1700 K and selected low temperature data.
- (t) Based on Refs. 1–3, 6, 7.
- (u) Based on Refs. 1–7.

### Preferred Values

$$k = [2.72 \cdot 10^{-6} \exp(-14800/T) + 3.2 \cdot 10^{-12} \exp(-215/T)] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the range } 240\text{--}1700 \text{ K.}$$

### Reliability

$\Delta \log k = \pm 0.2$  over the range 240–800 K, rising to  $\pm 0.5$  over the range 800–1700 K.

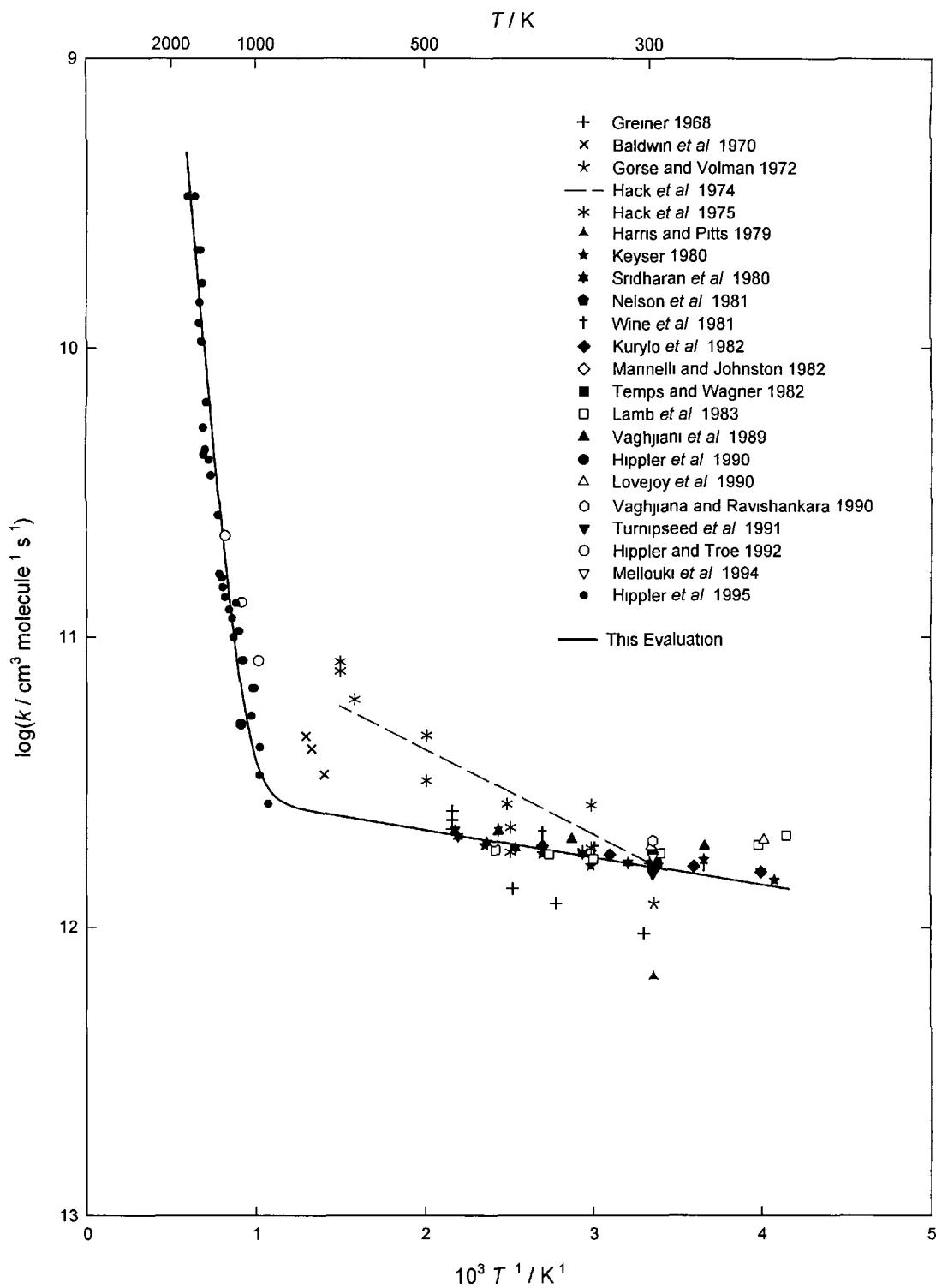
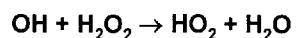
### Comments on Preferred Values

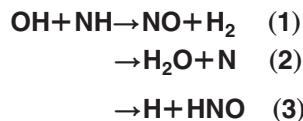
The data at low temperatures have been reviewed by the NASA and IUPAC Panels and we adopt their recommendations.<sup>19,20</sup> Studies prior to 1980<sup>21–25</sup> gave values of *k* approximately a factor of 2 lower at 298 K than those now accepted, probably due to the effects of secondary chemistry initiated by the HO<sub>2</sub> radicals produced. Since then the numerous studies cited in the Table<sup>1–8,10–12,14,16</sup> and others<sup>26–28</sup> have given results in excellent agreement in the range 240–460 K except for the study of Lamb *et al.*<sup>8</sup> which appears to give high values of *k* at the lowest temperatures studied.

At higher temperatures, the only study over a substantial range of temperatures is that of Hippler *et al.*<sup>17</sup> which gives values of *k* showing only a small increase with temperature up to  $\sim 800$  K in good agreement with the Arrhenius expression derived from the low temperature data. Above 800 K there is a sharp increase in *k* with temperature up to  $\sim 1570$  K. It is suggested that this behavior is due to formation of an intermediate complex with competition between its subsequent forward and backward dissociation. Values of *k* obtained in a number of other single temperature studies<sup>9,13,15,29,30</sup> are in reasonable agreement with the results of Hippler *et al.*<sup>17</sup> Hippler *et al.*<sup>17</sup> have derived an expression, which is the sum of two Arrhenius expressions, to fit their own and the low temperature results. This expression is taken as the basis of our preferred values but with substantial error limits at high temperatures until a more complete study of the pressure and temperature dependence of *k* is carried out.

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*Thermodynamic Data*

$$\begin{aligned}\Delta H^\circ_{298}(1) &= -301.3 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(1) &= -23.7 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 2.07 \cdot 10^{-2} T^{0.151} \exp(+36530/T) \\ &\quad (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

$$\begin{aligned}\Delta H^\circ_{298}(2) &= -168.6 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(2) &= -22.9 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 0.304 T^{0.063} \exp(+20400/T) \\ &\quad (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

$$\begin{aligned}\Delta H^\circ_{298}(3) &= -62.8 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(3) &= -29.7 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(3) &= 4.59 \cdot 10^{-4} T^{0.564} \exp(+7820/T) \\ &\quad (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data ( $k = k_1 + k_2 + k_3$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$8.3 \cdot 10^{-11}$	300	Hack and Kurzke, 1985 <sup>1</sup>	(a)
<i>Reviews and Evaluations</i>			
$k_2 = 3.3 \cdot 10^{-15} T^{1.2}$	298–3000	Cohen and Westberg, 1991 <sup>2</sup>	(b)
$k_3 = 3.3 \cdot 10^{-11}$	298–3000		
$8 \cdot 10^{-11}$	300–1000	CEC, 1992; 1994 <sup>3</sup>	(c)

**Comments**

- (a) Discharge flow study of the  $\text{NH}_2 + \text{O}_2$  reaction.  $\text{NH}_2$  was generated by the  $\text{F} + \text{NH}_3$  reaction and  $\text{O}_2$  added downstream.  $[\text{NH}_2]$ ,  $[\text{NH}]$ , and  $[\text{OH}]$  were monitored by LIF. Values of rate constants were derived by computer simulation of the concentration profiles. Results subject to considerable uncertainties
- (b) Values estimated by comparison with the kinetics of the reactions  $\text{OH} + \text{OH} \rightarrow \text{H} + \text{HO}_2$  and  $\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}$ .
- (c) Accepts value of Hack and Kurzke<sup>1</sup> assigning large error limits.

**Preferred Values**

$$k = 8 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the range } 300\text{--}2000 \text{ K.}$$

**Reliability**

$$\Delta \log k = \pm 0.5 \text{ at } 300 \text{ K, rising to } \pm 1 \text{ at } 2000 \text{ K.}$$

**Comments on Preferred Values**

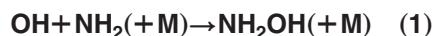
The preferred values are unchanged from our previous evaluations.<sup>3</sup> The only experimental study of this rate constant is very indirect and, although it is accepted as the pre-

ferred value, large error limits are assigned. The estimates of Cohen and Westberg<sup>2</sup> are of comparable magnitude and provide some support for our recommendations.

An important uncertainty is the branching ratios. Cohen and Westberg<sup>2</sup> have suggested that Channel (1), though exothermic, is a four center reaction and is likely to have a large activation energy. Their estimates suggest that Channel (3) provides the main contribution to the overall rate constant with Channel (2) only becoming significant at very high temperatures. A theoretical treatment by Sumathi *et al.*<sup>4</sup> suggests that the reaction proceeds through the formation of the adducts  $\text{NH}_2\text{O}$  and  $\text{HNOH}$  which are sufficiently energized to isomerize and dissociate to give, at 1 bar pressure,  $\text{H}_2 + \text{NO}$  as the predominant products [Channel (1)] with a significant contribution from  $\text{H} + \text{HNO}$  [Channel (3)]. There is also a channel leading to  $\text{O} + \text{NH}_2$ , which is endothermic and, on the basis of the kinetic data on its reverse, is not expected to be important. No recommendations are made for the branching ratios.

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#### Thermodynamic Data

$$\Delta H_{298}^{\circ}(1) = -277.7 \text{ kJ mol}^{-1}$$

$$\Delta S_{298}^{\circ}(1) = -141.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 3.75 \cdot 10^{-27} T^{-0.110} \exp(+33380/T) \text{ cm}^3 \text{ molecule}^{-1}$$

(300 ≤ T/K ≤ 5000)

$$\Delta H_{298}^{\circ}(2) = -112.0 \text{ kJ mol}^{-1}$$

$$\Delta S_{298}^{\circ}(2) = -8.36 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 0.526 T^{-0.056} \exp(+13450/T)$$

(300 ≤ T/K ≤ 5000)

$$\Delta H_{298}^{\circ}(3) = -23.4 \text{ kJ mol}^{-1}$$

$$\Delta S_{298}^{\circ}(3) = -24.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 1.55 \cdot 10^{-3} T^{0.446} \exp(+3120/T)$$

(300 ≤ T/K ≤ 5000)

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2 + k_3$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$k_1 = 3 \cdot 10^{-11} T^{0.2}$	200–400	Fagerström <i>et al.</i> , 1995 <sup>1</sup>	(a)
<i>Reviews and Evaluations</i>			
$k_2 = 1.5 \cdot 10^{-16} T^{1.5} \exp(230/T)$	250–3000	Cohen and Westberg, 1991 <sup>2</sup>	(b)
$k_3 = 1.8 \cdot 10^{-21} T^{2.6} \exp(870/T)$			
$k_3 = 3.3 \cdot 10^{-14} T^{0.405} \exp(-250/T)$	500–2500	CEC, 1992; 1994 <sup>3</sup>	(c)

#### Comments

- (a) Pulse radiolysis of SF<sub>6</sub>/H<sub>2</sub>O/NH<sub>3</sub> mixtures at total pressures of 0.5–1.0 bar. F atoms produced generated NH<sub>2</sub> and OH by abstraction from NH<sub>3</sub> and H<sub>2</sub>O, respectively. [NH<sub>2</sub>] and [OH] monitored by time-resolved absorption measurements at 597.7 nm and 309.0 nm, respectively. Values of  $k$  derived by simulation of reaction mechanism.
- (b) Estimated value for  $k_2$  based on a transition state theory treatment analogous to methods used successfully by Cohen and Westberg<sup>2</sup> in estimating values of  $k(\text{OH} + \text{NH}_3)$ . A value of  $k_2 = 1.7 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K is assumed in the estimation.  $k_3$  was estimated from  $k(\text{O} + \text{NH}_3)$  and the thermodynamic data.
- (c) Based on evaluation of data for  $k(\text{O} + \text{NH}_3)$  and thermodynamic data.

#### Preferred Values

$k_1 = 3.1 \cdot 10^{-11} T^{0.2} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 200–500 K at a pressure of 1 bar.

$k_3 = 4.2 \cdot 10^{-20} T^{2.3} \exp(140/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 300–2000 K.

#### Reliability

$\Delta \log k_1 = \pm 1$  over the range 200–500 K at a pressure of 1 bar.

$\Delta \log k_3 = \pm 0.3$  at 300 K, rising to  $\pm 0.5$  at 2000 K.

#### Comments on Preferred Values

The only direct measurement of the rate constant for any channel of this reaction is that of Fagerström *et al.*<sup>1</sup> for Channel (1). This is rather higher than the upper limit obtained by Diau *et al.*<sup>4</sup> and lower than that of Cheskis and Sarkisov,<sup>5</sup> both obtained indirectly. The value of Fagerström *et al.*<sup>1</sup> is accepted as the preferred value for  $k_1$  but, in the absence of confirmatory studies and any information on the pressure dependence of  $k_1$ , substantial error limits are assigned.

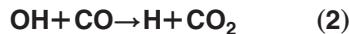
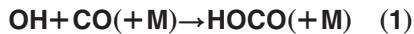
As the temperature is increased the decomposition of the hydroxylamine will become important but insufficient information is available to assess this quantitatively. Dean and Bozzelli<sup>6</sup> have used QRRK theory to analyze the addition process and have made theoretical estimates of the rate constant for H<sub>2</sub>O + NH formation by H abstraction. They conclude that at temperatures greater than ~1000 K the abstraction reaction predominates. The expression they derive for the abstraction reaction,  $k(\text{NH} + \text{H}_2\text{O}) = 4.0 \cdot 10^{-18} T^2 \times \exp(-25/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , gives values in reasonable agreement with the value obtained indirectly by Kimball-Linne and Hanson<sup>7</sup> in a flow reactor study at temperatures in the range 1050–1400 K.

The rate constant for Channel (3) is obtained from the reasonably reliable data for the reverse rate constant (this evaluation) and the thermodynamic data. The same procedure cannot be used to obtain values of  $k_2$  as the reaction of NH with H<sub>2</sub>O appears to proceed predominantly by a different channel.

## References

- <sup>1</sup>K. Fagerström, J. T. Jodkowski, A. Lund, and E. Ratajczak, Chem. Phys. Lett. **236**, 103 (1995).  
<sup>2</sup>N. Cohen and K. R. Westberg, J. Phys. Chem. Ref. Data **20**, 1211 (1991).  
<sup>3</sup>CEC, 1992; Supplement I, 1994 (see references in Introduction).

- <sup>4</sup>E. W.-G. Diau, T.-L. Tso, and Y.-P. Lee, J. Phys. Chem. **94**, 5261 (1990).  
<sup>5</sup>S. G. Cheskis and O. M. Sarkisov, Chem. Phys. Lett. **67**, 72 (1979).  
<sup>6</sup>A. M. Dean and J. W. Bozzelli, in *Combustion Chemistry II*, edited by W. C. Gardiner, Jr. (Springer, New York, 2001).  
<sup>7</sup>M. A. Kimball-Linne and R. K. Hanson, Combust. Flame **64**, 337 (1986).



## Thermodynamic Data

$$\begin{aligned}\Delta H^\circ_{298}(1) &= -129 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(1) &= -124 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 8.9 \cdot 10^{-26} T^{-0.2} \exp(+15680/T) \text{ cm}^3 \text{ molecule}^{-1} \\ (300 \leq T/K \leq 5000) &\end{aligned}$$

$$\begin{aligned}\Delta H^\circ_{298}(2) &= -102.2 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(2) &= -52.9 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 4.72 \cdot 10^{-7} T^{1.163} \exp(+12760/T) \\ (300 \leq T/K \leq 5000) &\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
<i>Low Pressure Range</i>			
$(1.44 \pm 0.15) \cdot 10^{-13}$	298	Greenblatt and Howard, 1989 <sup>1</sup>	(a)
$(1.0 \pm 0.1) \cdot 10^{-13}$	83	Frost, Sharkey, and Smith, 1993 <sup>2</sup>	(b)
$(1.05 \pm 0.15) \cdot 10^{-13}$	106		
$(2.0 \pm 0.35) \cdot 10^{-13}$	138		
$(1.8 \pm 0.05) \cdot 10^{-13}$	178		
$(1.78 \pm 0.05) \cdot 10^{-13}$	216		
$(1.7 \pm 0.2) \cdot 10^{-13}$	297		
$3.52 \cdot 10^{-12} \exp(-2630/T)$	1090–2370	Wooldridge, Hanson, and Bowman, 1994 <sup>3</sup>	(c)
$5.5 \cdot 10^{-18} T^{1.55} \exp(+402/T)$	300–3150	Lissianski <i>et al.</i> , 1995 <sup>4</sup>	(d)
$1.3 \cdot 10^{-13}$	298	Forster <i>et al.</i> , 1995 <sup>5</sup>	(e)
$4.17 \cdot 10^{-13}$	1155	Wooldridge, Hanson, and Bowman, 1996 <sup>6</sup>	(f)
$4.58 \cdot 10^{-13}$	1205		
$4.33 \cdot 10^{-13}$	1343		
$5.11 \cdot 10^{-13}$	1432		
$1.8 \cdot 10^{-12} \exp(-2720/T) + 1.6 \cdot 10^{-13} \exp(-60/T)$	80–900	Fulle <i>et al.</i> , 1996 <sup>7</sup>	(g)
$7.9 \cdot 10^{-17} T^{1.228} \exp(-35/T)$	1400–2600	Golden <i>et al.</i> , 1998 <sup>8</sup>	(h)
$1.6 \cdot 10^{-13}$	298		
<i>High Pressure Range</i>			
$9.7 \cdot 10^{-13}$	298	Forster <i>et al.</i> , 1995 <sup>5</sup>	(e)
$1.8 \cdot 10^{-11} \exp(-1847/T) + 1.6 \cdot 10^{-12} \exp(-135/T)$	90–819	Fulle <i>et al.</i> , 1996 <sup>7</sup>	(g)
<i>Reviews and Evaluations</i>			
$1.05 \cdot 10^{-17} T^{1.5} \exp(+250/T)$	300–2000	CEC; 1992, 1994 <sup>9</sup>	(i)
$k(P) = 1.5 \cdot 10^{-13} (1 + 0.6 P/\text{bar})$	200–300	NASA, 1997 <sup>10</sup>	(j)
$1.3 \cdot 10^{-13} [1 + (0.6 P/\text{bar})(300/T)^{1.0}]$	200–300	IUPAC, 1997 <sup>11</sup>	(k)
$k_0[\text{N}_2] = [\text{N}_2] 1.67 \cdot 10^{-11} \exp(-8050/T) + 1.50 \cdot 10^{-12}$	80–3000	Troe, 1998 <sup>12</sup>	(l)
$\exp(-2300/T) + 1.68 \cdot 10^{-13} \exp(-30/T)$	80–3000		
$k_\infty = 2.04 \cdot 10^{-9} \exp(-7520/T) + 1.83 \cdot 10^{-11} \exp(-1850/T)$	80–1000		
$+ 1.33 \cdot 10^{-12} \exp(-120/T)$	80–1000		
$k(P) = k_0 \{1 + [3.2P(\text{N}_2)/\text{bar}] \exp(-T/161)\}$	80–800		

## Comments

- (a) Discharge-flow study. Oxygen atoms were generated in the reactions  $\text{H} + \text{NO}_2$  or  $\text{F} + \text{H}_2\text{O}$ . O atom exchange

between  $^{18}\text{OH}$  and CO measured by laser magnetic resonance of reagent  $^{18}\text{OH}$  and product  $^{16}\text{OH}$ . Pressure range was 1.3–3.3 mbar.

- (b) Laser photolysis of  $\text{HNO}_3$  with laser induced fluores-

- cence detection of OH. Experiments conducted over the pressure range 2.6–13 mbar with Ar or N<sub>2</sub> bath gas. Modeling calculations using transition state and RRKM theories with inclusion of tunneling through the transition state.
- (c) Shock wave study of mixtures of HNO<sub>3</sub>/CO/Ar at pressures ranging between 0.19 and 0.82 bar. [OH] decay monitored by UV absorption. Rate coefficients extrapolated from a mechanism with 16 reactions.
  - (d) Shock wave study of the reaction H+CO<sub>2</sub>→OH+CO. [OH] decay monitored by absorption at 309.4 nm in N<sub>2</sub>O/H<sub>2</sub>/CO<sub>2</sub> mixtures and in ignition of CH<sub>4</sub>/O<sub>2</sub>/CO<sub>2</sub> mixtures. Rate coefficient expression obtained via the equilibrium constant and including a room temperature rate coefficient of 1.5·10<sup>-13</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and the high temperature results of Wooldridge, Hanson, and Bowman<sup>3</sup> and Yu, Wang, and Frenklach.<sup>12</sup>
  - (e) Laser flash photolysis experiments at pressures up to 150 bar He. OH generated by photolysis of N<sub>2</sub>O and the subsequent reaction of O(<sup>1</sup>D) with H<sub>2</sub>O. Detection of OH radicals by saturated laser induced fluorescence. The pressure dependence is expressed for the reactions OH+CO→HOCO\*→H+CO<sub>2</sub> and HOCO\*(+M)→HOCO(+M) and is given in analytical form.
  - (f) Kinetic study of HNO<sub>3</sub>/CO/Ar mixtures in incident shock waves. Simultaneous detection of OH and CO<sub>2</sub> by absorption at 306.7 nm and 4.2 μm, respectively. Observed concentration profiles interpreted by modeling with a mechanism comprising 16 reactions.
  - (g) Laser flash photolysis experiments between 1 and 700 bar He. Detection of OH radicals by saturated laser induced fluorescence. The data were represented with statistical unimolecular rate theory and expressed in analytical form. From experiments performed between 600 and 900 K, a reaction enthalpy of formation for the adduct HOCO ΔH<sub>r</sub><sup>0</sup>(OH+CO→HOCO)=−129±10 kJ mol<sup>−1</sup> at 0 K was determined.
  - (h) A laser photolysis/cw laser-induced fluorescence technique was employed at 293 K. OH was generated by the reaction of O(<sup>1</sup>D), formed by 193 nm photolysis of N<sub>2</sub>O, with H<sub>2</sub>O. The high temperature rate expression was derived from the reverse H+CO<sub>2</sub> reaction studied in a shock tube. HO and CO were monitored by laser absorption. A two-channel RRKM model of these and other results with five adjustable parameters was used to derive a general expression.
  - (i) The preferred value is compatible with flame simulations which are sensitive to the rate of this reaction.
  - (j) Weighted average of earlier data for M=N<sub>2</sub> at pressures below 1 bar.
  - (k) Evaluation of literature data. The equation reproduces the rate coefficients measured in the pressure range 0–1 bar of N<sub>2</sub> or air.
  - (l) Re-evaluation of the data of Ref. 7 and earlier literature data by detailed unimolecular rate modeling including multistep collisional energy transfer. Pressure dependent

dence of  $k$  near to the low pressure limit represented by  $k(P)=k_0[1+A_0 \exp(-T/T^*)P]$  with  $T^*=161$  K and  $A_0=2.0$ , 2.8, and 3.2 bar<sup>−1</sup> for M=He, Ar, and N<sub>2</sub>, respectively. The full pressure-dependent transition of  $k$  from  $k_0$  to  $k_\infty$  is expressed analytically by a more complicated expression; see Ref. 12.

### Preferred Values

$$k_0=[1.67 \cdot 10^{-11} \exp(-8050/T) + 1.50 \cdot 10^{-12} \exp(-2300/T) + 1.68 \cdot 10^{-13} \exp(-30/T)] \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

for M=N<sub>2</sub> over the range 80–3000 K.

$$k_\infty=[2.04 \cdot 10^{-9} \exp(-7520/T) + 1.83 \cdot 10^{-11} \exp(-1850/T) + 1.33 \cdot 10^{-12} \exp(-120/T)] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the range 80–1000 K.

$$k(P)=k_0[1+3.2(P/\text{bar})\exp(-T/161)]$$

for M=N<sub>2</sub> over the range 80–800 K.

### Reliability

$$\Delta \log k_0=\pm 0.1$$

for M=N<sub>2</sub> over the range 80–3000 K.

$$\Delta \log k_\infty=\pm 0.1$$

over the range 80–1000 K.

$$\Delta \log k(P)=\pm 0.1$$

for M=N<sub>2</sub> over the range 80–800 K.

### Comments on Preferred Values

The mechanism of the reaction of OH with CO proceeds via the formation of the HOCO radical intermediate as follows:



The energized intermediate HOCO may undergo decomposition back to the reactants or to the products H+CO<sub>2</sub> [Channel (2)] and, at sufficiently high gas densities, it may be collisionally stabilized [Channel (1)]. In this case, subsequent reactions of HOCO need to be considered. In addition, at high temperatures, collisionally stabilized HOCO may re-dissociate into OH+CO or H+CO<sub>2</sub> as is evident in nonexponential decays of [OH] in the presence of an excess of CO.<sup>7</sup> As a consequence both  $k_1$  and  $k_2$  are pressure dependent. The overall rate constant for OH removal ( $k$ ) is also pressure dependent and is given by  $k=(k_1+k_2)$ . [It should be noted that  $k$  does not include thermal redissociation of HOCO into OH+CO, which could be expressed in terms of  $k_1$ ,  $k_2$ ,  $K_c(1)$ , and  $K_c(2)$ .]

Preferred values are presented for  $k_0$  and  $k_\infty$ . At the high pressure limit HOCO will be the exclusive product and  $k_\infty=k_1$  (as [M]→∞). At lower pressures stabilization of the HOCO becomes negligible and the limiting low pressure rate constant,  $k_0$ , corresponds to the low pressure limiting rate constant for H+CO<sub>2</sub> formation, i.e.,  $k_0=k_2$  (as [M]→0). The pressure dependence between these extremes is complex and the papers of Fulle *et al.*<sup>7</sup> and Troe<sup>12</sup> should be consulted for a detailed account. However, a parameterized representation of the overall rate constant as a function of pressure has been derived for M=N<sub>2</sub> over a limited temperature range and is presented as  $k(P)$  in the Preferred Values.

The experiments of Greenblatt and Howard,<sup>1</sup> Frost, Sharkey, and Smith,<sup>2</sup> Wooldridge, Hanson, and Bowman,<sup>3,6</sup> Lissianski *et al.*,<sup>4</sup> Forster *et al.*,<sup>5</sup> Fulle, Hamann, and Hippler,<sup>7</sup> and Golden *et al.*<sup>8</sup> provide reliable rate coefficients over a very wide range of conditions. The data can be well represented in terms of unimolecular reaction rate theory; see Refs. 7, 8, and 12. We adopt here the most detailed analysis, that of Ref. 12, which provides a very good representation of all available experimental data over the wide range of temperatures and pressures studied.

The partitioning of  $k$  into  $k_1$  and  $k_2$  has been described in Refs. 7 and 12. Following Ref. 12, one has  $k_1 = k(P)(1+y)F(x)/(1+x)$  and  $k_2 = k_0[1 + (1-y)F(x)]$ , where  $x = k(P)/(k_\infty - k_0)$ ,  $y = k_0/(k_\infty - k_0)$ , and  $F$  is the broadening factor (see Introduction, Secs. 2.4, 2.5) with  $F_c = 0.49 + 0.51 \exp(-T/300)$ .  $k_0$ ,  $k_\infty$ , and  $k(P)$  are given as preferred values and the complicated dependence of  $k$  on temperature and pressure is discussed in more detail in Refs. 7 and 12, and using a selection of the available data<sup>1–3,6,7,13–15</sup> is illustrated in Figs. 1 and 2.

## References

- <sup>1</sup>G. D. Greenblatt and C. J. Howard, *J. Phys. Chem.* **93**, 1035 (1989).
- <sup>2</sup>M. J. Frost, P. Sharkey, and I. W. M. Smith, *J. Phys. Chem.* **97**, 12254 (1993).
- <sup>3</sup>M. S. Wooldridge, R. K. Hanson, and C. T. Bowman, 25th Symp. (Int.) Combustion, 1994, p. 741.
- <sup>4</sup>V. Lissianski, H. Yang, Z. Qin, M. R. Mueller, K. S. Shin, and W. C. Gardiner, Jr., *Chem. Phys. Lett.* **240**, 57 (1995).
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- <sup>6</sup>M. S. Wooldridge, R. K. Hanson, and C. T. Bowman, *Int. J. Chem. Kinet.* **28**, 361 (1996).
- <sup>7</sup>D. Fulle, H. F. Hamann, H. Hippler, and J. Troe, *J. Chem. Phys.* **105**, 983 (1996).
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- <sup>9</sup>CEC, 1992; CEC, Supplement I, 1994 (see references in Introduction).
- <sup>10</sup>NASA Evaluation No.12 (see references in Introduction).
- <sup>11</sup>IUPAC, Supplement V (see references in Introduction).
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- <sup>13</sup>A. R. Ravishankara and R. L. Thompson, *Chem. Phys. Lett.* **99**, 377 (1983).
- <sup>14</sup>C. D. Jonah, W. A. Mulac, and P. J. Zelinski, *J. Phys. Chem.* **88**, 4100 (1984); M. F. Beno, C. D. Jonah, and W. A. Mulac, *Int. J. Chem. Kinet.* **17**, 1090 (1985).
- <sup>15</sup>G. D. Greenblatt and C. J. Howard, *J. Chem. Phys.* **93**, 1035 (1989).

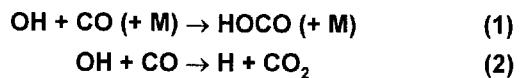


Fig. 1

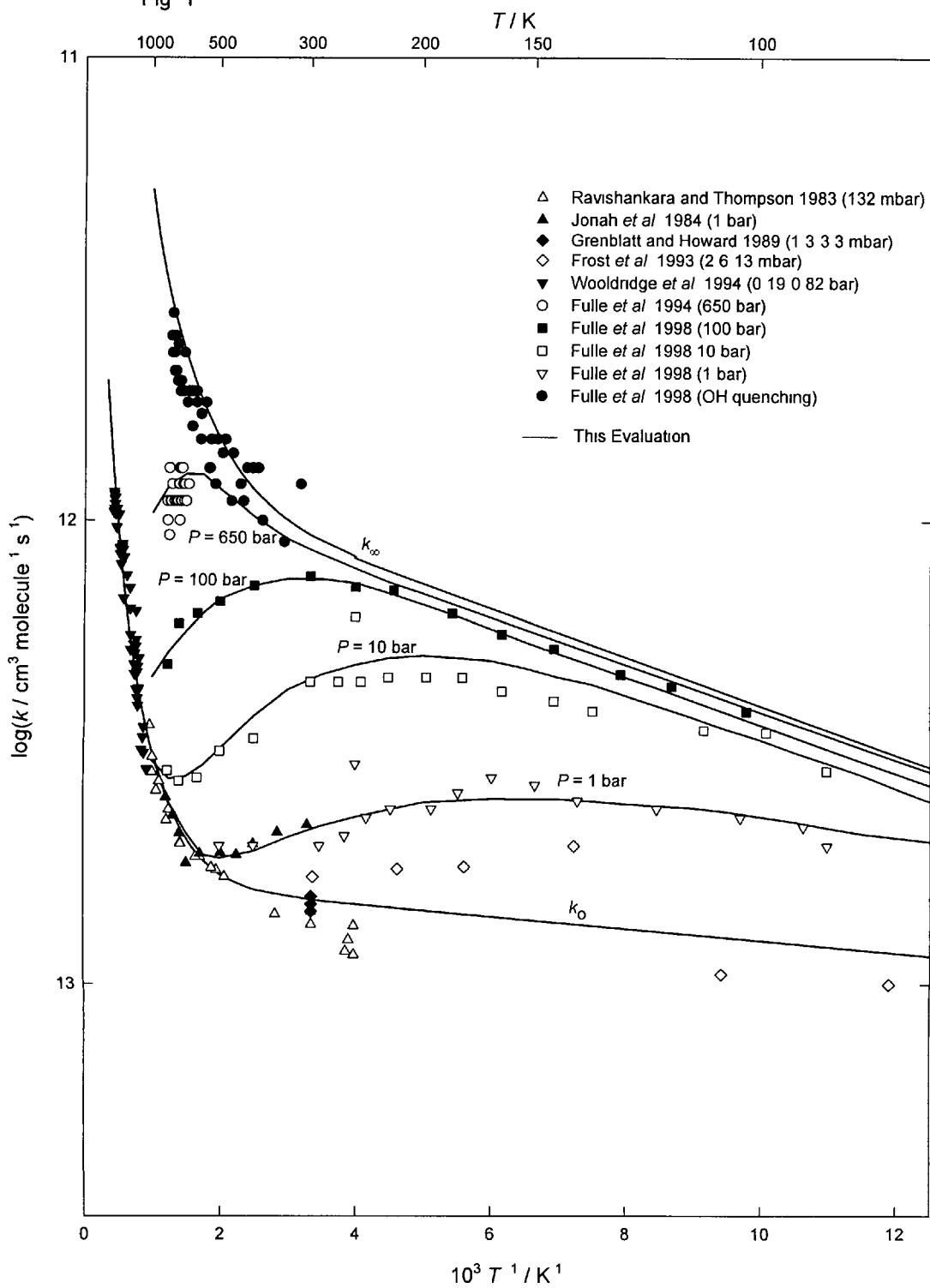
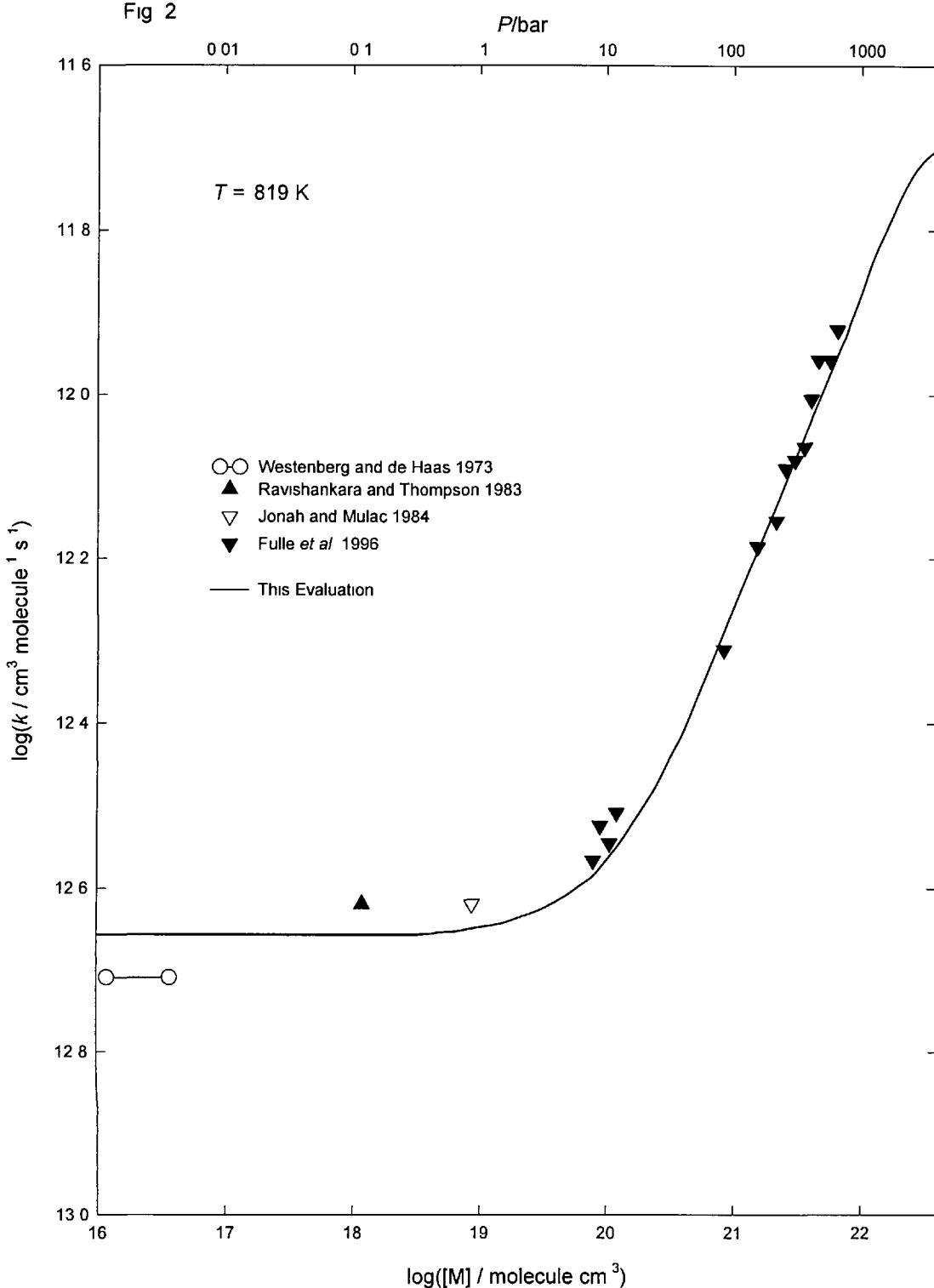
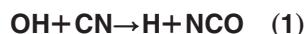




Fig 2





#### Thermodynamic Data

$$\begin{aligned}\Delta H_{298}^{\circ}(1) &= -127.6 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ}(1) &= -39.14 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 3.33 \cdot 10^{-6} T^{1.149} \exp(+15730/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

$$\begin{aligned}\Delta H_{298}^{\circ}(2) &= -88.7 \text{ J mol}^{-1} \\ \Delta S_{298}^{\circ}(2) &= -23.48 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 4.37 \cdot 10^{-4} T^{0.696} \exp(+10900/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Reviews and Evaluations</i>			
$1.0 \cdot 10^{-10}$	2300–2600	Morley, 1976 <sup>1</sup>	(a)
$9.5 \cdot 10^{-11}$	1950–2380	Haynes, 1977 <sup>2</sup>	(b)
$k_1 = 6.64 \cdot 10^{-11}$	1250–1863	Wooldridge, Hanson, and Bowman, 1996 <sup>3</sup>	(c)
<i>Reviews and Evaluations</i>			
$k_1 = 7 \cdot 10^{-11}$	1950–2840	Tsang, 1992 <sup>4</sup>	(d)
$k_2 = 1 \cdot 10^{-11} \exp(-1000/T)$			
$1.0 \cdot 10^{-10}$	1500–3000	CEC, 1992; 1994 <sup>5</sup>	(e)

#### Comments

- (a) Product concentration profiles (HCN, NH<sub>3</sub>, NO) in hydrocarbon/O<sub>2</sub> flames containing small additions of CH<sub>3</sub>CN and pyridine were determined by quadrupole mass spectrometry. Equilibrium between CN and HCN was assumed and the value of  $k$  was calculated from the [HCN] profile.
- (b) Study on premixed hydrocarbon/O<sub>2</sub> flames containing small additions of NH<sub>3</sub>, NO, or pyridine. Samples were removed by a water-cooled silica probe for analysis by infrared spectrophotometry (for [NO]), and absorption in NaOH for analysis of CN and NH species by ion selective electrodes. [H] was monitored by the Li/LiOH technique.
- (c) Shock tube study using HNO<sub>3</sub> (58–279 ppm)/HCN (573–843 ppm)/Ar mixtures at total pressures in the range 200–360 mbar. CN was generated by the OH + CN reaction. [CN] and [OH] were monitored by time resolved narrow line absorption.
- (d) Based on the data of Haynes<sup>2</sup> and Morley.<sup>1</sup>
- (e) Suggests that the main reaction channel is Channel (1) but values of Haynes<sup>2</sup> and of Morley<sup>1</sup> are upper limits and  $k_1$  is set slightly lower. Expression for  $k_2$  is based on the analogous reactions CN+HCl and CN+NH<sub>3</sub>.

#### Preferred Values

$k_1 = 6.7 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 1250–3000 K.

$k_2 = 1 \cdot 10^{-11} \exp(-1000/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 1250–3000 K.

#### Reliability

$\Delta \log k = \pm 0.2$  over the range 1250–3000 K.  
 $\Delta \log k = \pm 0.6$  over the range 1250–3000 K.

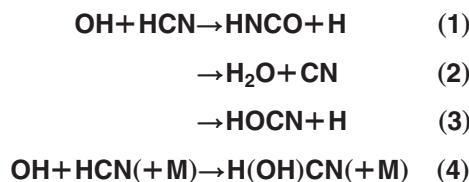
#### Comments on Preferred Values

Tsang<sup>4</sup> has suggested that Channel (1) should be the major channel at high temperatures and normal pressures and the recent study of Wooldridge *et al.*<sup>3</sup> supports this. The value of  $k_1$  obtained by Wooldridge *et al.*<sup>3</sup> is adopted as the preferred value. This channel is presumed to occur by formation of HOCH followed by its decomposition. Other products are possible and at very high pressures the HOCH may be stabilized but there is no information on these alternatives.

The reaction may also proceed by abstraction [Channel (2)]. Tsang's estimate<sup>4</sup> of  $k_2$  is adopted as the preferred value for  $k_2$  but with substantial error limits. On this basis [Channel (2)] only contributes a few percent to the overall reaction but Wooldridge *et al.*<sup>3</sup> have derived a value based on recommendations of Miller and Bowman<sup>6</sup> which assign it a larger activation energy and hence a larger contribution at the highest temperatures of the recommended range.

#### References

- <sup>1</sup> C. Morley, Combust. Flame **27**, 189 (1976).
- <sup>2</sup> B. S. Haynes, Combust. Flame **28**, 113 (1977).
- <sup>3</sup> S. T. Wooldridge, R. K. Hanson, and C. T. Bowman, Int. J. Chem. Kinet. **28**, 245 (1996).
- <sup>4</sup> W. Tsang, J. Phys. Chem. Ref. Data **21**, 753 (1992).
- <sup>5</sup> CEC, 1992; Supplement I, 1994 (see references in Introduction).
- <sup>6</sup> J. Miller and C. T. Bowman, Prog. Energy Combust. Sci. **15**, 287 (1992).

*Thermodynamic Data*

$$\begin{aligned}\Delta H^\circ_{298}(1) &= -70.3 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(1) &= -32.14 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 1.18 \cdot 10^{-4} T^{0.753} \exp(+8720/T) \\ &(300 \leq T/\text{K} \leq 4000)\end{aligned}$$

$$\begin{aligned}\Delta H^\circ_{298}(2) &= 21.34 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(2) &= 5.89 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 76.9 T^{-0.557} \exp(-2690/T) \\ &(300 \leq T/\text{K} \leq 5000)\end{aligned}$$

$$\begin{aligned}\Delta H^\circ_{298}(3) &= 36.8 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(3) &= -23.0 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(3) &= 1.35 \cdot 10^{-2} T^{0.218} \exp(-4330/T) \\ &(300 \leq T/\text{K} \leq 4000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data ( $k = k_1 + k_2 + k_3 + k_4$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$k_2 = 3.31 \cdot 10^{-11} \exp(-7554/T)$	1666–2300	Kanamaru and Daito, 1977 <sup>1</sup>	(a)
$k_2 = 1 \cdot 10^{-12}$	1800–2500	Roth, Löhr, and Hermanns, 1980 <sup>2</sup> .	(b)
$k_2 = 6.5 \cdot 10^{-18} T^{1.83} \exp(-5179/T)$	500–2000	Wooldridge, Hanson, and Bowman, 1995 <sup>3</sup>	(c)
<i>Reviews and Evaluations</i>			
$k_1 = 9.3 \cdot 10^{-30} T^{4.71} \exp(248/T)$	298–2500	Tsang and Herron, 1991 <sup>4</sup>	(d)
$k_2 = 3.6 \cdot 10^{-17} T^{1.5} \exp(-3887/T)$			
$k_3 = 5.3 \cdot 10^{-20} T^{2.45} \exp(-6100/T)$			
$k_2 = 1.5 \cdot 10^{-11} \exp(-5400/T)$	1500–2500	CEC, 1992; 1994 <sup>5</sup>	(e)
$1.2 \cdot 10^{-13} \exp(-400/T)$	200–300	NASA, 1997 <sup>6</sup>	(f)
$1.2 \cdot 10^{-13} \exp(-400/T)$ (at 1 bar)	290–440	IUPAC, 1997 <sup>7</sup>	(f)

**Comments**

- (a) Shock tube study; no experimental details given.
- (b) Shock tube study of Ar/HCN/N<sub>2</sub>O mixtures. [H] and [O] monitored by resonance absorption at 121.6 nm and 130.5 nm, respectively. [H] and [O] profiles fitted to 8-reaction mechanism but fit not very sensitive to  $k$ .
- (c) Shock tube study on HNO<sub>3</sub>/HCN/Ar mixtures at pressures in the range 0.1–1 bar. OH generated by the thermal decomposition of HNO<sub>3</sub> (10–280 ppm) in an excess of HCN (600–10000 ppm). [CN] and [OH] monitored by time-resolved laser absorption. Overall  $k$  deduced from the [OH] measurements and  $k_2$  from [OH] and [CN] determinations. The measurements were made over the range 1120–1960 K but the cited expression for  $k_2$  was extended to 500 K by use of data on the reverse reaction<sup>14</sup> and the thermochemistry, which had to be adjusted slightly to bring the data on forward and reverse rate constants into agreement with thermodynamic data.
- (d) Expression for  $k_2$  based on the data of Szekely *et al.*<sup>8</sup> for the reverse reaction together with the thermodynamics and an assumed  $T^{1.5}$  dependence of the pre-

exponential factor. The expressions for  $k_1$  and  $k_3$  are based on theoretical calculations of Miller and Melius.<sup>9</sup>

- (e) Based on data for the reverse reaction and the thermodynamics of the reaction.
- (f) Accepts the value of  $k_4^\infty$  obtained by Fritz *et al.*<sup>10,11</sup>

**Preferred Values**

$$k_2 = 6.5 \cdot 10^{-18} T^{1.83} \exp(-5180/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the range 500–2500 K.

$$k_2/k > 0.5 \text{ for } T > 1500 \text{ K.}$$

**Reliability**

$$\Delta \log k_2 = \pm 0.2 \text{ over the range 1000–2500 K, rising to} \pm 0.5 \text{ at 500 K.}$$

$$\Delta(k_2/k) = \pm 0.2 \text{ for } T > 1500 \text{ K.}$$

**Comments on Preferred Values**

The shock tube study of Wooldridge *et al.*<sup>3</sup> suggests that the only significant reaction channel at temperatures above 1200 K is Channel (2). The preferred expression for  $k_2$  is that obtained by Wooldridge *et al.*<sup>3</sup> which agrees well with the shock tube studies of Kanamaru and Daito<sup>1</sup> and of Roth

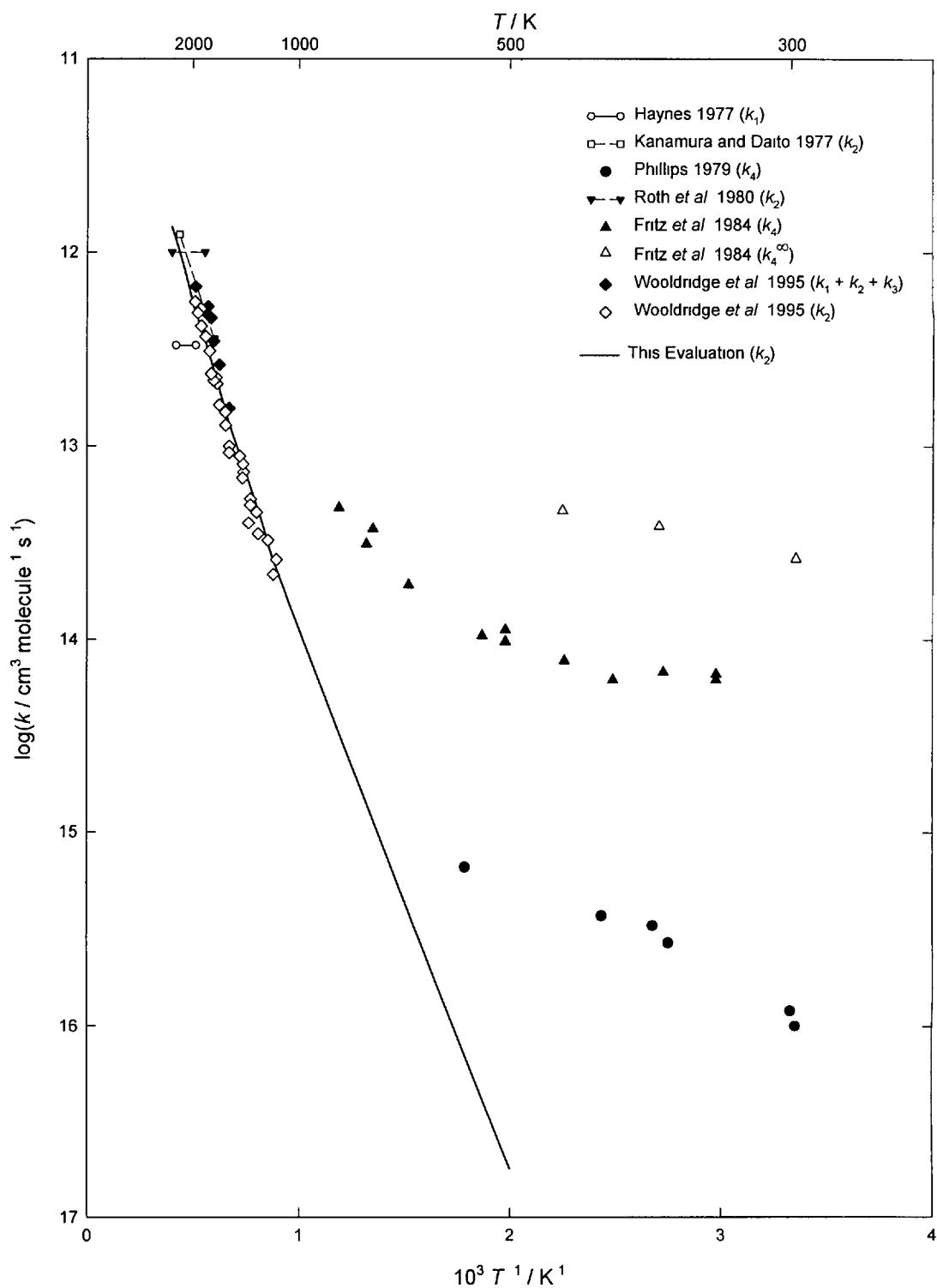
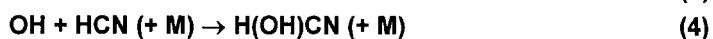
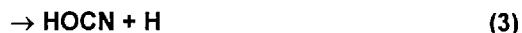
*et al.*<sup>2</sup> and with the flame study of Haynes.<sup>12</sup> There are no experimental data on  $k_1$  and  $k_3$ . The calculations of Miller and Melius,<sup>9</sup> recommended by Tsang and Herron,<sup>4</sup> offer a rough guide to the high temperature behavior although their calculations are not compatible with the low temperature results because they did not consider possible stabilization of the adduct [Channel (4)]. However, these calculations,<sup>9</sup> when taken together with the data of Wooldridge *et al.*, suggest a value of  $k_2/k > 0.5$  for  $T > 1500$  K, which we take as our recommendation for the branching ratio.

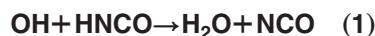
The situation at lower temperatures is less certain. The studies of both Phillips<sup>13</sup> and Fritz *et al.*<sup>10</sup> report a pressure dependent rate constant suggesting formation of a stabilized adduct [Channel (4)]. However, the values of  $k$  obtained in the studies of Fritz *et al.*<sup>10</sup> and Phillips<sup>13</sup> differ by factor of  $\sim 3$ . The results of Fritz *et al.*<sup>10</sup> give rise to the following Troe expressions for Channel (4):<sup>11</sup>  $k_4^\infty = 1.16 \cdot 10^{-13} \times \exp(-400/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ;  $k_4^0 = 1.5 \cdot 10^{-31} \times \exp(-875/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ ;  $F_c \sim 0.8$ . Fritz *et al.*<sup>10</sup> also see a strong increase in  $k$  at temperatures above 500 K, which they interpret as being due to the onset of Channel (2), but at 860 K, the highest temperature studied by them, the value of  $k$  obtained is higher than the value of  $k_2$  obtained by Wooldridge *et al.*<sup>3</sup> at  $\sim 1200$  K which may imply that be-

tween 860 K and 1200 K the addition reaction is reversed. Further studies are needed in this temperature regime to clarify the relation between the high and low temperature kinetics.

## References

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- <sup>6</sup>NASA Evaluation No. 12, 1997 (see references in Introduction).
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- <sup>10</sup>B. Fritz, K. Lorenz, W. Steinert, and R. Zellner, Oxidat. Commun. **6**, 353 (1984).
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#### Thermodynamic Data

$$\begin{aligned}\Delta H^\circ_{298}(1) &= -36.0 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(1) &= -1.51 \text{ J K}^{-1} \text{ mol}^{-1} \\ K(1) &= 6.00 T^{-0.291} \exp(+4230/T) \\ &(300 \leq T/\text{K} \leq 5000)\end{aligned}$$

$$\begin{aligned}\Delta H^\circ_{298}(2) &= -125.2 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(2) &= -14.13 \text{ J K}^{-1} \text{ mol}^{-1} \\ K(2) &= 3.53 \cdot 10^{-1} T^{-0.146} \exp(+15120/T) \\ &(300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$4.4 \cdot 10^{-12} \exp(-2788/T)$	624–875	Tully <i>et al.</i> , 1989 <sup>1</sup>	(a)
$\leq 2.5 \cdot 10^{-12}$	2120–2350	Mertens <i>et al.</i> , 1991 <sup>2</sup>	(b)
$6.03 \cdot 10^{-17} T^{1.5} \exp(-1809/T)$	620–1860	Wooldridge <i>et al.</i> , 1995 <sup>3</sup>	(c)
<i>Reviews and Evaluations</i>			
$k_1 = 1.06 \cdot 10^{-18} T^2 \exp(-1290/T)$	295–2500	Tsang, 1992 <sup>4</sup>	(d)

#### Comments

- (a) Pulsed laser photolysis at 193 nm of N<sub>2</sub>O/H<sub>2</sub>O/HNCO/He mixtures in a slow flow reactor at a pressure of 1 bar. [OH] monitored by time-resolved laser-induced fluorescence at 308 nm. The overall rate coefficient was determined from a pseudo-first order analysis of the decay of [OH].
- (b) Shock tube study using HNCO/N<sub>2</sub>O/Ar mixtures at total pressures in the range 0.4–1.0 bar. [OH] monitored by time-resolved laser absorption at 306.6 nm. An upper limit on the overall rate coefficient was obtained by computer simulation of the [OH] profiles using a detailed mechanism.
- (c) Shock tube study using HNCO/HNO<sub>3</sub>/Ar mixtures at total pressures in the range 0.2–0.4 bar and for temperatures from 1244 to 1858 K. [OH] monitored by time-resolved laser absorption at 306.6 nm. [CO<sub>2</sub>] monitored by time-resolved infrared laser absorption at 4.2 μm. Values of rate coefficients and product branching ratios,  $k_2/k$ , obtained by computer simulation of [OH] and [CO<sub>2</sub>] profiles using a detailed mechanism. The rate expression is a fit to the high-temperature shock tube data of Wooldridge *et al.*<sup>3</sup> and the lower temperature data of Tully *et al.*<sup>1</sup>
- (d) Assumes that the abstraction channel, (1), is the dominant channel and extrapolates the data of Tully *et al.*<sup>1</sup> using a standard  $T^2$  dependence for the pre-exponential factor by analogy with other OH reactions.

#### Preferred Values

$$k = 6.03 \cdot 10^{-17} T^{1.5} \exp(-1809/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the range 600–2300 K.

#### Reliability

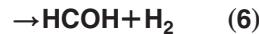
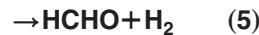
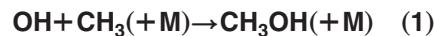
$$\Delta \log k = \pm 0.15 \text{ over the range 600–2300 K.}$$

#### Comments on Preferred Values

The preferred expression for  $k (= k_1 + k_2)$  is that reported by Wooldridge *et al.*<sup>3</sup> that was obtained by fitting their data and the lower temperature data of Tully *et al.*<sup>1</sup> The preferred expression is in very good agreement with the extrapolation of Tsang<sup>4</sup> for  $k_1$ . Wooldridge *et al.*<sup>3</sup> determined an upper limit on the branching ratio of  $k_2/k < 0.1$ , in the temperature range 1250–1860 K, consistent with Tully *et al.*<sup>1</sup> and with Tsang<sup>4</sup> who argued that the dominant product channel is reaction (1).

#### References

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- <sup>2</sup>J. D. Mertens, A. Y. Chang, R. K. Hanson, and C. T. Bowman, Int. J. Chem. Kinet. **24**, 279 (1992).
- <sup>3</sup>M. S. Wooldridge, R. K. Hanson, and C. T. Bowman, Int. J. Chem. Kinet. **28**, 361 (1996).
- <sup>4</sup>W. Tsang, J. Phys. Chem. Ref. Data **21**, 753 (1992).



#### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = -385.0 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = -137.96 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 3.19 \cdot 10^{-30} T^{0.942} \exp(+46760/T) \text{ cm}^3 \text{ molecule}^{-1}$$

(300 ≤ T/K ≤ 5000)

$$\Delta H^\circ_{298}(2) = 2.99 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = -0.16 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 20.6 \cdot T^{-0.442} \exp(-519/T)$$

(300 ≤ T/K ≤ 4000)

$$\Delta H^\circ_{298}(3) = 16.67 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = -19.18 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 3.61 \cdot 10^{-4} T^{0.815} \exp(-1714/T)$$

(300 ≤ T/K ≤ 5000)

$$\Delta H^\circ_{298}(4) = 51.67 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(4) = -33.70 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(4) = 3.67 \cdot 10^{-6} T^{1.171} \exp(-5660/T)$$

(300 ≤ T/K ≤ 5000)

$$\Delta H^\circ_{298}(5) = -292.1 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(5) = -28.43 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(5) = 7.89 \cdot 10^{-3} T^{0.174} \exp(+35270/T)$$

(300 ≤ T/K ≤ 5000)

$$\Delta H^\circ_{298}(6) = 22.69 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(6) = -6.99 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(6) = 3.95 \cdot 10^{14} T^{-4.962} \exp(-4620/T)$$

(300 ≤ T/K ≤ 5000)

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2 + k_3 + k_4 + k_5 + k_6$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	[M]/molecule $\text{cm}^{-3}$	Reference	Comments
<i>Rate Coefficient Measurements</i>				
$9.3 \cdot 10^{-11}$	296	$2.5 \cdot 10^{10} (\text{N}_2, \text{H}_2)$	Sworski, Hochanadel, and Ogren, 1980 <sup>1</sup>	(a)
$9.4 \cdot 10^{-11}$	298	$2.5 \cdot 10^{10} (\text{Ar} + \text{SF}_6)$	Anastasi <i>et al.</i> , 1991 <sup>2</sup>	(b)
$1.4 \cdot 10^{-11}$	1200	$5.7 \cdot 10^{18} (\text{Ar})$	Bott and Cohen, 1991 <sup>3</sup>	(c)
$8.0 \cdot 10^{-12}$	300	$7.2 \cdot 10^{15} (\text{He})$	Oser <i>et al.</i> , 1992 <sup>4</sup>	(d)
$2.2 \cdot 10^{-11}$		$2.7 \cdot 10^{16}$		
$6.0 \cdot 10^{-11}$		$1.5 \cdot 10^{17}$		
$1.2 \cdot 10^{-11}$	480	$1.6 \cdot 10^{16} (\text{He})$	Oser <i>et al.</i> , 1992 <sup>5</sup>	(d)
$2.2 \cdot 10^{-11}$		$3.8 \cdot 10^{16}$		
$4.4 \cdot 10^{-11}$		$1.4 \cdot 10^{17}$		
$7.6 \cdot 10^{-11}$	290	$(2.5-230) \cdot 10^{17} (\text{He})$	Hughes, Pereira, and Pilling, 1992 <sup>6</sup>	(e)
$9.7 \cdot 10^{-11}$	298	$2.1 \cdot 10^{18} (\text{SF}_6)$	Fagerström <i>et al.</i> , 1993 <sup>7</sup>	(b)
$1.00 \cdot 10^{-10}$		$4.2 \cdot 10^{18}$		
$1.22 \cdot 10^{-10}$		$1.23 \cdot 10^{19}$		
$1.30 \cdot 10^{-10}$		$2.46 \cdot 10^{19}$		
$(1.24-1.33) \cdot 10^{-10}$	283	$(2.2-25.9) \cdot 10^{18} (\text{SF}_6)$	Fagerström <i>et al.</i> , 1994 <sup>8</sup>	(f)
$(1.11-1.35) \cdot 10^{-10}$	298	$(2.1-24.6) \cdot 10^{18}$		
$(1.16-1.36) \cdot 10^{-10}$	331	$(1.9-22.1) \cdot 10^{18}$		
$(0.83-1.35) \cdot 10^{-10}$	361	$(1.7-20.3) \cdot 10^{18}$		
$(1.16-1.33) \cdot 10^{-10}$	373	$(6.7-19.7) \cdot 10^{18}$		
$k_1 = 2.0 \cdot 10^{-12}$	700	$6.8 \cdot 10^{15} (\text{He})$	Humpfer, Oser, and Grotheer, 1995 <sup>9</sup>	(g)
$k_5 = 1.7 \cdot 10^{-12}$	700			
$k_6 = 9.1 \cdot 10^{-11} \exp(-1500/T)$	600-700			
$(8.49-7.38) \cdot 10^{-11}$	290	$(2.5-226) \cdot 10^{17} (\text{He})$	Pereira <i>et al.</i> , 1997 <sup>10</sup>	(h)
$(4.80-5.79) \cdot 10^{-11}$	473	$(1.6-116) \cdot 10^{17}$		
$(2.44-3.59) \cdot 10^{-11}$	700	$(2.8-82) \cdot 10^{17}$		
$5.0 \cdot 10^{-11}$	298	$1.8 \cdot 10^{16} (\text{He})$	Deters <i>et al.</i> , 1998 <sup>11</sup>	(i)
$5.3 \cdot 10^{-11}$		$3.3 \cdot 10^{16}$		
$6.7 \cdot 10^{-11}$		$9.8 \cdot 10^{16}$		
$7.3 \cdot 10^{-11}$		$(1.1-11.5) \cdot 10^{18}$		
<i>Branching Ratios</i>				
$k_2/k$	298	$3.3 \cdot 10^{16} (\text{He})$	Deters <i>et al.</i> , 1998 <sup>11</sup>	(i)

$k/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$	T/K	[M]/molecule cm $^{-3}$	Reference	Comments
<i>Reviews and Evaluations</i>				
$k_\infty = 1.0 \cdot 10^{-10}$	300–2000		CEC, 1992; 1994 <sup>12</sup>	
$k_0[\text{He}] = [\text{He}] 2.3 \cdot 10^{-27}$	300			(j)
$k_0[\text{Ar}] = [\text{Ar}] 1.1 \cdot 10^{-28} (T/1000)^{-8.2}$	1000–2000			
$F_c = 0.18 \exp(-T/200)$	1000–2000			
$+ 0.82 \exp(-T/1438) \text{ for M=Ar}$				

### Comments

- (a) Flash photolysis of water vapor in CH<sub>4</sub> [CH<sub>3</sub>] was monitored by absorption at 216 nm. Analysis based on an 11 reaction scheme.
- (b) Pulse radiolysis of mixtures of CH<sub>4</sub>/H<sub>2</sub>O in the presence of Ar (1.23 bar) and SF<sub>6</sub> (66 mbar). The reactants, CH<sub>3</sub> and OH, were generated by the reaction of F with CH<sub>4</sub> and H<sub>2</sub>O, respectively. [CH<sub>3</sub>] was monitored by absorption spectroscopy at 216 nm.
- (c) Shock tube study of *t*-butyl hydroperoxide (to generate OH) and *t*-butylperoxide (to generate CH<sub>3</sub>) mixtures. [OH] monitored by absorption spectroscopy at 309 nm. Analysis based on a 6 reaction scheme. A fractional formation yield for CH<sub>3</sub>OH of 0.75 was found.
- (d) Discharge flow study in which CH<sub>3</sub> and OH were detected using time-of-flight mass spectrometry. Reactants generated from F+CH<sub>4</sub> and H+NO<sub>2</sub>. [CH<sub>3</sub>] was calibrated using the reaction CH<sub>3</sub>+NO<sub>2</sub>→CH<sub>3</sub>O+NO, while [OH] was calibrated using an excess of CH<sub>3</sub>CHO as scavenger. Analysis of the measurements was based on a 15 reaction model.
- (e) Pulsed laser photolysis of CH<sub>3</sub>COCH<sub>3</sub>/H<sub>2</sub>O/He mixtures at 193 nm to produce CH<sub>3</sub> in large excess over OH. [OH] was monitored by LIF and [CH<sub>3</sub>] by absorption at 216.4 nm. Data were modeled together with those of Oser *et al.*<sup>4</sup> using a master equation/inverse Laplace transform method.
- (f) Technique as in (b) but both [CH<sub>3</sub>] and [OH] were monitored by time resolved absorption spectroscopy at 216.4 nm and 309.0 nm respectively. Values of  $k$  based mainly on the [CH<sub>3</sub>] measurements.
- (g) Discharge flow study in which the CH<sub>3</sub> was generated by the pyrolysis of (CH<sub>3</sub>)<sub>2</sub>N<sub>2</sub> and the OH by the F+H<sub>2</sub>O reaction. The OH was in excess. Reactant and product concentrations were measured by mass spectrometry. The overall rate constant was extracted from the [CH<sub>3</sub>] decay profiles using a 21 reaction model. Channel rate constants were obtained by dividing the overall rate constant using branching ratios based on measurements of the products [CH<sub>3</sub>OH for Channel (1), H<sub>2</sub> for Channels (5) and (6), and the reaction of OD, to give H<sub>2</sub> and HD, was used to distinguish between (5) and (6)]. A comparison of rate constants between the two reactions suggests that any isotope effect is within the error limits.
- (h) Laser flash photolysis/LIF/absorption spectroscopy study as in (e). Only the ranges of values of  $k$  are cited

in the Table. Rate data were fitted using a master equation model coupled with inverse Laplace transformation to obtain microcanonical rate constants for dissociation, from canonical association rate coefficients, for Channels (1)–(4) and transition state calculations for Channels (5),(6). The model gives a satisfactory fit to the available experimental data but is not consistent with that from Refs. 5, 7 and 8.

- (i) Two experimental techniques were used; pulsed laser photolysis of CH<sub>3</sub>COCH<sub>3</sub>/H<sub>2</sub>/He mixtures at 193 nm with UV absorption monitoring of [CH<sub>3</sub>] and [OH] over the pressure range 45–467 mbar, where the rate coefficient was constant, and by discharge flow with [CH<sub>3</sub>], [OH], and [<sup>3</sup>CH<sub>3</sub>] being monitored by LMR over the range 0.7–4 mbar (He), where the rate coefficient falls off. This fall-off behavior was well reproduced by the model in Ref. 10. The discharge flow studies were used to obtain the branching ratio  $k_2/k$ .
- (j) Based on the data in Refs. 1–6.

### Preferred Values

$$k_1^\circ = 1.06 \cdot 10^{-10} T^{-6.21} \exp(-671/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \text{ for M=He over the range 298–2000 K.}$$

$$k_1^\infty = 7.2 \cdot 10^{-9} T^{-0.79} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the range 298–2000 K.}$$

$$F_{c,1} = 0.75 \exp(-T/210) + 0.25 \exp(-T/1434) \text{ for M=He over the range 298–2000 K.}$$

$$k_2^\circ = 1.8 \cdot 10^{-8} T^{-0.91} \exp(-275/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ for M=He over the range 298–2000 K.}$$

$$k_2^\infty = 6.4 \cdot 10^{-8} T^{5.8} \exp(485/T) \text{ s}^{-1} \text{ over the range 298–2000 K.}$$

$$F_{c,2} = 0.664 \exp(-T/3569) + 0.336 \exp(-T/108) + \exp(-3240/T) \text{ for M=He over the range 298–2000 K.}$$

$$k_3 = 1.2 \cdot 10^{-12} \exp(-2760/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the range 298–2000 K.}$$

$$k_4 = 2.0 \cdot 10^{-14} \exp(-6990/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the range 298–2000 K.}$$

$$k_5 = 5.3 \cdot 10^{-15} \exp(-2530/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the range 298–2000 K.}$$

$$k_6^\circ = 3.8 \cdot 10^{-14} T^{-0.12} \exp(209/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ for M=He over the range 298–2000 K.}$$

$$k_6^\infty = 1.14 \cdot 10^{-17} T^{8.0} \exp(1240/T) \text{ s}^{-1} \text{ over the range 298–2000 K.}$$

$$F_{c,6} = 0.295 \exp(-T/3704) + 0.705 \exp(-T/312) + \exp(-1238/T) \text{ for M=He over the range 298–2000 K.}$$

**Note.** The pressure dependent bimolecular rate constants for Channels (2) and (6) are given by  $k = \{k_0 k_\infty\}/(k_\infty - k_0)$

$+k_0[M])\}F$ , where  $F$  is the usual broadening factor. See Comments on Preferred Values.

### Reliability

$\Delta \log k_1^\infty = \pm 0.2$  at 298 K, rising to  $\pm 0.3$  at 2000 K.

$\Delta \log k_1^o = \pm 0.2$  at 298 K for M=He, rising to  $\pm 0.3$  at 2000 K.

$\Delta F_{c,1} = \pm 0.1$  for M=He over the range 298–2000 K.

$\Delta \log k_2^\infty = \pm 0.3$  over the range 298–2000 K.

$\Delta \log k_2^o = \pm 0.3$  for M=He over the range 298–2000 K.

$\Delta F_{c,2} = \pm 0.1$  for M=He over the range 298–2000 K.

$\Delta \log k_3 = \Delta \log k_4 = \Delta \log k_5 = \pm 1.0$  over the range 298–2000 K.

$\Delta \log k_6^\infty = \pm 1.0$  over the range 298–2000 K.

$\Delta \log k_6^o = \pm 1.0$  for M=He over the range 298–2000 K.

$\Delta F_{c,6} = \pm 0.1$  for M=He over the range 298–2000 K.

### Comments on Preferred Values

The reaction of OH with  $\text{CH}_3$  proceeds through the formation of a strongly bound complex which has available to it several decomposition channels. It may be collisionally stabilized [Channel (1)], decompose back to reactants, or proceed on to other products the most likely being those from channels (2)–(6). The  ${}^3\text{CH}_2$  which has been observed as a product could arise indirectly from the  ${}^1\text{CH}_2$  formed by Channel (2) or by direct production of  ${}^3\text{CH}_2 + \text{OH}$ . However, an *ab initio* calculation by Wilson and Balint-Kurti<sup>13</sup> suggests that the direct production will not compete with that formed via Channel (2). The rate constants, and hence the product distribution, are a complex function of temperature, pressure, and identity of the bath gas.

Most of the experimental studies have been carried out at close to ambient temperatures. Under such conditions the overall rate constant is relatively pressure independent at pressures above  $\sim 100$  mbar but exhibits fall-off at lower pressures. By 1 bar the rate constant is close to its high pressure limit and the reaction proceeds exclusively by  $\text{CH}_3\text{OH}$  formation. The overall rate constant in this “high pressure” regime is reasonably well characterized. Recent studies of Hughes *et al.*,<sup>6</sup> Peirera *et al.*,<sup>10</sup> and Deeters *et al.*<sup>11</sup> are in excellent agreement and are supported by the slightly higher results obtained in the older studies of Sworski *et al.*<sup>1</sup> and Anastasi *et al.*<sup>2</sup> However the results from the study of Fagerström *et al.*,<sup>7,8</sup> in which a technique similar to that of Anastasi *et al.*<sup>2</sup> was used, appear to be much too high.

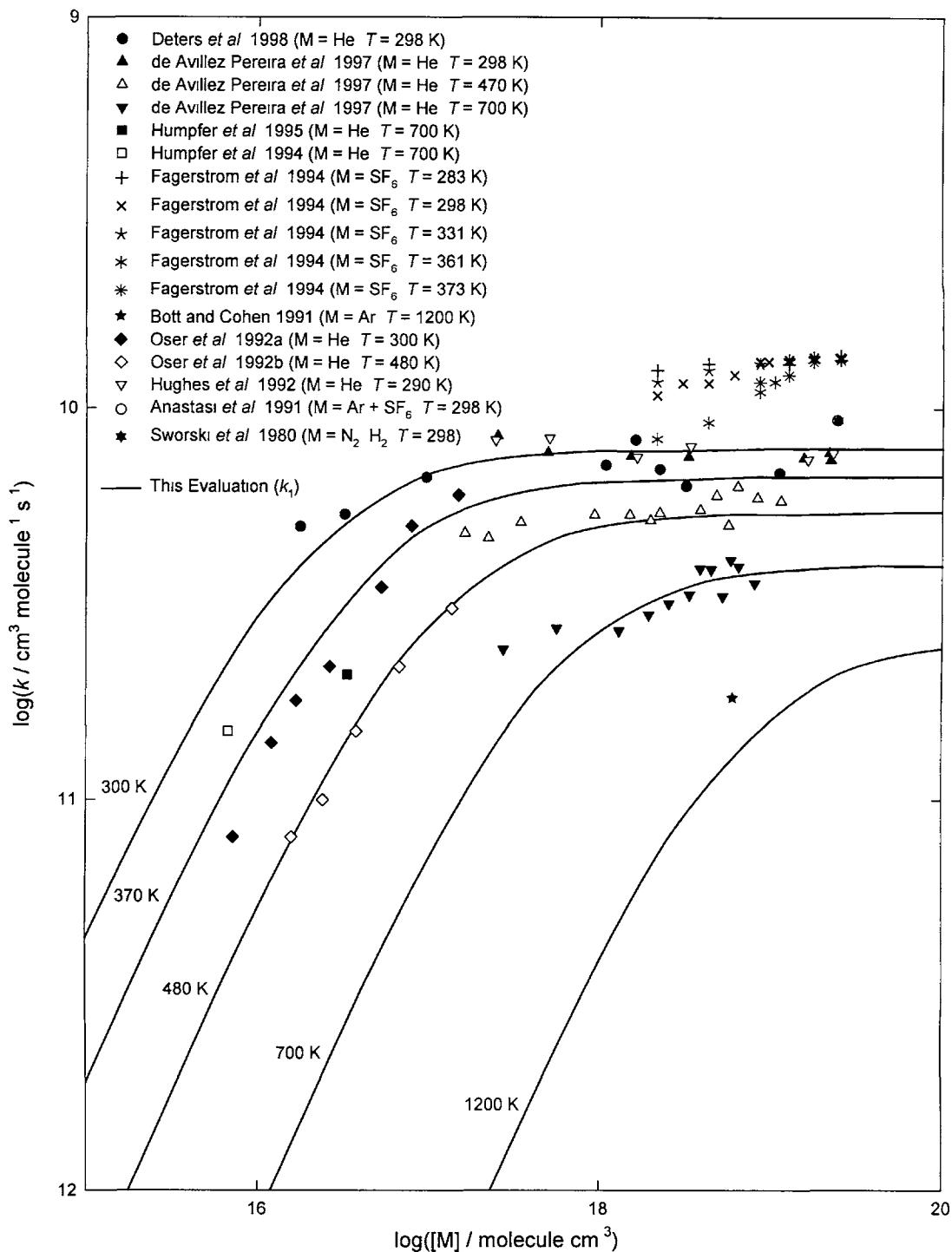
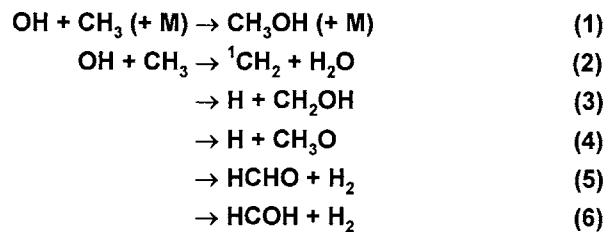
The behavior of the reaction at low pressures, where other channels compete with Channel (1), is much less clear. Deeters *et al.*<sup>11</sup> find Channel (2) to become the predominant channel at low temperatures and pressures, while Humpfer *et al.*,<sup>9</sup> working at 600–700 K, suggest a contribution from Channel (6) at their higher temperatures. The best guide to the branching behavior appears to be the expressions derived in the comprehensive modeling study by Pereira *et al.*<sup>10</sup> The experimental data for the overall reaction were fitted using a Master Equation treatment, rate constants for Channels (1)–(4) were derived using an Inverse Laplace Transform treat-

ment together with data from other studies, and for the minor channels, (5) and (6), RRKM theory was applied using the properties of the transition states derived by Walch.<sup>14</sup> The expressions so derived have been taken as our preferred values and give values that are in satisfactory agreement with results from most of the low temperature studies apart from those of Fagerström *et al.*,<sup>7,8</sup> Oser *et al.*,<sup>4,5</sup> and Humpfer *et al.*<sup>9</sup> There is good agreement with all of the data of Deters *et al.*,<sup>11</sup> with data for the rate constant for the reverse reaction  ${}^1\text{CH}_2 + \text{H}_2\text{O}$ , and with the channel efficiency for forming  $\text{CH}_3 + \text{OH}$ .<sup>10</sup> The rate constants for Channels (1), (2), and (6) are found to be strongly pressure dependent, whereas those for Channels (3), (4), and (5) are not. The parameters given for Channel (1) can be used in the usual Troe expressions for the rate constant of a recombination reaction but modification of the basic formalism is required for the rate constants of Channels (2) and (6). For Channels (2) and (6) the rate constants decrease as the pressure increases, in contrast to the usual Lindemann type fall-off behavior. This behavior has been represented using the following relationship which is analogous to the Troe formalism, namely  $k = \{k_0 k_\infty / (k_\infty + k_0[M])\}F$ , where  $F$  is the usual broadening factor. This expression should be used in conjunction with the recommended parameters in calculating values of  $k_2$  and  $k_6$ .

The preferred expressions show that, at temperatures close to 300 K, Channel (1) predominates but it becomes unimportant at temperatures above  $\sim 1000$  K. The only high temperature study is that of Bott and Cohen<sup>3</sup> who determined the overall  $k$  at 1200 K. Our preferred expressions, based on the low temperature data, predict a value within 20% of the value obtained by Bott and Cohen,<sup>10</sup> which is well within the error limits of the measurement. On this basis the temperature range of our recommendations for the high temperature channels, (2)–(6) is extended to 2000 K with appropriately substantial error limits.

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#### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = 385.0 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = 138.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 3.1 \cdot 10^{29} T^{-0.942} \exp(-46760/T) \text{ molecule cm}^{-3}$$

(300 ≤ T/K ≤ 5000)

$$\Delta H^\circ_{298}(3) = 401.7 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = 118.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 1.16 \cdot 10^{26} T^{-0.131} \exp(-48480/T) \text{ molecule cm}^{-3}$$

(300 ≤ T/K ≤ 5000)

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2 + k_3$ )

$k/\text{s}^{-1}$	T/K	[M]/molecule cm <sup>-3</sup>	Reference	Comments
<i>Rate Coefficient Measurements</i>				
<i>Low Pressure Range</i>				
$[\text{Ar}] 3.3 \cdot 10^{-7} \exp(-34400/T)$	1600–2100	$(7-230) \cdot 10^{17}$	Spindler and Wagner, 1982 <sup>1</sup>	(a)
$[\text{Ar}] 3.5 \cdot 10^{-8} \exp(-33436/T)$	1400–2200	$(6-30) \cdot 10^{17}$	Dombrowsky <i>et al.</i> , 1991 <sup>2</sup>	(b)
$[\text{Ar}] 7.0 \cdot 10^{-8} \exp(-33600/T)$	1400–2200	$(2-2.5) \cdot 10^{18}$	Koike <i>et al.</i> , 2000 <sup>3</sup>	(c)
<i>Intermediate Fall-off Range</i>				
$3.1 \cdot 10^1$	1600	$7.0 \cdot 10^{17}(\text{Ar})$	Spindler and Wagner, 1982 <sup>1</sup>	(a)
$1.4 \cdot 10^2$		$4.0 \cdot 10^{18}$		
$4.0 \cdot 10^2$		$2.3 \cdot 10^{19}$		
$3.4 \cdot 10^2$	1800	$7.0 \cdot 10^{17}(\text{Ar})$		
$1.6 \cdot 10^3$		$4.0 \cdot 10^{18}$		
$4.9 \cdot 10^3$		$2.3 \cdot 10^{19}$		
$2.3 \cdot 10^3$	2000	$7.0 \cdot 10^{17}(\text{Ar})$		
$1.1 \cdot 10^4$		$4.0 \cdot 10^{18}$		
$3.7 \cdot 10^4$		$2.3 \cdot 10^{19}$		
<i>High Pressure Range</i>				
$9.4 \cdot 10^{15} \exp(-45220/T)$	1600–2100	$(7-230) \cdot 10^{17}(\text{Ar})$	Spindler and Wagner, 1982 <sup>1</sup>	(a)
<i>Reviews and Evaluations</i>				
$k_0[\text{Ar}] = [\text{Ar}] 1.1 \cdot 10^{-7} \exp(-33080/T)$	1000–2000		CEC, 1994 <sup>4</sup>	(d)
$k_\infty = 1.7 \cdot 10^{16} \exp(-45740/T)$	1000–2000			
$F_c(\text{Ar}) = 0.18 \exp(-T/200) + 0.82 \exp(-T/1438)$	1000–2000			
$k_0[\text{N}_2] = [\text{N}_2] 4.9 \cdot 10^{20} T^{-7.35} \exp(-48037/T)$	300–2500		Held and Dryer, 1998 <sup>5</sup>	(e)
$k_\infty = 1.9 \cdot 10^{16} \exp(-46160/T)$	300–2500			
$F_c(\text{N}_2) = (1 - 0.414) \exp(-T/279) + 0.414 \exp(-T/5459)$	300–2500			

#### Comments

- (a) Study of CH<sub>3</sub>OH pyrolysis behind reflected shock waves in Ar. [CH<sub>3</sub>] and [OH] were monitored by absorption at 216 and 308 nm, respectively. High and low pressure rate coefficients obtained by extrapolation of the fall-off curves. Channel (1) is estimated to contribute about 75% and Channel (3) about 25% of the total rate.
- (b) Thermal decomposition of CH<sub>3</sub>OH studied behind incident shock waves. HO radicals monitored by absorption and H atoms by ARAS. Channel (1) contributes to 80% of the decomposition while Channel (3) is found

to contribute less than 5%. The probability for reaction (2) or a new channel leading to CH<sub>2</sub>O + H<sub>2</sub> is estimated to be about 10%–20%.

- (c) Infrared emission at 3.4 μm was used to monitor the pyrolysis of CH<sub>3</sub>OH/Ar mixtures in incident shock waves at pressures of 0.40–0.82 bar. Values of  $k$  were derived directly from the slopes of the emission profiles and also from  $t_{90}$  and computer modeling of a detailed mechanism.
- (d) The recommended rate data are mainly based on the theoretical analysis of the data of Spindler and Wagner<sup>1</sup> using unimolecular rate theory.<sup>6–8</sup>
- (e) Detailed modeling of CH<sub>3</sub>OH oxidation. A mechanism

with 89 reactions was employed to interpret literature data from studies carried out in static<sup>16–20</sup> and flow reactors,<sup>21–23</sup> shock tubes,<sup>24–27</sup> and premixed laminar flames.<sup>28–31</sup> Recommended rate data obtained from a fit of the RRKM results of Tsang<sup>9</sup> with Troe's fall-off formulation<sup>7</sup> using  $\langle \Delta E \rangle_{\text{down}} = 500 \text{ cm}^{-1}$ .

### Preferred Values

$k_0 = 1.1 \cdot 10^{-7} \exp(-33080/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for M = Ar over the range 1000–2000 K.

$k_\infty = 2.5 \cdot 10^{19} T^{-0.94} \exp(-47030/T) \text{ s}^{-1}$  over the range 1000–2000 K.

$F_c = 0.18 \exp(-T/200) + 0.82 \exp(-T/1438)$  for M = Ar over the range 1000–2000 K.

### Reliability

$\Delta \log k_0 = \pm 0.3$  for M = Ar over the range 1000–2000 K.

$\Delta \log k_\infty = \pm 0.5$  over the range 1000–2000 K.

$\Delta F_c = \pm 0.1$  for M = Ar over the range 1000–2000 K.

### Comments on Preferred Values

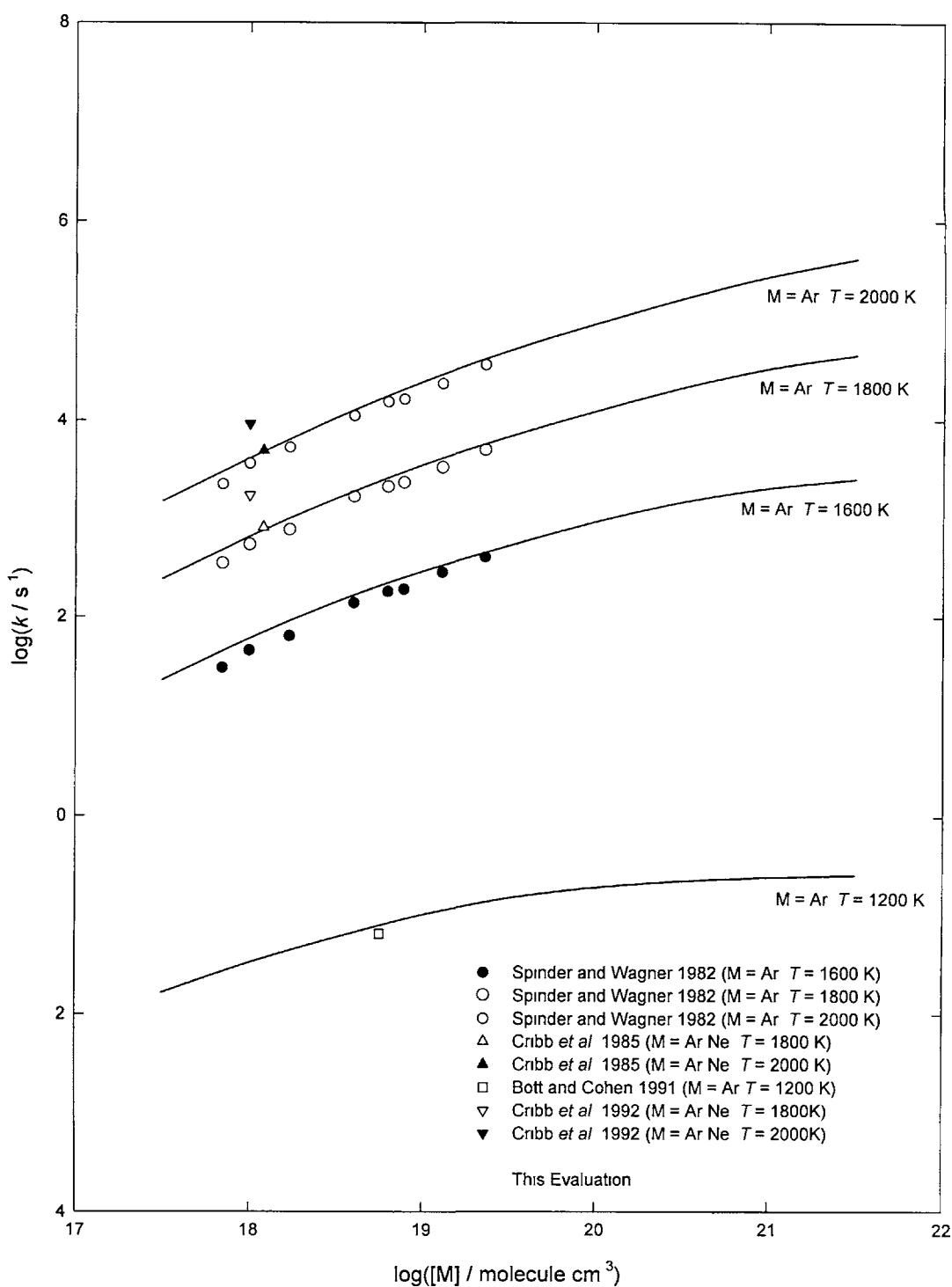
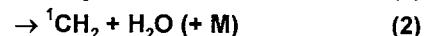
The recommended values are mainly based on the theoretical analysis of Spindler and Wagner<sup>1</sup> in terms of unimolecular rate theory.<sup>6–8</sup> The modeling leads to an almost temperature independent value of  $k_\infty = 7.0 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  between 200 and 2000 K for the reverse recombination reaction, in good agreement with data of Sworski *et al.*,<sup>10</sup> Anastasi *et al.*,<sup>11</sup> and the more recent determination of de Avillez Periera *et al.*<sup>12</sup> Therefore, because the available experimental data are far from the high pressure regime, we derived  $k_\infty$  from a recombination rate coefficient of  $k_\infty = 8.0 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,<sup>12</sup> and the given equilibrium constant. From the analysis of the fall-off curves, values for the collision efficiencies from 0.1 to 0.05 over the range 1600–2000 K were obtained. The results are consistent with the data of Cribb, Dove, and Yamazaki<sup>13</sup> and recombination data measured by Bott and Cohen.<sup>14</sup> According to Refs. 1, 2, 5, 13, and 15, the rate coefficient for Channel (3) is markedly smaller than that of Channel (1). The importance of Channel (2) or a new channel  $\text{CH}_3\text{OH}(+\text{M}) \rightarrow \text{CH}_2\text{O} + \text{H}_2(+\text{M})$  has been discussed by Dombrowsky *et al.*<sup>2</sup>

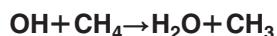
Xia *et al.*<sup>32</sup> have carried out *ab initio* molecular orbital and variational RRKM calculations on the reaction and derive expressions for  $k_\infty$  and  $k_0$  giving similar values over the range 1000–2000 K to our preferred expressions. Their calculations also suggest that the product branching ratios are

strongly pressure dependent with Channels (1) and (2) being dominant at high (>1.5 bar) and low (<7 mbar) pressures, respectively.

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*Thermodynamic Data*

$$\begin{aligned}\Delta H_{298}^{\circ} &= -59.86 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= 12.99 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 31.9 T^{-0.206} \exp(+6960/T) \\ &(300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$(1.1-1.8) \cdot 10^{-11}$	1225–1800	Fenimore and Jones, 1961 <sup>1</sup>	(a)
$1.4 \cdot 10^{-11}$	1750–2000	Wilson, O'Donovan, and Fristrom, 1968 <sup>2</sup>	(b)
$6.7 \cdot 10^{-12}$	1500	Peeters and Mahnen, 1973 <sup>3</sup>	(c)
$4.3 \cdot 10^{-12}$	1234	Bott and Cohen, 1989 <sup>4</sup>	(d)
$1.59 \cdot 10^{-20} T^{2.84} \exp(-978/T)$	223–420	Vaghjiani and Ravishankara, 1991 <sup>5</sup>	(e)
$4.0 \cdot 10^{-12} \exp(-1944/T)$	278–378	Finlayson-Pitts <i>et al.</i> , 1992 <sup>6</sup>	(f)
$9.65 \cdot 10^{-20} T^{2.58} \exp(-1082/T)$	293–800	Dunlop and Tully, 1993 <sup>7</sup>	(g)
$5.4 \cdot 10^{-15}$	292	Saunders <i>et al.</i> , 1993 <sup>8</sup>	(h)
$2.56 \cdot 10^{-12} \exp(-1765/T)$	233–343	Mellouki <i>et al.</i> , 1994 <sup>9</sup>	(i)
$1.89 \cdot 10^{-20} T^{2.82} \exp(-987/T)$	196–296	Gierczak <i>et al.</i> , 1997 <sup>10</sup>	(j)
<i>Reviews and Evaluations</i>			
$2.57 \cdot 10^{-17} T^{1.83} \exp(-1396/T)$	240–2500	CEC, 1992; 1994 <sup>11</sup>	(k)
$2.45 \cdot 10^{-12} \exp(-1775/T)$	220–300	NASA, 1997 <sup>12</sup>	(l)
$9.65 \cdot 10^{-20} T^{2.58} \exp(-1082/T)$	223–1234	Atkinson, 1997 <sup>13</sup>	(m)
$2.15 \cdot 10^{-12} \exp(-1735/T)$	240–300	IUPAC, 1999 <sup>14</sup>	(n)

**Comments**

- (a) Flame study on  $\text{CH}_4/\text{H}_2/\text{N}_2\text{O}/\text{O}_2$  mixtures at total pressures in the range 4–18.7 mbar.  $[\text{CH}_4]$ ,  $[\text{CO}_2]$ ,  $[\text{N}_2\text{O}]$ , and  $[\text{CO}]$  were monitored by mass spectrometry.  $[\text{H}]$  was estimated from the rate of removal of  $\text{N}_2\text{O}$  by the reaction  $\text{H} + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{OH}$  and  $[\text{OH}]$  was estimated from the kinetics of the  $\text{CO} + \text{OH}$  reaction. Assuming that removal of  $\text{CH}_4$  is solely by reaction with  $\text{OH}$  values of  $k/k(\text{CO} + \text{OH})$  were derived. Values of  $k$  cited in the Table were derived using values of  $k(\text{CO} + \text{OH})$  from the present evaluation.
- (b) Flame study on  $\text{CH}_4/\text{O}_2$  mixtures at 50 mbar pressure.  $[\text{CH}_4]$ ,  $[\text{CO}]$ ,  $[\text{CO}_2]$ , and  $[\text{H}_2\text{O}]$  were monitored by mass spectrometry. Values of  $k/k(\text{CO} + \text{OH})$  were obtained from the measured  $[\text{OH}]$  profiles. Values of  $k$  cited in the Table were derived using  $k(\text{CO} + \text{OH})$  from the present evaluation.
- (c) Flame study on  $\text{CH}_4/\text{O}_2$  mixtures at a total pressure of 53.3 mbar.  $[\text{CH}_4]$ ,  $[\text{H}_2\text{O}]$ ,  $[\text{O}_2]$ ,  $[\text{CO}]$ ,  $[\text{CO}_2]$ ,  $[\text{CH}_2\text{O}]$ ,  $[\text{CH}_3]$ ,  $[\text{CH}_3\text{O}_2]$ ,  $[\text{CH}_3\text{OH}]$ ,  $[\text{O}]$ ,  $[\text{OH}]$ ,  $[\text{H}_2]$ ,  $[\text{H}]$ , and  $[\text{HO}_2]$  were monitored by mass spectrometry. Values of  $k$  were calculated from the rate of removal of  $\text{CH}_4$ .
- (d) Shock tube study on  $\text{CH}_4/t\text{-butyl hydroperoxide}/\text{Ar}$  mixtures at total pressures of 1.1–1.3 bar.  $[\text{OH}]$  was monitored by resonance absorption behind the reflected shock. The OH resonance lamp was calibrated by shock heating  $\text{H}_2/\text{O}_2/\text{Ar}$  mixtures. Values of  $k$  were derived from the measured  $[\text{OH}]$  decay rate.

- (e) Broad band photolysis ( $\lambda = 165-185 \text{ nm}$ ) of  $\text{CH}_4/\text{H}_2\text{O}$  mixtures.  $[\text{OH}]$  was monitored by LIF using excitation at 281.1 nm and detection at 312.2 and 306.4 nm. In some experiments the OH was generated by pulsed laser photolysis of  $\text{H}_2\text{O}_2$  or  $\text{O}_3/\text{H}_2\text{O}$  mixtures. Values of  $k$  found to be independent of changes in the OH source, photolysis fluence, flow-rate of gases, pressure, or nature of diluent.
- (f) Discharge flow study using He carrier gas at a total pressure of 1.3 mbar. OH was generated by the  $\text{H} + \text{NO}_2$  reaction and the first order decay of  $[\text{OH}]$  in the presence of  $\text{CH}_4$  in large excess was monitored by resonance fluorescence.
- (g) Pulsed laser photolysis at 193 nm of  $\text{CH}_4/\text{H}_2\text{O}/\text{He}$  mixtures under slow flow conditions.  $[\text{OH}]$  was monitored by LIF at 307 nm. The agreement with the measurements of Vaghjiani and Ravishankara<sup>5</sup> was excellent and the expression for  $k$  cited is a fit to the data from the two studies.<sup>5,7</sup>
- (h) Pulsed laser photolysis at 193 nm or 248 nm of  $\text{N}_2\text{O}/\text{CH}_4/\text{He}$  mixtures under slow flow conditions.  $[\text{OH}]$  monitored by laser excitation at 282.150 nm and time resolved detection of the fluorescence at 308 nm.
- (i) Pulsed laser photolysis at 248 nm of  $\text{CH}_4/\text{H}_2/\text{O}_2/\text{He}$  under slow flow conditions.  $[\text{OH}]$  was monitored by LIF using excitation at 282 nm and detection at 309.4 nm.
- (j) Pulsed photolysis study using similar technique to (g). At temperatures close to room temperature broad band

photolysis of H<sub>2</sub>O was used as the OH source but at lower temperatures pulsed laser photolysis at 193 nm of N<sub>2</sub>O/H<sub>2</sub>O mixtures was used. The authors combined the results from this study with those from their previous study<sup>5</sup> to obtain the expression for *k* cited in the Table.

- (k) Accepts the expression derived by Madronich and Felder.<sup>15</sup>
- (l) Based on the data below 300 K of Refs. 5–10.
- (m) Derived from the data of Dunlop and Tully<sup>7</sup> and Vaghjiani and Ravishankara.<sup>5</sup>
- (n) This two parameter Arrhenius expression, to cover the limited temperature range 240–300 K, was derived from the three parameter expression given by Gierczak *et al.*<sup>10</sup>

### Preferred Values

$$k = 2.27 \cdot 10^{-18} T^{2.18} \exp(-1350/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the range 250–2400 K.

### Reliability

$\Delta \log k = \pm 0.1$  over the temperature range 250–350 K, rising to  $\pm 0.2$  at 800 K and  $\pm 0.3$  at 2400 K.

### Comments on Preferred Values

There have been numerous studies of this reaction<sup>1–10,15–45</sup> and the rate constant is well characterized over a wide temperature range. Our preferred values are based on the studies cited in the Table. The reaction is extremely important in atmospheric chemistry as well as combustion. Consequently, the data at atmospheric temperatures have been thoroughly evaluated by the NASA and IUPAC Panels<sup>12,14</sup> and, over a wider temperature range (223–1234 K), by Atkinson.<sup>13</sup> These recent reviews base their recommendations for low temperatures on the studies of Vaghjiani and Ravishankara,<sup>5</sup> Finlayson-Pitts *et al.*,<sup>6</sup> Dunlop and Tully,<sup>7</sup> Saunders *et al.*,<sup>8</sup> Mellouki *et al.*,<sup>9</sup> and Gierczak *et al.*<sup>10</sup> We accept their findings and base our preferred expression at these temperatures mainly on these studies.

The low temperature studies cited above<sup>5–10</sup> give values of *k* which agree to within about 10%; at higher temperatures (*T*>800 K) the data are more scattered. There are two pulsed photolysis studies<sup>15,33</sup> which overlap with the low temperature data and extend to temperatures above 1000 K. That of Tully and Ravishankara<sup>33</sup> is in fair agreement with the low temperature data and the similar study of Madronich and Felder<sup>15</sup> gives high values at low temperatures but above 1000 K appears to agree well with the other data at these temperatures. There are three shock tube studies<sup>4,30,31</sup> in the range 1100–1300 K. That of Bott and Cohen<sup>4</sup> is expected to be reliable since, using the same technique, they have obtained reliable data for a number of similar OH radical reactions. The shock tube study of Bradley *et al.*<sup>30</sup> is also in reasonable agreement with our preferred expression for *k* but the results obtained by Ernst *et al.*<sup>31</sup> are lower and show

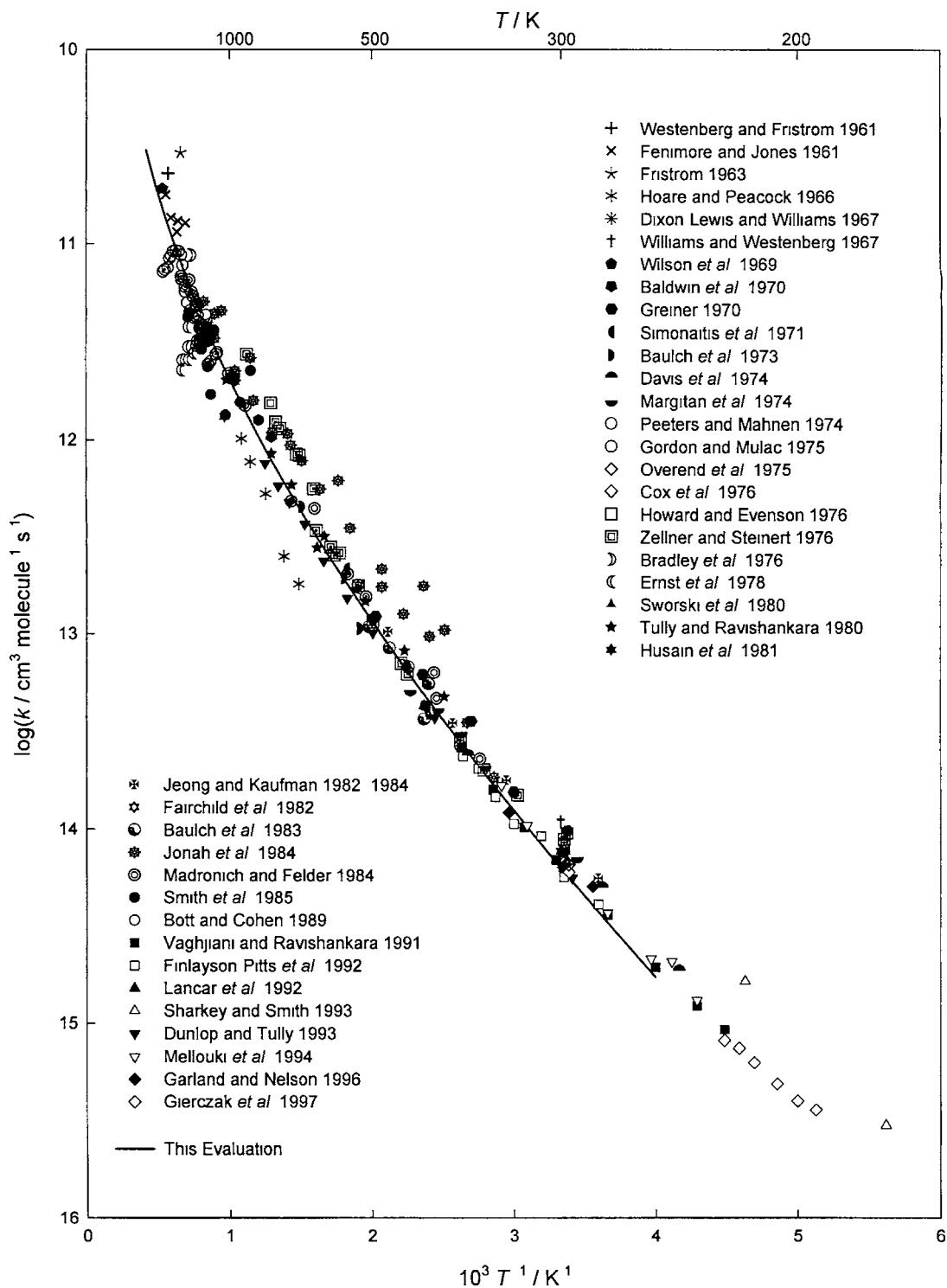
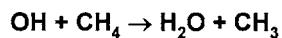
considerable scatter. In this temperature region the preferred expression is based mainly on the study of Bott and Cohen.<sup>4</sup> There is also a flame study of Dixon-Lewis and Williams<sup>16</sup> which is in excellent agreement with our preferred expression.

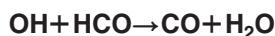
Most of the data at temperatures above 1500 K come from a number of older flame studies<sup>1,2,3,17,19</sup> which are of uncertain reliability but agree with the preferred expression to within a factor of  $\sim 2$ . There is also a shock tube study on CH<sub>4</sub> pyrolysis and oxidation by Hidaka *et al.*<sup>46</sup> who find that they can model their CO<sub>2</sub> production in fuel lean mixtures over the range 1800–2200 K using the expression proposed in our previous evaluations<sup>11</sup> which gives values in fair agreement with the present recommendations. The temperature range of our recommendations is extended to 2400 K on the basis of the flame studies (Refs. 1–3) and the shock tube study of Hidaka *et al.*<sup>46</sup> but with substantial error limits at high temperatures.

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*Thermodynamic Data*

$$\begin{aligned}\Delta H^\circ_{298} &= -432.6 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298} &= -21.69 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 0.709 T^{-0.342} \exp(+51940/T) \\ &(300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$1.8 \cdot 10^{-10}$	296	Temps and Wagner, 1984 <sup>1</sup>	(a)
<i>Reviews and Evaluations</i>			
$8.3 \cdot 10^{-11}$	1000–2500	Warnatz, 1984 <sup>2</sup>	(b)
$\sim 5 \cdot 10^{-11}$	300–2500	Tsang and Hampson, 1986 <sup>3</sup>	(c)
$7 \cdot 10^{-11} \exp(350/T)$	298–2000	Atkinson, 1989 <sup>4</sup>	(d)
$1.7 \cdot 10^{-10}$	300–2500	CEC, 1992; 1994 <sup>5</sup>	(e)

**Comments**

- (a) Discharge flow study of the reaction of OH with HCHO at a pressure of  $\sim 1.5$  mbar. [OH] and [HCO] monitored by laser magnetic resonance spectroscopy. Values of  $k$  were derived from the steady state concentrations of OH and HCO and, independently, from the rate of change of [OH] in the presence and absence of HCHO.
- (b) Estimate based on the available high temperature data.
- (c) Rate constant estimated to be close to collisional value
- (d) Based on the low temperature data of Temps and Wagner<sup>1</sup> and the value of  $(8 \pm 8) \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 1700–2000 K estimated by Seery<sup>6</sup> from induction time measurements.
- (e) Based on the data of Temps and Wagner,<sup>1</sup> Bowman,<sup>8</sup> and Browne *et al.*<sup>7</sup>

**Preferred Values**

$k = 1.8 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 296–2500 K.

**Reliability**

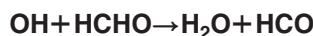
$\Delta \log k = \pm 0.3$  over the range 296–2500 K.

**Comments on Preferred Values**

The only direct study of the rate of this reaction is that of Temps and Wagner<sup>1</sup> at 298 K. Their value of the rate constant is accepted as the preferred value but with substantial error limits. The few high temperature data from flame<sup>7</sup> and shock tube<sup>6,8</sup> studies are largely derived from a complex kinetic analysis of species profile data and can only be considered as approximate. However, together with the low temperature data, they suggest a very small temperature coefficient for  $k$ , as implied also by the large value of  $k$ .

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*Thermodynamic Data*

$$\begin{aligned}\Delta H^\circ_{298} &= -127.3 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298} &= 10.7 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 40.4 T^{-0.315} \exp(+15110/T) \\ &(300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$1.25 \cdot 10^{-11} \exp(-88/T)$	299–426	Atkinson and Pitts, 1978 <sup>1</sup>	(a)
$1.05 \cdot 10^{-11}$	228–362	Stief <i>et al.</i> , 1980 <sup>2</sup>	(b)
$8.1 \cdot 10^{-12}$	296	Temps and Wagner, 1984 <sup>3</sup>	(c)
$8.4 \cdot 10^{-12}$	299	Niki <i>et al.</i> , 1984 <sup>4</sup>	(d)
$7.95 \cdot 10^{-12}$	298	Yetter <i>et al.</i> , 1989 <sup>5</sup>	(e)
$1.94 \cdot 10^{-11}$	1205	Bott and Cohen, 1991 <sup>6</sup>	(f)
<i>Reviews and Evaluations</i>			
$5.7 \cdot 10^{-15} T^{1.18} \exp(225/T)$	298–1600	Tsang and Hampson, 1986 <sup>7</sup>	(g)
$5.7 \cdot 10^{-15} T^{1.18} \exp(225/T)$	300–3000	CEC, 1992; 1994 <sup>8</sup>	(h)
$8.24 \cdot 10^{-18} T^2 \exp(753/T)$	228–1205	IUPAC, 1998 <sup>9</sup>	(i)

**Comments**

- (a) Pulsed vacuum UV photolysis; OH detected by time resolved LIF.
- (b) Flash photolysis; resonance fluorescence detection of OH.
- (c) Discharge flow; laser magnetic resonance detection of OH.
- (d) FTIR study of the products from  $\text{H}^{13}\text{CHO}$  and  $\text{C}_2\text{H}_4$  photo oxidation.  $k/k(\text{OH} + \text{C}_2\text{H}_4) = 0.99$  obtained at 0.92 bar pressure.  $k(\text{OH} + \text{C}_2\text{H}_4) = 8.48 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  used.
- (e) Discharge flow; resonance fluorescence detection of OH.
- (f) Shock-tube study with resonance absorption detection of OH.
- (g) Uses the low temperature data from Refs. 1 and 2 together with the high temperature data of Peeters and Mahnen<sup>10</sup> and Vandooren and Van Tiggelen.<sup>11</sup>
- (h) Accepts the recommendation of Tsang and Hampson.<sup>7</sup>
- (i) Fit of the function  $k = A T^2 \exp(B/T)$  to data shown in the Table.

**Preferred Values**

$k = 2.31 \cdot 10^{-11} \exp(-304/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 300–1500 K.

*Reliability*

$\Delta \log k = \pm 0.1$  at 300 K, rising to  $\pm 0.3$  at 1500 K.

*Comments on Preferred Values*

The preferred values are a two parameter fit to the data of Atkinson and Pitts,<sup>1</sup> Stief *et al.*,<sup>2</sup> Temps and Wagner,<sup>3</sup> Yetter

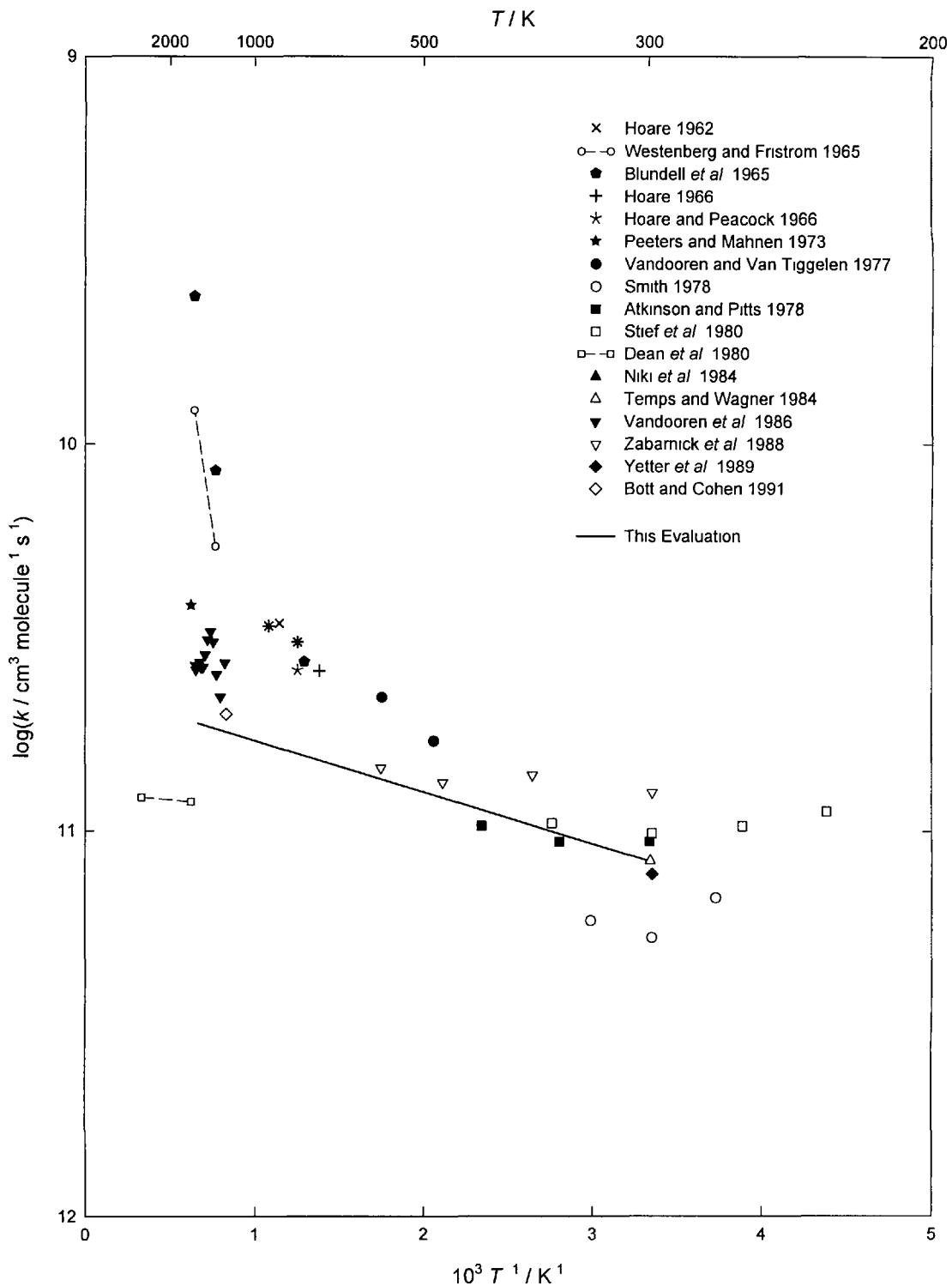
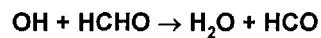
*et al.*,<sup>5</sup> Bott and Cohen<sup>6</sup> and the relative rate data of Niki *et al.*<sup>4</sup> There is considerable scatter over the whole temperature range, particularly at high temperatures, where we have based the preferred expression on the data of Bott and Cohen,<sup>6</sup> which is considered the most reliable in this regime. The earlier data of Peeters and Mahnen<sup>10</sup> at 1600 K and of Vandooren *et al.*<sup>11</sup> (1200–1600 K) provide some support. A transition state calculation by Zabarnick *et al.*<sup>12</sup> suggests that the Arrhenius plot may be substantially nonlinear but the scatter of the experimental data is too large to define the curvature with any confidence.

A number of other, mostly older, studies<sup>13–20</sup> are not used in deriving the preferred expression. They generally give much higher values than the more recent, and more reliable, measurements.

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#### Thermodynamic Data

$$\begin{aligned}\Delta H^{\circ}_{298}(1) &= -95.3 \text{ kJ mol}^{-1} \\ \Delta S^{\circ}_{298}(1) &= 9.19 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 12.1 T^{-0.121} \exp(+11220/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

$$\begin{aligned}\Delta H^{\circ}_{298}(2) &= -60.3 \text{ kJ mol}^{-1} \\ \Delta S^{\circ}_{298}(2) &= -5.33 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 0.12 T^{0.235} \exp(+7380/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$1.01 \cdot 10^{-12}$	292	Campbell, McLaughlin, and Handy, 1978 <sup>1</sup>	(a)
$1.06 \cdot 10^{-12}$	296	Overend and Paraskevopoulos, 1978 <sup>2</sup>	(b)
$1.00 \cdot 10^{-12}$	298	Ravishankara and Davis, 1978 <sup>3</sup>	(c)
$8.0 \cdot 10^{-11} \exp(-2265/T)$	1000–2000	Vandooren and Van Tiggelen, 1981 <sup>4</sup>	(d)
$1.10 \cdot 10^{-12}$	300	Barnes <i>et al.</i> , 1982 <sup>5</sup>	(e)
$0.94 \cdot 10^{-12}$	300	Tuazon <i>et al.</i> , 1983 <sup>6</sup>	(f)
$1.0 \cdot 10^{-11} \exp(-798/T)$	300–1020	Meier <i>et al.</i> , 1983 <sup>7</sup>	(g)
$4.8 \cdot 10^{-12} \exp(-480/T)$	240–440	Wallington and Kurylo, 1987 <sup>8</sup>	(h)
$0.88 \cdot 10^{-12}$	298	Pagsberg <i>et al.</i> , 1988 <sup>9</sup>	(i)
$5.9 \cdot 10^{-8} T^{2.65} \exp(444/T)$	294–866	Hess and Tully, 1989 <sup>10</sup>	(j)
$1.01 \cdot 10^{-12}$	298	McCaulley <i>et al.</i> , 1989 <sup>11</sup>	(k)
$0.90 \cdot 10^{-12}$	298	Nelson <i>et al.</i> , 1990 <sup>12</sup>	(l)
$1.00 \cdot 10^{-12}$	298		(m)
$8.64 \cdot 10^{-12}$	1205	Bott and Cohen, 1991 <sup>13</sup>	(n)
<i>Branching Ratio Measurements (<math>k_2/k</math>)</i>			
$0.11 \pm 0.04$	298	Hägele <i>et al.</i> , 1983 <sup>14</sup>	(o)
$0.22 \pm 0.07$	393		
$0.17 \pm 0.13$	298	Meier <i>et al.</i> , 1984 <sup>7</sup>	(g)
$0.25 \pm 0.08$	298		
0.17	298	Pagsberg <i>et al.</i> , 1988 <sup>10</sup>	(j)
$0.15 \pm 0.08$	298	McCaulley <i>et al.</i> , 1989 <sup>11</sup>	(k)
$0.15 \pm 0.05$	482	Dóbé <i>et al.</i> , 1994 <sup>15</sup>	(p)
$0.23 \pm 0.07$	612		
<i>Reviews and Evaluations</i>			
$1.1 \cdot 10^{-19} T^{2.53} \exp(-483/T)$	300–2000	Tsang, 1987 <sup>16</sup>	(q)
$k_2/k = 3.7 \exp(-1020/T)$	300–1205		
$6.01 \cdot 10^{-18} T^2 \exp(170/T)$	240–1205	Atkinson, 1994 <sup>17</sup>	(r)
$k_2/k = 0.15$	298		
$6.7 \cdot 10^{-12} \exp(-600/T)$	240–400	NASA, 1997 <sup>18</sup>	(s)
$3.1 \cdot 10^{-12} \exp(-360/T)$	240–300	IUPAC, 1999 <sup>19</sup>	(t)
$k_2/k = 0.15$	298		

#### Comments

- (a) Relative rate measurement in a static system. The CO<sub>2</sub> yield from H<sub>2</sub>O<sub>2</sub>/NO<sub>2</sub>/CO/CHOH mixtures was measured by GC. Comparison of CO<sub>2</sub> yields with those in presence of *n*-butane gave  $k/k(\text{OH} + \text{n-butane}) = 0.408$ .  $k(\text{OH} + \text{n-butane}) = 2.47 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ <sup>17,20</sup> used to obtain tabulated  $k$ .
- (b) Flash photolysis of H<sub>2</sub>O/CH<sub>3</sub>OH or N<sub>2</sub>O/H<sub>2</sub>/CH<sub>3</sub>OH mixtures. [OH] monitored by resonance absorption.
- (c) Flash photolysis of H<sub>2</sub>O/CH<sub>3</sub>OH/He mixtures. [OH] monitored by resonance fluorescence.
- (d) Lean methanol flames burning at 53 mbar pressure

sampled by molecular beam mass spectrometry. CO, CO<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>, CH<sub>3</sub>OH, HCHO, H<sub>2</sub>O, H, O, OH, CH<sub>3</sub>, and CH<sub>2</sub>OH (or CH<sub>3</sub>O from which it could not be distinguished) were monitored. Results were analyzed using steady state methods.

- (e) Relative rate study in a static system (420 dm<sup>3</sup> vessel) at atmospheric pressure. OH generated by decomposition of HO<sub>2</sub>NO<sub>2</sub> in the presence of NO or by photolysis of NO<sub>2</sub>/propene mixtures. [CH<sub>3</sub>OH] in the mixture monitored by GC and FTIR. Comparison with rate of ethene removal under identical conditions gave  $k/k(\text{OH} + \text{ethene}) = 0.16$  and 0.13 for the two radical

- sources.  $k(\text{OH} + \text{ethene}) = 8.4 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ <sup>17,20</sup> used to calculate  $k$ .
- (f) Relative rate study in static system ( $3500 \text{ dm}^3$  Teflon chamber). OH generated by reaction of  $\text{N}_2\text{H}_4$  with  $\text{O}_3$  in air in the presence of traces of  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{OCH}_3$ .  $[\text{CH}_3\text{OH}]$  and  $[\text{CH}_3\text{OCH}_3]$  monitored by FTIR.  $k/k(\text{OH} + \text{CH}_3\text{OCH}_3) = 0.314$  obtained.  $k(\text{OH} + \text{CH}_3\text{OCH}_3) = 3.01 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ <sup>17,20</sup> used to calculate  $k$ .
- (g) Discharge flow study. OH radicals produced by reaction of F atoms with  $\text{H}_2\text{O}$ .  $[\text{OH}]$  monitored by LIF at wavelengths near  $280 \text{ nm}$  in presence of large excess of  $\text{CH}_3\text{OH}$ . Branching ratios measured at room temperature by (i) detection of  $\text{CH}_3\text{O}$  by LIF at  $\sim 287 \text{ nm}$  and (ii) detection of  $\text{CH}_2\text{OH}$  by time-of-flight mass-spectrometry. In the former method the  $\text{CH}_3\text{O}$  signal was calibrated using the  $\text{F} + \text{CH}_3\text{OH}$  reaction and in the latter the  $\text{Cl} + \text{CH}_3\text{OH}$  reaction was used to calibrate the  $\text{CH}_2\text{OH}$  signal. No reasons could be suggested to explain the difference between the LIF result (0.25) for the branching ratios and that from the mass spectrometry (0.17).
- (h) Flash photolysis of  $\text{H}_2\text{O}/\text{CH}_3\text{OH}/\text{Ar}$  mixtures under slow flow conditions at total pressures in the range  $33\text{--}67 \text{ mbar}$ .  $[\text{OH}]$  monitored by resonance fluorescence at  $\sim 310 \text{ nm}$ .
- (i) Pulse radiolysis of  $\text{Ar}/\text{CH}_3\text{OH}$  mixtures with  $2 \text{ MeV}$  electrons from a Febetron. OH produced by  $\text{Ar}^* + \text{CH}_3\text{OH} \rightarrow \text{CH}_3 + \text{OH} + \text{Ar}$ .  $[\text{OH}]$  monitored by absorption at  $309 \text{ nm}$  to obtain  $k$ .  $[\text{CH}_3]$  monitored by absorption at  $216.4 \text{ nm}$  and  $[\text{CH}_2\text{OH}]$  obtained from its absorption spectrum over the range  $200\text{--}300 \text{ nm}$  to obtain branching ratio.
- (j) Pulsed laser photolysis at  $193 \text{ nm}$  of  $\text{N}_2\text{O}/\text{H}_2\text{O}/\text{CH}_3\text{OH}(\text{CD}_3\text{OH})/\text{He}$  mixtures under slow flow conditions.  $[\text{OH}]$  or  $[\text{OD}]$  monitored by LIF at wavelengths close to  $307 \text{ nm}$ . Total pressure  $\sim 900 \text{ mbar}$ .  $k(\text{CH}_3\text{OH})/k(\text{CD}_3\text{OH}) = 1.4 \exp(122/T)$  in range  $294\text{--}625 \text{ K}$  but the ratio falls off much more rapidly at higher temperatures.
- (k) Discharge flow study. OH or OD produced by reaction of H or D with  $\text{NO}_2$  in He carrier.  $[\text{OH}]$  or  $[\text{OD}]$  monitored by LIF at wavelengths close to  $307 \text{ nm}$  in large excess of the methanol.  $k$  measured for reaction of OH and OD with  $\text{CH}_3\text{OH}$ ,  $\text{CD}_3\text{OH}$ ,  $\text{CH}_3\text{OD}$ , and  $\text{CD}_3\text{OD}$ . Analysis of effects of isotopic substitution used to derive  $k_1/k_2$ .
- (l) Pulse radiolysis of  $\text{Ar}/\text{H}_2\text{O}/\text{CH}_3\text{OH}$  mixtures at  $1 \text{ bar}$  pressure.  $[\text{OH}]$  monitored by absorption at  $309 \text{ nm}$  using a Xe arc.
- (m) Relative rate study in a static system. OH produced by (1) photolysis of methyl nitrite/air mixtures at pressures close to  $1 \text{ bar}$  in a Teflon chamber with fluorescent lamps providing radiation in the region  $300\text{--}450 \text{ nm}$ , and (2) photolysis at  $254 \text{ nm}$  of  $\text{H}_2\text{O}_2/\text{N}_2$  mixtures. The concentrations of  $\text{CH}_3\text{OH}$  and  $[-\text{C}_6\text{H}_{12}^-]$  added to system were followed by GC.  $k/k(\text{OH} + [-\text{C}_6\text{H}_{12}^-]) = 0.134$  obtained from relative rates of removal of  $\text{CH}_3\text{OH}$  and  $[-\text{C}_6\text{H}_{12}^-]$ .  $k(\text{OH} + [-\text{C}_6\text{H}_{12}^-]) = 7.49 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ <sup>17,20</sup> used to obtain  $k$ .
- (n) Shock tube study using reflected shocks in  $\text{Ar}/(\text{CH}_3)_3\text{COOH}/\text{CH}_3\text{OH}$  mixtures. Shock speed measured and  $[\text{OH}]$  monitored by resonance absorption at  $309 \text{ nm}$ . Pressures close to  $1 \text{ bar}$  generated.
- (o) Pulsed laser photolysis at  $248 \text{ nm}$  of  $\text{HNO}_3/\text{CH}_3\text{OH}/\text{He}$  mixtures in a slow flow system.  $[\text{OH}]$  monitored by resonance fluorescence.  $[\text{CH}_3\text{O}]$  monitored at  $292 \text{ nm}$  and calibrated using the fluorescence excitation spectrum of the  $\text{CH}_3\text{O}$  produced by  $248 \text{ nm}$  photolysis of  $\text{CH}_3\text{ONO}$ .
- (p) Fast-flow discharge system used. OH generated by the  $\text{F} + \text{H}_2\text{O}$  reaction.  $\text{CH}_3\text{O}$  radicals, generated by the  $\text{OH} + \text{CH}_3\text{OH}$  reaction, were detected by LIF at  $292.8 \text{ nm}$  and the yields were compared with those from the  $\text{F} + \text{CH}_3\text{ONO}$  reaction.  $\text{CH}_2\text{OH}$  radicals, produced in the  $\text{OH} + \text{CH}_3\text{OH}$  reaction, were detected by reacting them with  $\text{O}_2$  to give  $\text{HO}_2$  which was detected by LMR and compared with the corresponding yields from the reaction of F with  $\text{CH}_2\text{O}$  in the presence of  $\text{O}_2$ .
- (q) Based on the room temperature values of Refs. 1–3, 7, 14 and a BEBO calculation. The expression for  $k_2/k$  is obtained from the results of Hägele *et al.*<sup>14</sup>
- (r) Least squares fit of the data from Refs. 2, 3, 6, 8, 9, 12, 13 to the expression  $k = C T^2 (-D/T)$ .
- (s) Based on the data of Refs. 2, 3, 7–9, 14, 21.
- (t) Based on the data of Refs. 2, 3, 8, 9, 11–13.

### Preferred Values

$k = 1.03 \cdot 10^{-17} T^{1.92} \exp(144/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range  $240\text{--}2000 \text{ K}$ .

$k_2/k = 0.15$  at  $300 \text{ K}$ .

### Reliability

$\Delta \log k = \pm 0.1$  at  $300 \text{ K}$ , rising to  $\pm 0.2$  at  $240 \text{ K}$  and to  $\pm 0.3$  at  $2000 \text{ K}$ .

$\Delta(k_2/k) = \pm 0.1$  at  $300 \text{ K}$ .

### Comments on Preferred Values

The rate constant is now well defined in the region of  $300 \text{ K}$  with excellent agreement between the results of Campbell *et al.*,<sup>1</sup> Overend and Paraskevopoulos,<sup>2</sup> Ravishankara and Davis,<sup>3</sup> Barnes *et al.*,<sup>5</sup> Tuazon *et al.*,<sup>6</sup> Wallington and Kurylo,<sup>8</sup> Pagsberg *et al.*,<sup>9</sup> Hess and Tully,<sup>10</sup> McCaulley *et al.*,<sup>11</sup> and Nelson *et al.*<sup>12</sup>

Studies over a temperature range also agree well. The preferred value for the temperature dependence is based on the work of Vandooren and Van Tiggelen,<sup>4</sup> Wallington and Kurylo,<sup>8</sup> Hess and Tully,<sup>10</sup> and Bott and Cohen.<sup>13</sup> There are also results from Meier *et al.*<sup>7</sup> and Hägele *et al.*<sup>14</sup> which fit this expression over most of their temperature range. The results of Greenhill and O'Grady<sup>21</sup> show more scatter and

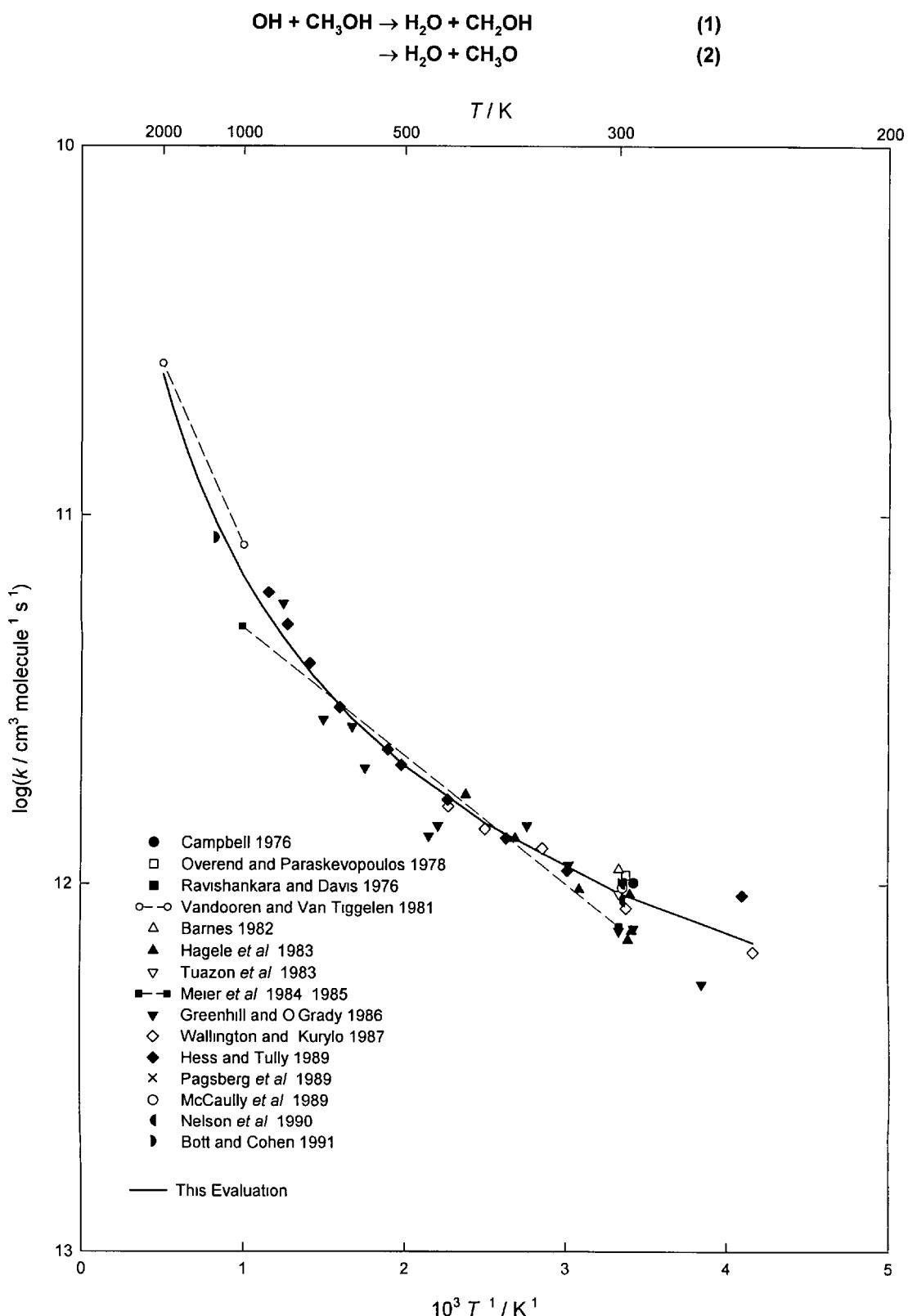
appear systematically low but are in general accord with the temperature variation of  $k$ .

There is general agreement that abstraction from the methyl group is likely to predominate at room temperature on the basis of the bond strengths involved in the abstraction process. This is reflected in the measured values of the branching ratios but they show substantial scatter covering the range  $k_2/k = 0.11\text{--}0.25$  at 298 K and ranging more widely at higher temperatures. The preferred value at 298 K is based on the results of Hägele *et al.*,<sup>14</sup> Meier *et al.*,<sup>7</sup> McCaulley *et al.*,<sup>11</sup> and Pagsberg *et al.*<sup>9</sup> Dóbé *et al.*<sup>15</sup> have estimated an even smaller value at 298 K on the basis of their results at higher temperatures.

At higher temperatures Hägele *et al.*<sup>14</sup> obtain a value of  $k_2/k = 0.23$  at 392 K and Dóbé *et al.*<sup>15</sup> obtain a very similar value, but at 612 K, Hess and Tully<sup>10</sup> have estimated that  $k_2/k$  will reach a value of  $\sim 0.5$  at 680 K on the basis of their measurements of  $k$  for isotopically substituted methanol, but this is about 100 K lower than would be suggested from an extrapolation of similar measurements of Hägele *et al.*<sup>14</sup> The existing data are not of sufficient consistency to make recommendations for the branching ratios at higher temperatures but the data suggest that Channel (2) will become comparable in importance to Channel (1) at  $\sim 1000$  K and become the predominant channel at temperatures higher than that.

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- <sup>13</sup>J. F. Bott and N. Cohen, *Int. J. Chem. Kinet.* **23**, 1075 (1991).
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- <sup>18</sup>NASA Evaluation No. 12, 1997 (see references in Introduction).
- <sup>19</sup>IUPAC, Supplement VII, 1999 (see references in Introduction).
- <sup>20</sup>R. Atkinson, *J. Phys. Chem. Ref. Data Monograph* 1 (1989).
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*Thermodynamic Data*

$$\Delta H^\circ_{298}(1) = -96.3 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = 9.17 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 3.83T^{0.012} \exp(+11340/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(2) = -120.8 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = 2.79 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 5.71 T^{-0.246} \exp(+14540/T) \\ (300 \leq T/\text{K} \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data ( $k = k_1 + k_2$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$2.93 \cdot 10^{-12} \exp(190/T)$	203–423	Vaghjiani and Ravishankara, 1989 <sup>1</sup>	(a)
$k_2 = 1.78 \cdot 10^{-12} \exp(220/T)$			
<i>Reviews and Evaluations</i>			
$k_1 = 1.2 \cdot 10^{-12} \exp(130/T)$	300–1000	CEC, 1992; 1994 <sup>2</sup>	(b)
$k_2 = 1.8 \cdot 10^{-12} \exp(220/T)$	300–1000		

**Comments**

- (a) Pulsed photolysis study with laser induced fluorescence detection of OH. First order decay of OH used to determine  $k_2$ . Because OH is regenerated rapidly from the CH<sub>2</sub>OOH produced in the first channel, the overall rate coefficient was determined from <sup>18</sup>OH loss and OH production from the reaction of <sup>18</sup>OH or OD with CH<sub>3</sub>OOH. A thorough investigation of the mechanism and discussion of the errors is given.
- (b) See Comments on Preferred Values.

**Preferred Values**

$k_1 = 1.2 \cdot 10^{-12} \exp(130/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 250–1000 K.

$k_2 = 1.8 \cdot 10^{-12} \exp(220/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 250–1000 K.

**Reliability**

$\Delta \log k_1 = \pm 0.2$  at 250 K, rising to  $\pm 0.4$  at 1000 K.

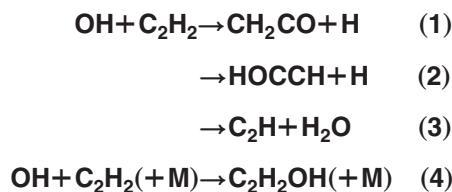
$\Delta \log k_2 = \pm 0.1$  at 250 K, rising to  $\pm 0.3$  at 1000 K.

**Comments on Preferred Values**

The preferred values are unchanged from the previous evaluation (CEC, 1994) and are based on the comprehensive and thorough study of Vaghjiani and Ravishankara.<sup>1</sup> An earlier 298 K determination of  $k_1$  by Niki *et al.*<sup>3</sup> using a relative rate method is consistent with the recommendation.

**References**

- <sup>1</sup>G. L. Vaghjiani and A. R. Ravishankara, *J. Phys. Chem.* **93**, 1948 (1989).
- <sup>2</sup>CEC, 1992; Supplement I, 1994 (see references in Introduction).
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*Thermodynamic Data*

$$\Delta H^\circ_{298}(1) = -94.8 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = -28.15 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 9.92 \cdot 10^{-4} T^{0.499} \exp(+11610/T) \\ (300 \leqslant T/\text{K} \leqslant 5000)$$

$$\Delta H^\circ_{298}(3) = 58.0 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = 17.47 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 3.04 \cdot 10^2 T^{-0.516} \exp(-7300/T) \\ (300 \leqslant T/\text{K} \leqslant 5000)$$

$$\Delta H^\circ_{298}(2) = 45.8 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = -20.90 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 1.50 \cdot 10^{-3} T^{0.610} \exp(-5360/T) \\ (300 \leqslant T/\text{K} \leqslant 5000)$$

$$\Delta H^\circ_{298}(4) = -152.3 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(4) = -122.23 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(4) = 1.89 \cdot 10^{-28} T^{0.714} \exp(+18470/T) \text{ cm}^3 \text{ molecule}^{-1} \\ (300 \leqslant T/\text{K} \leqslant 5000)$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data ( $k = k_1 + k_2 + k_3 + k_4$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$3.0 \cdot 10^{-12}$	1700–2000	Fenimore and Jones, 1964 <sup>1</sup>	(a)
$1.0 \cdot 10^{-11} \exp(-3500/T)$	1000–1700	Browne <i>et al.</i> , 1969 <sup>2</sup>	(b)
$k_4 = 3.0 \cdot 10^{-11} \exp(-3500/T)$	2000	Warnatz <i>et al.</i> , 1982 <sup>3</sup>	(c)
$2.7 \cdot 10^{-13}$	1100	Smith, Fairchild, and Crosley, 1984 <sup>4</sup>	(d)
$5.8 \cdot 10^{-13}$	1300		
$4.5 \cdot 10^{-11} \exp(-5300/T)$	1100–1273	Liu, Mulac, and Jonah, 1988 <sup>5</sup>	(e)
$1.53 \cdot 10^{-12}$	1700	Kaiser, 1990 <sup>6</sup>	(f)
$4.7 \cdot 10^{-13}$	1200	Bott and Cohen, 1990 <sup>7</sup>	(g)
$k_1 = 1.8 \cdot 10^{-11} \exp(-3600/T)$	1700–1900	Woods and Haynes, 1994 <sup>8</sup>	(h)
<i>Reviews and Evaluations</i>			
$k_4 \cdot [air] = [air] 5.5 \cdot 10^{-30}$	200–300	NASA, 1997 <sup>9</sup>	(i)
$k_4 \cdot [N_2] = [N_2] 5.0 \cdot 10^{-30} (T/300)^{-1.5}$	200–300	IUPAC, 1999 <sup>10</sup>	(j)
$1 \cdot 10^{-10} \exp(-6500/T)$	1000–2000	CEC, 1992; 1994 <sup>11</sup>	(k)

**Comments**

- (a) Acetylene/oxygen flames at atmospheric pressure with mass spectrometric sampling of the burned gas.
- (b) Acetylene flame, concentration profiles determined by absorption and emission spectroscopy. Computer simulation used to extract value of  $k$ .
- (c) Burner stabilized laminar flat acetylene/oxygen/argon flame; sampling nozzle with mass spectrometric analysis. Formation of  $\text{C}_4\text{H}_2$  was studied.
- (d) Pulsed  $\text{CO}_2$  laser photolysis of  $\text{SF}_6/\text{H}_2\text{O}_2/\text{N}_2/\text{C}_2\text{H}_2$  mixtures. OH detected by laser induced fluorescence. At 900 K the reaction shows a pressure dependence, but this is absent at 1100 and 1300 K, suggesting that the low temperature addition reaction is a minor channel at these higher temperatures.
- (e) Pulse radiolysis of  $\text{H}_2\text{O}/\text{C}_2\text{H}_2/\text{Ar}$  mixtures at a total pressure of 1 bar.  $[\text{OH}]$  monitored by time-resolved resonance absorption spectroscopy. The rate constant shows a complex pressure and temperature dependence below 1100 K as the addition channel becomes important.

- (f) Flame study on  $\text{C}_2\text{H}_2/\text{air}$  fuel rich flames at 1 bar pressure. Density-height profiles were determined for OH by absorption spectroscopy and for  $\text{CH}_4$  and  $\text{C}_2\text{H}_2$  by probe sampling. A computer simulation of the OH profile using a detailed mechanism was used to obtain  $k$ .
- (g) Shock tube study with UV absorption monitoring of  $[\text{OH}]$  which was generated from *t*-butyl hydroperoxide.
- (h) Laminar premixed ethylene/air flames, under sooting and nonsooting conditions.  $\text{C}_1\text{-}\text{C}_4$  hydrocarbon yields determined by gas chromatography and the results analyzed using the Miller-Melius model.<sup>12</sup> It is argued that channel (4) is reversible.
- (i) Based on the analysis of Smith *et al.*<sup>4</sup>
- (j) Based on the studies of Schmidt *et al.*,<sup>13</sup> Wahner and Zetzsch,<sup>14</sup> Bohn *et al.*,<sup>15</sup> Perry *et al.*,<sup>16</sup> Michael *et al.*,<sup>17</sup> Perry and Williamson,<sup>18</sup> the analysis of Smith *et al.*,<sup>4</sup> and the evaluation of Atkinson.<sup>19</sup>
- (k) Based largely on the studies of Fenimore and Jones<sup>1</sup> and Smith *et al.*<sup>4</sup>

### Preferred Values

$(k_1 + k_2 + k_3) = 1.3 \cdot 10^{-10} \exp(-6800/T)$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> over the range 1000–2000 K.

#### Reliability

$\Delta \log(k_1 + k_2 + k_3) = \pm 0.5$  at 1000 K, rising to  $\pm 1.0$  at 2000 K.

#### Comments on Preferred Values

The 1992 and 1994 CEC evaluations<sup>11</sup> ascribed reaction at high temperatures primarily to abstraction [Channel (3)] and used the measurements of Smith *et al.*<sup>4</sup> together with the reaction endothermicity to propose Arrhenius parameters. The same argument is retained here, with slight changes in the parameters reflecting updating of the thermodynamic data. The more recent rate measurements<sup>5–8,15,21</sup> for the overall rate constant are in reasonable agreement with this proposal.

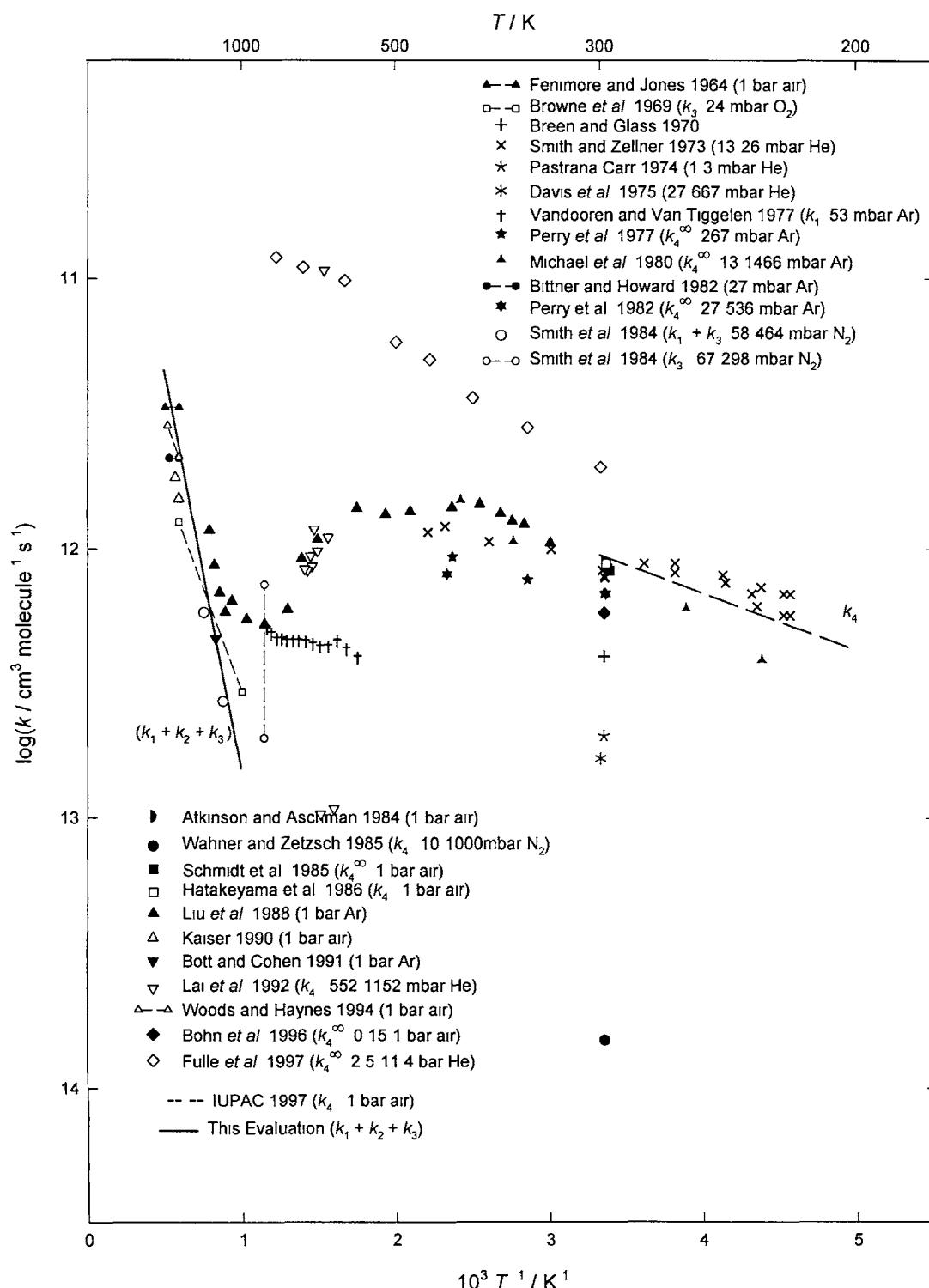
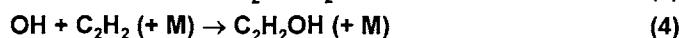
The mechanism of the reaction has been discussed in detail by Miller and Melius,<sup>12</sup> based on *ab initio* calculations. At low temperatures, the reaction proceeds primarily via an addition reaction to form the adduct HCC(H)OH. Both Fulle *et al.*<sup>21</sup> and Lai *et al.*<sup>22</sup> have studied OH concentration-time profiles in the system at temperatures around 700 K to extract the thermodynamic parameters of the adduct formation and redissociation reactions. At higher temperatures the adduct undergoes activated decomposition to form HOC<sub>2</sub>H + H, CH<sub>2</sub>CO + H, and CH<sub>3</sub> + CO, while Channel (3) proceeds by direct abstraction. Miller and Melius<sup>12</sup> provide calculated rate parameters for each of these channels. Their overall rate constant agrees with the expression recommended here to within a factor of 2 and their channel rate coefficients may be used to obtain some measure of the channel efficiencies. Channel (3) is shown to dominate (63% at 1000 K and 82% at 2000 K), with  $k_1/k = 0.24$  at 1000 K and 0.04 at 2000 K, and  $k_2/k = 0.1$  at 1000 K and 0.14 at 2000 K. The channel leading to CH<sub>3</sub> + CO is of low efficiency over the whole range.

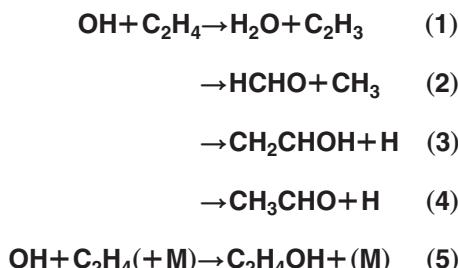
At temperatures below 1000 K and at pressures of  $\sim 1$  bar, the pressure dependent addition reaction begins to dominate. The rate data for the addition process have been evaluated by the NASA and IUPAC Panels whose findings we accept. The low temperature data have not been included in the Table but all of the data<sup>1–8,13–29</sup> are shown on the Arrhenius plot and a discussion of the low temperature data will be found in Refs.

9 and 10. Under combustion conditions the addition process is only significant at elevated pressures and the contribution of Channel (4) to the composite rate constant can be estimated using the following parameters:  $k_4^0 = 5.5 \cdot 10^{-30}$  cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup>,  $k_4^\infty = 3.8 \cdot 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>,  $F_{c,4} = 0.17 \exp(-51/T) + \exp(-T/204)$ .  $k_4^0$  is for N<sub>2</sub> and is taken from IUPAC.<sup>10</sup>  $k_4^\infty$  and  $F_{c,4}$  are values obtained by Fulle *et al.*<sup>21</sup> from studies using He as the bath gas.

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*Thermodynamic Data*

$$\begin{aligned} \Delta H^\circ_{298}(1) &= -31.7 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(1) &= 19.9 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 64.3 T^{-0.211} \exp(+3620/T) \\ &(300 \leq T/\text{K} \leq 5000) \end{aligned}$$

$$\begin{aligned} \Delta H^\circ_{298}(3) &= 1.49 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(3) &= 1.69 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(3) &= 5.00 \cdot 10^{-6} T^{1.832} \exp(+408/T) \\ &(300 \leq T/\text{K} \leq 5000) \end{aligned}$$

$$\begin{aligned} \Delta H^\circ_{298}(5) &= -125.6 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(5) &= -127.9 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(5) &= 3.44 \cdot 10^{-33} T^{2.297} \exp(+15600/T) \text{ cm}^3 \text{ molecule}^{-1} \\ &(300 \leq T/\text{K} \leq 5000) \end{aligned}$$

$$\begin{aligned} \Delta H^\circ_{298}(2) &= -51.8 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(2) &= 9.81 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 91.3 T^{-0.477} \exp(+6040/T) \\ &(300 \leq T/\text{K} \leq 5000) \end{aligned}$$

$$\begin{aligned} \Delta H^\circ_{298}(4) &= 113.2 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(4) &= -13.85 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(4) &= 8.18 \cdot 10^{-11} T^{3.102} \exp(+12430/T) \\ &(300 \leq T/\text{K} \leq 5000) \end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data ( $k = k_1 + k_2 + k_3 + k_4$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$5.7 \cdot 10^{-13}$	773	Badwin <i>et al.</i> , 1984 <sup>1</sup>	(a)
$2.4 \cdot 10^{-11} \exp(-2104/T)$	748–1173	Liu, Mulac, and Jonah, 1987 <sup>2</sup>	(b)
$2.5 \cdot 10^{-12}$	1220	Smith, 1987 <sup>3</sup>	(c)
$3.4 \cdot 10^{-11} \exp(-2992/T)$	651–901	Tully, 1988 <sup>4</sup>	(d)
$4.3 \cdot 10^{-12}$	$1200 \pm 17$	Bott and Cohen, 1991 <sup>5</sup>	(e)
<i>Reviews and Evaluations</i>			
$4 \times 87 \cdot 10^{-18} T^2 \exp(-1125/T)$	650–1220	Atkinson, 1989 <sup>6</sup>	(f)
$3.4 \cdot 10^{-11} \exp(-2990/T)$	650–1500	CEC, 1992; 1994 <sup>7</sup>	(g)

**Comments**

- (a) Addition of  $\text{C}_2\text{H}_4$  to slowly reacting  $\text{H}_2/\text{O}_2$  mixtures. Pressure change and product yields ( $\text{C}_2\text{H}_4\text{O}$ ,  $\text{HCHO}$ ,  $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{CH}_3\text{CHO}$ ) in early stages of reaction measured. Value of  $k$  is sensitive to  $\text{CO}$  and  $\text{HCHO}$  yields.
- (b) Pulse radiolysis of  $\text{H}_2\text{O}/\text{C}_2\text{H}_4$  mixtures in 1 bar Ar.  $[\text{OH}]$  monitored by resonance absorption. In the temperature range 343–563 K addition of OH to  $\text{C}_2\text{H}_4$  is dominant. In the range 563–748 K addition, adduct decomposition, and H-abstraction occur concurrently. Above 748 K H abstraction is dominant.
- (c) IR laser pyrolysis of flowing mixtures of  $\text{H}_2\text{O}_2/\text{CF}_4/\text{SF}_6/\text{C}_2\text{H}_4$  with  $[\text{OH}]$  monitored by LIF. Temperature determined from population of OH rotational states.
- (d) Laser photolysis of  $\text{N}_2\text{O}/\text{H}_2\text{O}/\text{C}_2\text{H}_4/\text{He}$  mixtures at 193 nm or  $\text{H}_2\text{O}/\text{C}_2\text{H}_4/\text{Ar}$  mixtures.  $[\text{OH}]$  monitored by laser induced fluorescence.  $k$  found to be independent of nature or pressure of bath gas.

- (e) Shock-tube study of  $t\text{-C}_4\text{H}_9\text{OH}/\text{C}_2\text{H}_4/\text{Ar}$  mixtures at temperatures near to 1200 K and pressures of 1 bar.  $[\text{OH}]$  monitored by UV absorption.
- (f) Derived from a fit of data of Smith<sup>3</sup> and Tully<sup>4</sup> to the expression  $k = C T^2 \exp(-D/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . This evaluation discusses in detail the low-temperature ( $< 600$  K) data for the addition reaction,  $\text{OH} + \text{C}_2\text{H}_4 + \text{M} \rightarrow \text{HOCH}_2\text{CH}_2 + \text{M}$ .
- (g) Accepts the expression of Tully.<sup>4</sup>

**Preferred Values**

$$(k_2 + k_3 + k_4) = 3.4 \cdot 10^{-11} \exp(-2990/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the range } 650\text{--}1500 \text{ K.}$$

**Reliability**

$$\Delta \log k = \pm 0.5 \text{ over the range } 650\text{--}1500 \text{ K.}$$

**Comments on Preferred Values**

Only the data for reactions (1)–(4) are evaluated here. The kinetics database for the addition reaction [Channel (5)] is

discussed at length in the evaluations of Atkinson<sup>6</sup> and IUPAC.<sup>8</sup>

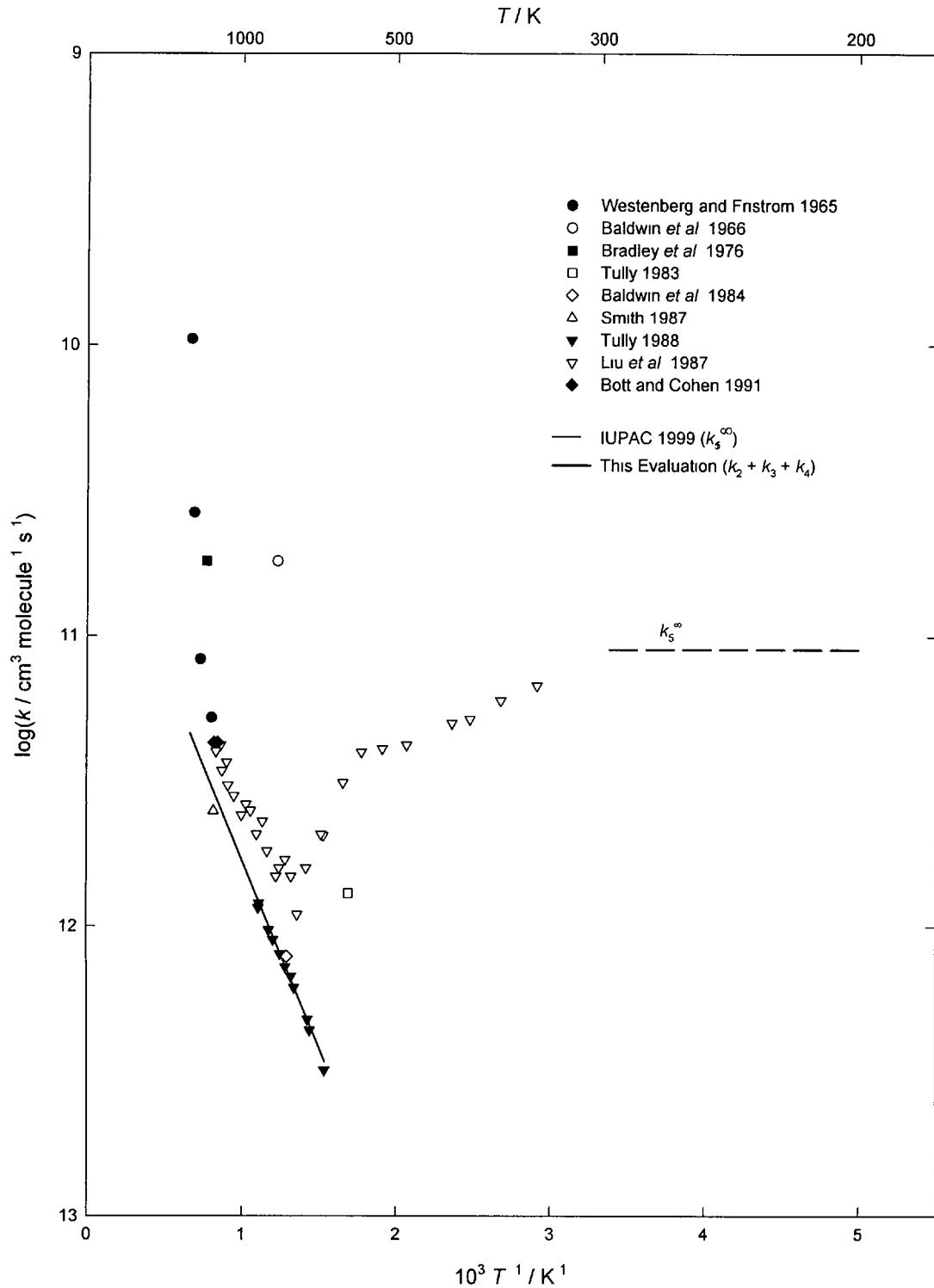
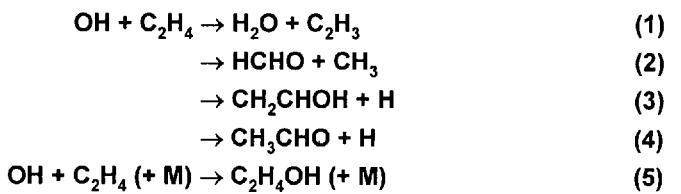
The direct rate constant measurements have all been carried out by monitoring the OH removal, which has usually been assumed to occur by hydrogen abstraction [Channel (1)]. However recent *ab initio* calculations by Hippler and Viskolcz<sup>9</sup> have cast doubt on the importance of the direct abstraction channel. Their calculations suggest that the direct abstraction reaction has a much smaller rate constant than suggested by the experimental studies, e.g., some 2 orders of magnitude smaller at 700 K. Instead, it is proposed that under high pressure conditions the reaction proceeds by addition and rapid equilibration of the reactants and adduct ( $\text{CH}_2\text{CH}_2\text{OH}$ ) which is followed by decomposition of the  $\text{CH}_2\text{CH}_2\text{OH}$  to  $\text{C}_2\text{H}_3\text{OH} + \text{H}$ , or by isomerization to  $\text{CH}_3\text{CHOH}$  and decomposition to  $\text{CH}_2\text{O} + \text{CH}_3$  or  $\text{CH}_3\text{CHO} + \text{H}$ . Furthermore, Hidaka *et al.*<sup>10</sup> find that the results in their shock tube study of  $\text{C}_2\text{H}_4$  oxidation at 1100–2100 K are best explained in terms of  $\text{H}_2\text{O} + \text{C}_2\text{H}_3$  formation. Further experimental studies are required to test these possibilities but, whereas in our previous evaluations<sup>7</sup> the high temperature rate constant data were assumed to refer to  $k_1$ , we now take  $k = (k_2 + k_3 + k_4)$ .

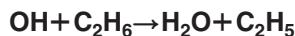
The theoretical calculations<sup>9</sup> suggest a complex pressure and temperature dependence of the overall rate constant for OH removal and this may in part explain the substantial scatter on the experimental data. The earlier studies<sup>11–14</sup> gave much higher values of  $k$  than more recent work and are not used in the present evaluation. The remaining studies<sup>1–5</sup> are

all cited in the Table. In his evaluation Atkinson<sup>6</sup> has discussed the values of  $k$  reported by Liu *et al.*,<sup>2</sup> which are substantially higher than those reported by Tully<sup>4</sup> at similar temperatures, and has suggested that the data of Liu *et al.*<sup>2</sup> may contain a contribution from stabilization of the adduct [Channel (5)]. The expression reported by Tully,<sup>4</sup> which we take as our preferred expression for  $k$ , gives lower values than those from the other studies but is compatible with the values found by Baldwin *et al.*,<sup>1</sup> Smith,<sup>3</sup> and Bott and Cohen.<sup>5</sup>

## References

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*Thermodynamic Data*

$$\begin{aligned}\Delta H_{298}^{\circ} &= -74.1 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= 23.23 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 3.44 \cdot 10^2 T^{-0.417} \exp(+8710/T) \\ &(300 \leq T/\text{K} \leq 4000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$1.08 \cdot 10^{-10} \exp(-2820/T)$	850–1600	Smets and Peeters, 1975 <sup>1</sup>	(a)
$1.43 \cdot 10^{-14} T^{1.05} \exp(-911/T)$	297–800	Tully, Ravishankara, and Carr, 1983 <sup>2</sup>	(b)
$8.51 \cdot 10^{-18} T^{2.06} \exp(-430/T)$	293–705	Tully <i>et al.</i> , 1986 <sup>3</sup>	(c)
$1.54 \cdot 10^{-11}$	1225	Bott and Cohen, 1991 <sup>4</sup>	(d)
$1.03 \cdot 10^{-11} \exp(-1110/T)$	231–377	Talukdar <i>et al.</i> , 1994 <sup>5</sup>	(e)
$8.37 \cdot 10^{-12}$	970	Koffend and Cohen, 1996 <sup>6</sup>	(d)
<i>Reviews and Evaluations</i>			
$1.2 \cdot 10^{-17} T^{2.0} \exp(-435/T)$	250–2000	CEC, 1992; 1994 <sup>7</sup>	(f)
$8.7 \cdot 10^{-12} \exp(-1070/T)$	220–380	NASA, 1997 <sup>8</sup>	(g)
$1.52 \cdot 10^{-17} T^{2.0} \exp(-498/T)$	226–1225	Atkinson, 1997 <sup>9</sup>	(h)
$7.8 \cdot 10^{-12} \exp(-1025/T)$	240–300	IUPAC, 1999 <sup>10</sup>	(i)

**Comments**

- (a) Concentration profiles of a number of species through the reaction zone of a  $\text{C}_2\text{H}_6/\text{O}_2$  flame at a pressure of 40 mbar were measured by quadrupole mass spectrometry.  $k$  was calculated throughout the flame front from  $[\text{C}_2\text{H}_6]$  and  $[\text{OH}]$  assuming OH to be the only species removing  $\text{C}_2\text{H}_6$  in the early stages of the reaction.
- (b) Flash photolysis of  $\text{H}_2\text{O}/\text{C}_2\text{H}_6/\text{Ar}$  mixtures under static conditions with  $[\text{C}_2\text{H}_6] \gg [\text{H}_2\text{O}]$ .  $[\text{OH}]$  was monitored by time resolved resonance fluorescence.
- (c) Pulsed laser photolysis at 193 nm of  $\text{N}_2\text{O}/\text{C}_2\text{H}_6/\text{He}$  mixtures in a slowly flowing system with  $[\text{C}_2\text{H}_6] \gg [\text{OH}]$ .  $[\text{OH}]$  was monitored by time resolved LIF detected at  $\sim 308$  nm.
- (d) Shock tube study on  $\text{CH}_4/t$ -butyl hydroperoxide/Ar mixtures at total pressures in the range 0.85–1.3 bar.  $[\text{OH}]$  was monitored by resonance absorption behind the reflected shock. The OH resonance lamp was calibrated by shock heating  $\text{H}_2/\text{O}_2/\text{Ar}$  mixtures. Values of  $k$  were derived from the measured  $[\text{OH}]$  decay rate
- (e) Pulsed laser photolysis at 248 nm of  $\text{H}_2\text{O}_2/\text{C}_2\text{H}_6/\text{He}$  mixtures in a slowly flowing system with  $[\text{C}_2\text{H}_6] \gg [\text{OH}]$ . The  $[\text{OH}]$  was monitored by time resolved LIF.
- (f) Adopts an expression similar to that derived by Cohen.<sup>50</sup>
- (g) Value at 298 K taken as the average of the values reported in Refs. 3, 5, 37, 39, 40, 42, and the unpublished results of Anderson and Stephens. The temperature coefficient is based on Refs. 5, 37, and unpublished results of Anderson and Stephens.
- (h) The data from Refs. 2–5, 21, 23, 25, 28, 29, 31, 34, 35,

37–39, 45, were fitted to the expression  $k = C T^2 \times \exp(-D/T)$ , where C and D are constants.

- (i) The expression derived by Atkinson<sup>9</sup> for the range 226–1225 K was accepted and the Arrhenius expression,  $k = A \exp(-B/T)$ , was derived from it for the range 240–300 K.

**Preferred Values**

$k = 1.52 \cdot 10^{-17} T^{2.0} \exp(-500/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 200–2000 K.

**Reliability**

$\Delta \log k = \pm 0.08$  at 298 K, rising to  $\pm 0.15$  at 200 K and to  $\pm 0.2$  at 2000 K.

**Comments on Preferred Values**

The rate constant for this reaction is well characterized over a wide temperature range, particularly at low temperatures because of its importance in atmospheric chemistry. The numerous studies at ambient temperatures and below<sup>2,3,5,13,14,17,20,21,23–25,27–45,47,48</sup> have been evaluated by the IUPAC<sup>10</sup> and NASA<sup>8</sup> Panels. We accept their recommendations for the range 200–300 K and do not cite in the Table the studies in this range.

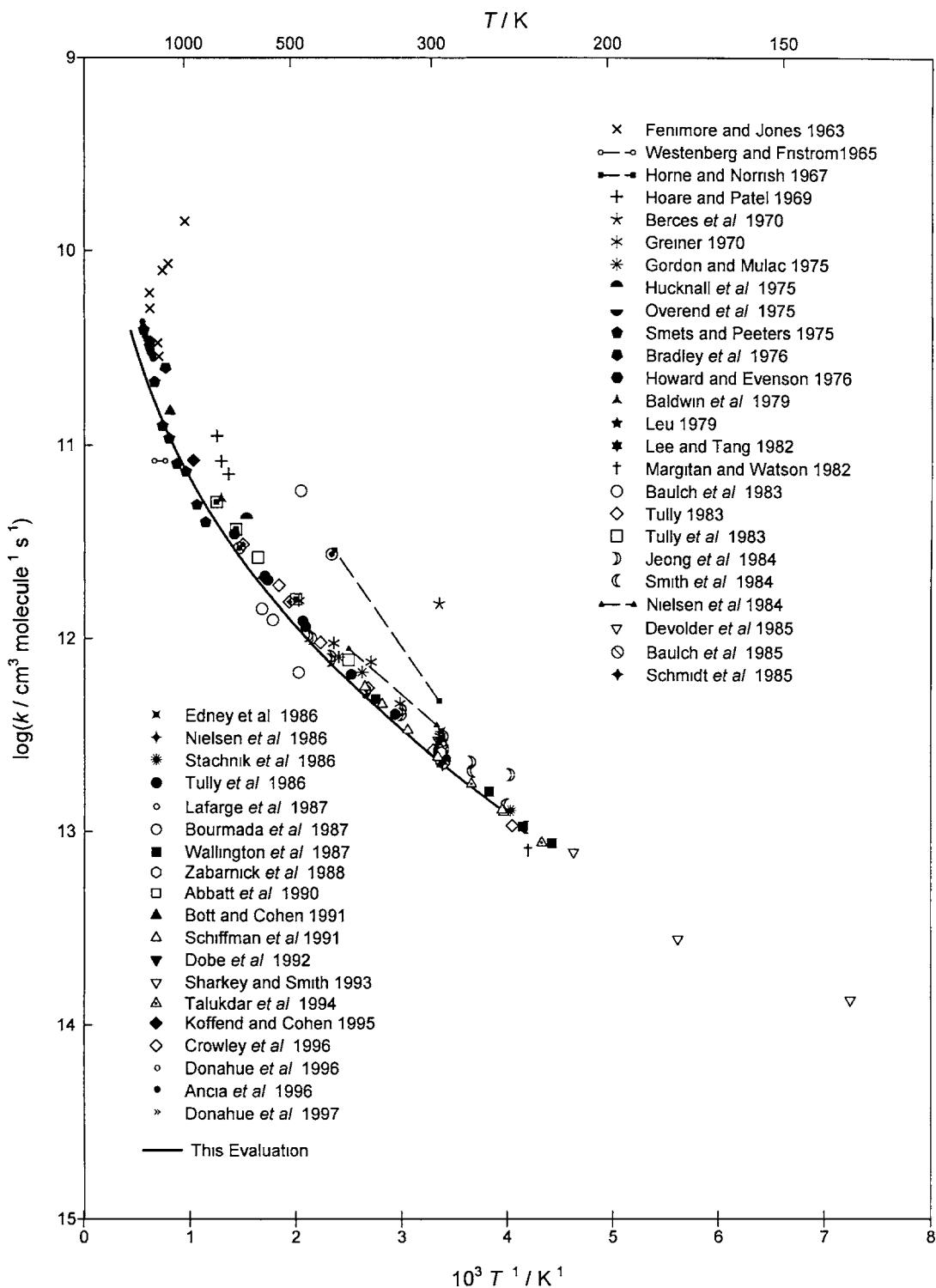
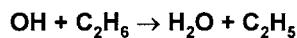
Among the measurements at temperatures above 300 K<sup>1–6,11–13,15–19,21,22,26,27,36,39,43,45,46</sup> there are a number of direct studies<sup>2,3,5,17,18,36,39,45,47,48</sup> and relative rate studies,<sup>16,26,43</sup> extending up to 800 K, which are in excellent agreement. The studies of Tully *et al.*<sup>2,3</sup> and Talukdar *et al.*<sup>5</sup> have been used to derive our preferred expression for  $k$  in this range. At

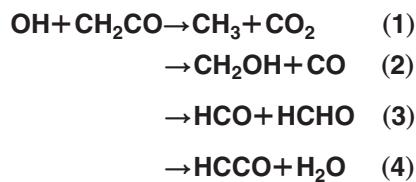
temperatures above 800 K the data are more scattered. In this region our recommendations are based mainly on the shock tube studies of Bott and Cohen (1225 K)<sup>4</sup> and Koffend and Cohen (970 K),<sup>6</sup> since their technique appears reliable and has produced satisfactory data for analogous reactions.

The expression derived by Atkinson,<sup>8</sup> using essentially the same data base as proposed here, is adopted as our preferred expression for  $k$ . It extrapolates reasonably well to the very scattered data at temperatures above 1500 K giving us confidence in extending the high temperature limit of our recommendations to 2000 K, with expanded error limits. Cohen and Westberg<sup>49</sup> derived a very similar expression in their 1983 evaluation of the rate data.

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*Thermodynamic Data*

$$\begin{aligned} \Delta H^\circ_{298}(1) &= -236.8 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(1) &= -17.93 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 0.466 T^{-0.252} \exp(+28500/T) \\ &(300 \leq T/\text{K} \leq 5000) \end{aligned}$$

$$\begin{aligned} \Delta H^\circ_{298}(3) &= -55.1 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(3) &= 17.47 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(3) &= 6.69 \cdot 10^2 T^{-0.733} \exp(+6580/T) \\ &(300 \leq T/\text{K} \leq 5000) \end{aligned}$$

$$\begin{aligned} \Delta H^\circ_{298}(2) &= -118.0 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(2) &= 15.83 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 3.57 \cdot 10^2 T^{-0.599} \exp(+14020/T) \\ &(300 \leq T/\text{K} \leq 5000) \end{aligned}$$

$$\begin{aligned} \Delta H^\circ_{298}(4) &= -56.1 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(4) &= 8.48 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(4) &= 68.4 T^{-0.449} \exp(+6550/T) \\ &(300 \leq T/\text{K} \leq 5000) \end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data ( $k = k_1 + k_2 + k_3 + k_4$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$1.8 \cdot 10^{-11}$	299	Hatakeyama <i>et al.</i> , 1985 <sup>1</sup>	(a)
$3.3 \cdot 10^{-11}$	298	Brown <i>et al.</i> , 1989 <sup>2</sup>	(b)
$6.2 \cdot 10^{-12} \exp(510/T)$	193–423		
$1.2 \cdot 10^{-11}$	296	Oehlers <i>et al.</i> , 1992 <sup>3</sup>	(c)
<i>Branching Ratios</i>			
$k_2/k = 0.6 \pm 0.1$	298	Grussdorf <i>et al.</i> , 1994 <sup>4</sup>	(d)
$k_3/k < 0.02$			
$k_4/k < 0.01$			
<i>Reviews and Evaluations</i>			
$1.5 \cdot 10^{-11}$	298	Atkinson, 1993 <sup>5</sup>	(e)
$1.7 \cdot 10^{-11}$	300–2000	CEC, 1992; 1994 <sup>6</sup>	(f)

**Comments**

- (a) Steady state photolysis of  $\text{CH}_3\text{ONO}/\text{O}_2/\text{NO}$  mixtures in an 11 dm<sup>3</sup> reactor with FTIR detection. Relative rate measurement vs propene with  $k(\text{OH} + \text{C}_3\text{H}_6)$  taken as  $8.0 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Ketene consumption and formation of both CO and HCHO formation were monitored. After correcting for OH+HCHO and for photolysis, the yield of HCHO was shown to be 70%–80%, and was attributed to  $\text{CH}_2\text{OH}$  formation [Channel (2)] followed by its reaction with  $\text{O}_2$ .
- (b) Discharge flow/resonance fluorescence study generating OH from  $\text{H} + \text{NO}_2$ . There was no evidence of any pressure dependence over the range 2.4–4.2 mbar
- (c) Discharge flow/LMR study, generating OH from  $\text{F} + \text{H}_2\text{O}$
- (d) Discharge flow/LMR study. OH and Cl were generated from  $\text{F} + \text{H}_2\text{O}$  and  $\text{F} + \text{HCl}$ , respectively. The  $\text{CH}_2\text{OH}$  product was calibrated against signals from  $\text{OH} + \text{CH}_3\text{OH}$  (yield of  $\text{CH}_2\text{OH} = 0.85$ ) and  $\text{Cl} + \text{CH}_3\text{OH}$  (yield  $\text{CH}_2\text{OH} = 1.0$ ). The two methods gave values for  $k_2/k$  of 0.56 and 0.69 respectively. Channel (3) was measured relative to  $\text{F} + \text{H}_2\text{CO}$  and Channel (4) relative to  $\text{F} + \text{CH}_2\text{CO}$ .

- (e) Mean of the values of Hatakeyama *et al.*<sup>1</sup> and Oehlers *et al.*<sup>3</sup>
- (f) Accepts the value recommended by Warnatz.<sup>7</sup>

**Preferred Values**

$$k = 2.8 \cdot 10^{-12} \exp(510/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the range } 296\text{--}1000 \text{ K.}$$

$$k_2/k = 0.6 \text{ at } 298 \text{ K}; k_3/k < 0.02 \text{ at } 298 \text{ K}; k_4/k < 0.01 \text{ at } 298 \text{ K.}$$

**Reliability**

$$\begin{aligned} \Delta \log k &= \pm 0.2 \text{ at } 296 \text{ K, rising to } 0.6 \text{ at } 1000 \text{ K.} \\ \Delta(k_2/k) &= \pm 0.2 \text{ at } 298 \text{ K.} \end{aligned}$$

**Comments on Preferred Values**

The available data at room temperatures range over a factor of  $\sim 3$ . We accept the value recommended by Atkinson<sup>5</sup> which is a mean of the values of Hatakeyama *et al.*<sup>1</sup> and Oehlers *et al.*<sup>3</sup> The only data at high temperatures come from a very indirect flame study by Vandooren and Van Tiggelen<sup>8</sup> who obtain a value of  $4.7 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over

the range 480–1000 K, suggesting a small positive temperature coefficient for  $k$  in contrast to the small negative value obtained in the more direct study of Brown *et al.*<sup>2</sup> at lower temperatures. Our preferred expression for  $k$  is obtained by combining our preferred value for  $k(298\text{ K})$  with the temperature dependence obtained by Brown *et al.*<sup>2</sup>

The most extensive measurements have been made at low pressures using discharge flow techniques: the measurements of Brown *et al.*<sup>2</sup> show no discernible pressure dependence over a limited pressure range. The scatter in the room temperature measurements of the rate constant make it difficult to draw conclusions on the pressure dependence from a comparison of the high and low pressure measurements. The absence of a pressure dependence observed by Brown *et al.*,<sup>2</sup> together with the observed rate parameters, suggests that the reaction occurs by addition followed by rapid decomposition of the adduct. Grussdorf *et al.*<sup>4</sup> have measured the branching ratios at low pressures at room temperature for a number of the possible channels and their values are accepted as our preferred values. Hatakeyama *et al.* obtained a value of  $k_2/k \sim 0.7\text{--}0.8$ . There are no data on the temperature dependence of the branching ratios but some insight into the temperature and pressure dependence of the branching ratios is

provided by the theoretical modeling of the reaction mechanism by Hou *et al.*<sup>9</sup> At low temperatures they find values of the branching ratios in agreement with the results of Grussdorf *et al.*,<sup>4</sup> together with contributions from Channel (1). At 1500 K the major channels are (1), (2), and (4). In the absence of experimental data these calculations probably offer the best guide to the high temperature branching ratios at this stage.

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### Thermodynamic Data

$$\begin{aligned}\Delta H^\circ_{298}(1) &= -122.8 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(1) &= 8.59 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 2.37 \cdot 10^3 T^{-0.936} \exp(+14320/T) \\ (300 \leqslant T/\text{K} \leqslant 5000)\end{aligned}$$

$$\begin{aligned}\Delta H^\circ_{298}(2) &= -102.3 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(2) &= 9.05 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 66.5 T^{-0.412} \exp(+12060/T) \\ (300 \leqslant T/\text{K} \leqslant 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

### Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$6.87 \cdot 10^{-12} \exp(257/T)$	299–426	Atkinson and Pitts, 1978 <sup>1</sup>	(a)
$5.52 \cdot 10^{-12} \exp(307/T)$	244–528	Michael, Keil, and Klemm, 1985 <sup>2</sup>	(b)
$1.7 \cdot 10^{-11}$	298	Balestra-Garcia, Le Bras, and MacLeod, 1992 <sup>3</sup>	(c)
$1.44 \cdot 10^{-11}$	298	Tyndall <i>et al.</i> , 1995 <sup>4</sup>	(d)
$4.31 \cdot 10^{-12} \exp(309/T)$	295–550	Taylor <i>et al.</i> , 1996 <sup>5</sup>	(e)
$1.89 \cdot 10^{-11} \exp(-597/T)$	600–900	D'Anna <i>et al.</i> , 2001 <sup>6</sup>	(f)
$1.44 \cdot 10^{-11}$	298	Sivakumaran and Crowley, 2003 <sup>7</sup>	(g)
$4.38 \cdot 10^{-12} \exp(366/T)$	201–348		
<i>Branching Ratios</i>			
$k_1/k = 0.93$	298	Cameron <i>et al.</i> , 2002 <sup>8</sup>	(h)
<i>Reviews and Evaluations</i>			
$3.89 \cdot 10^{-14} T^{0.73} \exp(560/T)$	250–1200	CEC, 1992; 1994 <sup>9</sup>	(i)
$5.6 \cdot 10^{-12} \exp(310/T)$	240–530	IUPAC, 1999; <sup>10</sup> Atkinson <sup>11</sup>	(j)

### Comments

- (a) Pulsed VUV flash photolysis of  $\text{H}_2\text{O}/\text{CH}_3\text{CHO}$  mixtures; resonance fluorescence detection of OH.
- (b) Discharge flow with resonance fluorescence detection of OH;  $\text{CH}_3\text{CO}$  shown to be the most probable product up to 530 K.
- (c) Pulsed laser photolysis study with resonance fluorescence detection of OH.
- (d) Discharge flow study with laser induced fluorescence detection of OH.
- (e) Laser photolysis; laser induced fluorescence detection OH. No pressure dependence of  $k$  observed in pressure range 132–950 mbar He. Sharp change in temperature dependence from negative to positive observed at ~600 K. Mechanism involving H atom abstraction from the  $\text{CH}_3$  group was dominant at elevated temperatures.
- (f) Relative rate study. OH radicals generated by photolysis of organic nitrite/synthetic air mixtures in a 250  $\text{dm}^3$  vessel in the presence of  $\text{CH}_3\text{CHO}$  and a reference compound (but-1-ene). Concentrations of the  $\text{CH}_3\text{CHO}$  and but-1-ene were monitored by long path FTIR.  $k/k_{\text{ref}} = 0.458 \pm 0.024$  obtained. Value of  $k$  cited obtained using  $k(\text{OH} + \text{but-1-ene}) = 3.13 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  from Atkinson.<sup>12</sup>
- (g) OH generated by pulsed laser photolysis of  $\text{H}_2\text{O}_2$  at 248 nm or  $\text{N}_2\text{O}/\text{H}_2\text{O}$  mixtures at 193 nm.  $[\text{OH}]$  was monitored by LIF at 309 nm. Experiments were carried out at total pressures of 66 or 132 mbar using He or Ar bath gas.
- (h) A series of studies in which the OH was generated in the presence of  $\text{CH}_3\text{CHO}$  by pulsed laser photolysis of  $\text{H}_2\text{O}_2$  or HONO.  $\text{CH}_3\text{CO}$  and  $\text{CH}_3$  were detected by transient absorption spectroscopy using diode array spectroscopy or absorption measurements at discrete wavelengths. H atoms were monitored by resonance fluorescence. As well as the value of  $k_1/k$  cited, upper limits of 0.03 for  $\text{CH}_3 + \text{HCOOH}$  production and 0.02 for  $\text{H} + \text{CH}_3\text{C(O)OH}$  production were established.
- (i) Based on the data of Atkinson and Pitts,<sup>1</sup> Michael et al.,<sup>2</sup> and Semmes et al.<sup>13</sup>
- (j) IUPAC expression is that derived by Atkinson,<sup>11</sup> based on the data of Atkinson and Pitts,<sup>1</sup> Michael et al.,<sup>2</sup> and Niki et al.<sup>14</sup>

### Preferred Values

$k = 4.8 \cdot 10^{-16} T^{1.35} \exp(792/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 280–1000 K.

$k_1/k = 0.93$  at 298 K.

### Reliability

$\Delta \log k = \pm 0.08$  at 280 K, rising to  $\pm 0.2$  at 1000 K.

$\Delta(k_1/k) = \pm 0.18$  at 298 K.

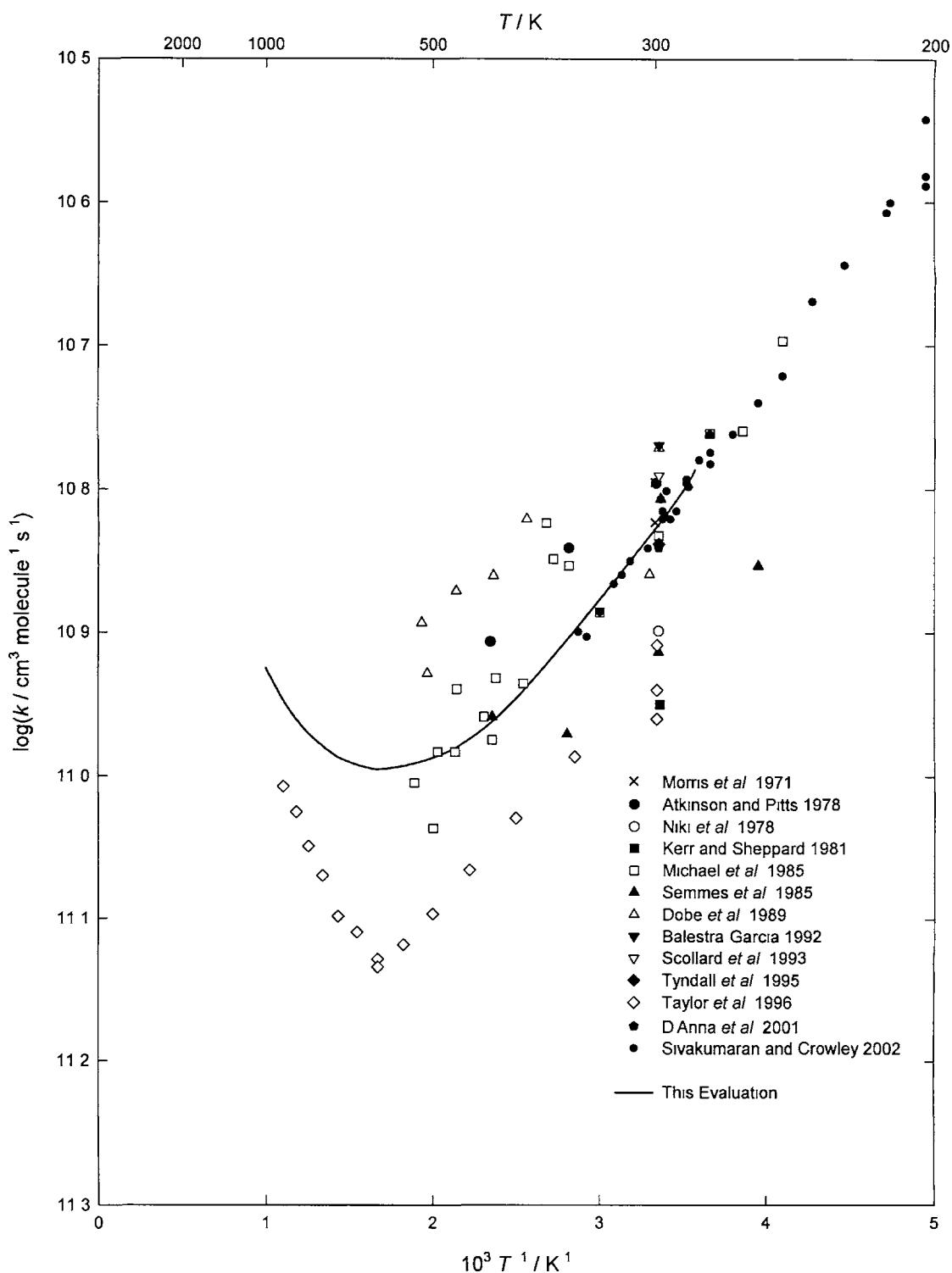
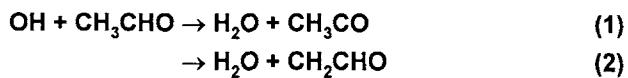
### Comments on Preferred Values

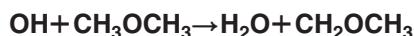
The preferred expression is a 3 parameter least squares fit to the data from the cited studies.<sup>1–7</sup> The measurements of Taylor et al.<sup>5</sup> cover an extended range to high temperatures where strong non-Arrhenius behavior is observed leading to reversal of slope of the temperature dependence. These results, however, are systematically 25% lower than data from the other studies in the range where they overlap; the data of Taylor et al.<sup>5</sup> were therefore scaled upward by Semmes et al.<sup>13</sup> who noted difficulties in accurate definition of  $[\text{CH}_3\text{CHO}]$  in the reaction mixtures. This procedure has been followed in the present evaluation. There are also a number of other studies<sup>15–18</sup> at ambient temperatures, thoroughly reviewed in Refs. 9, 10, and 11, which are not used in our evaluation. The preferred expression is in good agreement with that given by the IUPAC Panel<sup>10</sup> for the low temperature range.

It is usually assumed that the reaction occurs exclusively by Channel (1). The only direct measurement of the branching ratios tends to support this assumption. In the very careful study of Cameron et al.<sup>8</sup> it was shown that at 298 K the major, possibly only, channel is that leading to  $\text{H}_2\text{O} + \text{CH}_3\text{CO}$ . An upper limit of 25% could be established for any contribution from Channel (2).

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- <sup>17</sup>S. Dóbé, L. A. Khachatryan, and T. Bérces, *Ber. Bunsenges. Phys. Chem.* **99**, 847 (1989).
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*Thermodynamic Data*

$$\begin{aligned}\Delta H^\circ_{298} &= -95.0 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298} &= 19.7 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 2.19 \cdot 10^2 T^{-0.401} \exp(+11190/T) \\ &\quad (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$1.04 \cdot 10^{-11} \exp(-372/T)$	295–442	Tully and Droege, 1987 <sup>1</sup>	(a)
$6.30 \cdot 10^{-12} \exp(-234/T)$	230–372	Mellouki, Teton, and Le Bras, 1995 <sup>2</sup>	(b)
$3.39 \cdot 10^{-24} T^{4.11} \exp(1221/T)$	295–650	Arif, Dellinger, and Taylor, 1997 <sup>3</sup>	(c)
$1.51 \cdot 10^{-11} \exp(-496/T)$	263–364	DeMore and Bayes, 1999 <sup>4</sup>	(d)
$9.6 \cdot 10^{-12}$	753	Tranter and Walker, 2001 <sup>5</sup>	(e)
<i>Reviews and Evaluations</i>			
$1 \cdot 04 \cdot 10^{-11} \exp(-372/T)$	295–442	Atkinson, 1994 <sup>6</sup>	(f)

**Comments**

- (a) Pulsed laser photolysis at 193 nm of flowing He/N<sub>2</sub>O/H<sub>2</sub>O/CH<sub>3</sub>OCH<sub>3</sub> mixtures. [OH] monitored by LIF under pseudo first order conditions. Total pressure of 0.53 bar used.
- (b) Pulsed laser photolysis at 248 nm of flowing He/H<sub>2</sub>O<sub>2</sub>/CH<sub>3</sub>OCH<sub>3</sub> mixtures. [OH] monitored by LIF under pseudo first order conditions. Values of  $k$  independent of pressure.
- (c) Technique as in (a) but pressures of 0.97 bar used.
- (d) Relative rate technique using GC measurements to determine the fractional loss of dimethyl ether, by reaction with OH, compared to that of a reference compound. OH radicals were produced by 254 nm photolysis of O<sub>3</sub> in the presence of H<sub>2</sub>O or by 185 nm photolysis of an N<sub>2</sub>O/H<sub>2</sub> mixture. Reference compounds used were *n*-butane, *n*-pentane, and cyclohexane and the relative rates of reaction of these reference compounds with OH were also determined with respect to ethane, taking  $k(\text{OH} + \text{ethane}) = 1.29 \cdot 10^{-11} \times \exp(-1094/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .
- (e) Relative rates of consumption of H<sub>2</sub> and CH<sub>3</sub>OCH<sub>3</sub> were measured by GC when trace amounts of CH<sub>3</sub>OCH<sub>3</sub> were added to slowly reacting H<sub>2</sub>/O<sub>2</sub> mixtures. A wide range of compositions were used.  $k/k(\text{OH} + \text{H}_2)$  was obtained and combined with the value of  $k(\text{OH} + \text{H}_2)$  from this evaluation to derive  $k$ .
- (f) Review of low temperature data. Data of Tully and Droege<sup>1</sup> taken as basis of recommendation.

**Preferred Values**

$k = 8.2 \cdot 10^{-17} T^{1.73} \exp(176/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 250–1200 K.

*Reliability*

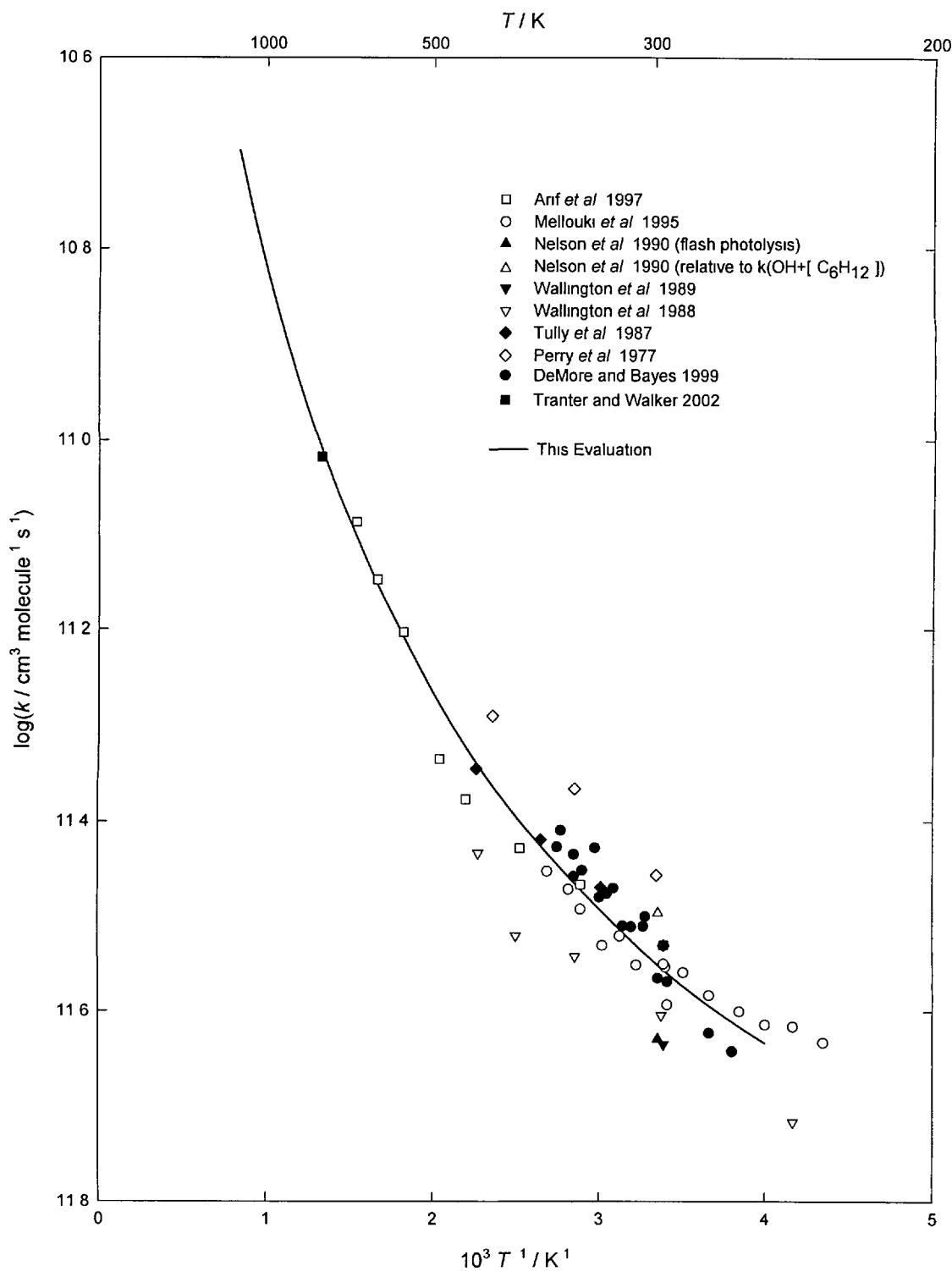
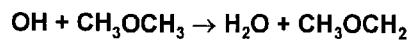
$\Delta \log k = \pm 0.1$  between 250 K and 500 K, rising to  $\pm 0.3$  at 1200 K.

*Comments on Preferred Values*

The data of Tully and Droege,<sup>1</sup> Mellouki *et al.*,<sup>2</sup> and Arif *et al.*<sup>3</sup> and DeMore and Bayes<sup>4</sup> are in excellent agreement in the temperature region where they overlap (295–364 K). At higher temperatures there is also good agreement between the results of Tranter and Walker<sup>5</sup> and Arif *et al.*<sup>3</sup> The preferred expression for  $k$  is based on these five studies which are cited in the Table. There are a number of other studies<sup>7–10</sup> which have not been used in deriving the preferred values but which are in fair agreement with it. The values of  $k$  obtained by Perry *et al.*<sup>7</sup> are approximately 25% higher, and those of Wallington *et al.*<sup>8</sup> are approximately 20% lower than those given by our preferred expression over the whole temperature ranges of both studies. The origins of these systematic differences are not clear. There is a similar degree of scatter among a number of single determinations of  $k$  at 295 K by relative rate techniques<sup>9,10</sup> and a pulse radiolysis study.<sup>10</sup>

**References**

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#### Thermodynamic Data

$$\begin{aligned}\Delta H^\circ_{298}(1) &= -95.6 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(1) &= 5.38 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 1.08 \cdot 10^2 T^{-0.625} \exp(+11240/T) \\ &(300 \leq T/\text{K} \leq 5000)\end{aligned}$$

$$\begin{aligned}\Delta H^\circ_{298}(3) &= -59.2 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(3) &= -1.04 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(3) &= 1.08 T^{-0.061} \exp(+7120/T) \\ &(300 \leq T/\text{K} \leq 5000)\end{aligned}$$

$$\begin{aligned}\Delta H^\circ_{298}(2) &= -80.0 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(2) &= -0.46 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 2.6 \cdot 10^{-2} T^{0.607} \exp(+9650/T) \\ &(300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2 + k_3$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$3.2 \cdot 10^{-12}$	292	Campbell <i>et al.</i> , 1976 <sup>1</sup>	(a)
$3.74 \cdot 10^{-12}$	296	Overend and Paraskevopoulos, 1978 <sup>2</sup>	(b)
$3.4 \cdot 10^{-11}$	294	Cox and Goldstone, 1982 <sup>3</sup>	(c)
$3.8 \cdot 10^{-12}$	303	Kerr and Stocker, 1986 <sup>4</sup>	(d)
$7.4 \cdot 10^{-12} \exp(-240/T)$	240–440	Wallington and Kurylo, 1987 <sup>5</sup>	(e)
$3.73 \cdot 10^{-19} T^{2.4} \exp(690/T)$	293–599	Hess and Tully, 1988 <sup>6</sup>	(f)
$3.04 \cdot 10^{-12}$	298	Nelson <i>et al.</i> , 1990 <sup>7</sup>	(g)
$3.33 \cdot 10^{-12}$	298		(h)
$(k_1 + k_3) = 8.80 \cdot 10^{-12}$	1204	Bott and Cohen, 1991 <sup>8</sup>	(i)
<i>Branching Ratios</i>			
$k_1/k = 0.75 \pm 0.15$	298	Meier <i>et al.</i> , 1987 <sup>9</sup>	(j)
$k_2/k \approx 0.15$	599	Hess and Tully, 1988 <sup>6</sup>	(k)
<i>Reviews and Evaluations</i>			
$6.18 \cdot 10^{-12} T^2 \exp(532/T)$	293–599	Atkinson, 1994 <sup>10</sup>	(l)
$7.0 \cdot 10^{-12} \exp(-235/T)$	240–600	NASA, 1997 <sup>11</sup>	(m)
$4.1 \cdot 10^{-12} \exp(-70/T)$	270–340	IUPAC, 1999 <sup>12</sup>	(n)
$k_2/k = k_3/k = 0.05$	298		

#### Comments

- (a) Relative rate study. Chain reaction initiated in  $\text{H}_2\text{O}_2/\text{NO}_2/\text{CO}$  mixtures containing  $\text{C}_2\text{H}_5\text{OH}$  and a reference hydrocarbon (*n*-butane).  $\text{CO}_2$  yield, measured by gas chromatography, could be related to  $k/(k(\text{OH} + \text{n-butane}))$ . Tabulated value of  $k$  derived using  $k(\text{OH} + \text{n-butane}) = 2.44 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .<sup>13</sup>
- (b) Flash photolysis of  $\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH}/\text{He}$  mixtures at a total pressure of 200 mbar. [OH] monitored by resonance absorption.
- (c) Relative rate study using a Teflon bag smog chamber. OH generated by photolysis of  $\text{HNO}/\text{synthetic air}$  mixtures in presence of  $\text{C}_2\text{H}_5\text{OH}$  and a reference compound (propene). The hydrocarbons were analyzed by

gas chromatography. The tabulated value of  $k$  was obtained using  $k(\text{OH} + \text{propene}) = 2.63 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .<sup>13</sup>

- (d) Technique as in (c). Ethene used as reference compound. Tabulated value of  $k$  obtained using  $k(\text{OH} + \text{ethene}) = 8.52 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .<sup>13</sup>
- (e) Flash photolysis of  $\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH}/\text{Ar}$  mixtures at total pressures in the range 33–66 mbar. [OH] monitored by resonance fluorescence.
- (f) Experiments were carried out using both  $^{16}\text{OH}$  and  $^{18}\text{OH}$ .  $^{16}\text{OH}$  was produced by the  $^{16}\text{O}({}^1\text{D}) + \text{H}_2\text{O}$  reaction using 193 nm laser photolysis of  $\text{N}_2{}^{16}\text{O}/\text{H}_2\text{O}$  mixtures.  $^{18}\text{OH}$  was produced by the 193 nm laser photolysis of  $\text{H}_2{}^{18}\text{O}$  alone. [OH] was monitored by laser induced fluorescence. The total pressures (He bath gas) was 920 mbar. The reaction was studied over

- the temperature range 293–749 K but the quoted expression is a fit to some of the data over the range 293–599 K [see Comments on Preferred Values and Comment (k)].
- (g) Pulse radiolysis of  $\text{H}_2\text{O}/\text{Ar}/\text{C}_2\text{H}_5\text{OH}$  mixtures using 2 MeV electrons from a Febetron at a total pressure of 1 bar.  $[\text{OH}]$  monitored by absorption at 309 nm in a multipass cell.
  - (h) Relative rate study using OH generated by UV photolysis of  $\text{CH}_3\text{ONO}$  or  $\text{H}_2\text{O}_2$  in air in a Teflon reaction chamber. Concentrations of  $\text{C}_2\text{H}_5\text{OH}$  and a reference compound ( $[-\text{C}_6\text{H}_{12}^-]$ ) also present were monitored by gas chromatography. The tabulated value of  $k$  is based on a value for  $k(\text{OH} + [-\text{C}_6\text{H}_{12}^-]) = 3.21 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .<sup>13</sup> Total pressure used was 970 mbar.
  - (i) Reflected shock waves through  $t\text{-BuOOH}/\text{C}_2\text{H}_5\text{OH}/\text{Ar}$  mixtures at pressures of 0.94–1.05 bar.  $[\text{OH}]$  monitored by resonance absorption. Rate constant for OH removal was determined. Since any  $\text{CH}_2\text{CH}_2\text{OH}$  produced via Channel (2) decomposes rapidly at these temperatures to produce  $\text{OH} + \text{C}_2\text{H}_4$ , the measured rate constant represents  $(k_1 + k_3)$ .
  - (j) A discharge flow system with OH radicals generated by the  $\text{F} + \text{H}_2\text{O}$  reaction and with  $[\text{OH}]$  monitored by LIF was used to determine  $k$ . The branching ratio was determined using a similar system with mass-spectrometric detection capable of detecting  $\text{CH}_3\text{CHOH}$  but none of the products from other channels.
  - (k) Technique as in (f). Experiments at 599 K measuring  $^{18}\text{OH}$  removal give  $(k_1 + k_2 + k_3)$ . Experiments with  $^{16}\text{OH}$  give only  $(k_1 + k_3)$  because at  $T > 599$  K the  $\text{CH}_3\text{CHOH}$  from Channel (2) decomposes rapidly to regenerate  $^{16}\text{OH}$ .
  - (l) Based on a fitting of the function  $k = A T^2 \exp(B/T)$  to the results of Hess and Tully.<sup>6</sup>
  - (m) Value of  $k$  at 298 K based on the data from Refs. 1–6, 16. The temperature dependence is based on the results of Wallington and Kurylo<sup>5</sup> and of Hess and Tully.<sup>6</sup>
  - (n) Based on the results of Hess and Tully.<sup>6</sup> Branching ratios were estimated using structure-reactivity correlations.<sup>14</sup>

### Preferred Values

$k = 3.0 \cdot 10^{-17} T^{1.78} \exp(425/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 290–1250 K.  
 $k_2/k = 0.15$  at 600 K.

### Reliability

$\Delta \log k = \pm 0.1$  at 290 K, rising to  $\pm 0.2$  at 1250 K.  
 $\Delta(k_2/k) = \pm 0.10$  at 600 K.

### Comments on Preferred Values

The preferred expression for  $k$  is obtained by combining

the value of  $k$  at  $\sim 298$  K, which is a mean of the values from Refs. 1–7 with the temperature dependence obtained by Hess and Tully.<sup>6</sup> The results of Meier *et al.*<sup>9,15</sup> and of Ravishankara and Davies<sup>16</sup> seem too low to be acceptable, those of Greenhill and O'Grady<sup>17</sup> too high, and these<sup>16,17</sup> are, therefore, not used in this evaluation. The unpublished results of Lorenz *et al.*<sup>18</sup> are consistently slightly lower ( $\sim 15\%$ ) than those of Hess and Tully<sup>6</sup> but provide support for their temperature dependence. The results of Wallington and Kurylo,<sup>5</sup> over the temperature range 240–440 K, are also in reasonable agreement with the preferred expression.

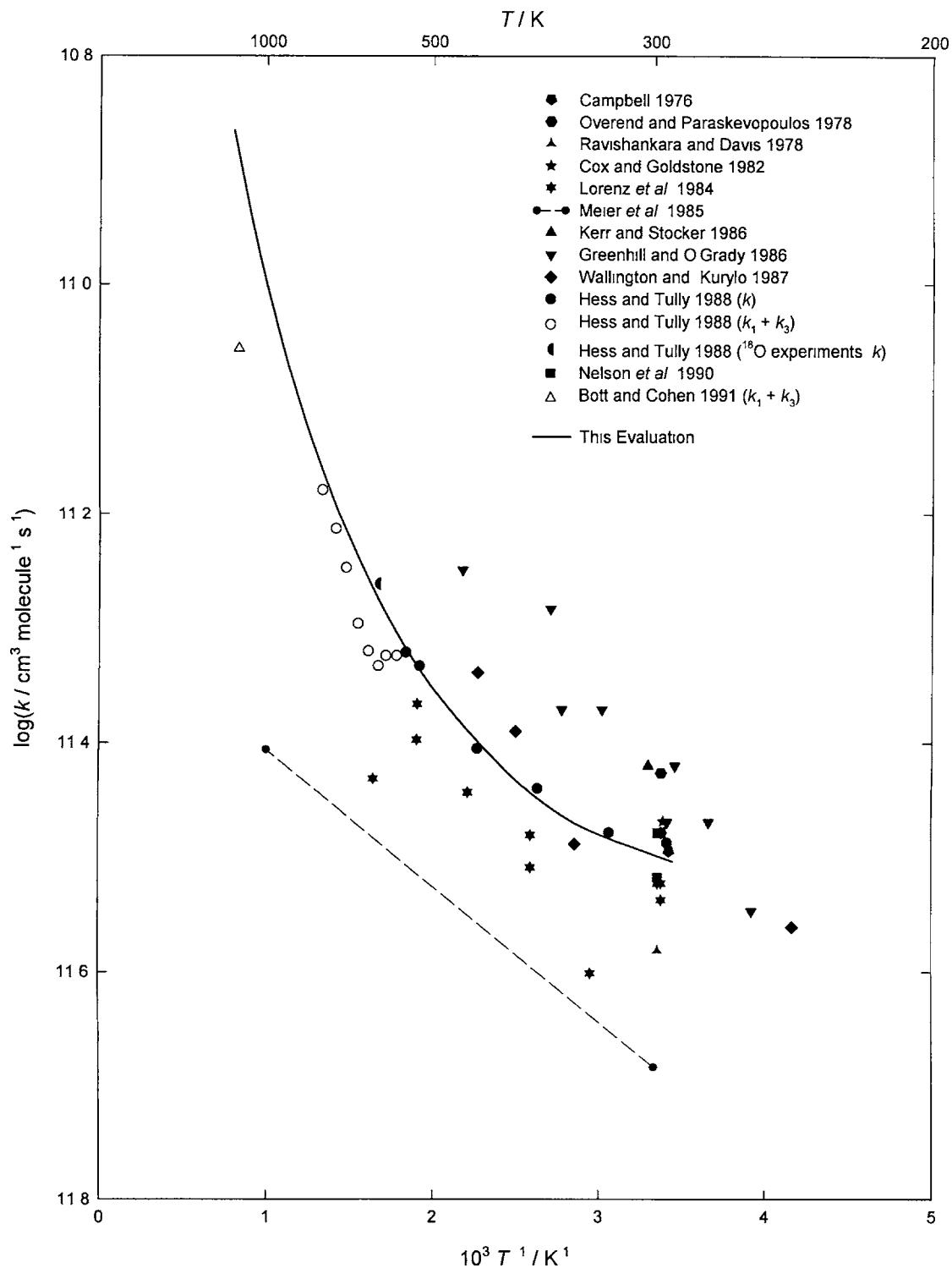
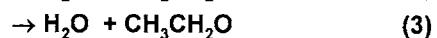
Hess and Tully<sup>6</sup> measured the rate constant for OH removal at temperatures higher than the upper limit of 599 K quoted in the Table. They found that above  $\sim 500$  K the apparent  $k$  for OH removal no longer increased with temperature as expected, which they attributed to the rapid decomposition of the  $\text{CH}_2\text{H}_2\text{OH}$  radical, produced via Channel (2), regenerating OH at these temperatures. By using  $^{18}\text{OH}$  as a reactant, which is not regenerated when the  $\text{CH}_2\text{CHOH}$  decomposes, they were able to show that at 599 K the value of  $k (= k_1 + k_2 + k_3)$  obtained from the rate of  $^{18}\text{OH}$  removal is consistent with the values measured at lower temperatures. Comparison of the results at 599 K from the  $^{16}\text{OH}$  and  $^{18}\text{OH}$  experiments also leads to a value for the branching ratio  $k_2/k$ . Because of the instability of the  $\text{CH}_2\text{CH}_2\text{OH}$  radical at high temperatures the study of Bott and Cohen,<sup>8</sup> who also monitored OH removal, also leads to a value of  $(k_1 + k_3)$  rather than  $k$ . The results of Bott and Cohen<sup>8</sup> suggest that the rate constants do not increase with temperature as rapidly as given by the expression of Hess and Tully<sup>6</sup> and this has been taken into account in deriving the preferred expressions.

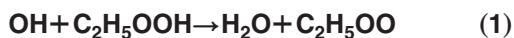
Apart from the Hess and Tully<sup>6</sup> value of  $k_2/k$  at 599 K, which is accepted as a preferred value, the only other study of the branching ratios is that of Meier *et al.*<sup>15</sup> who obtained  $k_1/k = (0.75 \pm 0.15)$  at 298 K. The IUPAC Evaluation Panel<sup>11</sup> have recommended values of  $k_2/k = k_3/k = 0.05$  at 298 K making use of Atkinson's structure-reactivity relationships.<sup>14</sup> This value is not inconsistent with the result of Meier *et al.*<sup>15</sup> but at this stage no recommendations are made for the low temperature regime. Marinov<sup>19</sup> has estimated values for the branching ratios by comparison with previously determined branching ratios for model compounds having chemical structures and bonding features similar to ethanol (propane and methane were the chosen reference compounds). Marinov<sup>19</sup> combines these ratios with the available rate data for the  $\text{OH} + \text{C}_2\text{H}_5\text{OH}$  reaction to derive expressions for  $k_1$ ,  $k_2$ , and  $k_3$ . These expressions are compatible with our preferred values and probably provide the best guide to the branching ratios at high temperatures.

### References

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- <sup>2</sup>R. Overend and G. Paraskevopoulos, J. Phys. Chem. **82**, 1329 (1978).
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<sup>11</sup>NASA Evaluation No.12, 1997 (see references in Introduction).  
<sup>12</sup>IUPAC, Supplement VII, 1999 (see references in Introduction).  
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<sup>18</sup>K. Lorenz, D. Rhäsa, and R. Zellner, quoted as a private communication in R. Atkinson, *J. Phys. Chem. Ref. Data Monograph* 1 (1989).  
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#### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = -135.4 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = -0.06 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 1.96 \cdot 10^2 T^{-0.06} \exp(+16130/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(2) = -105.2 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = 5.38 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 1.33 \cdot 10^2 T^{-0.601} \exp(+12400/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(3) = -73.9 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = 20.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 4.45 \cdot 10^2 T^{-0.517} \exp(+8660/T) \\ (300 \leq T/\text{K} \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2 + k_3$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
There are no experimental data for this reaction.			

#### Preferred Values

$k = 3.0 \cdot 10^{-12} \exp(190/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 250–1000 K.

$k_1/k = k_2/k = k_3/k = 0.33$  over the range 250–1000 K.

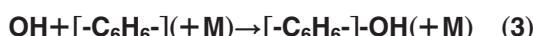
#### Reliability

$\Delta \log k = \pm 0.3$  at 250 K, rising to  $\pm 0.7$  at 1000 K.

$\Delta(k_1/k) = \Delta(k_2/k) = \Delta(k_3/k) = \pm 0.15$  over the range 250–1000 K.

#### Comments on Preferred Values

There are no experimental data for the reaction of OH with  $\text{C}_2\text{H}_5\text{OOH}$ . The overall rate expression, with Channels (1), (2), and (3) occurring at equal rates, is recommended by analogy with the  $\text{OH} + \text{CH}_3\text{OOH}$  reaction (see the  $\text{OH} + \text{CH}_3\text{OOH}$  data sheet).



#### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = -23.5 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = 24.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 8.35 \cdot 10^2 T^{-0.540} \exp(+2610/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(2) = 1.89 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = -23.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 3.12 \cdot 10^{-5} T^{1.188} \exp(-11/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(3) = -76.7 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = -111.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 1.11 \cdot 10^{-19} T^{-1.640} \exp(+7440/T) \text{ cm}^3 \text{ molecule}^{-1} \\ (300 \leq T/\text{K} \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2 + k_3$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$k_1 = 2.4 \cdot 10^{-11} \exp(-2260/T)$	450–1000	Tully <i>et al.</i> , 1981 <sup>1</sup>	(a)
$3.5 \cdot 10^{-11} \exp(-2300/T)$	790–1410	Madronich and Felder, 1985 <sup>2</sup>	(b)
$2.5 \cdot 10^{-11} \exp(-2050/T)$	790–1410	Felder and Madronich, 1986 <sup>3</sup>	(b)
$k_2 = 2.2 \cdot 10^{-11} \exp(-5330/T)$	1000–1150	He <i>et al.</i> , 1988 <sup>4</sup>	(c)
$k_1 = 1.89 \cdot 10^{-17} T^2 \exp(-1650/T)$	298–1050	Knispel <i>et al.</i> , 1990 <sup>5</sup>	(d)
<i>Reviews and Evaluations</i>			
$k_1 = 2.7 \cdot 10^{-16} T^{1.42} \exp(-732/T)$	400–1495	CEC, 1992; 1994 <sup>6</sup>	(e)
$k_2 = 2.2 \cdot 10^{-11} \exp(-5530/T)$	1000–1150		
$k_3 = 3.8 \cdot 10^{-12} \exp(-341/T)$	240–340		

#### Comments

- (a) Flash photolysis/resonance fluorescence study. Experiments conducted in the pressure range 26.7–267 mbar. The kinetic mechanism is discussed and an expression for the abstraction channel obtained.
- (b) High temperature flow reactor, OH generated by UV flash photolysis of water vapor at  $\lambda = 105 \text{ nm}$  or  $\lambda > 160 \text{ nm}$ . OH was detected by resonance fluorescence at 309 nm. Experimental pressures in the range 110–190 mbar.
- (c) Single-pulse shock tube study. Reactions of H and OH with phenol were studied. The rate coefficient,  $k_2$  was calculated from the equilibrium constant and the measured rate coefficient of the reverse reaction,  $k_{-2}$ .
- (d) Flash photolysis/resonance fluorescence study. OH generated by VUV photolysis of  $\text{H}_2\text{O}$  in 133 mbar Ar. Data analyzed to obtain  $k_1$  and combined with the high temperature data ( $T \geq 500 \text{ K}$ ) of Tully *et al.*<sup>1</sup> to derive the expression cited in the Table.
- (e) The preferred value for Channel (1) is based on the data of Tully *et al.*,<sup>1</sup> Lorenz and Zellner,<sup>7</sup> Madronich and Felder,<sup>2</sup> and Felder and Madronich<sup>3</sup> and for Channel (2) the preferred value is based on the work of He *et al.*<sup>4</sup> The recommended rate coefficient for the addi-

tion reaction is based on the data of Tully *et al.*,<sup>1</sup> Lorenz and Zellner,<sup>7</sup> Witte *et al.*,<sup>8</sup> Perry *et al.*,<sup>9</sup> and Edney *et al.*<sup>10</sup>

#### Preferred Values

$k_1 = 2.80 \cdot 10^{-11} \exp(-2302/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 298–1500 K.

$k_2 = 2.2 \cdot 10^{-11} \exp(-5330/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 1000–1150 K.

#### Reliability

$\Delta \log k_1 = \pm 0.3$  near room temperature, decreasing to  $\pm 0.1$  over the range 500–1500 K.

$\Delta \log k_2 = \pm 0.3$  over the temperature range 1000–1150 K.

#### Comments on Preferred Values

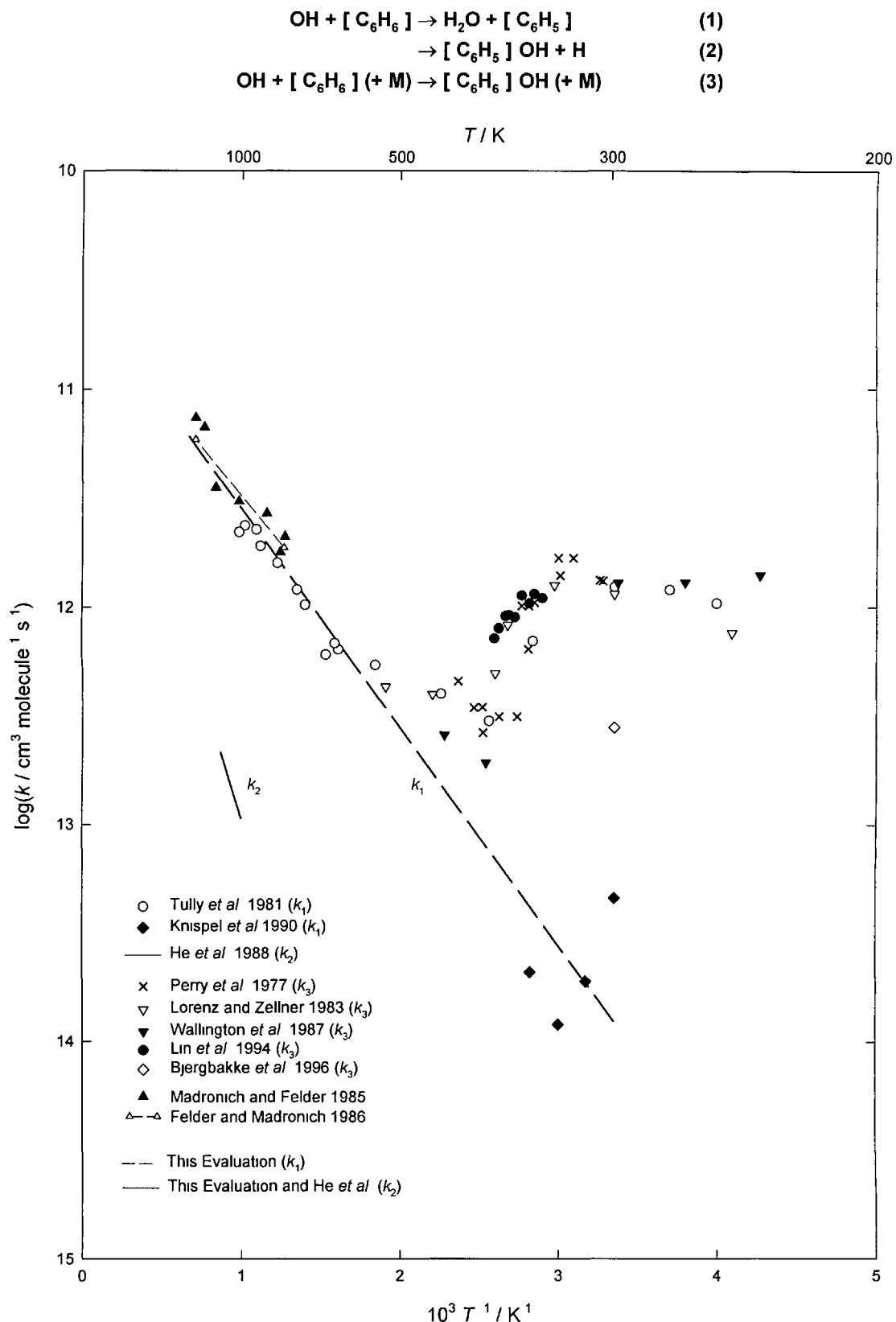
At  $T > 500 \text{ K}$  the abstraction of H atoms is the dominant channel.  $k_1$  was inferred from the low temperature data of Knispel *et al.*<sup>5</sup> and the high temperature data of Tully *et al.*<sup>1</sup> and of Felder and Madronich.<sup>3</sup> The displacement reaction, Channel (2) is not expected to be an elementary process, but to proceed via an intermediate adduct, hydroxycyclohexadienyl [generated in Channel (3)] at elevated temperatures. There are no directly measured values of  $k_2$ , and the only available data for the reverse reaction are those of He *et al.*<sup>4</sup>

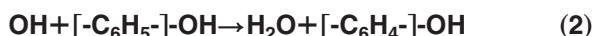
which we combine with the equilibrium constant (this evaluation) to give the recommended expression for  $k_2$ . The preferred value is unchanged from our previous evaluation.<sup>6</sup>

Reaction (3) is of little significance for the modeling of combustion reactions and no recommendation is given here. Values for  $k_3$  may be found in a recent review.<sup>11</sup> Some of the low temperature data relevant to  $k_3$ <sup>1,7,9,12–14</sup> are given on the Arrhenius plot to show the relationship between  $k_1$ ,  $k_2$ , and  $k_3$ .

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#### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = -134.9 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = 3.55 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 7.97 \cdot 10^{-1} T^{0.098} \exp(+16250/T) \\ (300 \leq T/\text{K} \leq 4000)$$

$$\Delta H^\circ_{298}(2) = -21.7 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = 15.22 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 1.85 \cdot 10^{-15} T^{4.623} \exp(+5750/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(3) = -92.5 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = -127.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 1.37 \cdot 10^{-31} T^{1.681} \exp(+11590/T) \text{ cm}^3 \text{ molecule}^{-1} \\ (300 \leq T/\text{K} \leq 5000)$$

Estimated thermodynamic data are only given for the 1,2 adduct. Other isomers are possible.  
See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2 + k_3$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$k_1 = 1.0 \cdot 10^{-11}$	1032	He, Mallard, and Tsang, 1988 <sup>1</sup>	(a)
$1.7 \cdot 10^{-12} \exp(+844/T)$	300–374	Knispel <i>et al.</i> , 1990 <sup>2</sup>	(b)
$(k_1 + k_2) = 5.6 \cdot 10^{-11} \exp(-880/T)$	323–374		
$3.7 \cdot 10^{-13} \exp(1267/T)$	301–373	Semadeni, Stocker, and Kerr, 1995 <sup>3</sup>	(c)
<i>Reviews and Evaluations</i>			
$(k_1 + k_2) = 1.0 \cdot 10^{-11}$	1000–1150	CEC, 1992; 1994 <sup>5</sup>	(d)
$k_3 = 2.8 \cdot 10^{-11}$	296		

#### Comments

- (a) This is an extension of the single-pulse shock tube study of the reaction  $\text{H} + [-\text{C}_6\text{H}_5\cdot] - \text{OH}$  by these authors (see  $\text{H} + [-\text{C}_6\text{H}_5\cdot] - \text{OH}$  data sheet), adding CO which reacts with OH to form H atoms leading to higher benzene yields. This process competes with the  $\text{OH} + [-\text{C}_6\text{H}_5\cdot] - \text{OH}$  reaction, thus rate data for the  $\text{OH} + [-\text{C}_6\text{H}_5\cdot] - \text{OH}$  reaction may be deduced. The value has been determined relative to  $k(\text{CO} + \text{OH}) = 1.2 \cdot 10^{-13} \exp(9.2 \cdot 10^{-4}T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . However, very large amounts of CO (about 30%) are required. The kinetic system is not simple and a further uncertainty is introduced from the reference reaction.
- (b) Flow reactor study in Ar bath gas. OH generated by pulsed photolysis of  $\text{H}_2\text{O}$  and monitored by resonance fluorescence at 308 nm. [OH] decay profile interpreted to give rate coefficients for the abstraction ( $k_1 + k_2$ ) and adduct ( $k_3$ ) forming channels.
- (c) Smog chamber study at 1 bar. Rate measured relative to  $k(\text{OH} + 1,3-\text{C}_4\text{H}_6) = 1.48 \cdot 10^{-11} \exp(448/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Ref. 4).
- (d) Preferred values based on the data of He, Mallard, and Tsang<sup>1</sup> for  $(k_1 + k_2)$  and of Rinke and Zetzsch<sup>6</sup> for  $k_3$ .

#### Preferred Values

$$(k_1 + k_2) = 1.6 \cdot 10^{-11} \exp(-443/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \\ \text{over the range } 320\text{--}1050 \text{ K.}$$

$$k_3 = 1.3 \cdot 10^{-12} \exp(914/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the range } 300\text{--}375 \text{ K.}$$

#### Reliability

$$\Delta \log(k_1 + k_2) = \pm 0.3 \text{ over the range } 320\text{--}1050 \text{ K.}$$

$$\Delta \log k_3 = \pm 0.4 \text{ over the range } 300\text{--}375 \text{ K.}$$

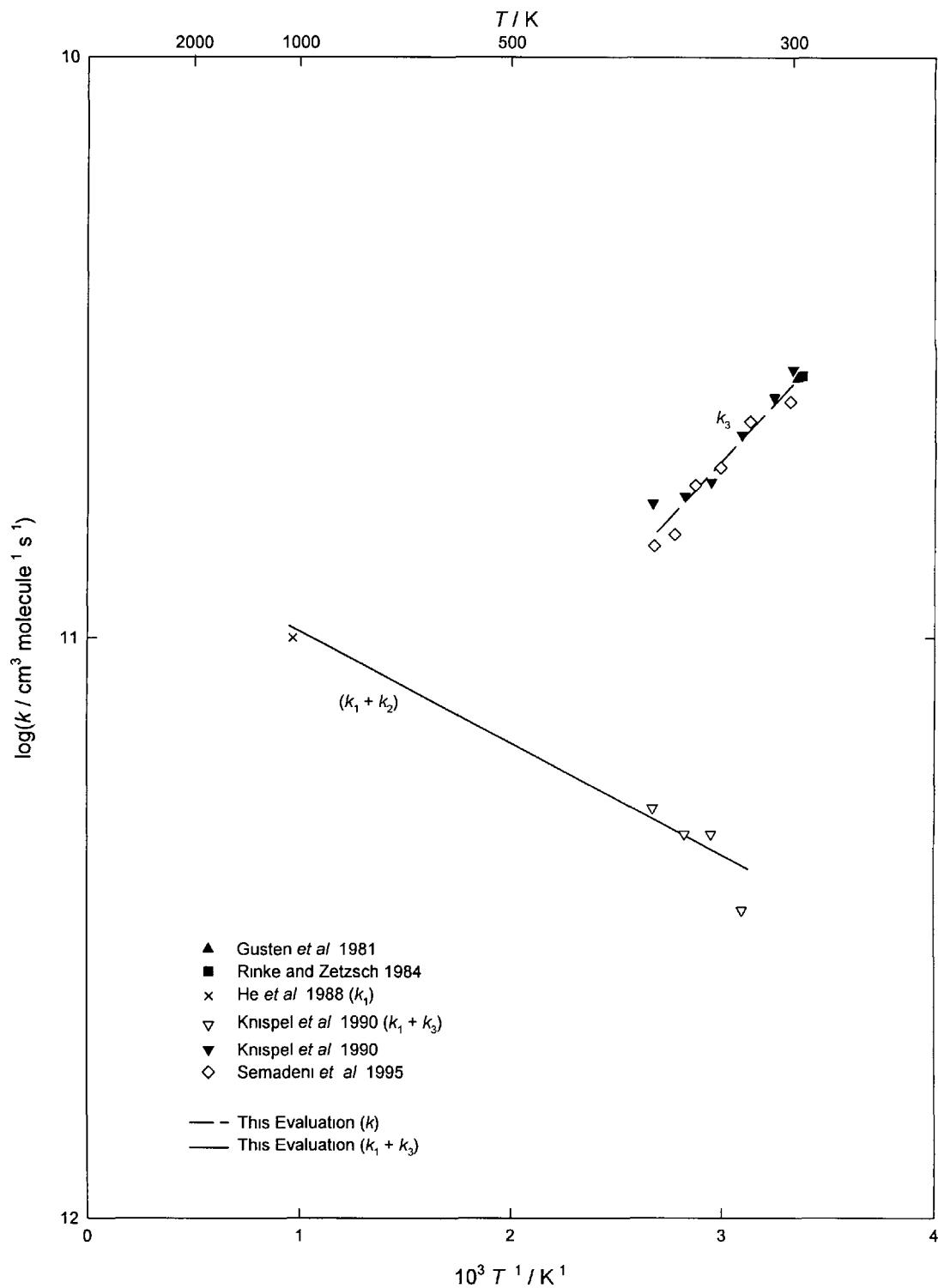
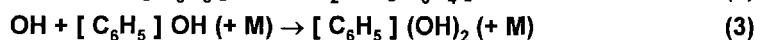
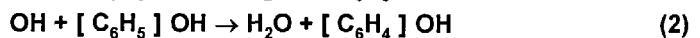
#### Comments on Preferred Values

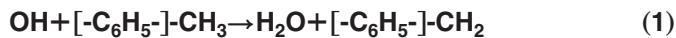
For temperatures  $< 400$  K the data of Knispel *et al.*<sup>2</sup> for the overall rate coefficient agrees well with that measured by Semadeni, Stocker, and Kerr.<sup>3</sup> The preferred value is a least squares fit to the data reported in these studies. Earlier measurements of the rate coefficient at room temperature by Güsten, Filby, and Schoof<sup>7</sup> and by Rinke and Zetzsch<sup>6</sup> are in good agreement with the recommendation. Knispel *et al.*<sup>2</sup> found that the branching ratio for abstraction,  $(k_1 + k_2)/k$ , increased from 0.15 to 0.30 over the range 323–374 K. The contribution to the overall rate coefficient of the abstraction reactions was negligible at lower temperatures. The only high temperature data is that of He, Mallard, and Tsang.<sup>1</sup> Combining their data with those of Knispel *et al.*<sup>2</sup> the expression given for the abstraction reaction can be determined. The contribution of Channel (2) may be estimated from the rate coefficient  $k(\text{OH} + [-\text{C}_6\text{H}_5\cdot]) = 2.80 \cdot 10^{-11} \exp(-2302/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (this evaluation); at 1000 K  $k_2$  is estimated to be 20% of  $(k_1 + k_2)$ . None of

the studies are free of potentially large errors and the assigned confidence limits reflect this.

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*Thermodynamic Data*

$$\Delta H^\circ_{298}(1) = -121.5 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = 3.98 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 1.23 \cdot 10^{-1} T^{0.492} \exp(+14510/T) \\ (300 \leqslant T/\text{K} \leqslant 5000)$$

$$\Delta H^\circ_{298}(2) = -23.6 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = 13.10 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 1.65 \cdot 10^2 T^{-0.504} \exp(+2640/T) \\ (300 \leqslant T/\text{K} \leqslant 5000)$$

$$\Delta H^\circ_{298}(3) = -87.3 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = -131.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 3.01 \cdot 10^{-32} T^{1.905} \exp(+10870/T) \text{ cm}^3 \text{ molecule}^{-1} \\ (300 \leqslant T/\text{K} \leqslant 5000)$$

Estimated thermodynamic data are only given for the 2,2 adduct. Other isomers are possible.

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data ( $k = k_1 + k_2 + k_3$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$k_1 = 5.0 \cdot 10^{-12} \exp(-453/T)$	380–473	Perry, Atkinson, and Pitts, 1977 <sup>1</sup>	(a)
$k_3 = 3.2 \cdot 10^{-13} \exp(805/T)$	296–325	Tully <i>et al.</i> , 1981 <sup>2</sup>	(b)
$k_1 = 2.1 \cdot 10^{-11} \exp(-1300/T)$	500–1000	Baldwin, Scott, and Walker, 1987 <sup>3</sup>	(c)
$k_3 = 3.8 \cdot 10^{-12} \exp(+180/T)$	213–298	Knispel <i>et al.</i> , 1990 <sup>4</sup>	(d)
$4.8 \cdot 10^{-12}$	773	Markert and Pagsberg, 1993 <sup>5</sup>	(e)
$k_1 = 2 \cdot 10^{-11} \exp(-1197/T)$	311–340	CEC, 1992; 1994 <sup>6</sup>	(f)
$k_3 = 2.2 \cdot 10^{-13} \exp(+1000/T)$	311–340		
$k_1 = 7 \cdot 10^{-13}$	338		
$k_3 = 5.7 \cdot 10^{-12}$	338		
<i>Reviews and Evaluations</i>			
$k_1 = 8.6 \cdot 10^{-15} T \exp(-440/T)$	300–1200		

**Comments**

- (a) Flash photolysis-resonance fluorescence study at total pressures of 133 mbar Ar bath gas. OH radicals generated by pulsed VUV photolysis of H<sub>2</sub>O. The addition channel is the dominant reaction pathway for temperatures below 325 K. The H atom abstraction reaction, Channel (1), was found to be the dominant pathway for temperatures above 380 K.
- (b) Flash photolysis-resonance fluorescence study. OH generated by pulsed photolysis of H<sub>2</sub>O at 165–185 nm. Total pressures in the range 27–133 mbar He, Ar or SF<sub>6</sub> bath gases. In addition, studies of the reactions of selectively deuterated toluenes were conducted. Rate expression given above corrected for ring abstraction reaction [Channel (2)].
- (c) Small amounts of toluene (0.05%–0.5%) were added to slowly reacting mixtures of H<sub>2</sub>+O<sub>2</sub>. Under the experimental condition the H<sub>2</sub>/O<sub>2</sub> reaction provides a reproducible source of H, O, and OH radicals. Measurement of the relative consumption of toluene and H<sub>2</sub> by gas chromatography permits evaluation of the rate coefficient for the reactions of H, O, and OH with toluene.
- (d) Flow reactor study in Ar bath gas. OH generated by

pulsed photolysis of H<sub>2</sub>O and monitored by resonance fluorescence at 308 nm. [OH] decay profile interpreted to give rate coefficients for the abstraction and adduct forming channels.

- (e) OH radicals generated from the pulsed radiolysis of H<sub>2</sub>O. Formation of benzyl [Channel (1)] and adduct [Channel (3)] monitored by time-resolved UV absorption spectroscopy in the wavelength region 200–400 nm.
- (f) See Comments on Preferred Values.

**Preferred Values**

$$k = 8.6 \cdot 10^{-15} T \exp(-440/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the range } 400–1200 \text{ K.}$$

**Reliability**

$$\Delta \log k = \pm 0.5 \text{ over the range } 400–1200 \text{ K.}$$

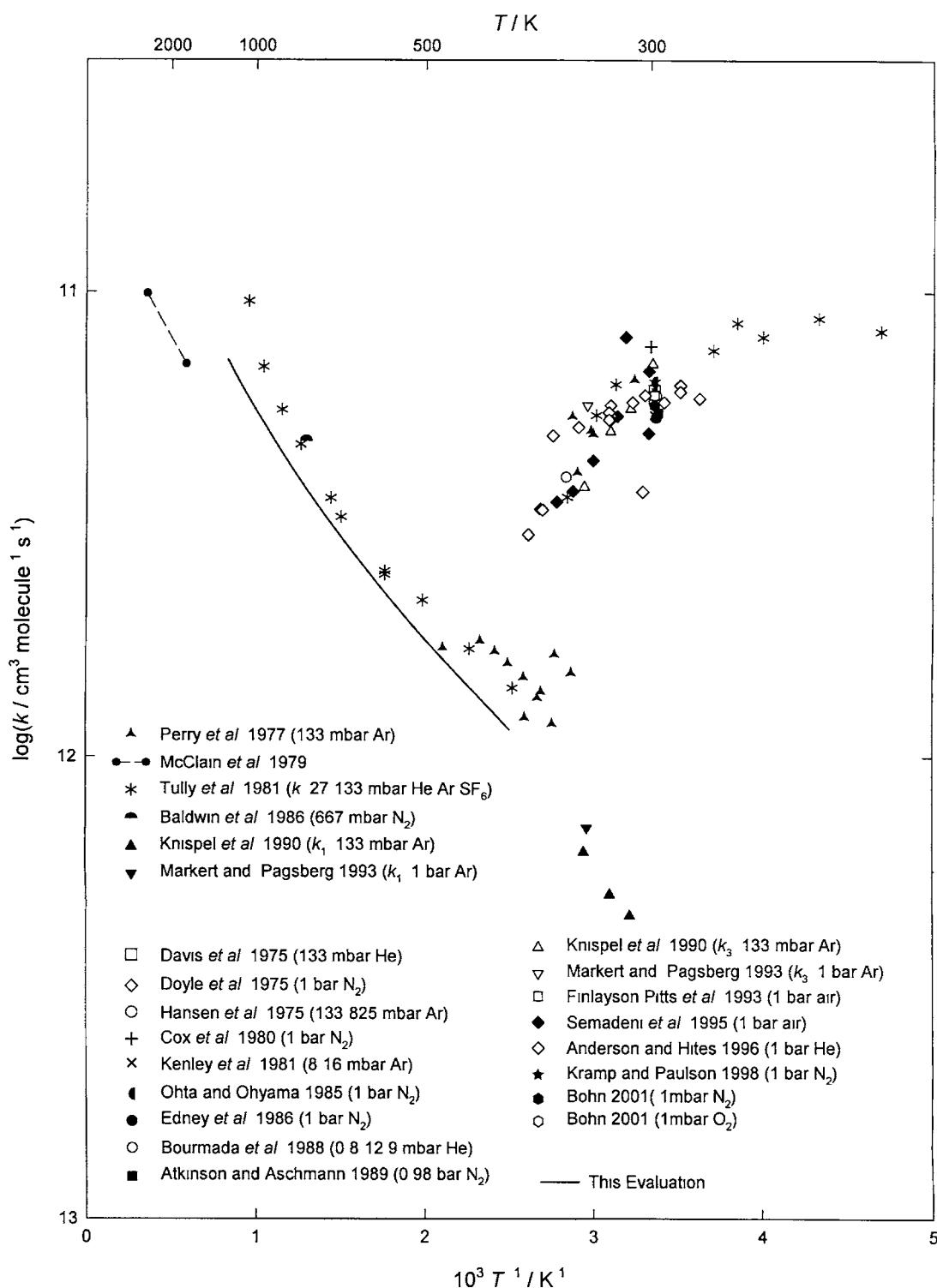
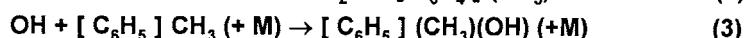
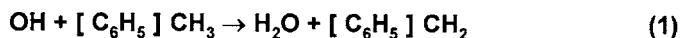
**Comments on Preferred Values**

The recommendation is unchanged from our previous evaluation.<sup>6</sup> At temperatures below about 400 K the addition reaction [Channel (3)] dominates. There have been numerous

studies conducted at  $T < 400$  K,<sup>7–20</sup> but the ill defined pressure dependence of the reaction does not allow us to make a recommendation for this channel. The mechanism and rate data for the reaction under atmospheric conditions has been reviewed by Atkinson.<sup>21</sup> The studies of Tully *et al.*<sup>2</sup> with  $[-\text{C}_6\text{H}_5]\text{-CD}_3$ ,  $[-\text{C}_6\text{D}_5\text{-}]\text{-CH}_3$ , and  $[-\text{C}_6\text{D}_5\text{-}]\text{-CD}_3$  show that at higher temperatures abstraction from the side chain seems to be the main reaction channel. Our present evaluation is based on the studies of Perry, Atkinson, and Pitts,<sup>1</sup> Tully *et al.*,<sup>2</sup> (after correction for ring abstraction) Baldwin, Scott, and Walker,<sup>3</sup> Knispel *et al.*,<sup>4</sup> and Markert and Pagsberg.<sup>5</sup> The indirect determination of McLain, Jachimowski, and Wilson<sup>22</sup> has not been included. Because of the rather high C-H bond energy in the aromatic ring the contribution of Channel (2) is estimated to be  $< 5\%$  for temperatures of about 1000 K, based on the recommended value for  $k(\text{OH} + [-\text{C}_6\text{H}_5\text{-}])$ .

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#### Thermodynamic Data

$$\Delta H^{\circ}_{298}(1) = -123.2 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298}(1) = 8.84 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 6.23 T^{-0.058} \exp(+14660/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^{\circ}_{298}(2) = -23.5 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298}(2) = 15.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 3.35 \cdot 10^{-44} T^{13.67} \exp(+10380/T) \\ (300 \leq T/\text{K} \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$1.4 \cdot 10^{-11}$	298	Niki <i>et al.</i> , 1978 <sup>1</sup>	(a)
$1.18 \cdot 10^{-11}$	298	Kerr and Sheppard, 1981 <sup>2</sup>	(b)
<i>Reviews and Evaluations</i>			
$1.29 \cdot 10^{-11}$	298	Atkinson, 1989 <sup>3</sup>	(c)
$1.3 \cdot 10^{-11}$	298–1500	CEC, 1994 <sup>4</sup>	(d)

#### Comments

- (a) FTIR study of photolysis of  $\text{C}_6\text{H}_5\text{CHO}/\text{C}_2\text{D}_4/\text{HONO}$  mixtures.  $k$  determined relative to  $k(\text{OH} + \text{C}_2\text{D}_4) = 8.78 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , which was measured relative to  $k(\text{OH} + \text{C}_2\text{H}_4)$  in the same study. Entry based on  $k(\text{OH} + \text{C}_2\text{H}_4) = 8.52 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .
- (b) GC analysis of reactant loss in photolysis of  $\text{C}_6\text{H}_5\text{CHO}/\text{C}_2\text{H}_4/\text{HONO}$  mixtures.  $k$  determined relative to  $k(\text{OH} + \text{C}_2\text{H}_4) = 8.52 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .
- (c) Based on data of Niki *et al.*<sup>1</sup> and Kerr and Sheppard.<sup>2</sup>
- (d) Accepts evaluation of Atkinson<sup>3</sup> with assumed zero activation energy to give temperature dependence.

#### Preferred Values

$k = 1.3 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 298–1500 K.

#### Reliability

$\Delta \log k = \pm 0.1$  at 298 K, rising to  $\pm 0.5$  at 1500 K.

#### Comments on Preferred Values

The preferred values are unchanged from our previous evaluation.<sup>4</sup> The relative rate values are considered reliable and the preferred value is a mean of the two published results<sup>1,2</sup> for 298 K. At room temperature it is apparent that the abstraction of the carbonyl H atom predominates<sup>3</sup> over addition to the aromatic ring. This is expected to apply up to at least 1000 K. Data for reactions of OH with other aldehydes suggests that the temperature coefficient for the major channel, carbonyl H abstraction, will be insignificant.

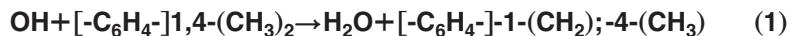
#### References

<sup>1</sup> H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, *J. Phys. Chem.* **82**, 132 (1978).

<sup>2</sup> J. A. Kerr and D. W. Sheppard, *Env. Sci. Technol.* **15**, 960 (1981).

<sup>3</sup> R. Atkinson, *J. Phys. Chem. Ref. Data, Monograph 1* (1989).

<sup>4</sup> CEC, Supplement 1, 1994 (see references in Introduction).



#### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = -121.2 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = -5.66 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 4.40 \cdot 10^{-6} T^{1.602} \exp(+15390/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(2) = -88.0 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = -139.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 1.99 \cdot 10^{-36} T^{3.060} \exp(+11650/T) \text{ cm}^3 \text{ molecule}^{-1} \\ (300 \leq T/\text{K} \leq 5000)$$

Estimated thermodynamic data are only given for the 2,5-(CH<sub>3</sub>);-1-(OH) adduct. Other isomers are possible. See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$k_1 = 6.4 \cdot 10^{-11} \exp(-1440/T)$	500–960	Nicovich, Thompson, and Ravishankara, 1981 <sup>1</sup>	(a)
$k_2 = 1.4 \cdot 10^{-11}$	298–300	Ohta and Ohyama, 1985 <sup>2</sup>	(b)
$k_2 = 1.3 \cdot 10^{-11}$	298	Edney, Kleindienst, and Corse, 1986 <sup>3</sup>	(c)
$k_2 = 1.3 \cdot 10^{-11}$	296	Atkinson and Aschmann, 1989 <sup>4</sup>	(d)
$k_2 = 1.3 \cdot 10^{-11}$	296		
<i>Reviews and Evaluations</i>			
$k_1 = 6.4 \cdot 10^{-11} \exp(-1440/T)$	500–960	CEC, 1992; 1994 <sup>5</sup>	(e)
$k_2 = 1.4 \cdot 10^{-11}$	298–320		

#### Comments

- (a) Flash photolysis-resonance fluorescence study. OH generated by pulsed photolysis of H<sub>2</sub>O in the wavelength region 165–185 nm. Experiments conducted in Ar bath gas over the pressure range 133–267 mbar
- (b) Relative rate measurements in a static reactor at total pressure of 1 bar N<sub>2</sub> bath gas. OH generated by photolysis of H<sub>2</sub>O<sub>2</sub> at 253.7 nm. Concentrations of *p*-xylene and reference substrate monitored by gas chromatography. Relative rate coefficient,  $k/k(\text{OH} + n\text{-C}_6\text{H}_{14}) = 2.31$ , converted to absolute value with  $k(\text{OH} + n\text{-C}_6\text{H}_{14}) = 5.45 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.<sup>6</sup>
- (c) Relative rate measurements in a static reactor at total pressure of 1 bar N<sub>2</sub> bath gas. OH generated by photolysis of CH<sub>3</sub>ONO in air with excess NO. Decay of reactant and reference substrate concentrations monitored by gas chromatography. Relative rate coefficient,  $k/k(\text{OH} + [\text{-C}_6\text{H}_{12}^-]) = 1.85$ , converted to absolute value with  $k(\text{OH} + [\text{-C}_6\text{H}_{12}^-]) = 7.21 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.<sup>3</sup>
- (d) Relative rate measurements in a static reactor at total pressure of 0.98 bar N<sub>2</sub> bath gas. OH generated by photolysis of CH<sub>3</sub>ONO in excess NO. Decay of reactant and reference substrate concentrations monitored by gas chromatography. Relative rate coefficient,  $k/k(\text{OH} + \text{C}_3\text{H}_6) = 0.488$ , converted to absolute value with  $k(\text{OH} + \text{C}_3\text{H}_6) = 2.63 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.<sup>3</sup>
- (e) See Comments on Preferred Values.

#### Preferred Values

$k_1 = 6.4 \cdot 10^{-11} \exp(-1440/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 500–960 K.

$k_2 = 1.4 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 298–320 K.

#### Reliability

$\Delta \log k_1 = \pm 0.1$  over the range 500–960 K.

$\Delta \log k_2 = \pm 0.1$  over the range 298–320 K.

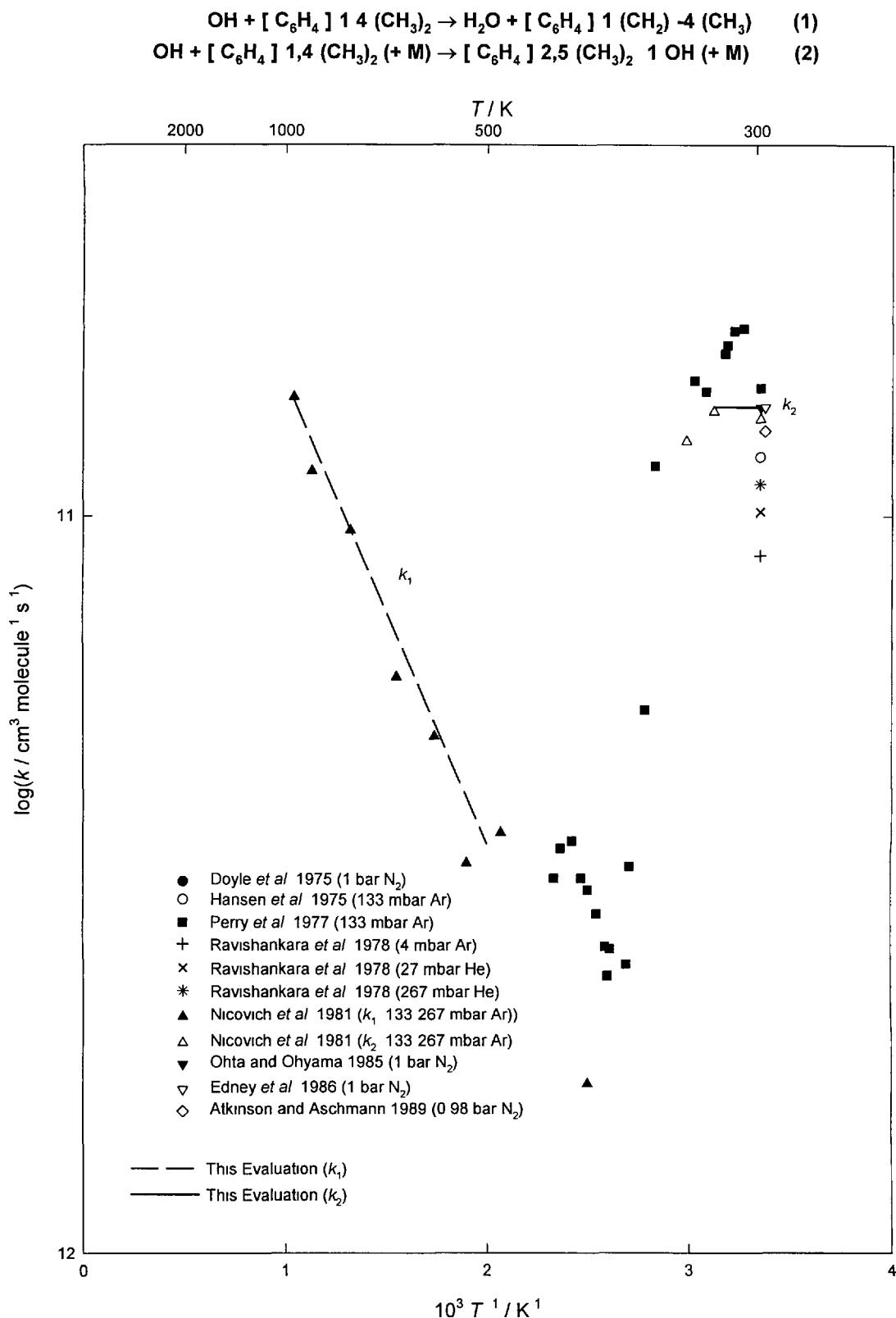
#### Comments on Preferred Values

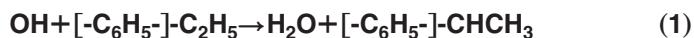
The preferred values are unchanged from our previous evaluations.<sup>5</sup>  $k_1$  is based on the data of Nicovich, Thompson, and Ravishankara,<sup>1</sup> and  $k_2$ , the rate constant for addition to the aromatic ring, is based on the data of Nicovich, Thompson, and Ravishankara,<sup>1</sup> Ohta and Ohyama,<sup>2</sup> Edney, Kleindienst, and Corse,<sup>3</sup> and Atkinson and Aschmann.<sup>4</sup> The data of Perry, Atkinson, and Pitts<sup>7</sup> were derived from fitting to a complex mechanism and have not been included in deriving the preferred values. The relative rate data of Doyle *et al.*<sup>8</sup> and Hansen, Atkinson, and Pitts<sup>9</sup> are in agreement with the preferred values. The data of Ravishankara *et al.*<sup>10</sup> were measured in the fall-off region. The recommended  $k_2$  is close to the high pressure limit. H-atom abstraction from the aromatic ring is not considered to be significant because of the high C-H bond energy involved.

#### References

- <sup>1</sup> J. M. Nicovich, R. L. Thompson, and A. R. Ravishankara, *J. Phys. Chem.* **85**, 2913 (1981).
- <sup>2</sup> T. Ohta and T. Ohyama, *Bull. Chem. Soc. Jpn.* **58**, 3029 (1985).

- <sup>3</sup>E. O. Edney, T. E. Kleindienst, and E. W. Corse, Int. J. Chem. Kinet. **18**, 1355 (1986).
- <sup>4</sup>R. Atkinson and S. M. Aschmann, Int. J. Chem. Kinet. **21**, 355 (1989).
- <sup>5</sup>CEC, 1992; Supplement I, 1994 (see References in Introduction).
- <sup>6</sup>R. Atkinson, J. Phys. Chem. Ref. Data **26**, 215 (1997).
- <sup>7</sup>R. A. Perry, R. Atkinson, and J. N. Pitts, Jr., J. Phys. Chem. **81**, 296 (1977).
- <sup>8</sup>G. J. Doyle, A. C. Lloyd, K. R. Darnall, A. M. Winer, and J. N. Pitts, Jr., Environ. Sci. Technol. **9**, 237 (1975).
- <sup>9</sup>D. A. Hansen, R. Atkinson, and J. N. Pitts, Jr., J. Phys. Chem. **79**, 1763 (1975).
- <sup>10</sup>A. R. Ravishankara, S. Wagner, S. Fischer, G. Smith, R. Schiff, R. T. Watson, G. Tesi, and D. D. Davis, Int. J. Chem. Kinet. **10**, 783 (1978).





#### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = -137.5 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = -16.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 8.45 \cdot 10^{-2} T^{0.115} \exp(+16500/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(3) = -23.5 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = 41.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 3.82 \cdot 10^3 T^{-0.452} \exp(+2640/T) \\ (300 \leq T/\text{K} \leq 3000)$$

$$\Delta H^\circ_{298}(2) = -73.9 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = 20.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 2.24 \cdot 10^2 T^{-0.427} \exp(+8720/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(4) = -88.0 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(4) = -139.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(4) = 1.99 \cdot 10^{-36} T^{3.060} \exp(+11650/T) \text{ cm}^3 \text{ molecule}^{-1} \\ (300 \leq T/\text{K} \leq 3000)$$

Estimated thermodynamic data are given only for the 2,2 adduct. Other isomers are possible.  
See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2 + k_3 + k_4$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$6.5 \cdot 10^{-12}$	305	Lloyd et al., 1976 <sup>1</sup>	(a)
$7.5 \cdot 10^{-12}$	298	Ravishankara et al., 1978 <sup>2</sup>	(b)
$7.1 \cdot 10^{-12}$	298		(c)
$8.0 \cdot 10^{-12}$	298		(d)
$6.3 \cdot 10^{-12}$	298	Ohta and Ohyama, 1985 <sup>3</sup>	(e)
<i>Reviews and Evaluations</i>			
$7.5 \cdot 10^{-12}$	298	CEC, 1992; 1994 <sup>4</sup>	(f)

#### Comments

- (a) Relative rate measurements in a static reactor at total pressure of 1 bar N<sub>2</sub> bath gas. OH generated by irradiation of hydrocarbon/NO<sub>x</sub>/air mixtures. Reactant and substrate concentration decays monitored by gas chromatography. Relative rate coefficient,  $k/k(\text{OH} + n\text{-C}_4\text{H}_{10}) = 2.65$ , converted to absolute value with  $k(\text{OH} + n\text{-C}_4\text{H}_{10}) = 2.44 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.<sup>5</sup>
- (b) Flash photolysis-resonance fluorescence study. OH generated by pulsed photolysis of H<sub>2</sub>O. Total pressure 4 mbar He bath gas.
- (c) See comment (b); total pressure 27 mbar He bath gas.
- (d) See comment (b); total pressure 270 mbar He bath gas.
- (e) Relative rate measurements in a static reactor at total pressure of 1 bar N<sub>2</sub> bath gas. OH generated by photolysis of H<sub>2</sub>O<sub>2</sub> at 253.7 nm. Concentrations of ethyl benzene and reference substrate monitored by gas chromatography. Relative rate coefficient,  $k/k(\text{OH} + n\text{-C}_6\text{H}_{14}) = 1.16$ , converted to absolute value with  $k(\text{OH} + n\text{-C}_6\text{H}_{14}) = 5.45 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.<sup>5</sup>
- (f) See Comments on Preferred Values. Rate coefficient is for  $P \leq 1$  bar.

#### Preferred Values

$$k_4 = 7.1 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K and } P \leq 1 \text{ bar.}$$

#### Reliability

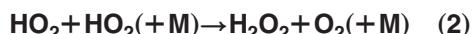
$$\Delta \log k_4 = \pm 0.1 \text{ at } 298 \text{ K.}$$

#### Comments on Preferred Values

This reaction has only been studied at room temperature. Thus the preferred value corresponds to the addition reaction, Channel (2). The relative rate coefficients have been revised to include recent recommended values for the reference rate coefficients.<sup>5</sup> There have been no recent published studies of this reaction, and the preferred value is the average of the cited data.<sup>1-3</sup>

#### References

- <sup>1</sup>A. C. Lloyd, K. R. Darnall, A. M. Winer, and J. N. Pitts, Jr., *J. Phys. Chem.* **80**, 789 (1976).
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- <sup>4</sup>CEC, 1992; Supplement I, 1994 (see references in Introduction).
- <sup>5</sup>R. Atkinson, *J. Phys. Chem. Ref. Data* **26**, 215 (1997).

*Thermodynamic Data*

$$\begin{aligned}\Delta H^{\circ}_{298}(1) &= \Delta H^{\circ}_{298}(2) = -163.5 \text{ kJ mol}^{-1} \\ \Delta S^{\circ}_{298}(1) &= \Delta S^{\circ}_{298}(2) = -18.5 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= K_c(2) = 4.53 \cdot 10^{-2} T^{0.143} \exp(+19680/T) \\ &(300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data ( $k = k_1 + k_2$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$7.0 \cdot 10^{-10} \exp(-6030/T) + 2.2 \cdot 10^{-13} \exp(+820/T)$ (At a pressure of 1 bar)	750–1100	Hippler, Troe, and Willner, 1990 <sup>1</sup>	(a)
<i>Reviews and Evaluations</i>			
$7.0 \cdot 10^{-10} \exp(-6030/T) + 2.2 \cdot 10^{-13} \exp(+820/T)$ $k_1 = 2.3 \cdot 10^{-13} \exp(+600/T)$ $k_2 = 1.7 \cdot 10^{-33} \exp(+1000/T)[\text{M}]$ $k_1 = 2.2 \cdot 10^{-13} \exp(+600/T)$ $k_2 = 1.9 \cdot 10^{-33} \exp(+980/T)[\text{N}_2]$	550–1250 200–300 230–420	CEC, 1994 <sup>2</sup> NASA, 1997 <sup>3</sup> IUPAC, 1997 <sup>4</sup>	(b) (c) (d)

**Comments**

- (a) A series of shock-tube studies were carried out between 750 and 1120 K employing two different sources of HO<sub>2</sub>, one being the thermal dissociation of H<sub>2</sub>O<sub>2</sub>, and the other, the thermal dissociation of CH<sub>3</sub>OOCH<sub>3</sub> in the presence of O<sub>2</sub>. Relative [HO<sub>2</sub>] and [H<sub>2</sub>O<sub>2</sub>] were monitored by UV absorption behind reflected shocks and [OH] was monitored by laser absorption at 308 nm behind incident shocks. The values of  $k$  derived were independent of Ar concentrations in the range (1–5) · 10<sup>-5</sup> mol cm<sup>-3</sup>. The data obtained are in excellent agreement with an earlier study<sup>5</sup> at ~1100 K using a similar technique. The values of  $k$  are obtained by fitting to a detailed mechanism and it was found that the fitting is sensitive to  $k(\text{OH} + \text{H}_2\text{O}_2)$  in a complex way, particularly at the higher temperatures. The rate constant expression was obtained by combining the high temperature data from this study with low temperature data as evaluated by the NASA<sup>3</sup> and IUPAC<sup>4</sup> Panels.
- (b) Accepts the expression of Hippler *et al.*<sup>1</sup>
- (c) The expression for  $k_1$  was based on the results of Cox and Burrows,<sup>6</sup> Thrush and Tyndall,<sup>7,8</sup> Kircher and Sander,<sup>9</sup> Sander,<sup>10</sup> Kurylo *et al.*,<sup>11</sup> and Takacs and Howard.<sup>12</sup> The recommendation for  $k_2$  was based on the studies of Sander *et al.*,<sup>13</sup> Simonaitis and Heicklen,<sup>14</sup> Kircher and Sander,<sup>9</sup> and Kurylo *et al.*<sup>11</sup>
- (d) The expressions derived by Kircher and Sander,<sup>9</sup> which are also recommended in the review of Wallington *et al.*,<sup>15</sup> are adopted.

**Preferred Values**

$$k_1 = [7.0 \cdot 10^{-10} \exp(-6030/T) + 2.2 \cdot 10^{-13} \exp(820/T)] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the range } 550\text{--}1250 \text{ K.}$$

*Reliability*

$\Delta \log k = \pm 0.15$  in the range 550–800 K, rising to  $\pm 0.4$  at 1250 K.

*Comments on Preferred Values*

The expression given by Hippler *et al.*<sup>1</sup> is adopted as our preferred expression for  $k$  over the range 550–1250 K, over which region  $k$  appears to be independent of pressure.<sup>3,4</sup> The results of Hippler *et al.*<sup>1</sup> are in excellent agreement with an earlier similar study of Troe<sup>5</sup> at 1100 K. The less precise study of Vardanyan *et al.*<sup>16</sup> at 800 K does not agree so well but supports the high values of  $k$  found by Troe *et al.*<sup>1</sup> at temperatures above 750 K. The data of Hippler *et al.*,<sup>1</sup> together with those of Lightfoot *et al.*,<sup>17</sup> confirm the existence of a deep minimum in the Arrhenius plot in the region 700–750 K. A theoretical estimate of  $k$  by Patrick, Golden, and Barker<sup>18</sup> predicts such a minimum but at the slightly higher temperature of 1000 K. The experimentally observed rapid increase in  $k$  with temperature above 800 K is unusually marked and, although good theoretical reasons can be advanced to explain it, its confirmation for this and related reactions is desirable. The sensitivity of  $k$  to temperature and lack of high temperature data make extrapolation of the Arrhenius plot beyond 1250 K very uncertain but fortunately the role of HO<sub>2</sub> radicals in combustion systems becomes less important above 1250 K.

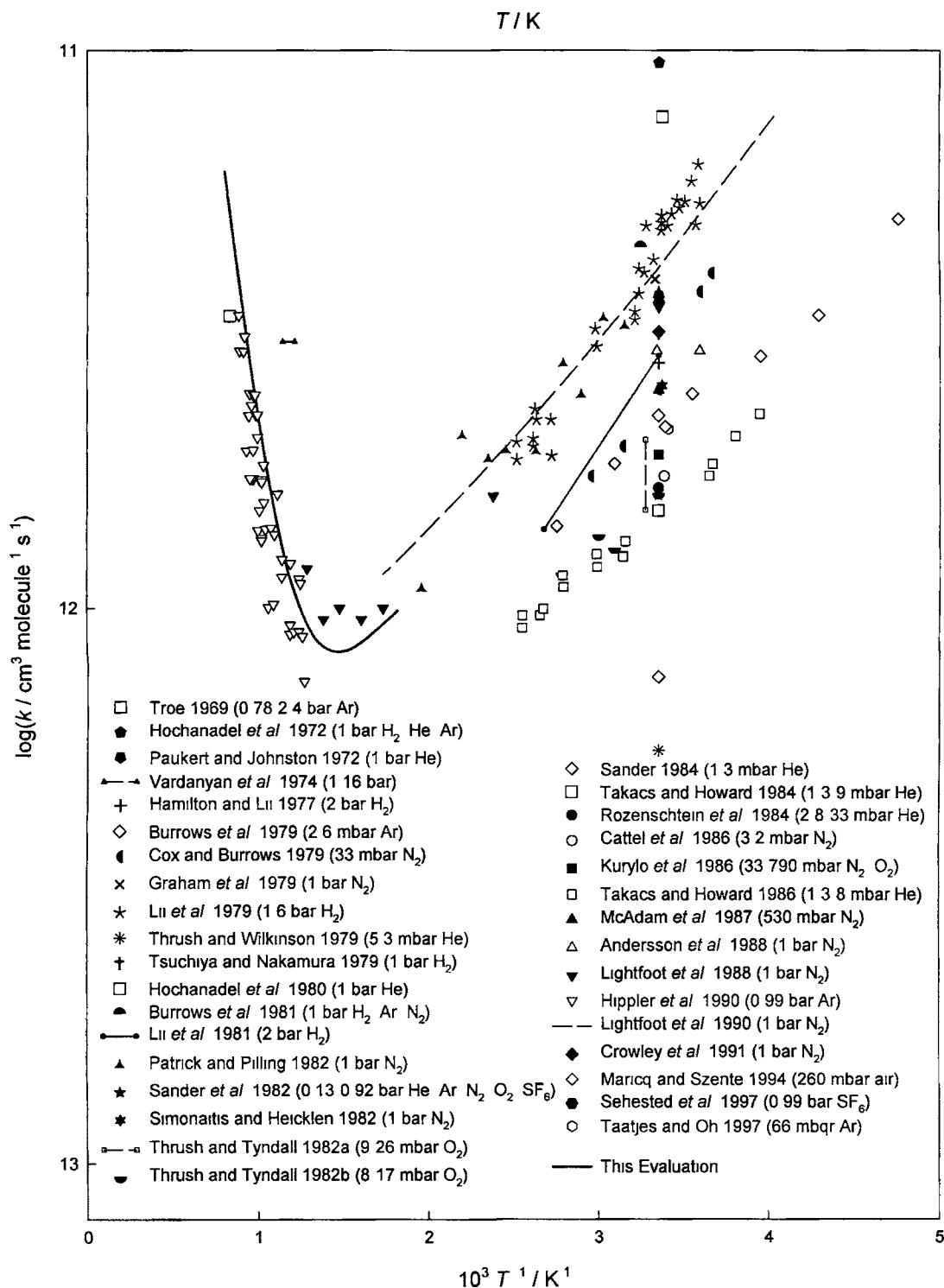
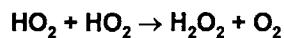
Below 550 K,  $k$  becomes pressure dependent and is par-

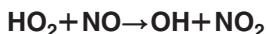
ticularly sensitive to polar gases such as H<sub>2</sub>O and NH<sub>3</sub>. There have been many studies<sup>6–15,17–41</sup> of the reaction at these lower temperatures because of its importance in atmospheric chemistry. These studies are not evaluated here but have been thoroughly reviewed in the evaluations of the NASA<sup>3</sup> and the IUPAC<sup>4</sup> Panels which should be consulted for details.

Our preferred expression for  $k$  is the sum of two terms. Between 550 K and 850 K both make significant contributions to  $k$  but above 850 K the single exponential expression  $k_1 = 7.0 \cdot 10^{-10} \exp(-6030/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  is sufficient.

## References

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- <sup>2</sup>CEC, 1992; Supplement I, 1994 (see references in Introduction).
- <sup>3</sup>NASA Evaluation No. 12, 1997 (see references in Introduction).
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- <sup>21</sup>E. J. Hamilton, Jr. and R.-R. Lii, *Int. J. Chem. Kinet.* **9**, 875 (1977).
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*Thermodynamic Data*

$$\begin{aligned}\Delta H_{298}^{\circ} &= -31.5 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= -16.1 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 0.134 T^{0.042} \exp(+3720/T) \\ &\quad (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$4.2 \cdot 10^{-12}$	1340–1760	Glänzer and Troe, 1975 <sup>1</sup>	(a)
$3.3 \cdot 10^{-12} \exp(254/T)$	232–403	Howard, 1979 <sup>2</sup>	(b)
$3.57 \cdot 10^{-12} \exp(226/T)$	423–1271	Howard, 1980 <sup>3</sup>	(c)
$3.0 \cdot 10^{-12} \exp(290/T)$	206–295	Seeley <i>et al.</i> , 1996 <sup>4</sup>	(d)
<i>Reviews and Evaluations</i>			
$3.5 \cdot 10^{-12} \exp(240/T)$	230–1270	Hanson and Salimian, 1984 <sup>5</sup>	(e)
$3.5 \cdot 10^{-12} \exp(250/T)$	230–430	NASA, 1997 <sup>6</sup>	(f)
$3.4 \cdot 10^{-12} \exp(270/T)$	200–400	IUPAC, 1997 <sup>7</sup>	(g)

**Comments**

- (a)  $[\text{NO}_2]$ ,  $[\text{HNO}_3]$ , and  $[\text{HO}_2]$  monitored by UV absorption in  $\text{HNO}_3/\text{NO}_2/\text{Ar}$  mixtures at 366 and 230 nm behind reflected shock waves. Values of  $k(\text{OH} + \text{NO}_2)$  were determined by modeling using a detailed kinetic scheme. Two sets of values of  $k(\text{OH} + \text{NO}_2)$  are quoted corresponding to extremes of the range of possible fitting parameters arising from uncertainties in the auxiliary kinetic data. The set of values corresponding most closely to currently accepted kinetic data has been chosen for plotting in the Figure. Values of  $k$ , obtained from  $k(\text{OH} + \text{NO}_2)$  values and equilibrium constants, are independent of temperature in the range covered. The value of  $k$  tabulated has been calculated using our expression for  $K$ .  $k = 7.5 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , based on an earlier value of  $K$  is given in the original paper.
- (b) Discharge flow system.  $\text{HO}_2$  generated by  $\text{H} + \text{O}_2 (+\text{M})$  or  $\text{F} + \text{H}_2\text{O}_2$  reaction. With the latter source the secondary reaction  $\text{OH} + \text{H}_2\text{O}_2$  is avoided by scavenging OH with added  $\text{CF}_3\text{Cl}$ .  $[\text{HO}_2]$  monitored by laser magnetic resonance. He carrier gas at total pressures of  $\sim 1$  mbar.
- (c) Technique as in (b). Results from the two studies<sup>2,3</sup> were combined by the author to give  $k = 3.51 \cdot 10^{-12} \exp(240/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the range 232–1271 K.
- (d) Discharge flow system operating in the turbulent flow regime over the pressure range 90–250 mbar with  $\text{N}_2$  carrier gas.  $\text{HO}_2$  generated by  $\text{H} + \text{O}_2 (+\text{M})$  reaction;  $[\text{HO}_2]$ ,  $[\text{OH}]$ , and  $[\text{NO}_2]$  monitored by high pressure chemical ionization mass spectrometry.
- (e) Based on the data of Howard<sup>3</sup> and of Glänzer and Troe.<sup>1</sup>

- (f) Based on the data of Howard and Evenson,<sup>14</sup> Leu,<sup>15</sup> Howard,<sup>2</sup> Glaschick-Schimpf *et al.*,<sup>16</sup> Hack *et al.*,<sup>18</sup> Thrush and Wilkinson,<sup>22</sup> Jemi-Alade and Thrush,<sup>20</sup> and Seeley *et al.*<sup>4</sup>
- (g) Mean of the results of Howard and Evenson,<sup>14</sup> Howard,<sup>2</sup> Leu,<sup>15</sup> Hack *et al.*,<sup>18</sup> Jemi-Alade and Thrush,<sup>20</sup> Thrush and Wilkinson,<sup>22</sup> and Seeley *et al.*<sup>4</sup> taken as the 298 K value. This value is combined with the temperature dependence of Howard<sup>2</sup> and of Seeley *et al.*<sup>4</sup>

**Preferred Values**

$k = 3.4 \cdot 10^{-12} \exp(250/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 200–2000 K.

*Reliability*

$\Delta \log k = \pm 0.15$  over the range 200–2000 K.

*Comments on Preferred Values*

In the early studies of this reaction indirect techniques were used to follow its progress and they yielded a range of low values of  $k$ .<sup>8–12</sup> With the advent of more direct monitoring techniques for  $\text{HO}_2$  and OH more consistent and much higher values of  $k$  were obtained.<sup>2–4,13–22</sup>

Because of the importance of the reaction in atmospheric chemistry most of the studies have been carried out at temperatures close to 300 K. These have been thoroughly reviewed by the NASA and IUPAC evaluation panels whose findings we accept.<sup>6,7</sup> On the Arrhenius plot, therefore, only the NASA and IUPAC values at 298 K are plotted as representative of the numerous determinations at, or close to, 298 K. The other data plotted are from studies in which the tem-

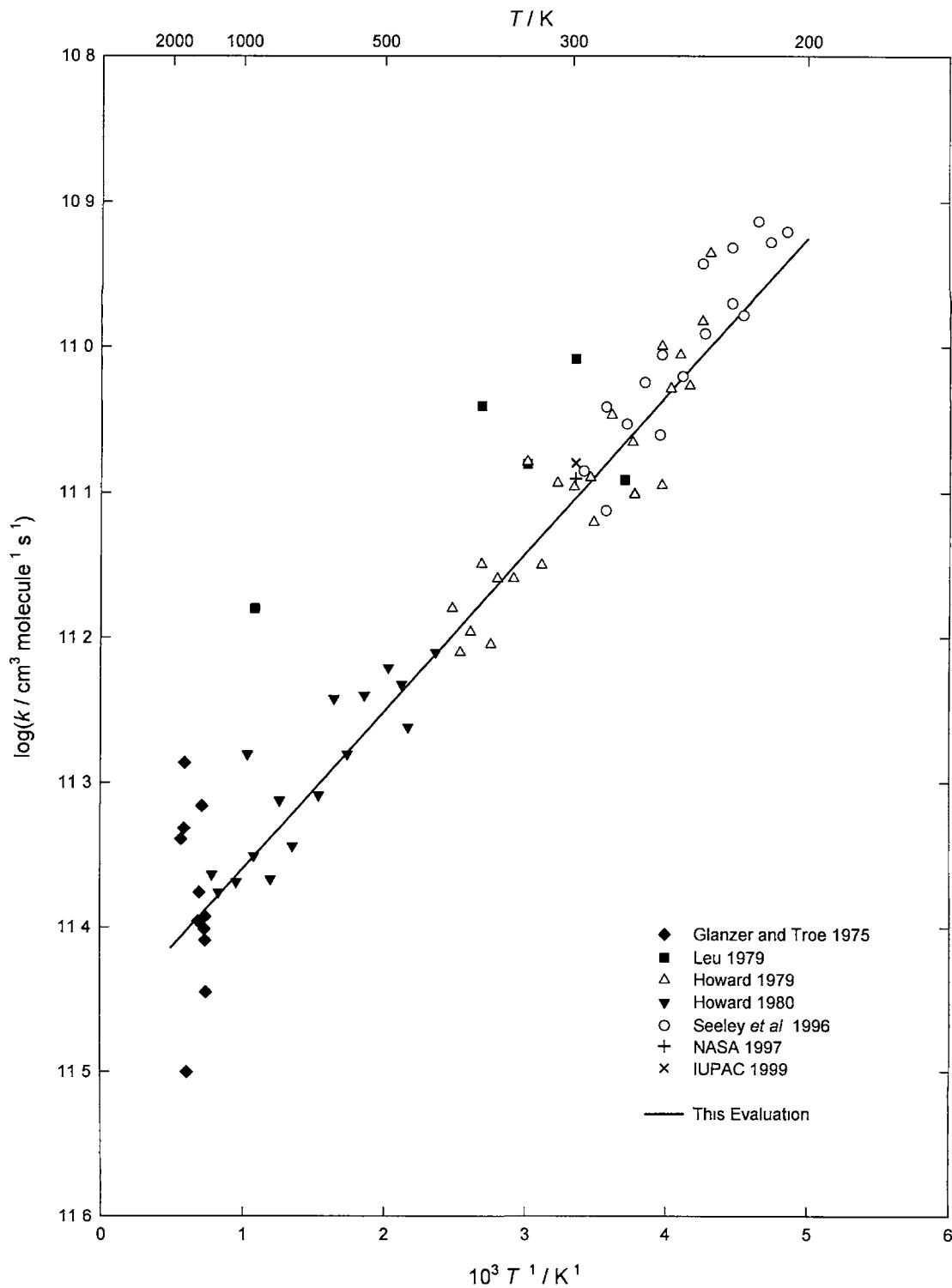
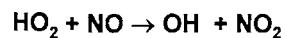
perature dependence of  $k$  has been determined using direct methods to follow the reaction. The one exception to that are the data of Glänzer and Troe<sup>1</sup> which were obtained from data on  $k(\text{OH} + \text{NO}_2)$  and the thermodynamic data.

The preferred expression for  $k$  is based largely on the results of Howard<sup>2,3</sup> and of Seeley *et al.*<sup>4</sup> The more scattered results of Leu<sup>15</sup> are in good agreement and, at higher temperatures, the results of Glänzer and Troe,<sup>1</sup> although involving a number of uncertainties [see comment (a)], also support the recommended expression.

Recent studies<sup>4,21</sup> up to pressures of 260 mbar have shown the rate constant to be independent of pressure. There are other reaction channels possible which have been investigated experimentally<sup>2,8</sup> and theoretically<sup>23</sup> but they do not appear to make a significant contribution.

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#### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = -332.0 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = -14.27 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 0.77 T^{-0.201} \exp(+39840/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(2) = -249.0 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = -25.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 1.72 \cdot 10^{-2} T^{0.104} \exp(+30070/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(3) = -97.7 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = -5.95 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 1.47 \cdot 10^{-5} T^{1.554} \exp(+12220/T) \\ (300 \leq T/\text{K} \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2 + k_3$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$2.5 \cdot 10^{-11}$	298	Cheskis and Sarkisov, 1978 <sup>1</sup>	(a)
$2.7 \cdot 10^{-11}$	349	Pagsberg, Eriksen, and Christensen, 1979 <sup>2</sup>	(b)
$2.6 \cdot 10^{-11}$	300–400	CEC, 1992; 1994 <sup>3</sup>	(c)
$3.4 \cdot 10^{-11}$	298	NASA, 1997 <sup>4</sup>	(d)

#### Comments

- (a) Relative rate measurement using flash photolysis of  $\text{NH}_3/\text{O}_2/\text{N}_2$  mixtures.  $[\text{NH}_2]$  monitored by intracavity laser absorption spectroscopy at 598 nm. Reported value of  $k$  is based on the measured value of  $k/k(\text{NH}_2 + \text{NH}_2) = 1.1$  at 750 mbar total pressure and the value<sup>5</sup>  $k(\text{NH}_2 + \text{NH}_2) = 2.5 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Measurements at 130 mbar gave the same value.
- (b) Pulse radiolysis of  $\text{NH}_3/\text{O}_2$  mixtures.  $[\text{NH}_2]$  monitored by absorption spectroscopy at 598 nm. Absence of any effect on the decay of  $[\text{NH}_2]$  interpreted as indicating that  $k(\text{HO}_2 + \text{NH}_2) = k(\text{H} + \text{NH}_2)$ . Value of  $k(\text{H} + \text{NH}_2)$  was determined in the same study.
- (c) Based on the data of Cheskis and Sarkisov<sup>1</sup> and of Pagsberg *et al.*<sup>2</sup>
- (d) Based on the data of Cheskis and Sarkisov,<sup>1</sup> Pagsberg *et al.*,<sup>2</sup> and unpublished results of Kurasawa and Lesclaux.<sup>6</sup>

#### Preferred Values

$k = 2.6 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 300–400 K.

#### Reliability

$\Delta \log k = \pm 0.3$  over the range 300–400 K.

#### Comments on Preferred Values

Only relative rate studies of this reaction at low temperatures are available. The values of  $k$  obtained are in good

agreement and are taken as the basis of our preferred values but substantial error limits are recommended.

The only information on the temperature dependence of  $k$  and the branching ratios come from theoretical calculations.<sup>7,8</sup> There is agreement that Channel (3) is the main reaction channel. The calculations of Sumathi and Peyerimhoff<sup>8</sup> suggest that it dominates over the range 300–2000 K and at pressures from 0.001 to 10 bar, with stabilization of the adduct  $\text{NH}_2\text{OOH}$  becoming important at higher pressures. However, the contributions from the remaining channels are highly uncertain, particularly the relative contributions of Channels (1) and (2). The calculations of Dean and Bozzelli<sup>7</sup> suggest that Channel (2) is the more important while those of Sumathi and Peyerimhoff<sup>8</sup> favor the other. Sumathi and Peyerimhoff<sup>8</sup> have derived expressions for the rate constants of all of the channels over the range 300–2000 K obtaining for  $k_1$ ,  $k_2$ , and  $k_3$  the expressions  $k_1 = 9.47 \cdot 10^{-9} T^{-1.12} \exp(-356/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,  $k_2 = 2.75 \cdot 10^{-20} T^{1.55} \exp(-1020/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,  $k_3 = 4.85 \cdot 10^{-7} T^{-1.32} \exp(-628/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and an overall rate constant of  $k = 4.07 \cdot 10^{-7} T^{-1.28} \exp(-587/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . In the absence of experimental data these expressions probably offer the best guide to the branching ratios. Their expression for  $k$  gives values in agreement with our preferred values well within the suggested error limits.

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<sup>3</sup> CEC, 1992; Supplement I, 1994 (see references in Introduction).

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ference on Photochemistry, Newport Beach, CA, March, 1980.

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<sup>8</sup> R. Sumathi and S. D. Peyerimhoff, *Chem. Phys. Lett.* **263**, 742 (1996).



#### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = -104.8 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = -9.94 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 1.17 \cdot 10^{-2} T^{0.462} \exp(+12790/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(2) = -235.3 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = -31.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 1.17 \cdot 10^{-2} T^{0.003} \exp(+28510/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(1) = -510.4 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = -15.47 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 1.64 T^{-0.377} \exp(+61340/T) \\ (300 \leq T/\text{K} \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2 + k_3$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$k_1 \approx 3 \cdot 10^{-11}$	1030–1115	Colket, Naegeli, and Glassman, 1977 <sup>1</sup>	(a)
<i>Reviews and Evaluations</i>			
$k_1 = 3 \cdot 10^{-11}$	600–1200	CEC, 1992; 1994 <sup>2</sup>	(b)

#### Comments

- (a) Study of the oxidation of  $\text{CH}_3\text{CHO}$  in a turbulent flow reactor at atmospheric pressure with end-product analysis by GC. Reaction (1) was proposed to account for the oxidation of  $\text{CH}_3$  and a value of  $k_1$  was selected to obtain rate coefficients for other reactions in the mechanism consistent with literature data.
- (b) Based on data of Colket *et al.*<sup>1</sup>

#### Preferred Values

$k_1 = 3 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 600–1200 K.

#### Reliability

$\Delta \log k_1 = \pm 1.0$  over the range 600–1200 K.

#### Comments on Preferred Values

The recommendation is unchanged from our previous evaluation<sup>2</sup> and is based on the indirect determination of

Colket *et al.*<sup>1</sup> but with large error limits assigned. Direct measurements of the rate coefficient and its temperature dependence are still needed.

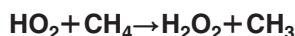
Zhu and Lin<sup>3</sup> have modeled the reaction using *ab initio* molecular orbital theory and variational RRKM theory to obtain values of the rate constants for the channels leading to  $\text{O}_2(^3\Sigma_g^-) + \text{CH}_4$ ,  $\text{O}_2(^1\Delta) + \text{CH}_4$ ,  $\text{CH}_3\text{O} + \text{OH}$ , and  $\text{H}_2\text{O} + \text{HCHO}$ . The formation of  $\text{CH}_3\text{O} + \text{OH}$  by an association/decomposition mechanism is found to dominate over the temperature range 300–3000 K and the rate constant is found to be independent of pressure up to 50 bar. The direct abstraction channel leading to  $\text{CH}_4 + \text{O}_2(^3\Sigma_g^-)$  is next in importance making a contribution to the overall rate constant of ~6% at 300 K and ~37% at 3000 K. The values derived for the rate constant,  $k_1$ , are higher than our preferred value by a factor of ~3 at 600 K and ~2 at 1200 K.

#### References

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<sup>2</sup> CEC, 1992; Supplement I, 1994 (see references in Introduction).

<sup>3</sup> R. Zhu and M. C. Lin, *J. Phys. Chem. A* **105**, 6243 (2001).

*Thermodynamic Data*

$$\begin{aligned}\Delta H^\circ_{298} &= 71.39 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298} &= 13.32 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 3.87 T^{0.140} \exp(-8780/T) \\ &\quad (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$4.2 \cdot 10^{-19}$	716	Baldwin, Jones, and Walker, 1988 <sup>1</sup>	(a)
<i>Reviews and Evaluations</i>			
$3.0 \cdot 10^{-13} \exp(-9350/T)$	300–2500	Tsang and Hampson, 1986 <sup>2</sup>	(b)
$1.5 \cdot 10^{-11} \exp(-12440/T)$	625–1275	Baldwin, Jones, and Walker, 1988 <sup>1</sup>	(c)
$1.5 \cdot 10^{-11} \exp(-12440/T)$	600–1000	CEC, 1992; 1994 <sup>3</sup>	(d)
$7.8 \cdot 10^{-20} T^{2.5} \exp(-10570/T)$	600–2000	Scott and Walker, 2002 <sup>4</sup>	(e)

**Comments**

- (a) Thermal decomposition of tetramethylbutane in the presence of O<sub>2</sub> was used as a source of HO<sub>2</sub> radicals. Tetramethylbutane/O<sub>2</sub>/CH<sub>4</sub>/N<sub>2</sub> mixtures were heated in a KCl coated vessel and product yields (*i*-butene, HCHO, CO, CH<sub>3</sub>OH) were measured by gas chromatography. A value of  $k/k^{1/2}(\text{HO}_2 + \text{HO}_2)$  was obtained from which the cited value of  $k$  has been derived using  $k(\text{HO}_2 + \text{HO}_2) = 8.4 \cdot 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 716 K (this evaluation).
- (b) Estimate based on the general relationship given by Walker<sup>5</sup> for  $k(\text{HO}_2 + \text{RH})$ .
- (c) The  $A$  factor (per C-H bond) was assumed to be the same as that found for the HO<sub>2</sub>+C<sub>2</sub>H<sub>6</sub> reaction and the activation energy was calculated using the value of  $k$  at 716 K obtained by Baldwin *et al.*<sup>1</sup> who used a slightly different value of  $k(\text{HO}_2 + \text{HO}_2)$  from that currently recommended.
- (d) The estimate of Baldwin *et al.*<sup>1</sup> [Comment (c)] was accepted but a narrower temperature range assigned.
- (e) Data base developed for reactions of HO<sub>2</sub> abstraction reactions from alkanes, alkenes, aromatic, and related compounds. Estimated rate constants were expressed in the form  $k = A T^{2.5} \exp(B/T)$ , based on the finding of Eiteneer *et al.*<sup>6</sup> that they could fit the results of four separate studies of the reaction HO<sub>2</sub>+HCHO→H<sub>2</sub>O<sub>2</sub>+CHO over the range 540–1600 K with the expression  $k = 6.8 \cdot 10^{-20} T^{2.5} \exp(-5136/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Preliminary calculations by Scott and Walker,<sup>4</sup> using the methods of Bozzelli and co-workers,<sup>7</sup> confirm that the  $T$  exponent should lie in the range 1.8–3.4. To obtain the expression for  $k(\text{HO}_2 + \text{CH}_4)$  the value of  $k$  obtained by Baldwin and Walker<sup>1</sup> at 716 K (cited in the Table) was used together

with an  $A$  factor per C-H bond identical with that for the HO<sub>2</sub>+C<sub>2</sub>H<sub>6</sub> reaction obtained experimentally<sup>8</sup> between 673 K and 793 K.

**Preferred Values**

$$k = 7.8 \cdot 10^{-20} T^{2.5} \exp(-10570/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the range 600–2000 K.

*Reliability*

$\Delta \log k = \pm 0.15$  between 600 K and 800 K, rising to  $\pm 0.3$  at 1000 K and  $\pm 0.7$  at 2000 K.

*Comments on Preferred Values*

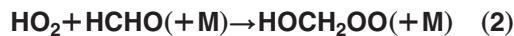
The only experimental determination of  $k$  is that by Baldwin *et al.*<sup>1</sup> at 716 K but the method used [Comment (a)] is known to give accurate data for other HO<sub>2</sub> reactions. The value of  $k/k^{1/2}(\text{HO}_2 + \text{HO}_2)$  determined experimentally is reliable and, in calculating  $k$ , the uncertainties in the reference rate constant (known to better than 20%) are reduced by 50% by virtue of the square root dependence on  $k(\text{HO}_2 + \text{HO}_2)$ , leading to a precise value of  $k$  at 716 K.

The preferred expression is that derived by Scott and Walker<sup>4</sup> as described in Comment (e). Scott and Walker<sup>4</sup> choose a non-Arrhenius form for the expression for  $k$  since experimental evidence for such a form for H-abstraction reactions is now widespread (see the data sheets on the HO<sub>2</sub>+HO<sub>2</sub>, CH<sub>3</sub>+C<sub>2</sub>H<sub>6</sub>, and O<sub>2</sub>+HCHO reactions) with a  $T$  exponent typically between 2 and 3. Hence the preferred expression should provide more reliable estimates of  $k$  at elevated temperatures than our previously recommended expression<sup>3</sup> and, consequently, the temperature range recommended for its use has been extended.

## References

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<sup>2</sup>W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data **15**, 1087 (1986).  
<sup>3</sup>CEC, 1992; Supplement I, 1994 (see references in Introduction).  
<sup>4</sup>M. Scott and R. W. Walker, Combust. Flame **129**, 365 (2002).

- <sup>5</sup>R. W. Walker, in *Gas Kinetics and Energy Transfer*, edited by P. G. Ashmore, Spec. Periodical Report, Chemical Society, London (1975), Vol. 1, p. 161.  
<sup>6</sup>B. Eiteneer, C.-L. Yu, M. Goldenberg, and M. Frenklach, J. Phys. Chem. A **102**, 5916 (1998).  
<sup>7</sup>C.-J. Chen and J. W. Bozzelli, J. Phys. Chem. A **104**, 9715 (2000).  
<sup>8</sup>R. R. Baldwin, C. E. Dean, M. R. Honeyman, and R. W. Walker, J. Chem. Soc. Faraday Trans. 1 **82**, 89 (1986).



### Thermodynamic Data

$$\begin{aligned}\Delta H^\circ_{298}(1) &= 1.77 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(1) &= 11.0 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 4.90 T^{0.032} \exp(-370/T) \\ &\quad (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

### Rate Coefficient Data ( $k = k_1$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$9.0 \cdot 10^{-16}$	773	Baldwin <i>et al.</i> , 1972; <sup>1</sup> 1979 <sup>2</sup>	(a)
$9.1 \cdot 10^{-13} \exp(-4523/T)$	943–995	Hochgreb <i>et al.</i> , 1990 <sup>3</sup>	(b)
$3.5 \cdot 10^{-13} \exp(-4620/T)$	541–773	Jemi-Alade, Lightfoot, and Lesclaux, 1986 <sup>4</sup>	(c)
$7.3 \cdot 10^{-18} T^2 \exp(-6038/T)$	1160–1890	Hidaka <i>et al.</i> , 1993 <sup>5</sup>	(d)
$6.8 \cdot 10^{-20} T^{2.5} \exp(-5136/T)$	1340–2270	Eiteneer <i>et al.</i> , 1998 <sup>6</sup>	(e)
<i>Reviews and Evaluations</i>			
$5.0 \cdot 10^{-12} \exp(-6580/T)$	600–1000	CEC, 1992; 1994 <sup>7</sup>	(f)
$k_2 = 6.7 \cdot 10^{-15} \exp(600/T)$	275–333	NASA, 1997 <sup>8</sup>	(g)
$k_2 = 9.7 \cdot 10^{-15} \exp(625/T)$	275–333	IUPAC, 1999 <sup>9</sup>	(h)

### Comments

- (a) Measurement of the effect of HCHO in reducing induction times leading to explosion at the second limit in  $\text{H}_2/\text{O}_2/\text{N}_2$  mixtures.<sup>1</sup> Using recommended value of  $k(\text{HO}_2 + \text{HO}_2)$  at 773 K ( $9.2 \cdot 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  [this evaluation]) gives  $k = (9.0 \pm 1.0) \cdot 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The value of  $k$  derived by Baldwin and Walker in a later paper<sup>2</sup> uses the same data and a different value of the reference rate constant.  
(b) Pyrolysis of  $\text{N}_2/\text{CH}_2/\text{O}_2$  mixtures at atmospheric pressure in a tubular flow reactor. Products sampled and analyzed by gas chromatography (CO,  $\text{CO}_2$ ,  $\text{CH}_2\text{O}$ ) and others ( $\text{O}_2$ ,  $\text{H}_2$ ) by on-line instrumentation. Substantial model fitted to rates of product formation. Results sensitive to the product  $k \cdot k(\text{H}_2\text{O}_2 + \text{M})/\text{cm}^6 \text{ mol}^{-2} \text{ s}^{-2}$ . Values obtained are  $(1.6 \pm 0.5) \cdot 10^{16}$  (944 K);  $(6.7 \pm 2.0) \cdot 10^{16}$  (994 K). Using  $k(\text{H}_2\text{O}_2 + \text{M})$  from the present evaluation gives the tabulated expression. Error limits on  $E/R$  are large ( $\pm 30\%$ ) due to the small temperature range covered.  
(c) Flash photolysis of HCHO/ $\text{O}_2$  mixtures or  $\text{Cl}_2/\text{HCHO}/\text{O}_2$  mixtures.  $[\text{HO}_2]$  and  $[\text{H}_2\text{O}_2]$  moni-

tored by UV absorption. Expression for  $k$  derived from unweighted least squares Arrhenius plot of their data over range 418–656 K together with the single temperature measurement of Baldwin *et al.*<sup>1,2</sup>

- (d) Shock-tube pyrolysis and oxidation of HCHO at total pressures between 1.4 and 2.5 bar. [HCHO] followed by time resolved IR-laser absorption and IR emission.  $k$  well defined by computer fit to [HCHO] decay.  
(e) Shock tube study on HCHO/ $\text{O}_2/\text{Ar}$  mixtures at total pressures in the range 0.7–2.5 bar. [CO] was monitored behind reflected shock waves by time resolved resonance laser absorption at  $2077.1 \text{ cm}^{-1}$ . The [CO] profiles were analyzed using the GRI-Mech 1.2. The expression for  $k_1$  cited is based on data from the present study together with data from Refs. 1–4.  
(f) Based on data of Baldwin *et al.*<sup>1,2</sup> and an assumed  $A$  factor of  $5.0 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .  
(g)  $k(298 \text{ K})$  taken as the average of the values of Su *et al.*<sup>10</sup> and Veyret *et al.*<sup>11,13</sup> The temperature dependence was taken from Veyret *et al.*<sup>13</sup>  
(h) Derived by taking the average of rate constants of Bar-

nes *et al.*<sup>12</sup> at 273 K and Veyret *et al.*<sup>13</sup> at 275 K and combining them with the *E/R* value of Veyret *et al.*<sup>13</sup>

### Preferred Values

$k_1 = 6.8 \cdot 10^{-20} T^{2.5} \exp(-5140/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 600–2000 K.

### Reliability

$\Delta \log k_1 = \pm 0.2$  at 600 K, rising to  $\pm 0.4$  at 2000 K.

### Comments on Preferred Values

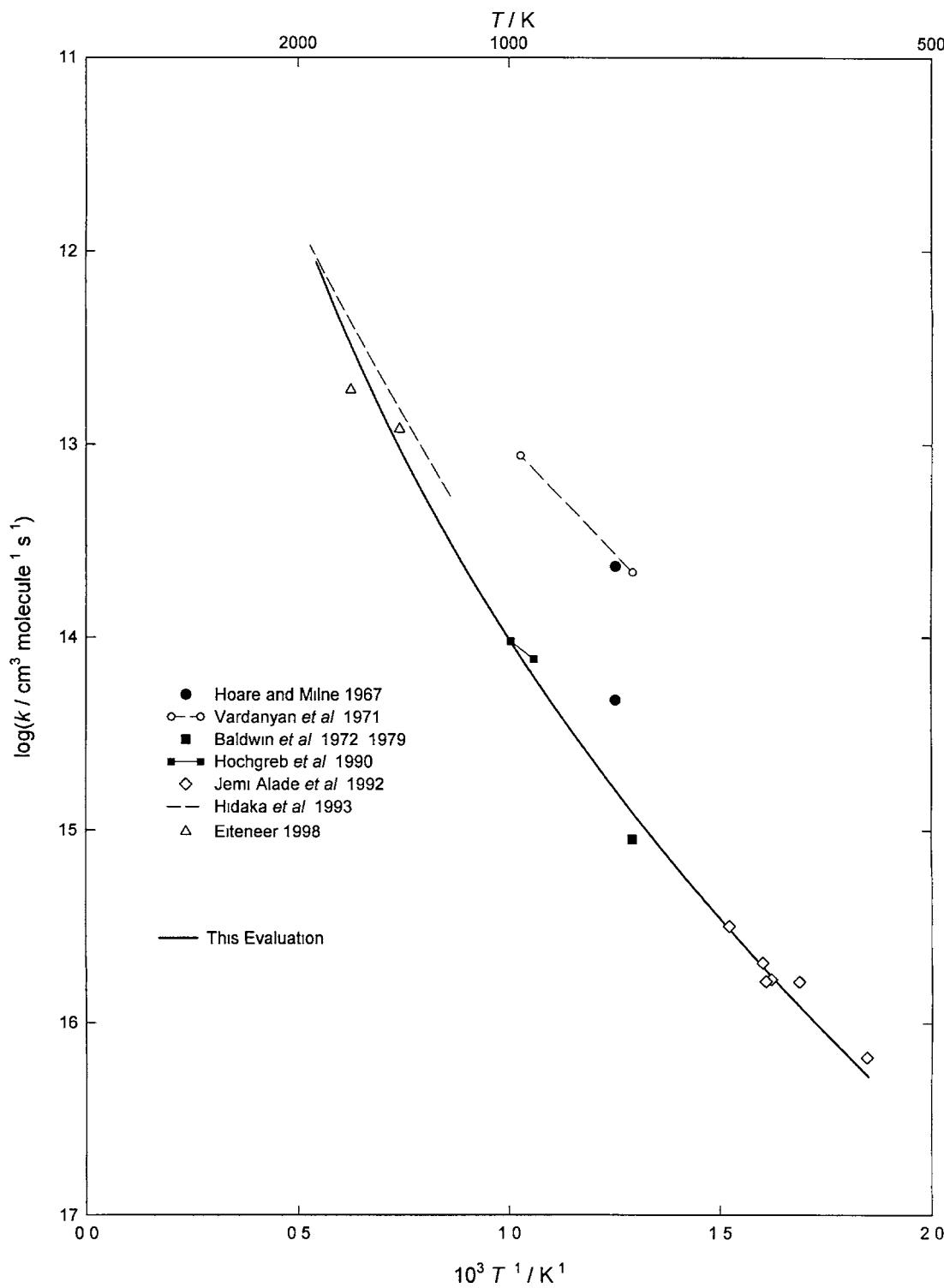
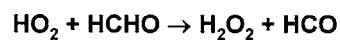
At low temperatures the reaction occurs by addition to form the adduct HOOCH<sub>2</sub>O which rapidly isomerizes to HOCH<sub>2</sub>OO [Channel (2)]. The data for this channel<sup>10–13</sup> have been evaluated by the NASA<sup>8</sup> and IUPAC<sup>9</sup> Panels whose publications should be consulted for details. Only the data for Channel (1), which predominates at high temperatures, are evaluated here. The IUPAC recommendation for  $k_2$  is  $k_2 = 9.7 \cdot 10^{-15} \exp(625/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 275–333 K.<sup>9</sup>

All of the more recent high temperature studies, i.e., those of Eiteneer *et al.*<sup>6</sup> Hidaka *et al.*,<sup>5</sup> Jemi-Alade *et al.*,<sup>4</sup> and Hochgreb *et al.*<sup>3</sup> are in quite good agreement with the earlier studies of Baldwin *et al.*<sup>1,2</sup> and form the basis for our preferred expression for  $k$ . Eiteneer *et al.*<sup>6</sup> have reviewed the same data and from them have derived the expression for  $k$

cited in the Table, which we have adopted as our preferred expression. Earlier studies<sup>14–16</sup> at these temperatures give much higher values which are not considered reliable.

### References

- <sup>1</sup>R. R. Baldwin, A. R. Fuller, D. Longthorn, and R. W. Walker, *J. Chem. Soc. Faraday Trans. 1* **68**, 1362 (1972).
- <sup>2</sup>R. R. Baldwin and R. W. Walker, 17th Symp. (Int.) Combustion, 1979, p. 525.
- <sup>3</sup>S. Hochgreb, R. A. Yetter, and F. L. Dryer, 23rd Symp. (Int.) Combustion, 1990, p. 171.
- <sup>4</sup>A. A. Jemi-Alade, P. D. Lightfoot, and R. Lesclaux, *Chem. Phys. Lett.* **195**, 25 (1992).
- <sup>5</sup>Y. Hidaka, T. Taniguchi, H. Tanaka, T. Kamesawa, K. Inami, and H. Kawano, *Combust. Flame* **92**, 365 (1993).
- <sup>6</sup>B. Eiteneer, C.-L. Yu, M. Goldenberg, and M. Frenklach, *J. Phys. Chem. A* **102**, 5196 (1998).
- <sup>7</sup>CEC, 1992; Supplement 1, 1994 (see references in Introduction).
- <sup>8</sup>NASA Evaluation No 12, 1997 (see references in Introduction).
- <sup>9</sup>IUPAC, Supplement VII, 1999 (see references in Introduction).
- <sup>10</sup>F. Su, J. G. Calvert, J. H. Shaw, H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, *Chem. Phys. Lett.* **65**, 221 (1979).
- <sup>11</sup>B. Veyret, J.-C. Rayez, and R. Lesclaux, *J. Phys. Chem.* **86**, 3424 (1982).
- <sup>12</sup>I. Barnes, K. H. Becker, E. H. Fink, A. Reimer, F. Zabel, and H. Niki, *Chem. Phys. Lett.* **115**, 1 (1985).
- <sup>13</sup>B. Veyret, R. Lesclaux, M.-T. Rayez, J.-C. Rayez, R. A. Cox, and G. K. Moortgat, *J. Phys. Chem.* **93**, 2368 (1989).
- <sup>14</sup>D. E. Hoare and G. S. Milne, *Trans. Faraday Soc.* **63**, 101 (1967).
- <sup>15</sup>R. R. Baldwin, D. H. Langford, M. J. Matchan, R. W. Walker, and D. H. Yorke, 13th Symp. (Int.) Combustion, 1971, p. 251.
- <sup>16</sup>I. A. Vardanyan, G. A. Sachyan, and A. B. Nalbandyan, *Combust. Flame* **17**, 315 (1971).





### Rate Coefficient Data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$6 \cdot 10^{-11}$	298	Grotheer <i>et al.</i> , 1985 <sup>1</sup>	(a)
<i>Reviews and Evaluations</i>			
$2.0 \cdot 10^{-11}$	300–2500	Tsang, 1987 <sup>2</sup>	(b)

### Comments

- (a) Discharge flow study of the reaction of  $\text{CH}_2\text{OH}$  with  $\text{O}_2$ .  $\text{CH}_2\text{OH}$  radicals were generated by the  $\text{Cl} + \text{CH}_3\text{OH}$  reaction in He carrier gas at pressures of  $< 2$  mbar. Products and reactant concentrations were monitored by mass spectrometry.  $k$  was derived from the measured  $[\text{HO}_2]$  profile as a function of  $\text{O}_2$ . The authors suggest an uncertainty factor of  $\sim 2$ .
- (b) Estimate. Basis of estimate not given.

### Reliability

$$\Delta \log k = \pm 0.5 \text{ at } 298 \text{ K.}$$

### Comments on Preferred Values

Only limited accuracy is claimed for the sole measurement of this rate constant.<sup>1</sup> Until further studies are available this value is accepted but substantial error limits are assigned. The likely products of the reaction are  $\text{HCHO} + \text{H}_2\text{O}_2$ .

### References

- <sup>1</sup>H.-H. Grotheer, G. Riekert, U. Meier, and Th. Just, Ber. Bunsenges. Phys. Chem. **89**, 187 (1987).  
<sup>2</sup>W. Tsang, J. Phys. Chem. Ref. Data **16**, 471 (1987).

### Preferred Values

$$k = 6 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$



### Thermodynamic Data

$$\begin{aligned}\Delta H^\circ_{298}(1) &= -160.7 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(1) &= -21.7 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 6.5 \cdot 10^{-2} T^{0.042} \exp(+17850/T) \\ (300 \leqslant T/\text{K} \leqslant 5000)\end{aligned}$$

$$\begin{aligned}\Delta H^\circ_{298}(2) &= -373.0 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(2) &= 113.8 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 1.35 \cdot 10^{30} T^{-1.684} \exp(+44400/T) \text{ molecule cm}^{-3} \\ (300 \leqslant T/\text{K} \leqslant 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

### Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$k = 4.8 \cdot 10^{-12}$	300	Moortgat <i>et al.</i> , 1989 <sup>1</sup>	(a)
$k_1 = 3.5 \cdot 10^{-12}$	300		(b)
$k = 4.4 \cdot 10^{-13} \exp(780/T)$	248–573	Lightfoot, Veyret, and Lesclaux, 1990 <sup>2</sup>	(c)
$k = 2.9 \cdot 10^{-13} \exp(862/T)$	248–678	Lightfoot <i>et al.</i> , 1991 <sup>3</sup>	(d)
$k_2 = 1.6 \cdot 10^{-15} \exp(1730/T)$	218–298	Elrod <i>et al.</i> , 2001 <sup>4</sup>	(e)
<i>Branching Ratio Measurements</i>			
$k_1/k = 0.92 [920 \text{ mbar}]$	295	Wallington and Japar, 1990 <sup>5</sup>	(f)
$k_1/k = 0.92 [20–920 \text{ mbar}]$	295	Wallington, 1991 <sup>6</sup>	(f)
$\ln(k_1/k_2) = 6.21 - 1160/T$	218–298	Elrod <i>et al.</i> , 2001 <sup>4</sup>	(e)
<i>Reviews and Evaluations</i>			
$k = 5.6 \cdot 10^{-13} \exp(640/T)$	250–600	Wallington, Dagaut, and Kurylo, 1992 <sup>7</sup>	(g)
$k = 4.1 \cdot 10^{-13} \exp(790/T)$	230–680	Lightfoot <i>et al.</i> , 1992 <sup>8</sup>	(h)
$k = 4.1 \cdot 10^{-13} \exp(790/T)$	298–700	CEC, 1994 <sup>9</sup>	(i)
$k = 3.8 \cdot 10^{-13} \exp(800/T)$	228–573	NASA, 1997 <sup>10</sup>	(j)
$k = 3.8 \cdot 10^{-13} \exp(780/T)$	225–580	IUPAC, 1999 <sup>11</sup>	(k)
$k_1 = 4.15 \cdot 10^{-13} \exp(750/T)$	228–573	Tyndall <i>et al.</i> , 2001 <sup>12</sup>	(l)

### Comments

- (a) Rate coefficient determinations made prior to 1989 have not been listed explicitly. The measurements can be found in Refs. 13–20 which have been reviewed in earlier evaluations.<sup>10,11</sup>
- (b) Modulated photolysis of  $\text{CH}_3\text{CHO}/\text{O}_2/\text{N}_2$  mixtures at atmospheric pressure with long path length UV and FTIR absorption detection. Composite absorptions due to  $\text{CH}_3\text{O}_2$  and  $\text{HO}_2$  recorded at 220 and 250 nm. The wave forms were analyzed simultaneously with an assumed reaction scheme. The absorption cross sections used were for  $\text{CH}_3\text{O}$ ,  $\sigma_{250}[\text{CH}_3\text{O}_2]=4.16 \cdot 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ ,  $\sigma_{220}/\sigma_{250}=0.81$ , and for  $\text{HO}_2$ ,  $\sigma_{220}[\text{HO}_2]=4.0 \cdot 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ ,  $\sigma_{250}[\text{HO}_2]=0.5 \cdot 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ .  $k_1$  was determined by simulating the growth of  $[\text{CH}_3\text{OOH}]$  and the concentration of other products with an assumed reaction scheme.
- (c) Flash photolysis of  $\text{Cl}_2/\text{CH}_4/\text{CH}_3\text{OH}/\text{O}_2/\text{N}_2$  mixtures with UV absorption detection at 210 and 260 nm. Simultaneous analysis of composite absorption profiles. Cross sections of  $\text{CH}_3\text{O}_2$  and  $\text{HO}_2$  at the two wavelengths were derived from studies on the two self-reactions (with either  $\text{CH}_3\text{OH}$  or  $\text{CH}_4$  removed) and  $\text{NOCl}$  used as an actinometer ( $\sigma_{260}[\text{CH}_3\text{O}_2]=3.6 \cdot 10^{-18}$ ,  $\sigma_{210}[\text{CH}_3\text{O}_2]=2.5 \cdot 10^{-18}$ ,  $\sigma_{260}[\text{HO}_2]=0.3 \times 10^{-18}$ ,  $\sigma_{210}[\text{HO}_2]=5.3 \cdot 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ ).
- (d) Flash photolysis of  $\text{O}_2/\text{CH}_4/\text{CH}_3\text{OH}$  mixtures between 600 K and 719 K with UV absorption detection. The earlier data of Lightfoot *et al.*<sup>2</sup> were reanalyzed using temperature dependent absorption cross sections<sup>21</sup> and combined with the results of this study.
- (e) Turbulent flow technique in which  $\text{CH}_3\text{O}_2$  was generated by the reaction  $\text{F}+\text{CH}_4$  followed by  $\text{CH}_3+\text{O}_2+\text{M}$ , and  $\text{HO}_2$  was generated by  $\text{H}+\text{O}_2+\text{M}$ . Chemical ionization mass spectrometry was used to detect  $\text{HCHO}$ ,  $\text{CH}_3\text{O}_2$ ,  $\text{CH}_3\text{OOH}$ ,  $\text{CH}_3\text{O}$ ,  $\text{HO}_2$ , and  $\text{NO}_2$ . Second order kinetics conditions were used and absolute concentrations of  $\text{CH}_3\text{O}_2$  and  $\text{HO}_2$  were determined by titration with  $\text{NO}$  and measurement of the calibrated  $\text{NO}_2$  signal. Values of the rate constants were determined by detailed modeling of product and reactant profiles.  $\text{CH}_3\text{OOH}$  was shown to be the major product and both the  $[\text{CH}_3\text{OOH}]$  and  $[\text{CH}_3\text{O}_2]$  profiles were shown to be consistent with the kinetic model being used. Values of  $k_2$  were derived from measurements at 130 mbar. Expression for  $k_1/k_2$  uses  $k_1=(k-k_2)$  and the NASA<sup>10</sup> value of  $k$  to obtain  $k_1$ .
- (f) Growth of  $\text{CH}_3\text{OOH}$  compared to loss of  $\text{CH}_4$  following the photolysis of  $\text{F}_2/\text{CH}_4/\text{H}_2/\text{air}$  mixtures using long path length FTIR spectroscopy.<sup>5</sup> Conditions arranged so that  $\text{CH}_3\text{O}_2$  reacted predominantly with  $\text{HO}_2$ . Complications arising from secondary chemistry were mainly avoided by using  $\text{F}_2$ . The yield of

$\text{CH}_3\text{OOH}$  appeared independent of pressure between 20 and 920 mbar although corrections for  $\text{CH}_3\text{F}$  formation were made at the lowest pressures.<sup>6</sup>

- (g) Based on a single Arrhenius fit of all the available kinetic data excluding the determination by Kan *et al.*<sup>15</sup> Both values reported by Jenkin *et al.*<sup>19</sup> and Moortgat *et al.*<sup>1</sup> were included. The reaction was assumed to give only  $\text{CH}_3\text{OOH}$  and  $\text{O}_2$  as reported by Wallington and Japar.<sup>4</sup>
- (h) The preferred value at 298 K is a simple mean of the rate parameters derived by Cox and Tyndall,<sup>14</sup> Jenkin *et al.*,<sup>19</sup> Moortgat *et al.*,<sup>1</sup> and Lightfoot *et al.*,<sup>2,3</sup> which excludes the low values reported by Kurylo *et al.*<sup>18</sup> and Kan *et al.*<sup>15</sup> The temperature coefficient was obtained as a rounded-off average of the three latest temperature-dependent studies (Dagaut *et al.*,<sup>20</sup> Lightfoot *et al.*,<sup>2</sup> and Lightfoot *et al.*<sup>3</sup>), with the A factor adjusted to give the recommended value of  $k_{298}$ .
- (i) See Comments on Preferred Values.
- (j)  $k_{298}$  is the averaged value of data from Cox and Tyndall,<sup>14</sup> McAdam *et al.*,<sup>16</sup> Kurylo *et al.*,<sup>18</sup> Jenkin *et al.*,<sup>19</sup> Moortgat *et al.*,<sup>1</sup> and Lightfoot *et al.*<sup>2</sup> E/R is derived from the data of Cox and Tyndall,<sup>14</sup> Dagaut *et al.*,<sup>20</sup> and Lightfoot *et al.*<sup>2</sup>
- (k)  $k_{298}$  is the mean of the values of Cox and Tyndall,<sup>14</sup> Jenkin *et al.*,<sup>19</sup> Dagaut *et al.*,<sup>20</sup> Moortgat *et al.*,<sup>1</sup> and Lightfoot *et al.*<sup>3</sup> E/R is that reported by Lightfoot *et al.*<sup>3</sup>
- (l) Based mainly on the studies of Lightfoot *et al.*<sup>2</sup> and Dagaut *et al.*<sup>20</sup> together with those of Cox and Tyndall,<sup>14</sup> Jenkin *et al.*,<sup>19</sup> and Moortgat *et al.*<sup>1</sup>

### Preferred Values

$k=4.2 \cdot 10^{-13} \exp(750/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 225–700 K.

$$k_2/k=0.1 \text{ at } 298 \text{ K.}$$

### Reliability

$$\Delta \log k = \pm 0.1 \text{ at } 225 \text{ K, rising to } \pm 0.3 \text{ at } 700 \text{ K.}$$

$$\Delta k_2/k = \pm 0.05 \text{ at } 298 \text{ K.}$$

### Comments on Preferred Values

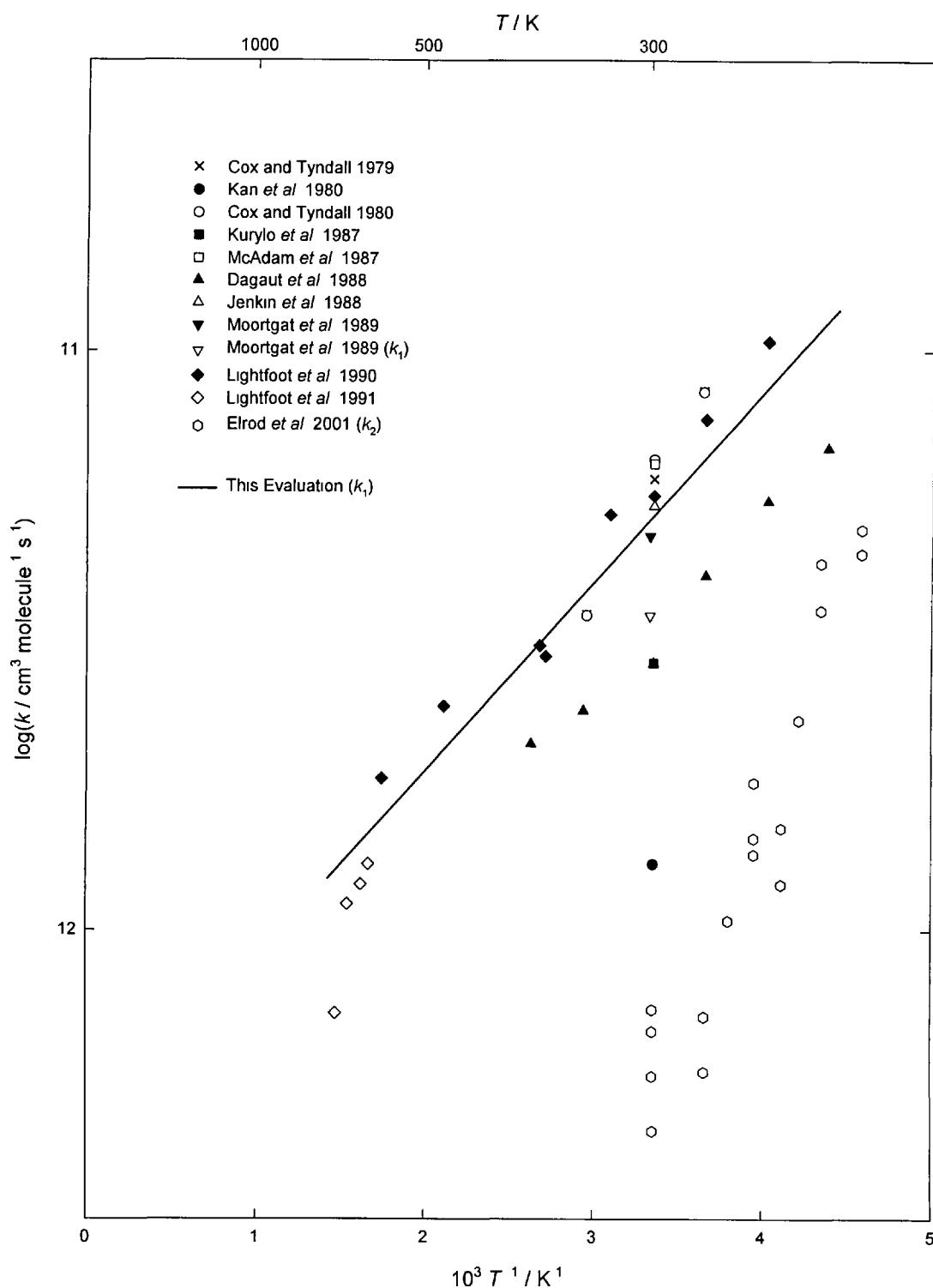
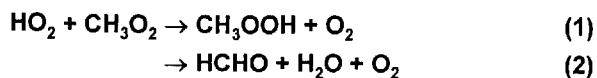
The independent reviews undertaken by Wallington *et al.*,<sup>7</sup> Lightfoot *et al.*,<sup>8</sup> and Tyndall *et al.*<sup>12</sup> have critically evaluated the kinetic and mechanistic data available on this reaction. The preferred expression is that given by Tyndall *et al.*,<sup>12</sup> which is very similar to that of Lightfoot *et al.*<sup>8</sup> Basically the same kinetics data base was used by Tyndall *et al.*,<sup>12</sup> and Lightfoot *et al.*,<sup>8</sup> but Tyndall *et al.*<sup>12</sup> evaluated the absorption cross sections of the peroxy species including more recent data and were able to reanalyze a number of previous studies in terms of these new cross section eventually arriving at an expression for  $k$  slightly different from that of Lightfoot *et al.*<sup>8</sup> The earlier review of Wallington *et al.*<sup>7</sup> did not incorporate the extensive high temperature

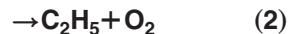
data from the Bordeaux group<sup>3</sup> in reaching their recommendations and included the kinetic measurements of Kurylo *et al.*<sup>18</sup> in their Arrhenius analysis which gives a value of the rate constant significantly lower at 298 K than all of the other direct measurements. The temperature dependence reported by Kurylo and co-workers (Dagaut *et al.*<sup>20</sup>) is, however, in very good agreement with the other recent temperature dependent studies, suggesting a possible systematic error in the absolute  $k$  values of Kurylo *et al.*<sup>18</sup> (see Arrhenius plot).

The studies of Wallington and Japar,<sup>5</sup> Wallington,<sup>6</sup> and Elrod *et al.*<sup>4</sup> indicate that Channel (1) is the major reaction pathway. Further support for this is provided by Lightfoot *et al.*<sup>3</sup> who could only interpret their high temperature data if the reaction was assumed to give mainly CH<sub>3</sub>OOH and O<sub>2</sub>. However, the studies of Wallington *et al.*<sup>6</sup> and Elrod *et al.*<sup>4</sup> also suggest that there is a small contribution from Channel (2) of ~10% at 298 K. If the temperature dependence of  $k_2$  determined by Elrod *et al.*<sup>4</sup> persists to higher temperatures this contribution will become <1% at temperatures above ~700 K.

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*Thermodynamic Data*

$$\Delta H^\circ_{298}(1) = -79.4 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = -21.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 4.71 \cdot 10^{-3} T^{0.393} \exp(+9700/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(2) = 54.8 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = 3.99 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 1.04 T^{0.070} \exp(-6580/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(3) = 97.4 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = 20.20 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 7.44 T^{0.141} \exp(-11840/T) \\ (300 \leq T/\text{K} \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data ( $k = k_1 + k_2 + k_3$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$k_1 = 1.05 \cdot 10^{-11} \exp(-9590/T)$	673–773	Baldwin <i>et al.</i> , 1984 <sup>1</sup>	(a)
$k_1 = 4.7 \cdot 10^{-12} \exp(-8612/T)$	673–773	Baldwin, Dean, and Walker, 1986 <sup>2</sup>	(b)
$k_1 = 6.3 \cdot 10^{-12} \exp(-8985/T)$	673–773	Baldwin, Stout, and Walker, 1991 <sup>3</sup>	(c)
<i>Reviews and Evaluations</i>			
$3.7 \cdot 10^{-12} \exp(-8650/T)$	600–900	CEC, 1992; 1994 <sup>4</sup>	(d)

**Comments**

- (a) Thermal decomposition of tetramethylbutane in the presence of O<sub>2</sub> was used as a source of HO<sub>2</sub> radicals. Tetramethylbutane/O<sub>2</sub>/C<sub>2</sub>H<sub>4</sub>/N<sub>2</sub> mixtures were heated in a KCl coated vessels and product yields were measured by gas chromatography. Major products were *i*-butene and C<sub>2</sub>H<sub>4</sub>O. Values of  $k/k^{1/2}(\text{HO}_2 + \text{HO}_2)$  were obtained from which we have derived the cited expression of  $k$  using the expression for  $k(\text{HO}_2 + \text{HO}_2)$  from the present evaluation. The  $k/k^{1/2}(\text{HO}_2 + \text{HO}_2)$  values were found to increase slightly with increase in pressure. The higher pressure values were considered more reliable and were used in calculating  $k$ . It was later shown<sup>2</sup> that the values of  $k$  above 723 K are slightly too high.
- (b) Study on the competitive oxidation of C<sub>2</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub> using the thermal decomposition of tetramethylbutane in the presence of O<sub>2</sub> as a source of HO<sub>2</sub> radicals. Tetramethylbutane/O<sub>2</sub>/C<sub>2</sub>H<sub>4</sub>/C<sub>3</sub>H<sub>6</sub>/N<sub>2</sub> mixtures were heated in a boric acid coated vessel and product yields (C<sub>2</sub>H<sub>4</sub>O, C<sub>3</sub>H<sub>6</sub>O) were measured by gas chromatography. Values of  $k/k(\text{HO}_2 + \text{C}_3\text{H}_6)$  were obtained using the expression for  $k(\text{HO}_2 + \text{C}_3\text{H}_6)$  of Baldwin *et al.*<sup>5</sup>
- (c) Technique as in (a) but a boric acid coated vessel was used which is considered to yield more reliable results because of the lack of surface effects. Results from this study were combined with those from previous studies to derive the expression for  $k$  cited.
- (d) Based on Refs. 1,2.

**Preferred Values**

$k_1 = 6.3 \cdot 10^{-12} \exp(-8990/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 600–900 K.

$k_2 = 1.0 \cdot 10^{-13} T^{0.07} \exp(-6580/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 700–1500 K.

**Reliability**

$\Delta \log k_1 = \pm 0.15$  over the temperature range 600–750 K, rising to  $\pm 0.25$  at 900 K.

$\Delta \log k_2 = \pm 0.2$  at 700 K, rising to  $\pm 0.4$  at 1500 K.

**Comments on Preferred Values**

Experimental data are available only for Channel (1). No absolute determinations have been made and all of the relative rate measurements are based on determination of oxirane yields. The expression for  $k_1$  derived in the study of Baldwin *et al.*<sup>3</sup> incorporates measurements from other studies and is considered the most reliable. The other data available consist of earlier studies by Walker,<sup>6</sup> and Baldwin and Walker,<sup>7</sup> both of which are in agreement with the recommendations, a study by Hoare and Patel<sup>8</sup> which is not considered reliable, and a study by Arsentiev *et al.*<sup>9</sup> in which the autoxidation of ethane was followed by ESR monitoring of the total peroxy radical concentration and measurement of the products. Over the small temperature range used, 637–688 K, Arsentiev *et al.*<sup>9</sup> obtain for the rate constant for peroxy removal the expression  $2.1 \cdot 10^{-12} \exp(-6810/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Under their conditions HO<sub>2</sub> is likely to be the predominant peroxy radical but the expression obtained gives values a

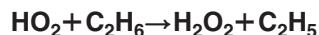
factor of 10 greater than the expression obtained by Baldwin *et al.*<sup>1–3</sup>

The Arrhenius parameters obtained by Baldwin *et al.*<sup>1–3</sup> for  $k_1$  are consistent with those found for the analogous reaction of HO<sub>2</sub> with a number of alkenes<sup>3,10</sup> and, on this basis, it has been argued that they refer to the addition of HO<sub>2</sub> to C<sub>2</sub>H<sub>4</sub> to form CH<sub>2</sub>CH<sub>2</sub>OOH.<sup>1,11</sup> However, there are difficulties in reconciling this mechanism, particularly the magnitude of the activation energy, with the rate parameters of the C<sub>2</sub>H<sub>5</sub>+O<sub>2</sub> reaction (see the data sheet on C<sub>2</sub>H<sub>5</sub>+O<sub>2</sub>). *Ab initio* calculations<sup>12</sup> show that, while the HO<sub>2</sub>+C<sub>2</sub>H<sub>4</sub> reaction leads to formation of C<sub>2</sub>H<sub>5</sub>O<sub>2</sub> via a small energy barrier that lies below the threshold energy for formation of C<sub>2</sub>H<sub>5</sub>O<sub>2</sub>, formation of C<sub>2</sub>H<sub>4</sub>O requires crossing to another potential energy surface *via* a conical intersection. The experiments of Baldwin *et al.*<sup>1–3</sup> used high O<sub>2</sub> concentrations so that any C<sub>2</sub>H<sub>5</sub> formed in their experiments would rapidly regenerate reactants which may have affected their interpretation. The calculations of Miller and Klippenstein,<sup>13</sup> which provide the best interpretation of the C<sub>2</sub>H<sub>5</sub>+O<sub>2</sub> reaction, did not consider the OH+C<sub>2</sub>H<sub>4</sub>O channel, except to establish that its yield was small. Further work is required on Channel (1) to establish its mechanism. For the present the preferred expression for  $k_1$  is taken as that of Baldwin *et al.*<sup>3</sup> and the

value of  $k_2$  is obtained from the equilibrium constant and the value of the rate constant for the reverse reaction.

## References

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### Thermodynamic Data

$$\begin{aligned}\Delta H_{298}^{\circ} &= 54.86 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= 23.6 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 27.5 T^{-0.016} \exp(-6730/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the origin source of the Thermodynamic Data.

### Rate Coefficient Data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$1.83 \cdot 10^{-11} \exp(-10260/T)$	673–773	Baldwin <i>et al.</i> , 1986 <sup>1</sup>	(a)
<i>Reviews and Evaluations</i>			
$4.9 \cdot 10^{-13} \exp(-9770/T)$	300–800	Walker, 1977 <sup>2</sup>	(b)
$2.22 \cdot 10^{-11} \exp(-10335/T)$	500–1000	CEC, 1992; 1994 <sup>3</sup>	(c)
$1.18 \cdot 10^{-19} \exp(-8480/T)$	500–2000	Scott and Walker, 2002 <sup>4</sup>	(d)

### Comments

- (a) Thermal decomposition of tetramethylbutane in the presence of O<sub>2</sub> was used as a source of HO<sub>2</sub> radicals. Tetramethylbutane/O<sub>2</sub>/C<sub>2</sub>H<sub>6</sub>/N<sub>2</sub> mixtures were heated in KCl and boric acid coated vessels and product yields (*i*-butene, C<sub>2</sub>H<sub>4</sub>) were measured by gas chromatography. Values of  $k/k^{1/2}(\text{HO}_2 + \text{HO}_2)$  were obtained from

which we have derived the cited expression of  $k$  using the expression for  $k(\text{HO}_2 + \text{HO}_2)$  from the present evaluation.

- (b) Estimate based on the rate constants for HO<sub>2</sub> attack on *i*-butane and 2,3-dimethylbutane.  
 (c) Accepts the expression of Baldwin *et al.*<sup>1</sup>  
 (d) Results of the study of Baldwin *et al.* over the range 673–793 K fitted to the non-Arrhenius expression

A  $T^{2.5} \exp(B/T)$ , following a detailed review of HO<sub>2</sub> abstraction reactions and the establishment of a data base for such reactions.<sup>4</sup> The  $T$  exponent of 2.5 was assumed to be the same as that for the HO<sub>2</sub>+HCHO reaction, as obtained by Eiteneer *et al.*<sup>5</sup> (see HO<sub>2</sub>+HCHO data-sheet).

### Preferred Values

$$k = 1.83 \cdot 10^{-19} T^{2.5} \exp(-8480/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the range 500–2000 K.

#### Reliability

$\Delta \log k = \pm 0.15$  over the range 500–800 K, rising to  $\pm 0.3$  at 1000 K and  $\pm 0.7$  at 2000 K.

#### Comments on Preferred Values

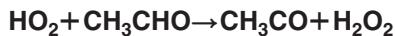
The only reliable experimental determinations of  $k$  are those of Baldwin *et al.*<sup>1</sup> They are in excellent agreement with a similar study on the HO<sub>2</sub>+tetramethylbutane reaction in which only primary H atoms are abstracted.<sup>4,6</sup> The earlier relative rate studies of Hoare and Patel<sup>7</sup> were considered by

the authors themselves to be unreliable. Baldwin *et al.*<sup>1</sup> obtained values of  $k/k^{1/2}(\text{HO}_2 + \text{HO}_2)$  and, in calculating  $k$  from them, the uncertainties in the reference rate constant are reduced by 50% by virtue of the square root dependence on  $k(\text{HO}_2 + \text{HO}_2)$ , leading to precise values of  $k$  between 500 K and 800 K.

The preferred expression for  $k$  should give a considerably more reliable prediction of  $k$  at elevated temperatures than the Arrhenius form recommended in our previous evaluation.<sup>3</sup> The reaction HO<sub>2</sub>+C<sub>2</sub>H<sub>6</sub> is unlikely to be an important reaction in combustion systems above  $\sim 1500$  K.

### References

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#### Thermodynamic Data

$$\begin{aligned}\Delta H_{298}^\circ &= 6.27 \text{ kJ mol}^{-1} \\ \Delta S_{298}^\circ &= 8.92 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 2.9 \cdot 10^2 T^{-0.589} \exp(-1250/T) \\ (300 \leqslant T/\text{K} \leqslant 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

### Rate Coefficient Data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$2.8 \cdot 10^{-12} \exp(-5350/T)$	1030–1115	Colket <i>et al.</i> , 1975 <sup>1</sup>	(a)
<i>Reviews and Evaluations</i>			
$5.0 \cdot 10^{-12} \exp(-6000/T)$	900–1200	CEC, 1992; 1994 <sup>2</sup>	(b)

### Comments

- (a) The oxidation of CH<sub>3</sub>CHO was studied by heating CH<sub>3</sub>CHO/O<sub>2</sub>/Air mixtures in a turbulent flow reactor. Concentrations of stable species (CH<sub>3</sub>CHO, H<sub>2</sub>, CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, CO<sub>2</sub>, CH<sub>3</sub>, HCHO) were measured at points along the reactor by gas chromatography. The results were modeled using a reaction scheme of 25 reactions and rate constants were derived for 4 reactions.
- (b) See Comments on Preferred Values.

### Preferred Values

$$k = 6.8 \cdot 10^{-20} T^{2.5} \exp(-5135/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the range 600–1500 K.

#### Reliability

$\Delta \log k = \pm 0.4$  over the range 600–1000 K, rising to  $\pm 0.7$  at 1500 K.

#### Comments on Preferred Values

The only determination of  $k$  is that of Colket *et al.*<sup>1</sup> over

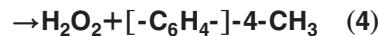
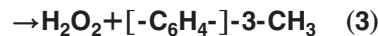
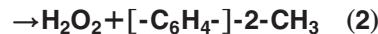
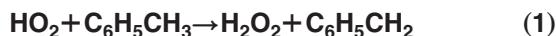
the temperature range 1030–1115 K. Extrapolation of this expression to 713 K gives  $k = 1.55 \cdot 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  compared with  $k(\text{HO}_2 + \text{C}_2\text{H}_5\text{CHO}) = 1.6 \cdot 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for specific attack on the aldehydic C-H bond at the same temperature.<sup>3</sup> This agreement appears to support the expression given by Colket *et al.*,<sup>1</sup> on the assumption that the aldehydic C-H bonds in the two compounds are kinetically identical. However, the Arrhenius parameters of Colket *et al.*<sup>1</sup> are probably too low, as also seen when the expression is expressed in the preferred non-Arrhenius form  $k = 9.1 \cdot 10^{-21} T^{2.5} \exp(-3153/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  which compares with  $k = 6.8 \cdot 10^{-20} T^{2.5} \exp(-5135/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the reaction  $\text{HO}_2 + \text{HCHO}$  obtained from an excellent fit to four independent sets of experimental data between 540 K and 1600 K.<sup>4</sup> Given the similarities in the enthalpies of reaction concerned (within  $\sim 4 \text{ kJ mol}^{-1}$ ) the expression for  $k(\text{HO}_2 + \text{HCHO})$  is also recommended for use with the  $\text{HO}_2 + \text{CH}_3\text{CHO}$  reaction. This expression predicts a value of  $k$  at 1070 K 20% higher than that found by Colket *et al.*<sup>1</sup> and

50% lower than that given by the expression for  $k(\text{HO}_2 + \text{C}_2\text{H}_5\text{CHO})$  cited above.

At low temperatures the reaction occurs by addition and at atmospheric pressure the adduct,  $\text{CH}_3\text{CH}(\text{OH})\text{O}_2$ , rapidly equilibrates with the reactants.<sup>5,6</sup> The rate constants for the forward and reverse reactions and the equilibrium constant have been measured over the range 298–373 K by Tomas *et al.*<sup>5</sup>

## References

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- <sup>6</sup> C. M. Roehl, D. Bauer, and G. K. Moortgat, J. Phys. Chem. **100**, 4038 (1996).



### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = 7.53 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = 4.31 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 1.49 \cdot 10^{-2} T^{0.839} \exp(-896/T) \quad (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(3) = 105.4 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = 13.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 22.7 T^{-0.171} \exp(-12850/T) \quad (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(2) = 105.4 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = 13.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 20.0 T^{-0.157} \exp(-12850/T) \quad (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(4) = 105.4 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(4) = 8.43 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(4) = 12.5 T^{-0.171} \exp(-12850/T) \quad (300 \leq T/\text{K} \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

### Rate Coefficient Data ( $k = k_1 + k_2 + k_3 + k_4$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$6.3 \cdot 10^{-17}$	773	Baldwin, Scott, and Walker, 1992 <sup>1</sup>	(a)
$5 \cdot 10^{-10} \exp(-11070/T)$	1150–1250	Eng <i>et al.</i> , 1998 <sup>2</sup>	(b)
$k_1 = 9.1 \cdot 10^{-17}$	773	Scott and Walker, 2002 <sup>3</sup>	(c)
<i>Reviews and Evaluations</i>			
$k_1 = 6.6 \cdot 10^{-13} \exp(-5680/T)$	600–1000	CEC, 1994 <sup>4</sup>	(d)
$k_2 = 9 \cdot 10^{-12} \exp(-14500/T)$	600–1000		
$k_1 = 1.7 \cdot 10^{-20} T^{2.5} \exp(-5090/T)$	600–1200	Scott and Walker, 2002 <sup>3</sup>	(e)
$k_2 = k_3 = 3.0 \cdot 10^{-20} T^{2.5} \exp(-13900/T)$	600–1200		
$k_4 = 1.5 \cdot 10^{-20} T^{2.5} \exp(-13900/T)$	600–1200		

### Comments

- (a) Study of the relative rate of consumption of H<sub>2</sub> and C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> when traces of toluene were added to slowly reacting H<sub>2</sub>/O<sub>2</sub> mixtures. Preliminary analysis of the results gave value of  $k/k^{1/2}(\text{HO}_2 + \text{HO}_2) = 6.5 \cdot 10^{-11}$  (cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>)<sup>1/2</sup> at 773 K. The cited value of  $k$  has been obtained using  $k^{1/2}(\text{HO}_2 + \text{HO}_2)$  from the present evaluation.
- (b) Shock tube study on toluene/O<sub>2</sub>/Ar mixtures. Benzyl radical concentrations were monitored by UV absorption at 257 nm behind reflected shocks at total pressures between 2 and 4 bar. Initially the benzyl concentration profiles were analyzed using a detailed mechanism but this analysis showed that a simplified mechanism applied and this was used to derive values of  $k$ .
- (c) More extensive study of system as described in Comment (a). Wider range of mixtures used permitted a more precise determination of the ratio  $k/k^{1/2}(\text{HO}_2 + \text{HO}_2)$ .
- (d) The  $A$  factor was estimated from the  $A$  factor per C-H bond for the HO<sub>2</sub>+(CH<sub>3</sub>)<sub>3</sub>CC(CH<sub>3</sub>)<sub>3</sub> reaction<sup>5</sup> with a reduction of a factor of 8 per C-H bond due to loss of entropy of activation from increased electron delocalization in the emerging C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub> radical. This  $A$  factor was combined with the value of  $k$  at 773 K from Baldwin *et al.*<sup>1</sup> to obtain the activation energy. A normal  $A$  factor coupled to the thermochemistry was used to obtain the parameters for attack on the ring.
- (e) Use was made of the fact that, for any particular RH, H abstractions by HO<sub>2</sub> and Br have virtually identical enthalpies of reaction and that the differences in activation energy for HO<sub>2</sub> and Br reactions with RH are virtually constant for a similar temperature range but over a wide range of enthalpies of reaction. The single value<sup>3</sup> of  $k_1 = 9.1 \cdot 10^{-17}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> was fitted to a non-Arrhenius expression using the parameters for the HO<sub>2</sub>+HCHO reaction (see data sheet) as models, and a reduction of a factor of 4 in the  $A$  factor per C-H bond for the loss of entropy of activation due to the formation of the electron-delocalized benzyl radical. The data of Eng *et al.*<sup>2</sup> were not used in the fit.

### Preferred Values

$k_1 = 1.55 \cdot 10^{-19} T^{2.5} \exp(-7390/T)$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> over the range 600–1500 K.

$k_2 = k_3 = 3.0 \cdot 10^{-20} T^{2.5} \exp(-13900/T)$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> over the range 600–1200 K.

$k_4 = 1.5 \cdot 10^{-20} T^{2.5} \exp(-13900/T)$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> over the range 600–1200 K.

### Reliability

$\Delta \log k_1 = \pm 0.3$  over the range 600–800 K, rising to  $\pm 0.7$  at 1500 K.

$\Delta \log k_2 = \Delta \log k_3 = \Delta \log k_4 = \pm 0.5$  over the range 600–800 K, rising to  $\pm 1$  at 1200 K

### Comments on Preferred Values

The values of  $k$  reported by Eng *et al.*<sup>2</sup> and by Scott and Walker<sup>3</sup> are seemingly incompatible. Taking the value of  $k = 4.9 \cdot 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 1200 K from the data of Eng *et al.*<sup>2</sup> and coupling it with the value of  $k$  at 773 K from Scott and Walker<sup>3</sup> gives impossibly high Arrhenius parameters. The experiments of Eng *et al.*<sup>2</sup> were designed primarily to determine  $k(\text{O}_2 + \text{C}_6\text{H}_5\text{CH}_3 \rightarrow \text{HO}_2 + \text{C}_6\text{H}_5\text{CH}_2)$ , and  $k$  was obtained from the acceleration in the rate of benzyl formation due to radical attack on the C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>, which was attributed entirely to HO<sub>2</sub>. In consequence their value of  $k$  has to be seen as a maximum value, which may be seriously in error if the mechanism is more complex. The low overall rates involved may also contribute to increased error. The more recent data<sup>6,7</sup> for  $k(\text{H} + \text{C}_6\text{H}_5\text{CH}_3 \rightarrow \text{C}_6\text{H}_5\text{CH}_2)$  at high temperatures when combined with  $k(\text{H} + \text{HCHO})$  from this evaluation gives the ratio  $k(\text{X} + \text{HCHO})/k(\text{X} + \text{C}_6\text{H}_5\text{CH}_3) = 2.0$  at 1200 K for X=H. When X=HO<sub>2</sub>, a higher ratio is expected because of the higher energy barriers involved, but use of Eng *et al.*'s data in combination with the very reliable expression for HO<sub>2</sub>+HCHO, which covers the range 540–1600 K, and gives a ratio of 0.5. This discrepancy provides good evidence that the values of Eng *et al.*<sup>2</sup> are about a factor of 4 too high. This view is also consistent with the thermochemistry of the reaction which would otherwise predict very high values for the rate constant of the reverse reaction.

On the other hand, based on the values of  $k$  obtained for similar reactions, Scott and Walker's<sup>3</sup> value of  $k_1$  is expected to be accurate to  $\pm 20\%$ . If their value was doubled, nearly all of the C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> in their system would be removed by HO<sub>2</sub> radicals and be totally inconsistent with the observed kinetics.

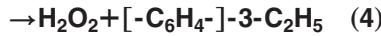
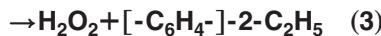
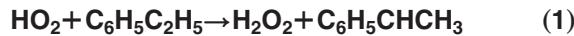
In order to achieve some compatibility in obtaining our preferred expression, the values of Eng *et al.*,<sup>2</sup> attributed to  $k_1$ , were reduced by a factor of 3 while those of Scott and Walker<sup>3</sup> were doubled and the resultant values were fitted to the non-Arrhenius expression  $k = A T^{2.5} \exp(B/T)$ , based on the expression for  $k(\text{HO}_2 + \text{HCHO})$  obtained from the excellent fit to four sets of data over the range 540–600 K (see data sheet). However, given the similar enthalpies of reaction for Channel (1) and the HO<sub>2</sub>+HCHO reaction, the difference between the values of the constants in the exponential terms in the expressions for  $k$  for the two reactions, 7390 K and 5135 K, respectively, is probably too high, and adds to the view that the results of Eng *et al.*<sup>2</sup> are too high by up to a factor of 10. An expression with a higher temperature exponent, ( $\sim 4$ ), due to the decreasing effect of electron delocalization in the benzyl radical on the  $A$  factor as the temperature increases, could also reduce the discrepancy.

Preferred values for  $k_2$ ,  $k_3$ , and  $k_4$  are based on the thermochemistry of the reaction channels and the similar reaction enthalpy of the HO<sub>2</sub>+CH<sub>4</sub> reaction.

## References

- <sup>1</sup>R. R. Baldwin, M. Scott, and R. W. Walker, 21st Symp. (Int.) Combustion, 1986, p. 991.  
<sup>2</sup>R. A. Eng, C. Fittschen, A. Gebert, P. Hibomvschi, H. Hippler, and A.-N. Unterreiner, 27th Symp. (Int.) Combustion, 1998, p. 211.  
<sup>3</sup>M. Scott and R. W. Walker, Combust. Flame **129**, 365 (2002).

- <sup>4</sup>CEC, Supplement I, 1994 (see references in Introduction).  
<sup>5</sup>R. R. Baldwin, M. W. M. Hisham, A. Keen, and R. W. Walker, J. Chem. Soc. Faraday Trans. 1 **77**, 1165 (1982).  
<sup>6</sup>M. Braun-Unkhoff, P. Frank, and Th. Just, 22nd Symp. (Int.) Combustion, 1988, p. 1053.  
<sup>7</sup>H. Hippler, C. Reihs, and J. Troe, Z. Phys. Chem. N. F. **167**, 1 (1990).  
<sup>8</sup>H. Hippler, C. Reihs, and J. Troe, 23rd Symp. (Int.) Combustion, 1991, p. 31.



### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = -8.48 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = -15.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 4.38 \cdot 10^{-3} T^{0.572} \exp(+1095/T) \quad (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(2) = 55.1 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = 20.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 11.6 T^{0.030} \exp(-6690/T) \quad (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(3) = 105.5 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = 42.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 1.98 \cdot 10^2 T^{0.005} \exp(-12770/T) \quad (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(4) = 105.5 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(4) = 42.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(4) = 1.98 \cdot 10^2 T^{0.005} \exp(-12770/T) \quad (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(5) = 105.5 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(5) = 9.42 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(5) = 3.78 T^{0.006} \exp(-12770/T) \quad (300 \leq T/\text{K} \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

### Rate Coefficient Data ( $k = k_1 + k_2 + k_3 + k_4 + k_5$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$2.75 \cdot 10^{-16}$	773	Scott, and Walker, 2002 <sup>1</sup>	(a)
<i>Reviews and Evaluations</i>			
$k_1 = 4.4 \cdot 10^{-13} \exp(-5680/T)$	600–1000	CEC, 1992 <sup>2</sup>	(b)
$k_2 = 5.3 \cdot 10^{-12} \exp(-9760/T)$	600–1000		
$k_3 = k_4 = k_5 = 9 \cdot 10^{-12} \exp(-14500/T)$	600–1000		
$k_1 = 1.13 \cdot 10^{-20} T^{2.5} \exp(-5090/T)$	600–1200	Scott and Walker, 2002 <sup>1</sup>	(c)
$k_2 = 5.9 \cdot 10^{-20} T^{2.5} \exp(-8480/T)$	600–1200		
$k_3 = k_4 = 3.0 \cdot 10^{-20} T^{2.5} \exp(-13900/T)$	600–1200		
$k_5 = 1.5 \cdot 10^{-20} T^{2.5} \exp(-13900/T)$	600–1200		

### Comments

- (a) Study of the relative rate of consumption of  $\text{H}_2$  and  $\text{C}_6\text{H}_5\text{C}_2\text{H}_5$  when traces of  $\text{C}_6\text{H}_5\text{C}_2\text{H}_5$  were added to slowly reacting  $\text{H}_2/\text{O}_2$  mixtures. Analysis of the results gave a value of  $k/k^{1/2}(\text{HO}_2 + \text{HO}_2) = 2.6 \cdot 10^{-10} (\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})^{1/2}$  at 773 K. The cited value of  $k$  has been obtained using  $k^{1/2}(\text{HO}_2 + \text{HO}_2)$  from the present evaluation. The value of  $k(\text{HO}_2 + \text{HO}_2)$  is accurately known and effects of any error in it, when calculating  $k$  from the rate constant ratio, are reduced by a factor of 2 because of the square root dependence.

- (b) Estimated expressions based on a comparison with data on the  $\text{HO}_2 + \text{C}_6\text{H}_5\text{CH}_3$  reaction.<sup>3</sup>  
(c) Use was made of the fact that, for any particular RH, H abstractions by  $\text{HO}_2$  and Br have virtually identical enthalpies of reaction and that the differences in activation energy for  $\text{HO}_2$  and Br reactions with RH are virtually constant for a similar temperature range, but over a wide range of enthalpies of reaction. The value of  $k_1 = 2.58 \cdot 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was obtained from  $k$  by subtracting 50% of  $k(\text{HO}_2 + \text{C}_2\text{H}_6)$  (see data sheet) to allow for attack (6.5%) at the  $\text{CH}_3$  group. This

single value was fitted to a non-Arrhenius expression using the parameters for the HO<sub>2</sub>+HCHO reaction (see data sheet) as models, and a reduction of a factor of 4 in the *A* factor per C-H bond for the loss of entropy of activation due to the formation of the electron-delocalized radical.

### Preferred Values

$k_1 = 1.03 \cdot 10^{-19} T^{2.5} \exp(-6805/T)$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> over the range 600–1500 K.

$k_2 = 5.9 \cdot 10^{-20} T^{2.5} \exp(-8480/T)$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> over the range 600–1500 K.

$k_3 = k_4 = 3.0 \cdot 10^{-20} T^{2.5} \exp(-13900/T)$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> over the range 600–1500 K.

$k_5 = 1.5 \cdot 10^{-20} T^{2.5} \exp(-13900/T)$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> over the range 600–1500 K.

### Reliability

$\Delta \log k_1 = \pm 0.3$  over the range 600–800 K, rising to  $\pm 0.7$  at 1500 K.

$\Delta \log k_2 = \pm 0.3$  over the range 600–800 K, rising to  $\pm 0.5$  at 1500 K.

$\Delta \log k_3 = \Delta \log k_4 = \Delta \log k_5 = \pm 0.5$  over the range 600–800 K, rising to  $\pm 1.0$  at 1500 K.

### Comments on Preferred Values

Only the single value of  $k_1$  at 773 K is available<sup>1</sup> but it shows excellent consistency on thermochemical grounds with the experimental data on  $k(\text{HO}_2 + \text{C}_6\text{H}_5\text{CH}_3)$ . Both were determined relative to  $k^{1/2}(\text{HO}_2 + \text{HO}_2)$  which, as indicated in Comment (a), is known reliably. The comments on the preferred values for the HO<sub>2</sub>+C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> reaction (see data sheet) are pertinent. Both reactions involve the formation of electron-delocalized radicals, the abstraction of labile H atoms, and are near thermoneutral. Thus the differences in activation energy for the two reactions should correspond to approximately 50% of the difference in the reaction enthalpies.

As for the other H-abstraction reactions of HO<sub>2</sub> previously evaluated here, the rate constant is fitted to the expression  $k = A T^{2.5} \exp(B/T)$ . In calculating  $k_1$  from  $k$  allowance is made for attack at the CH<sub>3</sub> group (6.5%). The *A* factor per C-H bond for Channel (1) is assumed to be the same as that for the reaction HO<sub>2</sub>+C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>→H<sub>2</sub>O<sub>2</sub>+C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub> and the energy term is calculated using the experimental value of  $k$ .<sup>1</sup> The difference in the activation energies for the reactions of the two alkylbenzenes is approximately 5 kJ mol<sup>-1</sup> which is approximately 50% of the difference in the reaction enthalpies, as expected (see above). However, as explained in the comments on the preferred values for the HO<sub>2</sub>+C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> reaction (see data sheet), the expression for  $k$  may give values significantly too high at temperatures above 1000 K.

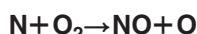
$k_2$  is taken as 50% of  $k(\text{HO}_2 + \text{C}_2\text{H}_6)$  (see data sheet). Preferred values for  $k_3$ ,  $k_4$ , and  $k_5$  are based on the thermochemistry of these channels and the similar reaction enthalpy of HO<sub>2</sub>+CH<sub>4</sub>.

### References

<sup>1</sup>M. Scott and R. W. Walker, Combust. Flame **129**, 365 (2002).

<sup>2</sup>CEC, Supplement I, 1994 (see references in Introduction).

<sup>3</sup>R. R. Baldwin, M. Scott, and R. W. Walker, 21st Symp. (Int.) Combustion, 1986, p. 991.



### Thermodynamic Data

$$\Delta H^\circ_{298} = -133 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298} = 13.37 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c = 11.8 T^{-0.117} \exp(+15950/T) \\ (300 \leq T/\text{K} \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

### Rate Coefficient Data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$3 \cdot 10^{-12} \exp(-3100/T)$	390–520	Kistiakowski and Volpi, 1957 <sup>1</sup>	(a)
$3 \cdot 10^{-12}$	1575	Kaufman and Decker, 1959 <sup>2</sup>	(b)
$1.4 \cdot 10^{-11} \exp(-3600/T)$	412–755	Clyne and Thrush, 1961 <sup>3</sup>	(c)
$6.3 \cdot 10^{-12} \exp(-3500/T)$	453–603	Vlastaras and Winkler, 1967 <sup>4</sup>	(d)
$2.34 \cdot 10^{-11} \exp(-4000/T)$	300–910	Wilson, 1967 <sup>5</sup>	(e)
$5.5 \cdot 10^{-12} \exp(-3200/T)$	280–333	Becker, Groth, and Kley, 1969 <sup>6</sup>	(f)
$1.08 \cdot 10^{-16}$	302	Clarke and Wayne, 1970 <sup>7</sup>	(g)
$7.5 \cdot 10^{-17}$	300	Westenberg, Roscoe, and de Haas, 1970 <sup>8</sup>	(e)
$2.6 \cdot 10^{-11}$	2880	Livesey, Roberts, and Williams, 1971 <sup>9</sup>	(h)

$k/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$	T/K	Reference	Comments
$7.2 \cdot 10^{-17}$	298	Winkler <i>et al.</i> , 1986 <sup>10</sup>	(i)
$8.8 \cdot 10^{-17}$	298	Barnet, Marston, and Wayne, 1987 <sup>11</sup>	(j)
$2 \cdot 10^{-18} T^{2.15} \exp(-2557/T)$	400–1220	Fernandez, Goumri, and Fontijn, 1998 <sup>12</sup>	(k)
<i>Reviews and Evaluations</i>			
$1.5 \cdot 10^{-14} T \exp(-3270/T)$	298–5000	CEC, 1994 <sup>13</sup>	(l)
$1.5 \cdot 10^{-11} \exp(-3600/T)$	200–300	NASA, 1997 <sup>14</sup>	(m)

### Comments

- (a) N atoms produced in a discharge reacted with O<sub>2</sub> in a low pressure stirred flow reactor. Change in steady state [N] on addition of amounts of O<sub>2</sub> monitored by mass spectrometry.
- (b) Relative rate study using oxygen photosensitized reactions in NO/O<sub>2</sub> mixtures with [NO] decay monitored by UV spectrophotometric detection of NO<sub>2</sub>.  $k(N + O_2)/k(N + NO) = 0.07$  measured at 1575 K and  $k(N + O_2)$  obtained using the value recommended in the present evaluation.
- (c) Discharge flow study of the reaction of N atoms with O<sub>2</sub> in large excess. [N] monitored by end point titration with NO.
- (d) Discharge flow study of the reaction of N atoms with O<sub>2</sub> in large excess.  $k$  determined by measuring [N] and [O] as a function of distance. [N] determined by end point titration with NO followed further downstream by measurement of total [O] by titration with excess NO<sub>2</sub>.
- (e) Discharge flow study of the reaction of N atoms with O<sub>2</sub> in large excess. [N] monitored by electron spin resonance spectroscopy.
- (f) Static system with N atoms produced by a discharge and reacted with O<sub>2</sub> in a stainless steel vessel at low pressures (0.1–100  $\mu\text{bar}$ ). Relative [N] monitored using the N+N afterglow intensity.
- (g) Discharge flow study of the reaction of N atoms with O<sub>2</sub> in large excess. [N] monitored at points down the tube by addition of excess NO and measuring  $\Delta[\text{NO}]$  using a photoionization detector.
- (h) Study using a premixed atmospheric pressure propane/O<sub>2</sub> flame to which N<sub>2</sub> had been added. [NO] profile measured by probe sampling and chemical analysis of the burned gases. [OH] monitored by UV absorption. Value of  $k$  obtained at the mean flame temperature using a relatively simple mechanism for which the [NO] fit is more sensitive to  $k(O + NO)$  than  $k(N + O_2)$ .  $k$  is misquoted in the abstract of the original reference.
- (i) Discharge flow study of N atoms reacting with N<sub>2</sub>. Vibrational state distribution of the NO produced was measured using a multiphoton ionization technique.  $k/k(N + NO)$  measured for NO in specific vibrational states. Quoted value of  $k$  based on  $k(N + NO)$  from this evaluation.

- (j) Discharge flow study of the reaction of N atoms with O<sub>2</sub> in large excess. [N] monitored using the intensity of the N+N afterglow.
- (k) Vacuum UV flash photolysis of N<sub>2</sub>O/O<sub>2</sub>/Ar mixtures at total pressures in the range 133–266 mbar. [N] monitored by time resolved resonance fluorescence.
- (l) Based on data from Refs. 1–11, cited in the Table.
- (m) Least squares fit to the data of Refs. 1, 5–8, 10, 11, cited in the Table.

### Preferred Values

$$k = 9.7 \cdot 10^{-15} T^{1.01} \exp(-3120/T) \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$$

over the range 280–5000 K.

### Reliability

$\Delta \log k = \pm 0.2$  over the range 280–1500 K, rising to  $\pm 0.5$  at 5000 K.

### Comments on Preferred Values

The new study by Fernandez *et al.*<sup>12</sup> is in excellent agreement with our previous evaluation<sup>13</sup> giving only slightly lower values of  $k$  over the temperature range covered (400–1220 K). Fernandez *et al.*<sup>12</sup> have carried out a semi-empirical fit of their results using Transition State Theory. They obtain the expression,  $k = 9.72 \cdot 10^{15} T^{1.01} \times \exp(-3121/T) \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ , using a value of  $E_0^\# = 27.4 \text{ kJ mol}^{-1}$ . This expression is an excellent fit to all of the results cited in the Table and is adopted as our preferred expression for  $k$ .

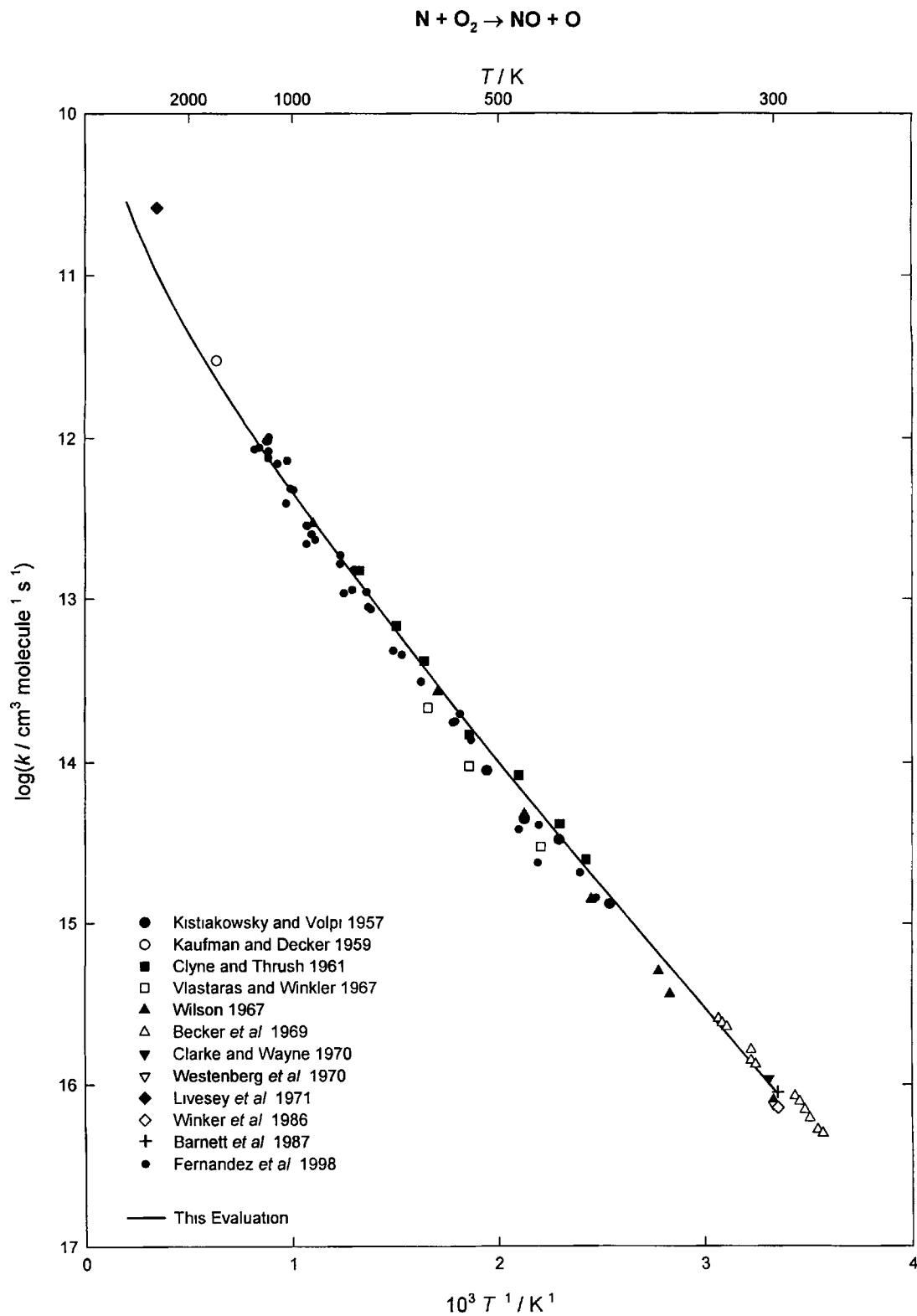
There have been a number of recent relevant theoretical studies,<sup>15–17</sup> all of them in general agreement with the experimental results.

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#### Thermodynamic Data

$$\begin{aligned}\Delta H^\circ_{298}(1) &= -201.6 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(1) &= -11.7 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 4.28 \cdot 10^{-2} T^{0.250} \exp(+25340/T) \\ (300 \leq T/\text{K} \leq 5000) \end{aligned}$$

$$\begin{aligned}\Delta H^\circ_{298}(2) &= 93.6 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(2) &= 5.29 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 1.06 T^{0.081} \exp(-11500/T) \\ (300 \leq T/\text{K} \leq 5000) \end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$k_1 = 5 \cdot 10^{-11}$	298	Howard and Smith, 1980 <sup>1</sup>	(a)
$k_1 = 2.21 \cdot 10^{-10} T^{-0.25}$	250–515	Howard and Smith, 1981 <sup>2</sup>	(b)
$k_1 = 2 \cdot 10^{-10} T^{-0.17}$	103–294	Smith and Stewart, 1994 <sup>3</sup>	(b)
<i>Reviews and Evaluations</i>			
$k_2 = 3.3 \cdot 10^{-11} T^{-0.1} \exp(-10700/T)$	500–3000	Cohen and Westberg, 1991 <sup>4</sup>	(c)
$k_1 = 3.8 \cdot 10^{-11} \exp(85/T)$	250–500	IUPAC, 1992 <sup>5</sup>	(d)
$k_1 = 4.7 \cdot 10^{-11}$	300–2500	CEC, 1994 <sup>6</sup>	(e)

#### Comments

- (a) Discharge flow system used to generate a steady state concentration of N atoms. A much lower concentration of OH radicals was produced by flash photolysis of  $\text{H}_2\text{O}$  and the decay of [OH] monitored under pseudo first order conditions by resonance fluorescence. [N] was determined by end point titration with NO.
- (b) Discharge flow system used to generate a steady state concentration of N atoms. A much lower concentration of OH radicals were generated by pulsed laser photolysis of  $\text{HNO}_3$  and the [OH] monitored by time resolved LIF. The very low temperatures were achieved by expansion through a Laval nozzle. The pressure range was 1–8 mbar.
- (c) Estimated using Transition State Theory.
- (d) Mean of the 298 K values of Campbell and Thrush,<sup>7</sup> Howard and Smith,<sup>1,2</sup> and Brune *et al.*<sup>8</sup>
- (e) Based on Refs. 1,2,7,8.

#### Preferred Values

$k_1 = 1.8 \cdot 10^{-10} T^{-0.2} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 100–2500 K.

#### Reliability

$\Delta \log k_1 = \pm 0.1$  at 300 K, rising to  $\pm 0.3$  at 100 K and to  $\pm 0.4$  at 2500 K

#### Comments on Preferred Values

The only direct measurements of  $k$  are at low temperatures. At 300 K the data are in good agreement, with the two measurements of the temperature coefficient of  $k$  suggesting a small negative dependence. The preferred expression is based on the data of Howard and Smith,<sup>1–3</sup> which is supported by the data of Campbell and Thrush<sup>7</sup> and Brune *et al.*<sup>8</sup>

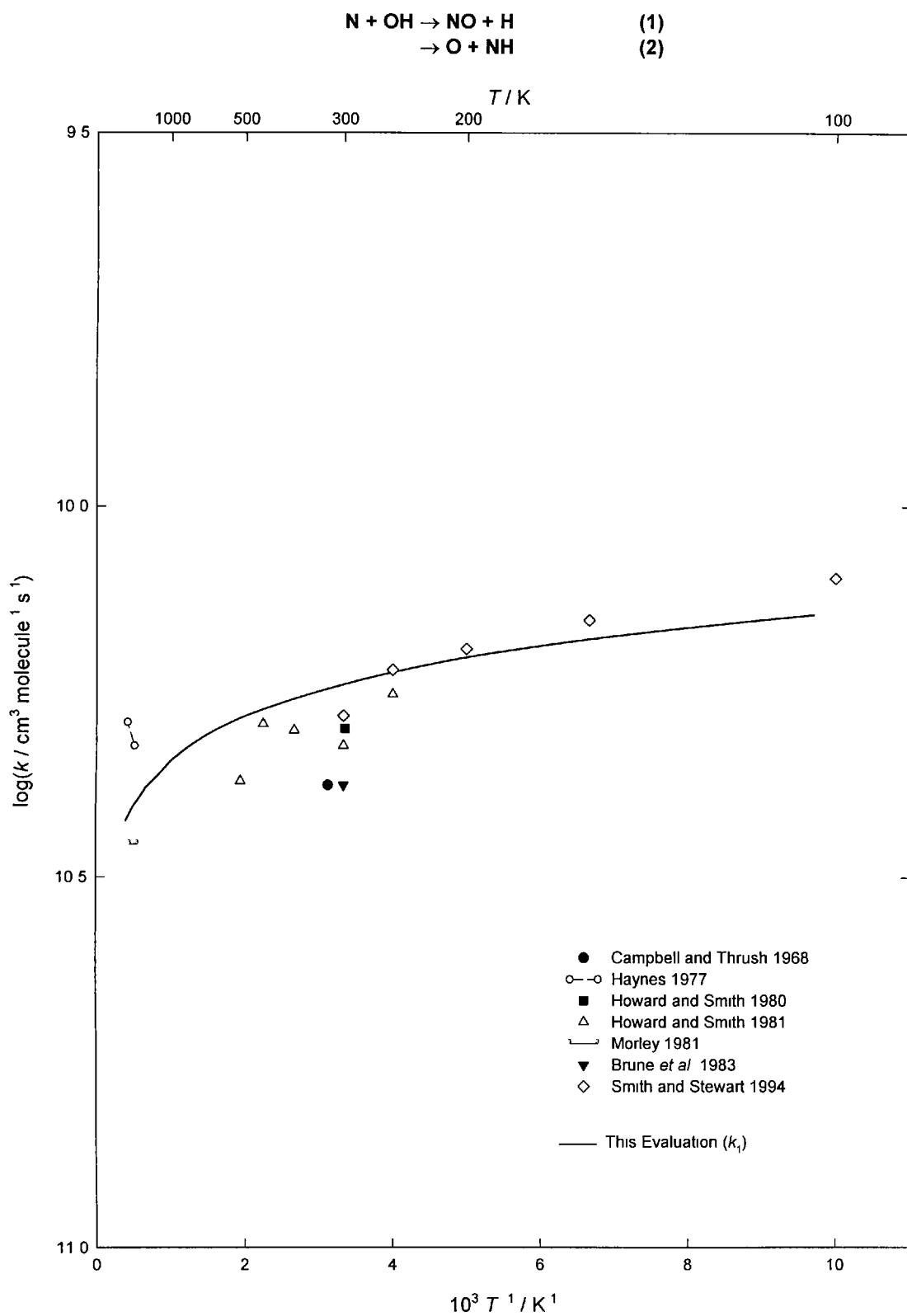
These data on  $k$  are assigned to Channel (1) since, as discussed later, Channel (2) is not believed to contribute significantly.

There are no direct measurements of  $k_1$  at high temperatures but extrapolation of the preferred expression to 2500 K gives values lower by a factor of  $\sim 2$  than those calculated from the data on the reverse reaction and the equilibrium constant, which is well within the error limits associated with all of the quantities involved. The flame studies of Haynes<sup>9</sup> and Morley<sup>10</sup> also give values in reasonable agreement. The temperature range for use of the preferred expression is therefore extended to high temperatures with appropriate error limits.

There are no direct measurements of  $k_2$ . The sparse data on the reaction of O with NH when combined with the thermodynamic data suggest a value of  $k_2$  of  $\sim 3 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 3000 K, which is in fair agreement with the value estimated from the expression recommended by Cohen and Westberg,<sup>4</sup> suggesting that Channel (2) makes little contribution over the range covered by our recommendations.

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**N+NO→N<sub>2</sub>+O***Thermodynamic Data*

$$\begin{aligned}\Delta H_{298}^{\circ} &= -313.8 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= -11.3 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 0.517 T^{-0.088} \exp(+37000/T) \\ &(300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$3 \cdot 10^{-11}$	298	Lin, Parkes, and Kaufman, 1970 <sup>1</sup>	(a)
$3.4 \cdot 10^{-11}$	196–400	Lee <i>et al.</i> , 1978 <sup>2</sup>	(b)
$3.4 \cdot 10^{-11}$	298	Cheah and Clyne, 1980 <sup>3</sup>	(c)
$3.2 \cdot 10^{-11}$	298	Stief <i>et al.</i> , 1988 <sup>4</sup>	(d)
$3.7 \cdot 10^{-11}$	1251–3152	Michael and Lim, 1992 <sup>5</sup>	(e)
$3.32 \cdot 10^{-11}$	1550–3660	Mick <i>et al.</i> , 1993 <sup>6</sup>	(f)
$2.2 \cdot 10^{-11} \exp(100/T)$	213–369	Wennberg <i>et al.</i> , 1994 <sup>7</sup>	(c)
<i>Reviews and Evaluations</i>			
$7.1 \cdot 10^{-11} \exp(-790/T)$	1400–4000	CEC, 1994 <sup>8</sup>	(g)
$2.1 \cdot 10^{-11}$	200–300	NASA, 1997 <sup>9</sup>	(h)

**Comments**

- (a) Discharge flow study. [N] monitored by resonance absorption spectroscopy calibrated by chemical titration with NO.  $k$  determined from measurements of depletion in [N] with varying [NO] at a fixed reaction time.
- (b) Direct determination of  $k$  using two different techniques under pseudo first order conditions with [NO]  $\gg$  [N] and detection of N atoms by atomic resonance fluorescence. A discharge flow study ( $P=1\text{--}3$  mbar He) gave  $k=2.7 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ; a flash photolysis study ( $P=25\text{--}920$  mbar N<sub>2</sub>) gave  $k=4.0 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . No temperature or pressure dependence of  $k$  could be detected with certainty within the scatter of the data, nor could any cause be found for the difference between the two values. The mean value was therefore reported with 25% error limits.
- (c) Discharge flow study. [N] monitored by atomic resonance fluorescence in an excess of NO.
- (d) Discharge flow study with relative concentration of reactants and products determined by mass spectrometry.  $k$  determined from decay of [NO] in an excess of N atoms. The measurements on the N+NO reaction were used to assess the validity of the technique for applying it to the N+CH<sub>3</sub> reaction.
- (e) Shock tube study in which N atoms were generated behind reflected shock waves by pulsed laser photolysis at 193 nm of NO/Ar or Kr mixtures. First order decay of [N] monitored by atomic resonance spectroscopy.
- (f) Shock tube study on SiH<sub>4</sub>/NO/Ar mixtures at total pressures in the range 0.4–1.5 bar. N atoms were pro-

duced from the reaction of Si atoms with NO. [Si] and [N] were monitored by time resolved atomic resonance absorption. Values of  $k$  were obtained by detailed chemical modeling.

- (g) Accepts the expression of Davidson and Hanson.<sup>10</sup>
- (h) Based on the studies of Wennberg *et al.*<sup>7</sup> and Lee *et al.*<sup>2</sup>

**Preferred Values**

$k=3.5 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 210–3700 K.

*Reliability*

$\Delta \log k=\pm 0.3$  over the range 210–3700 K.

*Comments on Preferred Values*

There is a substantial scatter in the measurements of  $k$  and considerable uncertainty about its temperature dependence. There are numerous studies at low temperatures.<sup>1–4,7,11–19</sup> In their evaluation the NASA Panel suggest that the most reliable of them are those of Wennberg *et al.*<sup>7</sup> and Lee *et al.*<sup>2</sup> which indicate a value of  $k$  of  $3.5 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 300 K, which is supported by the studies of Lin *et al.*,<sup>1</sup> Cheah and Clyne,<sup>3</sup> and Stief *et al.*<sup>4</sup> Wennberg *et al.*<sup>7</sup> also find a small negative temperature coefficient for  $k$  but if this is accepted throughout the whole temperature range it predicts values of  $k$  at high temperatures rather lower than the most reliable measured values at elevated temperatures.

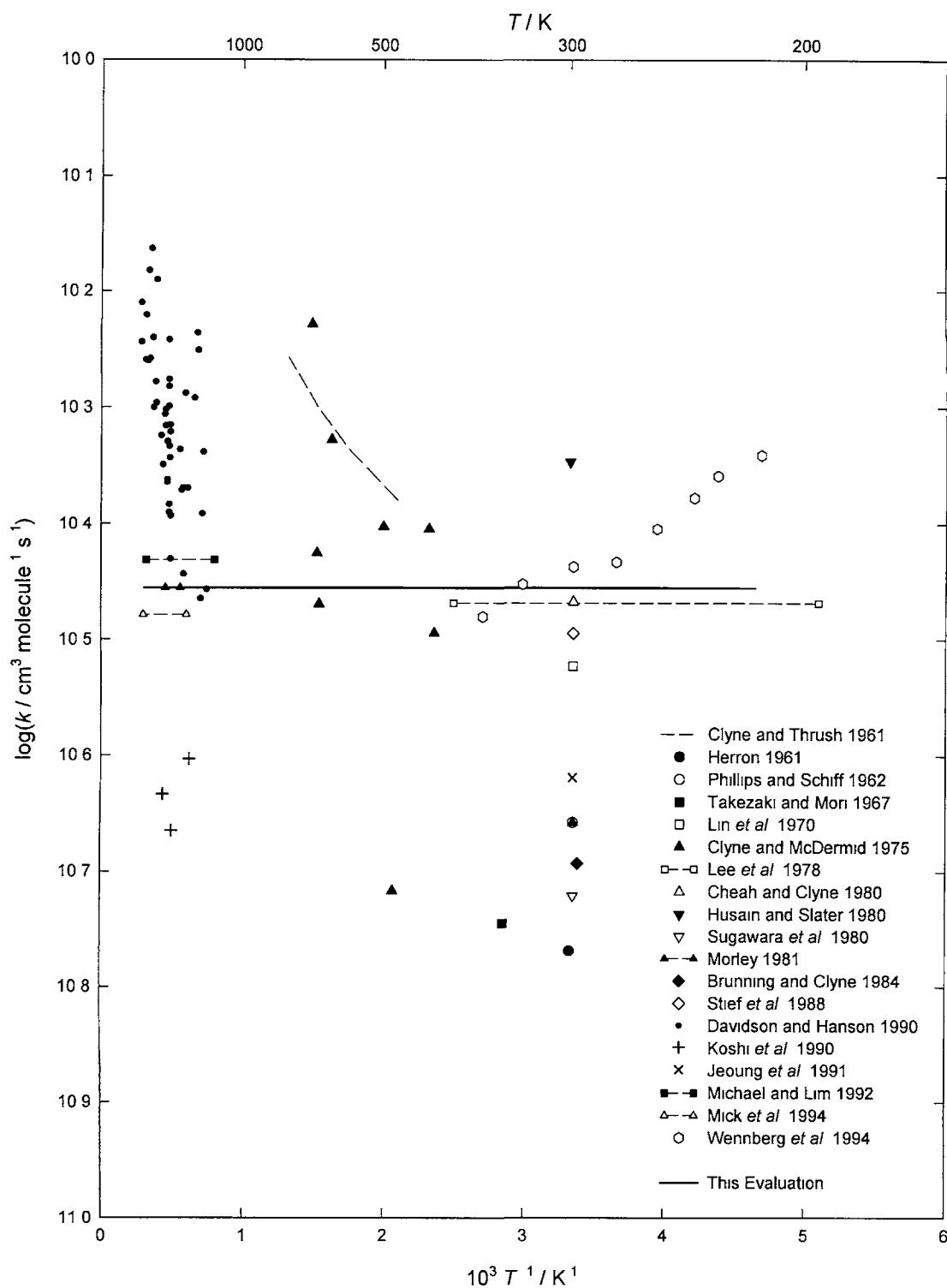
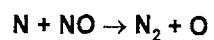
From among the studies at higher temperatures<sup>5,6,10,20</sup> our previous evaluation<sup>8</sup> accepted the expression obtained by Davidson and Hanson.<sup>10</sup> However, a more recent study by

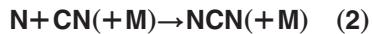
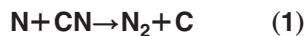
Michael and Lim,<sup>5</sup> using very similar methods, gives values of  $k$  of similar magnitude but fails to reproduce the temperature dependence which Davidson and Hanson<sup>10</sup> observed, instead giving a temperature independent  $k$  with a value of  $3.7 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . This result is supported by the study of Mick *et al.*<sup>6</sup> and the flame study of Morley<sup>21</sup> but the shock tube study of Koshi *et al.*<sup>20</sup> gives a value some 40% lower.

In view of the uncertainty about the small temperature dependence of  $k$ , a temperature independent  $k$  is recommended which is consistent with the high and low temperature data within the fairly substantial scatter. It is also consistent with the data on the reverse rate constant and the thermodynamic data within the error limits of all of these quantities. A quasi-classical trajectory calculation by Duff and Sharma<sup>22</sup> giving values of  $k$  for the range 100–1000 K and an atmospheric modeling study<sup>23</sup> are also compatible with the recommendations.

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#### Thermodynamic Data

$$\begin{aligned}\Delta H_{298}^{\circ}(1) &= -191.4 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ}(1) &= -6.22 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 1.55 T^{-0.161} \exp(+22930/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

$$\begin{aligned}\Delta H_{298}^{\circ}(2) &= -435.1 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ}(2) &= -129.5 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 4.55 \cdot 10^{-30} T^{1.198} \exp(+52490/T) \text{ cm}^3 \text{ molecule}^{-1} \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$1.0 \cdot 10^{-10}$	300	Whyte and Phillips, 1983 <sup>1</sup>	(a)
$3.24 \cdot 10^{-13} \exp(1770/T)$	300–534	Atakan <i>et al.</i> , 1992 <sup>2</sup>	(b)
$<8.3 \cdot 10^{-13}$	750		
$6.6 \cdot 10^{-11}$	3050–4430	Natarajan, Woike, and Roth, 1997 <sup>3</sup>	(c)
<i>Reviews and Evaluations</i>			
$k_1 = 3 \cdot 10^{-10}$	300–2500	CEC, 1992; 1994 <sup>4</sup>	(d)

#### Comments

- (a) Fast flow discharge study at total pressures of 2–4.6 mbar. CN radicals were generated by pulsed laser photolysis of  $\text{C}_2\text{N}_2$  at 193 nm and N atoms produced by a discharge in  $\text{N}_2$ . [N] was determined by titration with NO and [CN] decay in an excess of N atoms was monitored by LIF.
- (b) Pulsed laser photolysis at 193 nm of  $\text{C}_2\text{N}_2$  used to produce CN radicals in a flowing  $\text{N}_2/\text{N}/\text{He}$  mixture, the N atoms having been produced by a discharge in the  $\text{N}_2/\text{He}$  mixture prior to mixing with  $\text{C}_2\text{N}_2$ . [CN] monitored by time resolved LIF in an excess of N atoms.
- (c) Shock tube study using highly diluted  $\text{C}_2\text{N}_2/\text{NO}/\text{Ar}$  mixtures at 1.5 bar. [N] monitored by time resolved ARAS behind reflected shock waves and [N] profile simulated by computer modeling.
- (d) Based on the data of Whyte and Phillips<sup>1</sup> and older high temperature data.

#### Preferred Values

$k_1 = 9.8 \cdot 10^{-10} T^{-0.40} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 300–3000 K.

#### Reliability

$\Delta \log k_1 = \pm 0.3$  at 300 K, rising to  $\pm 0.5$  at 3000 K.

#### Comments on Preferred Values

There are only a limited number of studies of this reaction.<sup>1–3,5–7</sup> The relationship between the data obtained at low temperatures and those at high temperatures is unclear and there are uncertainties in the reaction mechanism.

At high temperatures (3000–8000 K) the data scatter over a factor of approximately 20 with no clear indication of the temperature dependence.<sup>3,5–7</sup> There are, however, two concordant studies of the reverse of Channel (1) at high temperatures (see  $\text{C} + \text{N}_2$  data sheet) which, when combined with the thermodynamic data, predict a value of  $k_1 = 4 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 3000–4000 K. This is in reasonable agreement with the most recent study of Natarajan *et al.*<sup>3</sup>

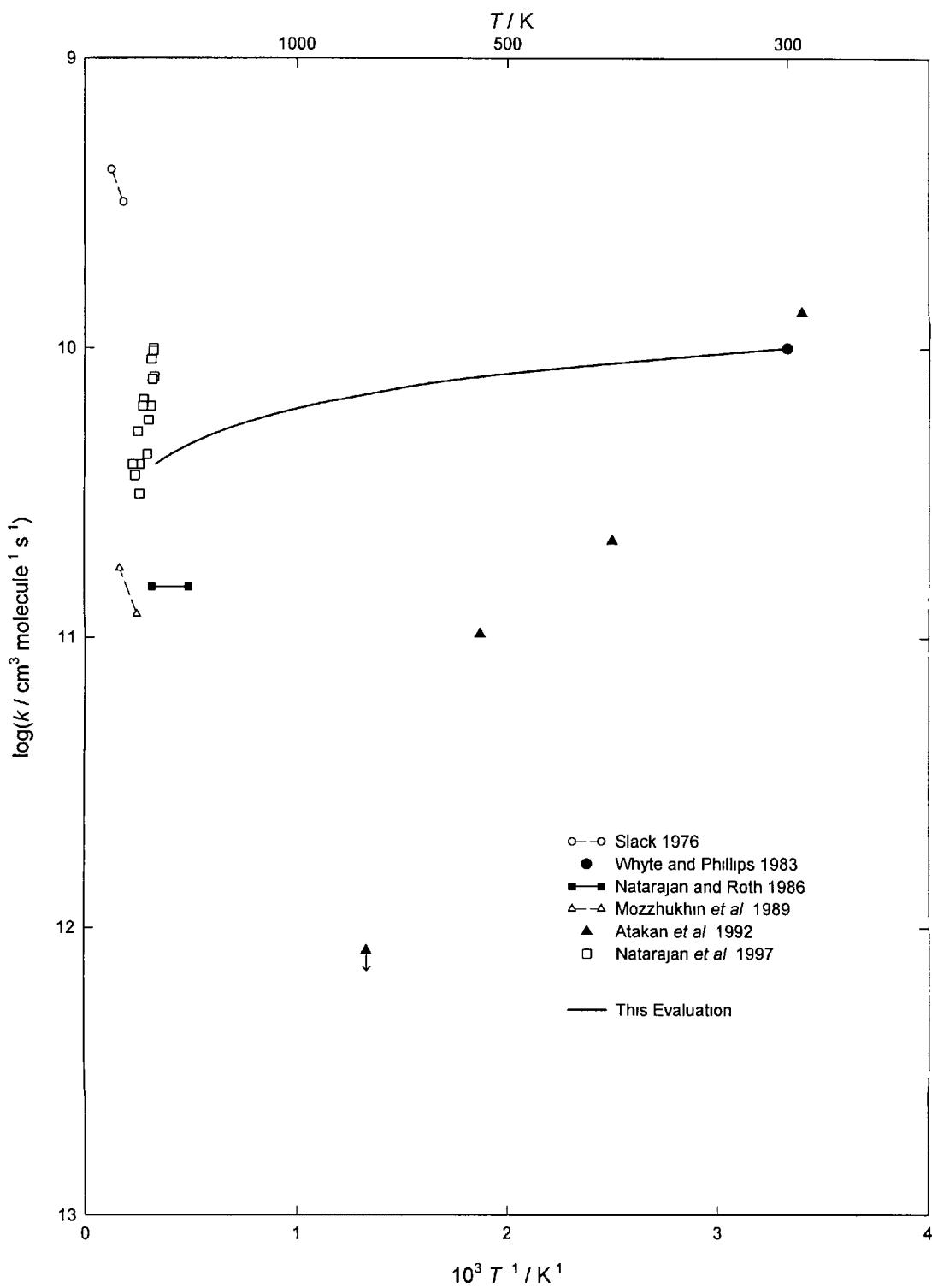
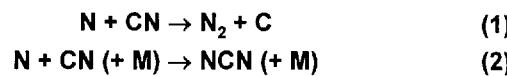
The values of  $k_1$  predicted by the data on the reverse of Channel (1) together with the thermodynamic data are also in excellent agreement with the values of  $k$  obtained by Whyte and Phillips<sup>1</sup> and Atakan *et al.*<sup>2</sup> at 300 K but this agreement must be treated with some caution because of the long extrapolation of the data on the reverse reaction which were obtained at temperatures above 2000 K. The data on the reverse of Channel (1) also predicts only a small negative value for  $E/R$  but Atakan *et al.*<sup>2</sup> find that  $k$  decreases by 2 orders of magnitude in going from 300 K to 750 K which is suggestive of adduct formation. A theoretical treatment of the reaction by Moskaleva and Lin<sup>8</sup> suggests that the reaction goes through formation of NCN, a cyclic *c*-NCN radical, and CNN but it also predicts that  $k_1$  should have a small positive temperature dependence in contrast to the negative value found by Atakan *et al.*<sup>2</sup> There has been no study of the pressure dependence of the rate constant at low temperatures but the theoretical treatment of Moskaleva and Lin<sup>8</sup> suggests that the high pressure limit for the reaction should have been reached by 1 bar. The preferred expression for  $k$  is based on the studies of Natarajan *et al.*<sup>3</sup> at high temperatures and those of Whyte and Phillips<sup>1</sup> and Atakan *et al.*<sup>2</sup> at temperatures close to 300 K, fitting the data to  $T^n$  temperature dependence.

There are values for  $k_2$ , of doubtful reliability, from a number of older studies<sup>9–11</sup> in which the combination of N

atoms to form N<sub>2</sub> in the presence of CN radicals has been studied. The mechanism has been assumed to involve the sequence N+CN→NCN, N+NCN→N<sub>2</sub>+CN with, usually, no consideration of the role of Channel (1). The kinetic data obtained have been reviewed by Baulch *et al.*<sup>12</sup>

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#### Thermodynamic Data

$$\begin{aligned}\Delta H^\circ_{298}(1) &= -710.2 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(2) &= 3.73 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 4.15 \cdot 10^3 T^{-1.197} \exp(+85020/T) \\ (300 \leq T/\text{K} \leq 5000) \end{aligned}$$

$$\begin{aligned}\Delta H^\circ_{298}(2) &= -74.0 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(2) &= 27.9 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 1.29 \cdot 10^4 T^{-0.899} \exp(+8610/T) \\ (300 \leq T/\text{K} \leq 5000) \end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$k_1 = 3.3 \cdot 10^{-11}$	1700	Lifshitz and Frenklach, 1980 <sup>1</sup>	(a)
$k_2 = 1.7 \cdot 10^{-12}$	1700		
$5.5 \cdot 10^{-11}$	298	Brownword, Hancock, and Heard, 1997 <sup>2</sup>	(b)
<i>Reviews and Evaluations</i>			
$k_1 = 3.3 \cdot 10^{-11}$	1700	CEC, 1992; 1994 <sup>3</sup>	(c)

#### Comments

- (a) Measurement of the induction times to ignition behind reflected shock waves in  $\text{C}_2\text{N}_2/\text{O}_2/\text{Ar}$  mixtures. Values of  $k$  obtained by fitting to a detailed mechanism by computer simulation. The fitting was reasonably sensitive to  $k_1$  but not to  $k_2$ .
- (b) NCO radicals generated by pulsed multiphoton dissociation of phenyl isocyanate (infrared  $\text{CO}_2$  laser radiation) in the presence of N atoms generated in a microwave discharge. [NCO] monitored by time resolved laser induced fluorescence. [N] determined by titration with NO. Bath gases were Ar/N<sub>2</sub> mixtures at total pressures of  $\sim 5$  mbar.
- (c) Based on Ref. 1.

#### Preferred Values

$$k_1 = 2.3 \cdot 10^{-10} T^{-0.25} \text{ over the range } 298\text{--}1700 \text{ K.}$$

#### Reliability

$$\Delta \log k_1 = \pm 0.2 \text{ at } 298 \text{ K, rising to } \pm 0.5 \text{ at } 1700 \text{ K.}$$

#### Comments on Preferred Values

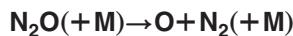
Since our previous evaluations<sup>3</sup> Brownword *et al.*<sup>2</sup> have measured the overall rate constant at 298 K obtaining a value

slightly higher than the only other value, at 1700 K, on which our previous preferred values were based. The present preferred values are a fit to the two values assuming a  $T^n$  dependence of the rate constant with substantial error limits suggested at high temperatures.

There are no direct determinations of the branching ratios. However measurements of the rate constant for the reverse of Channel (2),<sup>4,5</sup> at temperatures in the region of 2000–4000 K, when combined with the thermodynamic data, suggest that Channel (2) will be insignificant throughout the whole temperature range. If then the low temperatures products are  $\text{CO} + \text{N}_2$ , Brownword *et al.*<sup>2</sup> also argue that, on the grounds of spin conservation, one of them is likely to be in an excited triplet state.

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*Thermodynamic Data*

$$\begin{aligned}\Delta H_{298}^{\circ} &= 167.1 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= 132.7 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 2.32 \cdot 10^{29} T^{-1.103} \exp(-20340/T) \text{ molecule cm}^{-3} \\ (300 \leqslant T/\text{K} \leqslant 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{s}^{-1}$	T/K	[M]/molecule cm <sup>-3</sup>	Reference	Comments
<i>Rate Coefficient Measurements</i>				
<i>Low Pressure Range</i>				
$[\text{Ar}]8.3 \cdot 10^{-10} \exp(-29000/T)$	1500–2500	$(3.0\text{--}1204) \cdot 10^{18}$	Olszewski, Troe, and Wagner, 1966 <sup>1</sup>	(a)
$[\text{Ar}, \text{Kr}, \text{N}_2]2.4 \cdot 10^{-10} \exp(-25805/T)$	1815–3365		Monat, Hanson, and Kruger, 1977 <sup>2</sup>	(b)
$[\text{Ar}]4.5 \cdot 10^{-10} \exp(-27180/T)$	2100–3200	$(2.5\text{--}7.7) \cdot 10^{18}$	Dean and Steiner, 1977 <sup>3</sup>	(c)
$[\text{Ar}]2.4 \cdot 10^{-9} \exp(-30800/T)$	1500–2250	$7 \cdot 10^{18}$	Roth and Just, 1977 <sup>4</sup>	(d)
$[\text{He}]1.9 \cdot 10^{-15}$	2000	$(3.6\text{--}24) \cdot 10^{18}$	Endo, Glänsler, and Troe, 1979 <sup>5</sup>	(e)
$[\text{Ar}]3.5 \cdot 10^{-16}$				
$[\text{N}_2]4.5 \cdot 10^{-16}$				
$[\text{Ar}]6.2 \cdot 10^{-10} \exp(-27660/T)$	1685–2560	$(5\text{--}20) \cdot 10^{18}$	Sulzmann, Kline, and Penner, 1980 <sup>6</sup>	(f)
$[\text{Ar}]7.3 \cdot 10^{-10} \exp(-28180/T)$	1700–2500	$(6\text{--}60) \cdot 10^{18}$	Zaslonko, <i>et al.</i> , 1980 <sup>7</sup>	(g)
$[\text{Ar}]2.7 \cdot 10^{-9} \exp(-30994/T)$	1700–2300	$(2.9\text{--}9.3) \cdot 10^{18}$	Fujii <i>et al.</i> , 1986 <sup>8</sup>	(h)
$[\text{Ar}]1.7 \cdot 10^{-9} \exp(-30430/T)$	1600–2500	$(2.9\text{--}4.6) \cdot 10^{18}$	Fujii <i>et al.</i> , 1989 <sup>9</sup>	(i)
$[\text{Ar}]2.5 \cdot 10^{-6} T^{-1.0} \exp(-2900/T)$	1500–5000	$(6.4\text{--}8.2) \cdot 10^{19}$	Zuev and Starikovskii, 1991 <sup>10</sup>	(j)
$[\text{Ar}]6.6 \cdot 10^{-10} \exp(-28230/T)$	1000–3000	$(5.4\text{--}7.2) \cdot 10^{18}$	Johnsson, Glarborg, and Dam-Johansen, 1992 <sup>11</sup>	(k)
$[\text{Ar}, \text{Kr}]5.25 \cdot 10^{-10} \exp(-27921/T)$	1546–2500	$3.3 \cdot 10^{18}$	Michael and Lim, 1992 <sup>12</sup>	(l)
$[\text{Ar}]1.0 \cdot 10^{-8} \exp(-31870/T)$	1000–1400	$6.0 \cdot 10^{18}$	Glarborg, Johnsson, and Dam-Johansen, 1994 <sup>13</sup>	(m)
$[\text{N}_2]1.5 \cdot 10^{-9} \exp(-29030/T)$	1103–1173	$(9.7\text{--}68) \cdot 10^{18}$	Allen, Yetter, and Dryer, 1995 <sup>14</sup>	(n)
$[\text{Ar}]6.6 \cdot 10^{-10} \exp(-28505/T)$	1750–3100	$(7.1\text{--}19000) \cdot 10^{17}$	Röhrlig <i>et al.</i> , 1996 <sup>15</sup>	(o)
$[\text{Ar}]1.18 \cdot 10^{-9} \exp(-29096/T)$	1195–2494	$(2.6\text{--}5.4) \cdot 10^{18}$	Ross <i>et al.</i> , 1997 <sup>16</sup>	(p)
<i>High Pressure Range</i>				
$1.3 \cdot 10^{11} \exp(-30000/T)$	1400–2100	$(2.8\text{--}1570) \cdot 10^{18}$	Olszewski, Troe and Wagner, 1966 <sup>1</sup>	(a)
$1.7 \cdot 10^{11} \exp(-29000/T)$	1750–2000	$(7.3\text{--}73) \cdot 10^{18}$	Zuev and Starikovskii, 1991 <sup>10</sup>	(j)
$4.2 \cdot 10^9 \exp(-27000/T)$	1000–3000	$(5.4\text{--}7.2) \cdot 10^{18}$	Johnsson, Glarborg, and Dam-Johansen, 1992 <sup>11</sup>	(k)
$7.91^{10} \exp(-28190/T)$	1103–1173	$(9.7\text{--}68) \cdot 10^{18}$	Allen, Yetter, and Dryer, 1995 <sup>14</sup>	(n)
$1.3 \cdot 10^{12} \exp(-31511/T)$	1750–3100	$(7.1\text{--}19000) \cdot 10^{17}$	Röhrlig <i>et al.</i> , 1996 <sup>15</sup>	(o)
<i>Reviews and Evaluations</i>				
$k_\infty = 1.3 \cdot 10^{11} \exp(-30000/T)$	900–2100		Baulch <i>et al.</i> , 1973 <sup>17</sup>	(q)
$k_0[\text{Ar}] = [\text{Ar}]8.3 \cdot 10^{-10} \exp(-29000/T)$	1300–2500		Hanson and Salimian, 1985 <sup>18</sup>	(r)
$k_0[\text{Ar}, \text{Kr}] = [\text{Ar}, \text{Kr}]1.15 T^{-2.5} \exp(-32710/T)$	1500–3600		Tsang and Herron, 1991 <sup>19</sup>	(s)
$k_\infty = 1.3 \cdot 10^{11} \exp(-30000/T)$	700–2500			
$k_0[\text{N}_2] = [\text{N}_2]1.2 \cdot 10^{-6} T^{-0.73} \exp(-31600/T)$				
$k_0[\text{CO}_2] = [\text{CO}_2]2 \cdot 10^{-6} T^{-0.67} \exp(-31300/T)$				
$F_c(\text{N}_2) = 1.167 - 1.25 \cdot 10^{-4} T$				
$F_c(\text{CO}_2) = 1.167 - 1.25 \cdot 10^{-4} T$				
$k_0[\text{Ar}] = [\text{Ar}]6.6 \cdot 10^{-10} \exp(-28230/T)$	1000–3000		Dean and Bozzelli, 2000 <sup>20</sup>	(t)

**Comments**

- (a) Shock wave study.  $[\text{N}_2\text{O}]$  decay monitored by IR emission at 4.5  $\mu\text{m}$  and UV absorption at 230–250 nm. Data in incident and reflected shocks obtained from both IR and UV measurements are in agreement.
- (b)  $\text{N}_2\text{O}$  decomposition investigated by the shock tube technique. IR emission from the 4.5  $\mu\text{m}$  vibration-rotation band of  $\text{N}_2\text{O}$  was used to monitor the decay as a function of time.
- (c) Shock tube study of  $\text{N}_2\text{O}/\text{CO}/\text{Ar}$  mixtures. The decom-

position was followed monitoring the emission from  $\text{CO}_2$  generated following the reaction  $\text{O} + \text{CO}$ .

- (d) Shock wave study of mixtures of  $\text{CH}_4$  (10–25 ppm) and  $\text{N}_2\text{O}$  (5–150 ppm) diluted in Ar.  $[\text{O}]$  measured by atomic resonance absorption spectroscopy at 130.5 nm.
- (e) Thermal dissociation of  $\text{N}_2\text{O}$  studied behind reflected shock waves.  $[\text{N}_2\text{O}]$  decay determined by UV absorption at 230 nm. Theoretical analysis of weak collision effects for several bath gases (He, Ne, Ar, Kr, Xe,  $\text{N}_2$ , and  $\text{CF}_4$ ).
- (f) Thermal decomposition of  $\text{N}_2\text{O}$  studied behind reflected shock waves. The decay of  $\text{N}_2\text{O}$  was deter-

- mined from N<sub>2</sub>O emission at 4.52  $\mu\text{m}$ . [NO] was measured by correlation spectroscopy at 225.9 nm, NO was formed in the reaction O+N<sub>2</sub>O→2NO.
- (g) Pyrolysis of N<sub>2</sub>O in shock waves. [N<sub>2</sub>O] decay measured by absorption at 240 nm. Effects of Ar, He, N<sub>2</sub>, and CO as bath gases were investigated. When CO was present, [O] was measured by the emission at 405 nm arising from the recombination reaction, O+CO.
- (h) Shock tube study of the system NH<sub>3</sub>/N<sub>2</sub>O/Ar. N<sub>2</sub>O dissociation followed by N<sub>2</sub>O infrared emission at 4.52  $\mu\text{m}$ .
- (i) Pyrolysis of N<sub>2</sub>O investigated behind reflected shock waves. O atom formation detected by atomic resonance absorption spectroscopy at 130 nm.
- (j) Thermal decomposition of N<sub>2</sub>O was determined spectroscopically by ultrasonic wave reflection in N<sub>2</sub>O/Ar mixtures.
- (k) Thermal decomposition of N<sub>2</sub>O measured in a laminar flow reactor. N<sub>2</sub>O was analyzed by IR spectroscopy. Experiments were conducted over the temperature range 1000–1350 K. The rate coefficients found by kinetic modeling were  $k=[\text{Ar}]8.5 \cdot 10^{-10} \exp(-28864/T)$ ,  $k=[\text{N}_2]1.66 \cdot 10^{-9} \times \exp(-28906/T)$  and  $k=[\text{He}]3.9 \cdot 10^{-9} \times \exp(-29250/T)$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. The measured rate coefficient for M=Ar was combined with high temperature data published prior to 1991 from Ref. 21 to calculate the rate coefficient cited for T in the range 1000–3000 K.
- (l) Unimolecular decomposition of N<sub>2</sub>O investigated in reflected shock waves. O atoms monitored by atomic resonance absorption spectroscopy at 130 nm.
- (m) See comment (k). Relative efficiencies with respect to Ar are; Ar:N<sub>2</sub>:O<sub>2</sub>:CO<sub>2</sub>:H<sub>2</sub>O=1.0:1.7:1.4:3.0:12.
- (n) N<sub>2</sub>O decomposition investigated in a variable pressure flow reactor. Mixtures of approximately 1% in N<sub>2</sub> and water vapor were studied. Profiles of N<sub>2</sub>O, O<sub>2</sub>, NO, NO<sub>2</sub>, and H<sub>2</sub>O were measured by FTIR. Rate coefficients extracted from a mechanism with 52 reactions.
- (o) Thermal decomposition of N<sub>2</sub>O studied behind shock waves. N<sub>2</sub>O monitored by IR emission at 4.5  $\mu\text{m}$ . The observed concentration profile was analyzed with a mechanism comprising 9 reactions. The pressure dependence was described by a simple Lindemann fit.
- (p) Reflected shock tube study of N<sub>2</sub>O pyrolysis. O atom concentrations monitored by atomic resonance absorption spectroscopy.
- (q) Evaluation of the literature up to 1971. The  $k_0$  and  $k_\infty$  values of Olschewski *et al.*<sup>1</sup> were adopted for recommendation.
- (r) Evaluation of the literature up to 1981. The recommended value is mainly based on data from Monat *et al.*,<sup>2</sup> Dean and Steiner,<sup>3</sup> Roth and Just,<sup>4</sup> and Endo *et al.*<sup>5</sup>
- (s) Evaluation of the literature up to 1989.  $k_\infty$  based on values of Olschewski *et al.*<sup>1</sup>  $k_0$  based on the evaluations of Baulch *et al.*<sup>17</sup> and Hanson and Salimian<sup>18</sup> with slight adjustment to reproduce the rate data of Johnston.<sup>22</sup>
- (t) Evaluation of the literature up to 1996;  $k_0$  value based on the recommendations of Johnsson *et al.*<sup>11</sup>

## Preferred Values

$k_0 = 1.0 \cdot 10^{-9} \exp(-28910/T)$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for M=Ar over the range 1000–3000 K.

$k_\infty = 9.9 \cdot 10^{10} \exp(-29140/T)$  s<sup>-1</sup> over the range 1000–3000 K.

$F_c = (1.167 - 1.25 \cdot 10^{-4}T)$  for M=Ar over the range 1000–3000 K.

## Reliability

$\Delta \log k_0 = \pm 0.3$  for M=Ar over the range 1000–3000 K.

$\Delta \log k_\infty = \pm 0.5$  over the range 1000–3000 K.

$\Delta F_c = \pm 0.1$  for M=Ar over the range 1000–3000 K.

## Comments on Preferred Values

The published data are in very good agreement. The preferred value for  $k_0$  is based on the data of Olschewski *et al.*<sup>1</sup> (which also formed the basis for the evaluations of Baulch<sup>17</sup> and Tsang and Herron<sup>19</sup>) and the data from Monat *et al.*,<sup>2</sup> Dean and Steiner,<sup>3</sup> Roth and Just,<sup>4</sup> Sulzmann *et al.*,<sup>6</sup> Zaslonko *et al.*,<sup>7</sup> Fujii *et al.*,<sup>8,9</sup> Johnsson *et al.*,<sup>11</sup> Michael and Lim,<sup>12</sup> Glarborg *et al.*,<sup>13</sup> Allen *et al.*,<sup>14</sup> Röhrig *et al.*,<sup>15</sup> and Ross *et al.*<sup>16</sup> The preferred  $k_\infty$  is based on the data of Olschewski *et al.*,<sup>1</sup> Zuev and Starikovskii,<sup>10</sup> Johnsson *et al.*,<sup>11</sup> Allen *et al.*,<sup>14</sup> and Röhrig *et al.*<sup>15</sup>

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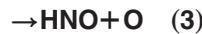
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#### Thermodynamic Data

$$\Delta H_{298}^o(1) = -229.2 \text{ kJ mol}^{-1}$$

$$\Delta S_{298}^o(1) = 8.08 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 11.1 T^{-0.193} \exp(+27450/T) \quad (300 \leq T/K \leq 5000)$$

$$\Delta H_{298}^o(2) = -105.4 \text{ kJ mol}^{-1}$$

$$\Delta S_{298}^o(2) = -31.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 4.65 \cdot 10^{-4} T^{0.558} \exp(+12880/T) \quad (300 \leq T/K \leq 5000)$$

$$\Delta H_{298}^o(3) = -0.2 \text{ kJ mol}^{-1}$$

$$\Delta S_{298}^o(3) = -4.64 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 1.32 \cdot 10^{-1} T^{0.197} \exp(+133/T) \quad (300 \leq T/K \leq 500)$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2 + k_3$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$1.26 \cdot 10^{-12} \exp(-770/T)$	268–543	Hack, Kurzke, and Wagner, 1985 <sup>1</sup>	(a)
$3.17 \cdot 10^{-11} \exp(-6968/T) + 1.5 \cdot 10^{-13} \exp(-770/T)$	985–1729	Hennig, Röhrig, and Wagner, 1993 <sup>2</sup>	(b)
$5.81 \cdot 10^{-11} \exp(-8600/T)$	293–793	Mertens <i>et al.</i> , 1994 <sup>3</sup>	(c)
$k_1 = 7.47 \cdot 10^{-16} T^{0.79} \exp(-601/T)$	298–2200	Römming and Wagner, 1996 <sup>4</sup>	(d)
$(k_2 + k_3) = 3.49 \cdot 10^{-11} \exp(-7962/T)$	1200–2200		
<i>Reviews and Evaluations</i>			
$(k_1 + k_2) = 1.3 \cdot 10^{-13} \exp(-770/T)$	270–550	CEC, 1994 <sup>5</sup>	(e)
$k_3 = 6.5 \cdot 10^{-11} \exp(-9000/T)$	2200–3500		

#### Comments

- (a) Discharge flow study in which NH was generated by the reaction sequence  $\text{F} + \text{NH}_3 \rightarrow \text{NH}_2 + \text{HF}$ ,  $\text{NH}_2 + \text{F} \rightarrow \text{NH} + \text{HF}$ . [O] and [H] monitored by time resolved resonance fluorescence and [NH] and [OH] by laser induced fluorescence. Reaction  $\text{NH} + \text{O}_2(^1\Delta_g) \rightarrow$  products also studied;  $k \leq (1 \pm 2) \cdot 10^{-5} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  obtained.
- (b) Shock tube studies at bath gas pressures of Ar in the range 410–720 mbar. NH generated by the thermal decomposition of  $\text{HN}_3$  in the presence of  $\text{O}_2$ . [NH] and [OH] were monitored in incident shock waves by time resolved laser absorption at 336 and 308 nm, respectively. [OH] profiles, fitted with a detailed mechanism, demonstrated 100% reaction via Channel (1) up to 800 K and decreasing to 0 at 2000 K.
- (c) Shock tube study in which NH was generated by the thermal dissociation of  $\text{HNCO}$ . [NH] and [OH] monitored by cw laser absorption at 336 and 307 nm, respectively. Values of  $k$  obtained by fitting [NH] profile using a detailed reaction mechanism.

(d) Shock tube study in which NH was produced from the thermal dissociation of  $\text{HN}_3$ . [NH] was monitored by time resolved laser absorption at 336.10 nm. H and O atom formation were followed by ARAS at 121.6 and 130.5 nm, respectively. The bath gas was Ar at total pressures in the range 54–1300 mbar. Experimental results were obtained over the temperature range 1200–2200 K. The expression for  $k_1$  was obtained by combining results from this study with those from other studies.<sup>1,2,3,6</sup>

(e) See Comments on Preferred Values.

#### Preferred Values

$k_1 = 1.5 \cdot 10^{-13} \exp(-770/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 250–3300 K.

$k_3 = 4.0 \cdot 10^{-11} \exp(-6970/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 250–3300 K.

#### Reliability

$\Delta \log k_1 = \pm 0.4$  over the range 250–3300 K.

$\Delta \log k_3 = \pm 0.1$  over the range 250–3300 K.

#### Comments on Preferred Values

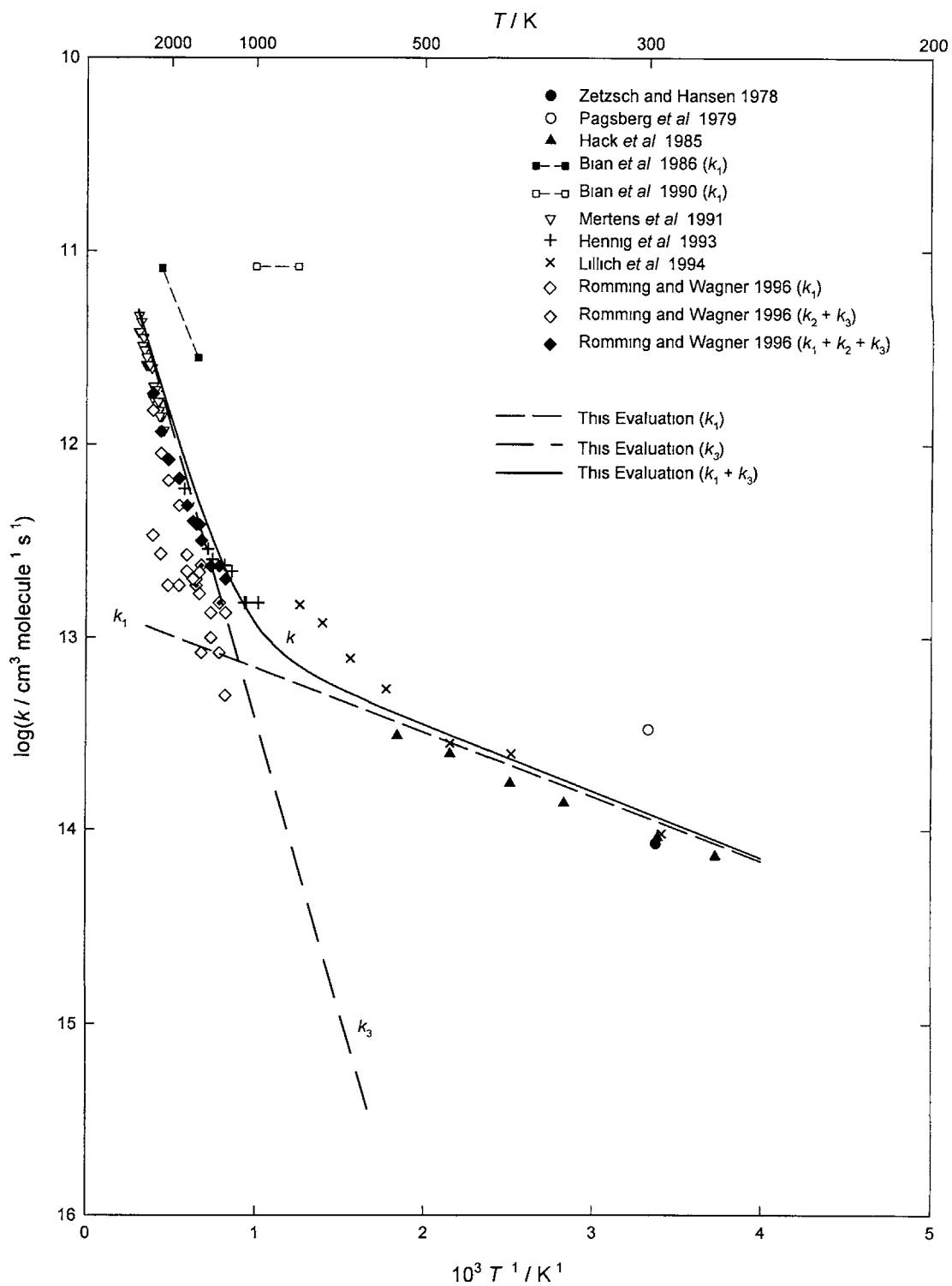
The recommended expressions for  $k_1$  and  $k_3$  are based on the data of Hennig *et al.*,<sup>2</sup> Romming and Wagner,<sup>4</sup> Hack *et al.*,<sup>1</sup> and Mertens *et al.*<sup>3</sup> The studies of Lillich *et al.*<sup>6</sup> and Zetzsch and Hansen<sup>7</sup> are in excellent agreement with our recommendations and the upper limit of Pagsberg *et al.*<sup>8</sup> is also compatible, but the data of Bian *et al.*,<sup>9,10</sup> which were derived from a complex system, appear to be too high. In their studies of products Hack *et al.*<sup>1</sup> detected OH but not H or O and hence concluded that Channel (1) is dominant at low temperatures. The studies at higher temperature<sup>2–4</sup> are compatible with this and with the emergence of Channel (3) as the dominant high temperature channel.

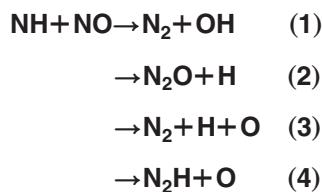
The potential energy surface has been investigated using BAC-MP4 calculations.<sup>11</sup> RRKM rate coefficients<sup>11</sup> based on this surface agree well with experimental data and also suggest the dominance of Channel (1) at low temperatures, and of Channel (3) at high temperatures. There are no experimental data on the rate coefficient for Channel (2) but both the

theoretical treatments and experimental studies suggest that it is unimportant over the whole temperature range.

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*Thermodynamic Data*

$$\begin{aligned}
 \Delta H_{298}^{\circ}(1) &= -409.7 \text{ kJ mol}^{-1} \\
 \Delta S_{298}^{\circ}(1) &= -16.56 \text{ J K}^{-1} \text{ mol}^{-1} \\
 K_c(1) &= 4.68 \cdot 10^{-1} T^{-0.174} \exp(+49200/T) \\
 &\quad (300 \leq T/\text{K} \leq 5000)
 \end{aligned}$$

$$\begin{aligned}
 \Delta H_{298}^{\circ}(3) &= 20.3 \text{ kJ mol}^{-1} \\
 \Delta S_{298}^{\circ}(3) &= 75.35 \text{ J K}^{-1} \text{ mol}^{-1} \\
 K_c(3) &= 1.13 \cdot 10^{23} T^{-0.046} \exp(-2290/T) \text{ molecule cm}^{-3} \\
 &\quad (300 \leq T/\text{K} \leq 5000)
 \end{aligned}$$

$$\begin{aligned}
 \Delta H_{298}^{\circ}(2) &= -146.8 \text{ kJ mol}^{-1} \\
 \Delta S_{298}^{\circ}(2) &= -57.31 \text{ J K}^{-1} \text{ mol}^{-1} \\
 K_c(2) &= 6.56 \cdot 10^{-7} T^{1.057} \exp(+18050/T) \\
 &\quad (300 \leq T/\text{K} \leq 5000)
 \end{aligned}$$

$$\begin{aligned}
 \Delta H_{298}^{\circ}(4) &= 51.9 \text{ kJ mol}^{-1} \\
 \Delta S_{298}^{\circ}(4) &= -6.36 \text{ J K}^{-1} \text{ mol}^{-1} \\
 K_c(4) &= 3.85 \cdot 10^{-2} T^{0.339} \exp(-6070/T) \\
 &\quad (300 \leq T/\text{K} \leq 5000)
 \end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data ( $k = k_1 + k_2 + k_3 + k_4$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$4.8 \cdot 10^{-11}$	300	Cox, Nelson, and McDonald, 1985 <sup>1</sup>	(a)
$5.78 \cdot 10^{-11}$	269–373	Harrison, Whyte, and Phillips, 1986 <sup>2</sup>	(b)
$k_1 = 2.0 \cdot 10^{-11}$	2000	Vandooren <i>et al.</i> , 1991 <sup>3</sup>	(c)
$k_1 = 1.4 \cdot 10^{-11}$			
$k_2 = 3.3 \cdot 10^{-12}$			
$2.8 \cdot 10^{-10} \exp(-6400/T)$	2220–3350	Mertens <i>et al.</i> , 1991 <sup>4</sup>	(d)
$4.7 \cdot 10^{-11}$	300	Yamasaki <i>et al.</i> , 1991 <sup>5</sup>	(e)
$4.5 \cdot 10^{-11}$	3500	Yokoyama, Sakane, and Fueno, 1991 <sup>6</sup>	(f)
$5.4 \cdot 10^{-11}$	298	Hack, Wagner, and Zasykin, 1994 <sup>7</sup>	(g)
$2.5 \cdot 10^{-10} T^{-1.6} \exp(-457/T)$	293–1085	Lillich <i>et al.</i> , 1994 <sup>8</sup>	(h)
$4.8 \cdot 10^{-11}$	295	Okada <i>et al.</i> , 1994 <sup>9</sup>	(i)
$1.66 \cdot 10^{-11}$	1300–2200	Römming and Wagner, 1996 <sup>10</sup>	(j)
<i>Branching Ratios</i>			
$k_1/k = 0.19 \pm 0.10$	2940–3040	Mertens <i>et al.</i> , 1991 <sup>4</sup>	(d)
$k_1/k = 0.32 \pm 0.07$	3207–3637	Yokoyama, Sakane, and Fueno, 1991 <sup>6</sup>	(f)
$k_2/k = 0.8 \pm 0.4$	298	Durant, 1994 <sup>11</sup>	(k)
$k_1/k = 0.09$	298	Hack, Wagner, and Zasykin, 1994 <sup>7</sup>	(g)
$k_1/k = 0.30 \pm 0.09$	295	Okada <i>et al.</i> , 1994 <sup>9</sup>	(i)
$k_2/k = 0.65 \pm 0.17$			
$k_2/k = 0.84 \pm 0.40$	298	Wolf, Yang, and Durant, 1994 <sup>12</sup>	(k)
$k_2/k = 0.77 \pm 0.08$	298	Quandt and Hershberger, 1995 <sup>13</sup>	(l)
<i>Reviews and Evaluations</i>			
$5.0 \cdot 10^{-11}$	270–380	CEC 1992, 1994 <sup>14</sup>	(m)
$2.8 \cdot 10^{-10} \exp(-6400/T)$	2220–3350		
$4.9 \cdot 10^{-11}$	200–300	NASA, 1997 <sup>17</sup>	(n)

**Comments**

- (a) Pulsed laser photolysis of  $\text{N}_2\text{H}_4/\text{He}/\text{NO}$  mixtures at 266 nm in flowing system.  $[\text{NH}]$  decay monitored by laser induced fluorescence at 304.85 nm.
- (b) Pulsed laser photolysis of  $\text{N}_2\text{H}_4/\text{Ar}/\text{NO}$  mixtures at 248 nm in flowing system.  $[\text{NH}]$  decay monitored by laser induced fluorescence at 336 nm. He,  $\text{N}_2$ , and  $\text{N}_2\text{O}$  also used as carrier gases gave same result.
- (c) Ammonia oxygen flame study, reactant and product

analysis by molecular beam sampling mass spectrometry. The observed concentration profiles were fitted to a complex mechanism. Two values of  $k_1$  are given corresponding to different values for the rate coefficient of the  $\text{NH}_2 + \text{NO}$  reaction to which the measurements are sensitive at 2000 K. Our evaluation of the  $\text{NH}_2 + \text{NO}$  rate data favors the value  $k_4(\text{NH}_2 + \text{NO}) = 2.0 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

- (d) Shock tube study. NH produced by the thermal disso-

- ciation of HNCO. Time histories of  $[\text{NH}(X^3\Sigma)]$  and  $[\text{OH}(X^2\Pi)]$  measured behind the shock waves cw laser absorption at 336 and 307 nm, respectively. Results fitted to a large reaction mechanism.
- (e) NH produced by pulsed laser photolysis of HNCO and  $\text{CHBr}_3/\text{NO}$  at 193 nm in 27 mbar Ar.  $[\text{NH}]$ ,  $[\text{OH}]$ , and  $[\text{H}]$  probed by laser induced fluorescence. Results on branching ratio that favor OH channel were due to misinterpretation of data caused by the production of vibrationally excited OH and are superseded by Ref. 9.
  - (f) Shock tube studies at 3500 K on the decomposition of HNCO in HNCO/NO/Ar mixtures.  $[\text{NH}]$  and  $[\text{OH}]$  followed by UV emission at 337 nm and 309 nm, respectively. Pressures ranged from 280 to 1160 mbar.  $[\text{OH}]$  calibration made on the basis of  $\text{H}_2/\text{O}_2/\text{Ar}$  experiments conducted under the same conditions.
  - (g) Electronically excited NH produced by the pulsed laser photolysis of  $\text{N}_3\text{H}$  at 248 nm. NH in ground state produced by quenching with Xe. Detection of NH and OH by laser induced fluorescence at 336.2 nm and 308.3 nm, respectively. Experiments carried out at 14.8 mbar.
  - (h) NH produced by pulsed laser photolysis of HNCO at 193 nm in the presence of excess xenon to relax electronically excited NH. Ground state NH and OH detected by laser induced fluorescence at 336 nm and 308.3 nm, respectively. Reaction pressure was in the range 34–39 mbar.  $[\text{OH}]$  calibration from  $\text{H}_2\text{O}_2$  photolysis experiments.
  - (i) Electronically excited NH produced by the pulsed laser photolysis of HNCO at 193 nm and quenched by addition of Xe, in a bath gas of He at 27 mbar total pressure. NH in the ground state was detected by laser induced fluorescence at 336 nm, OH was detected by LIF at 308 and 314 nm, and H by VUV LIF at 121.567 nm. Rate constants for  $v=0$  and  $v=1$  levels of NH were determined; vibrational excitation is unimportant.
  - (j) NH produced in incident shock tube studies on the thermal decomposition of  $\text{HN}_3$ . NH concentrations determined by narrow linewidth laser absorption detection at 336.1 nm. H and O atom formation was followed by ARAS at 121.6 and 130.5 nm, respectively. Total pressures were in the range 0.25–1.2 bar.
  - (k) Discharge flow experiments in a quartz reactor with mass spectrometric detection of products. NH generated from the reactions of excess F with  $\text{NH}_3$ . Total pressures were in the range 1–3.3 mbar.
  - (l) Electronically excited NH produced by the pulsed laser photolysis of  $\text{N}_3\text{H}$  and relaxed to its ground state by quenching with Xe. Time resolved infrared spectroscopy used to detect  $\text{N}_2\text{O}$ . NH concentration determined from laser power, absorption coefficient, and quantum yield. 30% estimated accuracy. Typical pressures were 2.7 mbar Xe with 1.3 mbar  $\text{SF}_6$ .
  - (m) Evaluation of data published to 1991. Recommendation based on the studies of Refs. 1, 2, 15, and 16 over the temperature range 270–380 K, and Ref. 3 over the range 2220–3350 K.

- (n) Recommendation based on the studies of Refs. 1, 2, and 15.

### Preferred Values

$$k = [5.7 \cdot 10^{-9} T^{-0.78} \exp(-40/T) + 7.4 \cdot 10^{-10} \times \exp(-10540/T)] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the range 298–3300 K.

$$(k_1 + k_2) = 5.7 \cdot 10^{-9} T^{-0.78} \exp(-40/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the range 298–3300 K.

$$(k_3 + k_4) = 7.4 \cdot 10^{-10} \exp(-10540/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the range 298–3300 K.

$$k_1/k = 0.2 \text{ at } 298 \text{ K.}$$

$$k_2/k = 0.8 \text{ at } 298 \text{ K.}$$

### Reliability

$$\Delta \log k = \pm 0.3 \text{ over the range 298–3300 K.}$$

$$\Delta \log(k_1 + k_2) = \pm 0.3 \text{ over the range 298–1200 K, increasing to } \pm 0.5 \text{ for the range 2000–3300 K.}$$

$$\Delta \log(k_3 + k_4) = \pm 0.3 \text{ over the range 298–1200 K, increasing to } \pm 0.5 \text{ for the range 2000–3300 K.}$$

$$\Delta(k_1/k) = \Delta(k_2/k) = \pm 0.15 \text{ at } 298 \text{ K.}$$

### Comments on Preferred Values

There is now a considerable body of data which indicates that the overall rate coefficient exhibits a slow decrease with temperature in the range 298 K to approximately 2000 K with a rapid increase at higher temperatures. The preferred expression for  $k$  is a fit to the data of Cox *et al.*,<sup>1</sup> Harrison *et al.*,<sup>2</sup> Yamasaki *et al.*,<sup>5</sup> Hack *et al.*,<sup>7</sup> Lillich *et al.*,<sup>8</sup> Okada *et al.*,<sup>9</sup> Römming and Wagner,<sup>10</sup> Mertens *et al.*,<sup>4</sup> and Vandoren *et al.*<sup>3</sup> The studies of Gordon *et al.*,<sup>18</sup> Hansen *et al.*,<sup>19</sup> Roose *et al.*,<sup>20</sup> and Yokoyama *et al.*<sup>6</sup> appear to give low values of  $k$ . The QRRK calculation of Bozzelli *et al.*<sup>21</sup> show qualitative agreement with the experimental observations, with a slight increase in  $k$  at high temperatures caused by the increase availability of Channel (3) but other theoretical studies<sup>22,23</sup> are in poor agreement with experiment.

At high temperatures the rapid increase in  $k$  above 2000 K appears to be due to the growing predominance of Channel (4) which may subsequently produce  $\text{N}_2 + \text{H} + \text{O}$  by the rapid decomposition of  $\text{N}_2\text{H}$  [Channel (3)] and the high temperature term in our preferred expression for  $k$  is assigned to  $(k_3 + k_4)$ . Support for this comes from a flame and modeling study<sup>24</sup> in which an expression for  $k_{-4}$  was derived for the temperature range 1200–2500 K. Combination of the expression obtained for  $k_{-4}$  with the thermodynamic data for Channel (4) gives  $k_4 = 7.4 \cdot 10^{-10} T^{0.339} \exp(-10540/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  which is in reasonable agreement with our preferred expression.

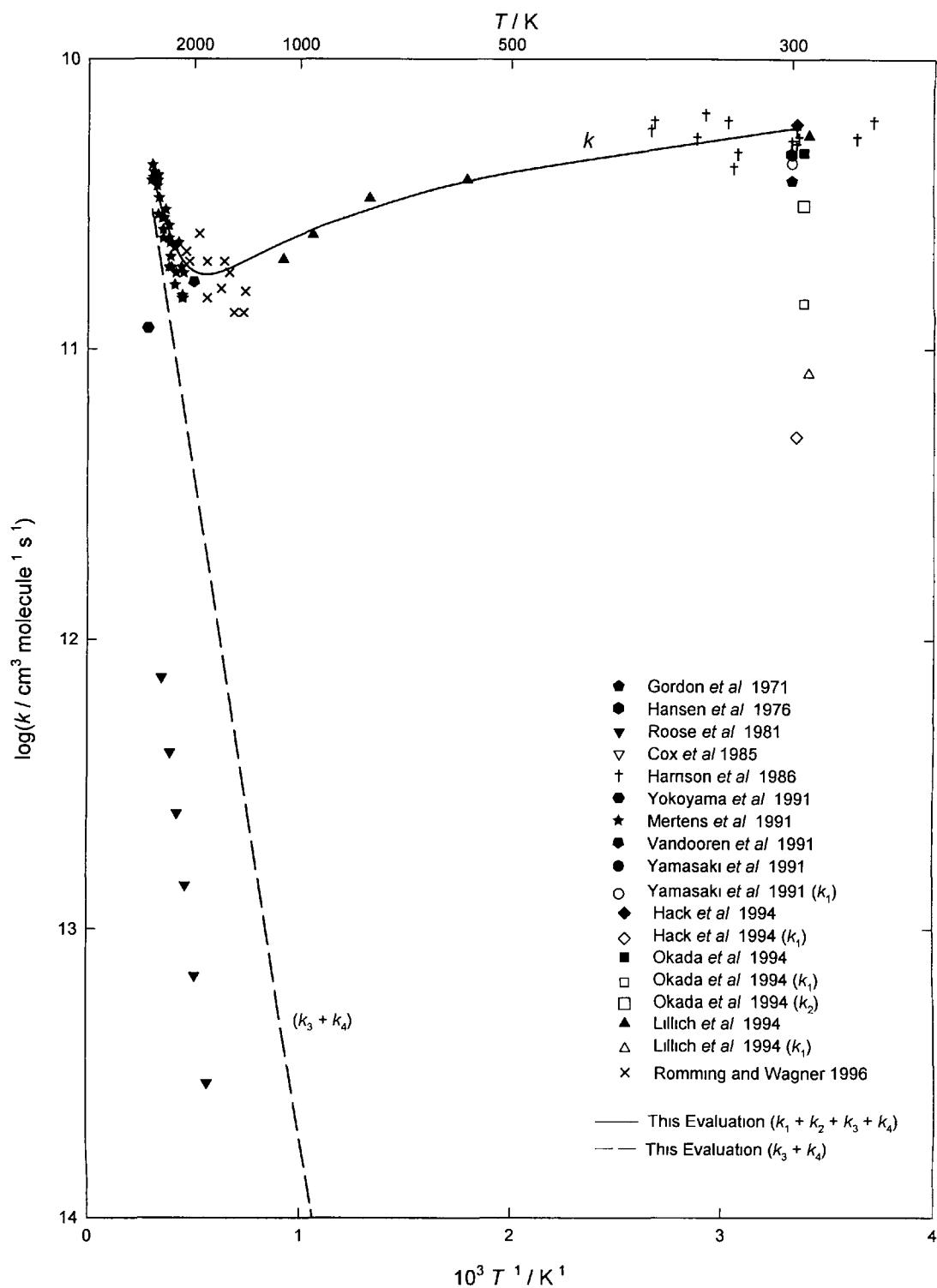
The low temperature term in our expression for  $k$  is assigned to  $(k_1 + k_2)$ . At low temperatures there is evidence for the occurrence of Channels (1) and (2), with Channel (2) predominating. Branching ratio measurements at  $\sim 300$  K cover the range  $k_2/k = 0.65–0.91$ . The earlier value of  $k_2/k = 0$  from Yamasaki *et al.*<sup>5</sup> is now known to be in error

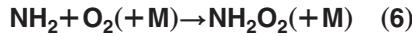
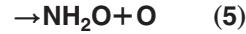
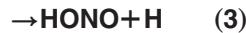
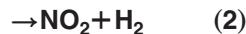
and has been superseded by the measurements of Okada *et al.*<sup>9</sup> from the same laboratory. Our preferred value at 298 K is the mean of the values of Durant,<sup>11</sup> Hack *et al.*,<sup>7</sup> Okada *et al.*,<sup>9</sup> Wolf *et al.*,<sup>12</sup> and Quandt and Hershberger.<sup>13</sup> The branching fraction,  $k_1/k$ , calculated theoretically by Simonson *et al.*<sup>25</sup> and Szichman and Baer<sup>26</sup> agrees with our preferred value. There are no experimental studies to show how  $k_1/k_2$  varies with temperature. A theoretical treatment by Miller and Melius<sup>27</sup> suggests that  $k_1/k$  increases from 0.19 to 0.30 over the range 300–3500 K. Unfortunately Channels (3) and (4) were not considered in their work, but this study and more recent theoretical predictions<sup>22,26</sup> probably offer the best guide to the relative importance of Channel (1) in relation to Channel (2) as the temperature increases.

High temperature studies of OH yields give some indication of  $k_1/k$  at  $T \geq 2000$  K but the evidence is conflicting and not adequate to make recommendations at this stage. Thus Mertens *et al.*<sup>4</sup> find  $k_1/k = 0.19 \pm 0.10$  at 2940–3040 K but Yokoyama *et al.*<sup>6</sup> obtain a higher value ( $k_1/k = 0.32 \pm 0.07$ ) at 3207–3637 K, whereas our preferred value for  $(k_1 + k_2)/k$  would predict a decline in  $k_1/k$  as temperature increases in this regime. If the value of  $k_1/k$  of Mertens *et al.*<sup>4</sup> is combined with the theoretical value of  $k_1/k_2 = 0.41$  of Miller and Melius<sup>26</sup> at 3000 K a value of  $(k_1 + k_2)/k = 0.65$  is predicted compared with the value of 0.67 given by our preferred expressions. Thus our preferred expressions for  $k$  and  $(k_1 + k_2)$  are compatible with the Mertens *et al.*<sup>4</sup> value of  $k_1/k$  but not with the higher value of Yokoyama *et al.*<sup>6</sup>

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#### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = -341.0 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = -0.27 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 5.84 T^{-0.249} \exp(+40900/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(3) = -51.0 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = -31.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 7.7 \cdot 10^{-6} T^{1.199} \exp(+6490/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(5) = 125.8 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(5) = -4.68 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(5) = 1.10 \cdot 10^{-6} T^{1.919} \exp(-14450/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(2) = -156.4 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = -29.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 3.88 \cdot 10^{-3} T^{0.340} \exp(+18820/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(4) = -45.4 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(4) = 4.59 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(4) = 2.06 T^{0.003} \exp(+4680/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(6) = -27.8 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(6) = -135.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(6) = 7.2 \cdot 10^{-37} T^{3.207} \exp(+4600/T) \text{ cm}^3 \text{ molecule}^{-1} \\ (300 \leq T/\text{K} \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2 + k_3 + k_4 + k_5 + k_6$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$< 6 \cdot 10^{-21}$	296	Tyndall <i>et al.</i> , 1991 <sup>1</sup>	(a)
$3.65 \cdot 10^{-10} \exp(-12628/T)$	1450–2300	Hennig <i>et al.</i> , 1995 <sup>2</sup>	(b)
$k_4 = 1.66 \cdot 10^{-11} \exp(-13230/T)$			
$k_5 = 9.96 \cdot 10^{-11} \exp(-15034/T)$			
<i>Reviews and Evaluations</i>			
$< 3 \cdot 10^{-18}$	298	CEC, 1992; 1994 <sup>3</sup>	(c)
$< 6 \cdot 10^{-21}$	298	NASA, 1997 <sup>4</sup>	(d)
$< 6 \cdot 10^{-21}$	298	IUPAC, 1997 <sup>5</sup>	(d)

#### Comments

- (a) Photolysis of  $\text{NH}_3$  in the presence of  $\text{O}_2$ .  $[\text{NO}]$ ,  $[\text{NO}_2]$ , and  $[\text{N}_2\text{O}]$  were monitored by FTIR spectroscopy. The upper limit to the rate constant was based on computer simulation of a substantial reaction mechanism.
- (b) Shock tube study on  $\text{N}_2\text{H}_4/\text{O}_2/\text{Ar}$  mixtures.  $[\text{NH}_2]$ ,  $[\text{NH}]$ , and  $[\text{OH}]$  were monitored by time resolved laser absorption spectroscopy. In separate experiments  $[\text{O}]$  and  $[\text{H}]$  were monitored by ARAS. Values of  $k_4$  and  $k_5$  were obtained from computer simulations of a detailed mechanism.  $\text{NH}$  was not detected, and from the analysis of the  $[\text{H}]$  it was concluded that the contribution from any channel leading to  $\text{H}$  was small. The  $[\text{O}]$  profile indicated that the  $\text{NO}_2$  forming channel contributed less than 10%.

- (c) Based on the study of Lesclaux and Demissy.<sup>6</sup>
- (d) Based on the study of Tyndall *et al.*<sup>1</sup>

#### Preferred Values

$k = 3.65 \cdot 10^{-10} \exp(-12630/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 1400–2400 K.

$k_1 = 2.9 \cdot 10^{-10} \exp(-12420/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 1400–2400 K.

$k_4 = 1.66 \cdot 10^{-11} \exp(-13230/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 1400–2400 K.

$k_5 = 1.0 \cdot 10^{-10} \exp(-15030/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 1400–2400 K.

#### Reliability

$\Delta \log k = \pm 0.4$  over the range 1400–2400 K.

$\Delta \log k_1 = \pm 0.5$  over the range 1400–2400 K.

$\Delta \log k_4 = \pm 0.5$  over the range 1400–2400 K.

$\Delta \log k_5 = \pm 0.5$  over the range 1400–2400 K.

#### Comments on Preferred Values

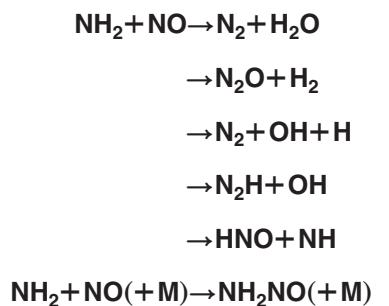
At low temperatures this reaction is too slow to be studied by the usual fast reaction techniques and the most reliable studies<sup>1,6–12</sup> only provide upper limits to  $k$ . The NASA and IUPAC Panels have reviewed the low temperature data and recommend the upper limit from the study of Tyndall *et al.*<sup>1</sup> The very small value of this upper limit suggests that if the adduct,  $\text{NH}_2\text{OO}$ , is formed its stability is low and it is of no importance in combustion.

There are few data at higher temperatures. The most reliable study appears to be that of Hennig *et al.*<sup>2</sup> on which we base our preferred values. They obtained values for the rate constants of Channels (4) and (5) and the overall rate constant for  $\text{NH}_2$  removal. Their results are consistent with radical ( $\text{NH}$ ,  $\text{OH}$ ,  $\text{H}$ ,  $\text{O}$ ) production contributing less than 15% to the primary reaction and 85%–90% leading to stable products with Channel (1) being predominant. The value of  $k_1$  recommended has therefore been obtained by taking the difference between the total rate constant for  $\text{NH}_2$  removal and the contributions of the other two channels observed by Hennig *et al.*<sup>2</sup> The other high temperature data come from a shock tube study on  $\text{NH}_3/\text{O}_2/\text{H}_2/\text{H}_2\text{O}$  mixtures by Fujii *et al.*,<sup>13</sup> in which induction times were measured, and a study by Dean *et al.*,<sup>14</sup> in which  $\text{NH}_3/\text{O}_2$  mixtures were passed through a hot tubular reactor and the NO profiles modeled. In both studies Channel (4) was taken as the main reaction channel and values of  $k_4$  were derived. The values of Dean *et al.*<sup>14</sup> are compatible with the preferred expression for  $k_4$  but those of Fujii *et al.*<sup>13</sup> are much higher.

A recent theoretical study of the reaction by Sumathi and Peyerimhoff<sup>15</sup> concludes that the main reaction channel at high temperatures is Channel (5), a conclusion also reached by Melius and Binckley.<sup>16</sup> However, provisionally the experimental findings, pointing to Channel (1) as the predominant reaction, are accepted.

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*Thermodynamic Data*

$$\Delta H^{\circ}_{298}(1) = -521.6 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298}(1) = -24.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 0.246 T^{-0.230} \exp(+62650/T)$$

(300 ≤ T/K ≤ 5000)

$$\Delta H^{\circ}_{298}(3) = -24.7 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298}(3) = 84.6 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 3.29 \cdot 10^2 T^{0.760} \exp(+2940/T)$$

(300 ≤ T/K ≤ 5000)

$$\Delta H^{\circ}_{298}(5) = 183.8 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298}(5) = -3.49 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(5) = 0.185 T^{0.195} \exp(-22070/T)$$

(300 ≤ T/K ≤ 5000)

$$\Delta H^{\circ}_{298}(2) = -197.7 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298}(2) = -54.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 5.48 \cdot 10^{-6} T^{-0.840} \exp(+23990/T)$$

(300 ≤ T/K ≤ 5000)

$$\Delta H^{\circ}_{298}(4) = 4.61 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298}(4) = 2.87 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(4) = 0.427 T^{0.188} \exp(-522/T)$$

(300 ≤ T/K ≤ 4000)

$$\Delta H^{\circ}_{298}(6) = -184.1 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298}(6) = -162.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(6) = 7.9 \cdot 10^{-33} T^{1.463} \exp(+22600/T) \text{ cm}^3 \text{ molecule}^{-1}$$

(300 ≤ T/K ≤ 5000)

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data ( $k = k_1 + k_2 + k_3 + k_4 + k_5 + k_6$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$2.8 \cdot 10^{-7} T^{-1.67}$	216–480	Stief <i>et al.</i> , 1982 <sup>1</sup>	(a)
$1.7 \cdot 10^{-11}$	298	Dreier and Wolfrum, 1985 <sup>2</sup>	(b)
$1.3 \cdot 10^{-11}$	298		
$1.66 \cdot 10^{-11}$	295	Andresen <i>et al.</i> , 1982 <sup>3</sup>	(c)
$1.81 \cdot 10^{-11}$	298	Whyte and Phillips, 1983 <sup>4</sup>	(d)
$5.6 \cdot 10^{-6} T^{-2.2}$	295–620	Bulatov <i>et al.</i> , 1989 <sup>5</sup>	(e)
$1.3 \cdot 10^{-8} T^{-1.17}$	294–1025	Atakan, Wolfrum, and Weller, 1990 <sup>6</sup>	(f)
$2.2 \cdot 10^{-11}$	298	Pagsberg <i>et al.</i> , 1991 <sup>7</sup>	(g)
$2.2 \cdot 10^{-12} \exp(525/T)$	297–673	Diau <i>et al.</i> , 1994 <sup>8</sup>	(h)
$(2.9–6.0) \cdot 10^{-12}$	1466–2141	Vandooren, Bian, and Van Tiggelen, 1994 <sup>9</sup>	(i)
$5.43 T^{-4.02} \exp(-1034/T)$	293–612	Wolf, Yang, and Durant, 1994 <sup>10</sup>	(j)
$1.4 \cdot 10^{-11}$	298	Yu and Lin, 1994 <sup>11</sup>	(k)
$1.38 \cdot 10^{-10} T^{-0.57} \exp(300/T)$	305–1037	Park and Lin, 1997 <sup>12</sup>	(l)
$(k_3 + k_4) = 1.4 \cdot 10^{-14} T^{0.53} \exp(998/T)$	300–1000		
$(k_3 + k_4) = 1.53 \cdot 10^{-1} T^{-3.02} \exp(-9589/T)$	1000–2000		
$k_2 = 1.37 \cdot 10^{-9} T^{-0.93} \exp(192/T)$	300–1000		
$k_2 = 5.36 \cdot 10^{-10} T^{-0.98} \exp(1311/T)$	1000–2000		
$1.65 \cdot 10^{-7} T^{-1.54} \exp(-93/T)$	203–813	Wolf, Yang, and Durant, 1997 <sup>13</sup>	(m)
$2.2 \cdot 10^{-11} \exp(-4212/T)$	1400–2800	Deppe <i>et al.</i> , 1997 <sup>14</sup>	(n)
$3.5 \cdot 10^{-8} T^{-1.34}$	300–2500	Song <i>et al.</i> , 2000 <sup>15</sup>	(o)
$1.14 \cdot 10^{-8} T^{-1.203} \exp(106/T)$	200–2500	Song <i>et al.</i> , 2001 <sup>16</sup>	(o)
<i>Branching Ratios</i>			
$(k_3 + k_4)/k = 0.10 \pm 0.02$	295	Bulatov <i>et al.</i> , 1989 <sup>5</sup>	(e)
$(k_3 + k_4)/k = 0.14 \pm 0.03$	470		
$(k_3 + k_4)/k = 0.20 \pm 0.04$	620		
$(k_3 + k_4)/k = 0.10 \pm 0.025$	300	Atakan, Wolfrum, and Weller, 1990 <sup>6</sup>	(f)
$(k_3 + k_4)/k = 0.11 \pm 0.03$	420		
$(k_3 + k_4)/k = 0.12 \pm 0.03$	520		
$(k_3 + k_4)/k = 0.12 \pm 0.03$	600		
$(k_3 + k_4)/k = 0.15 \pm 0.04$	700		
$(k_3 + k_4)/k = 0.15 \pm 0.04$	784		

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
$(k_3 + k_4)/k = 0.167 \pm 0.045$	865		
$(k_3 + k_4)/k = 0.176 \pm 0.05$	900		
$(k_3 + k_4)/k = 0.19 \pm 0.05$	1000		
$(k_3 + k_4)/k = 0.10$	299	Stephens <i>et al.</i> , 1993 <sup>17</sup>	(p)
$(k_3 + k_4)/k = 0.10$	656		
$(k_3 + k_4)/k = 0.15$	950		
$(k_3 + k_4)/k = 0.17$	1173		
$(k_3 + k_4)/k = 0.57$	1466	Vandooren, Bian, and Van Tiggelen, 1994 <sup>9</sup>	(i)
$(k_3 + k_4)/k = 0.58$	1671		
$(k_3 + k_4)/k = 0.75$	1841		
$(k_3 + k_4)/k = 0.61$	1958		
$(k_3 + k_4)/k = 0.70$	2038		
$(k_3 + k_4)/k = 0.74$	2098		
$(k_3 + k_4)/k = 0.82$	2141		
$(k_3 + k_4)/k = 0.27$	950	Halbgewachs <i>et al.</i> , 1996 <sup>18</sup>	(q)
$(k_3 + k_4)/k = 0.28$	1000		
$(k_3 + k_4)/k = 0.40$	1050		
$(k_3 + k_4)/k = 0.35$	1100		
$(k_3 + k_4)/k = 0.45$	1150		
$(k_3 + k_4)/k = 0.43$	1173		
$(k_3 + k_4)/k = 0.48$	1200		
$(k_3 + k_4)/k = 0.10$	302	Park and Lin, 1996 <sup>19</sup>	(r)
$(k_3 + k_4)/k = 0.14$	527		
$(k_3 + k_4)/k = 0.18$	695		
$(k_3 + k_4)/k = 0.20$	800		
$(k_3 + k_4)/k = 0.24$	930		
$(k_3 + k_4)/k = 0.28$	1004		
$(k_3 + k_4)/k = 0.30$	1060		
$k_1/k = 0.7$	298	Quandt and Hershberger, 1996 <sup>20</sup>	(s)
$(k_3 + k_4)/k = 2.02 \cdot 10^{55} T^{-15.484} \exp(-22370/T)$	1211–1369	Glarborg <i>et al.</i> , 1997 <sup>21</sup>	(t)
$(k_3 + k_4)/k = 0.090 \pm 0.002$	298	Wolf, Yang, and Durant, 1997 <sup>13</sup>	(m)
$(k_3 + k_4)/k = 5.8 \cdot 10^3 T^{-0.951} \exp(-3560/T)$	1410–2810	Deppe <i>et al.</i> , 1999 <sup>14</sup>	(n)
$(k_3 + k_4)/k = 0.5 + 3.36 \cdot 10^{-4}(T - 1600)$	1340–1670	Votsmeier <i>et al.</i> , 1999 <sup>22</sup>	(u)
$k_1 = 4.33 \cdot 10^{-5} T^{-2.369} \exp(-436/T)$	400–1900	Song <i>et al.</i> , 2001 <sup>16</sup>	(v)
$k_4 = 7.1 \cdot 10^{-14} T^{0.294} \exp(438/T)$			
$(k_3 + k_4)/k = 0.59$	1826	Song <i>et al.</i> <sup>23</sup>	(w)
$(k_3 + k_4)/k = 0.58$	1829		
$(k_3 + k_4)/k = 0.61$	1897		
$(k_3 + k_4)/k = 0.61$	1907		
$(k_3 + k_4)/k = 0.62$	1938		
$(k_3 + k_4)/k = 0.62$	1945		
$(k_3 + k_4)/k = 0.63$	1975		
$(k_3 + k_4)/k = 0.62$	2005		
$(k_3 + k_4)/k = 0.63$	2048		
$(k_3 + k_4)/k = 0.659$	2066		
$(k_3 + k_4)/k = 0.63$	2069		
$(k_3 + k_4)/k = 0.64$	2089		
$(k_3 + k_4)/k = 0.65$	2127		
$(k_3 + k_4)/k = 0.66$	2136		
$(k_3 + k_4)/k = 0.66$	2159		
<i>Reviews and Evaluations</i>			
$1.8 \cdot 10^{-12} \exp(650/T)$	220–2000	CEC, 1992; 1994 <sup>24</sup>	(x)
$1.6 \cdot 10^{-9} T^{-0.85}$	300–2000	Diau <i>et al.</i> , 1994 <sup>8</sup>	(y)
$k_2 = 7.9 \cdot 10^{-9} T^{-1.1} \exp(-98/T)$	300–2000		
$(k_3 + k_4) = 6.6 \cdot 10^{-13} \exp(196/T)$	300–2000		
$k_2 = 2.17 \cdot 10^{-8} T^{-1.25}$	300–1400	Glarborg <i>et al.</i> , 1995 <sup>25</sup>	(z)
$(k_3 + k_4) = 4.67 \cdot 10^{-11} T^{-0.55}$	300–1400		
$(k_3 + k_4)/k = 2.2 \cdot 10^{-3} T^{0.7}$	300–1400		
$(k_3 + k_4)/k = 0.1$	300	Diau and Smith, 1996 <sup>26</sup>	(aa)
$(k_3 + k_4)/k = 0.85$	3000		
$4 \cdot 10^{-12} \exp(450/T)$	200–300	NASA, 1997 <sup>27</sup>	(ab)
$8.23 \cdot 10^{-8} T^{-1.5}$	210–500	IUPAC, 1998 <sup>28</sup>	(ac)
$k_1/k = 0.9$	298		
$(k_3 + k_4)/k = 9.69 \cdot 10^{-3} - 1.31 \cdot 10^{-4} T + 3.96 \cdot 10^{-7} T^2$	300–1670	Park and Lin, 1999 <sup>29</sup>	(ad)
$- 9.72 \cdot 10^{-11} T^3$			
$(k_3 + k_4) = 2.37 \cdot 10^{-17} T^{1.40} \exp(894/T)$			
$k_1 = 2.0 \cdot 10^{-7} T^{-1.61} \exp(-150/T)$			

### Comments

- (a) Flash photolysis study.  $[\text{NH}_2]$  was monitored by time-resolved laser induced fluorescence at 600 nm after excitation of the  $\text{NH}_2$  with 597.7 nm radiation.
- (b) Flow reactor study in which  $\text{NH}_2$  radicals were produced by laser flash photolysis of  $\text{NH}_3$  at 193 nm.  $[\text{NH}_2]$  and the product concentration,  $[\text{N}_2]$ , were monitored by coherent anti-Stokes Raman spectroscopy (CARS). An independent value of  $k$  was obtained by monitoring vibrationally excited  $\text{H}_2\text{O}$  by time-resolved infrared fluorescence.
- (c) Flow reactor study in which  $\text{NH}_2$  radicals were produced by laser flash photolysis at 193 nm.  $[\text{OH}]$  was monitored by laser induced fluorescence. No H atom production could be detected using ARAS.
- (d) Flash photolysis of  $\text{NH}_3/\text{NO}$  mixtures with  $[\text{NH}_2]$  monitored by time-resolved laser induced fluorescence at 597.7 nm.
- (e)  $\text{NH}_2$  was generated by photolysis of  $\text{NH}_3$  ( $\lambda > 193$  nm) and detected via intracavity laser absorption in a quartz reactor. Total pressure 13–28 mbar. Branching ratios determined from the changes in  $\text{NH}_2$  decay with changing  $\text{NH}_3$  concentrations.
- (f) Pulsed laser photolysis of  $\text{NH}_3/\text{NO}$  mixtures at 193 nm and detection of OH in heated quartz reactor.  $[\text{OH}]$  was monitored by time-resolved laser induced fluorescence. The total pressures were in the range 4–136 mbar  $\text{N}_2$ .
- (g) Pulse radiolysis of  $\text{Ar}/\text{SF}_6/\text{NH}_3$  mixtures.  $\text{NH}_2$  was generated by the  $\text{F}+\text{NH}_3$  reaction and its concentration monitored by absorption at 597.6 nm.  $[\text{OH}]$  was obtained from absorption at 309 nm in the presence of NO at 1 bar total pressure. Results suggest that the OH formation channel contributes no more than 7% to the overall reaction.
- (h) Pulsed laser photolysis at 193 nm of  $\text{NH}_3/\text{NO}/\text{Ar}$  mixtures at a total pressure of 67 mbar.  $[\text{NH}_2]$  decay monitored using cavity ring down laser absorption at 537.6 nm. Branching ratios were investigated with RRKM calculations.
- (i) Mass spectrometric sampling of near stoichiometric  $\text{NH}_3/\text{NO}/\text{Ar}$  (6.7% Ar) flame at 72 mbar. Species detected include  $\text{H}$ ,  $\text{H}_2$ ,  $\text{NH}_2$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{N}_2$ ,  $\text{N}_2\text{O}$ , NO. Results based on an analysis using a complex mechanism.
- (j) Pulsed laser photolysis of  $\text{NH}_3/\text{NO}$  mixtures.  $[\text{NH}_2]$  monitored by time-resolved continuous-wave laser-induced fluorescence. The total pressure was 17 mbar Ar.
- (k) Pulsed laser photolysis of  $\text{NH}_3/\text{NO}$  mixtures at 193 nm.  $[\text{NH}_2]$  monitored by cavity ring down laser absorption between 536 and 539 nm.
- (l) Pulsed laser photolysis of  $\text{NH}_3/\text{NO}/\text{He}$  mixtures at 193 nm in a quartz reactor under slow flow conditions and total pressures in the range 3–13 mbar. The  $[\text{NO}]$  reactant and  $[\text{H}_2\text{O}]$  product were monitored by mass spectrometry. Rate constants were derived from kinetic modeling of the  $[\text{NO}]$  and  $[\text{H}_2\text{O}]$  profiles. Product branching was determined by addition of CO and mass spectrometric detection of  $\text{CO}_2$  produced by the reaction  $\text{OH}+\text{CO}\rightarrow\text{H}+\text{CO}_2$  and kinetic modeling of the  $[\text{OH}]$ . The results from this study and from the study Halbegewachs *et al.*<sup>18</sup> were later reinterpreted to accommodate changes in the model. See Comment (bb)
- (m) Rate coefficients determined in quartz and aluminum flow reactors at 13–130 mbar Ar total pressure.  $\text{NH}_2$  radicals were generated by laser photolysis of  $\text{NH}_3$  at 193 nm and  $[\text{NH}_2]$  was monitored by continuous-wave laser-induced fluorescence. Branching ratios were determined in a discharge-flow apparatus with mass spectrometric detection of products.  $\text{NH}_2$  radicals were generated by the reaction of F atoms with  $\text{NH}_3$ . The OH yield was determined by titration with CO and detection of the  $\text{CO}_2$  product.
- (n) Shock wave study of hydrazine decomposition in the presence of NO at pressures in the range 0.17–4.27 bar.  $[\text{NH}_2]$ ,  $[\text{NH}]$ , and  $[\text{OH}]$  were monitored by narrow line absorption detection at 597.365, 336.100, and 308.417 nm, respectively, and  $[\text{H}]$  and  $[\text{O}]$  by ARAS at 121.6 nm and 130.4 nm. The branching ratio for Channel (5) was determined to be 3% at 1583 K and 9% at 2116 K. The expression given in the Table for branching ratio is our fit to the experimental data. Individual data points are shown in the figure.
- (o) Basically the same technique was used in the two shock tube studies of Song *et al.*<sup>15,16</sup> In the first of them<sup>15</sup> reflected shock waves in  $\text{CH}_3\text{NH}_2/\text{NO}/\text{Ar}$  mixtures at pressures in the range 1.00–1.38 bar were used and the study covered the temperature range 1716–2507 K. In the second,<sup>16</sup>  $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$  was used as the source of  $\text{NH}_2$  radicals instead of  $\text{CH}_3\text{NH}_2$ , which allowed a lower temperature range to be investigated (1263–1726 K), and the pressure range was 1.14–1.45 bar.  $[\text{NH}_2]$  was monitored by frequency modulated absorption spectroscopy at  $16739.79 \text{ cm}^{-1}$ . Detailed kinetic modeling was used to simulate the  $[\text{NH}_2]$  profiles and values of the rate constant were obtained from the change in the profiles in the presence and absence of NO. In the first study<sup>15</sup> the cited expression for  $k$  the authors combine their data with low temperature data to give the expression cited. The expression cited in the Table for the second study<sup>16</sup> is a fit, derived by the authors, to their own data from the two studies<sup>15,16</sup> and the lower temperature data of Wolf *et al.*<sup>13</sup>
- (p) Pulsed laser photolysis of  $\text{NH}_3/\text{NO}$  mixtures at 193 nm.  $[\text{NH}_3]$ ,  $[\text{NH}_2]$ ,  $[\text{OH}]$ , and  $[\text{H}_2\text{O}]$  were monitored by infrared absorbance. The total pressure was 23 mbar. The mass balance based on OH and  $\text{H}_2\text{O}$  yields ranged from 70% to 94% at 1173 K.
- (q) Pyrolysis of  $\text{NH}_3/\text{NO}$ , and  $\text{NH}_3/\text{NO}/\text{CO}$  mixtures in argon in a quartz reactor.  $[\text{NH}_3]$ ,  $[\text{NO}]$ ,  $[\text{CO}]$ , and  $[\text{CO}_2]$  were monitored by FTIR. The total pressure was near to 1 bar, with Ar as the bath gas. Branching ratios were obtained from modeling using a detailed mecha-

- nism. The results from this study and from the studies of Park and Lin<sup>19,29</sup> were later reinterpreted to accommodate changes in the model. See Comment (dd).
- (r) Pulsed laser photolysis of NH<sub>3</sub>/NO/He mixtures at 193 nm and total pressures in the range 7–13 mbar. Branching ratios were determined from mass spectrometric detection of NH<sub>2</sub>, H<sub>2</sub>O, and CO<sub>2</sub>. The OH yield was determined by reaction with CO and measurement of the CO<sub>2</sub> produced.
- (s) Pulsed laser photolysis of NH<sub>3</sub>/NO mixtures at 193 nm and 1.3 mbar SF<sub>6</sub> total pressure. [H<sub>2</sub>O] and [NO] were monitored by infrared laser absorption.
- (t) Pyrolysis in a quartz flow reactor of NH<sub>3</sub>/NO/O<sub>2</sub> and CO/NH<sub>3</sub>/NO/O<sub>2</sub> mixtures. Low oxygen concentrations were employed to reduce complications of secondary reactions. Total pressures were in the range 1.12–1.27 bar of the N<sub>2</sub> carrier gas. [NO], [CO], [CO<sub>2</sub>] were determined spectrophotometrically and [O<sub>2</sub>] paramagnetically. Branching ratios were derived by kinetic modeling with a 318 reaction mechanism.<sup>29</sup> This work supersedes the studies of Kasuya *et al.*<sup>30</sup> and Kjargaad *et al.*<sup>31</sup> The expression given in table for branching ratio is our fit to experimental data. Individual data points are shown in the figure.
- (u) Shock tube study with generation of NH<sub>2</sub> from NH<sub>3</sub> by laser photolysis. [NH<sub>2</sub>] was monitored by frequency-modulation laser absorption spectroscopy. Branching ratios were determined from shape of NH<sub>2</sub> concentration profile as a function of time.
- (v) Reevaluation of the authors previous work, Votsmeier *et al.*<sup>22</sup> making use of the new values of *k* from the authors' latest study<sup>16</sup> shows that the branching ratios are in good agreement with the calculated values of Miller and Klippenstein.<sup>39</sup> Expressions quoted are calculated using the branching ratios of Miller and Klippenstein<sup>39</sup> and the authors' values of *k*.
- (w) Measurement of [NH<sub>2</sub>] by frequency modulation absorption behind reflected shock waves in monomethylamine (CH<sub>3</sub>NH<sub>2</sub>)/NH<sub>3</sub>/NO/Ar mixtures at pressures in the range 1.1–1.2 bar. The branching ratio was determined by kinetic modeling with a detailed, 125-reaction, mechanism with the branching ratio as a fitting parameter. The resulting branching ratios are consistent with the calculated values of Miller and Klippenstein<sup>39</sup> and the previous experimental determination of Votsmeier *et al.*<sup>22</sup>
- (x) Evaluation of work up to 1991. The preferred room temperature rate coefficient is based on data of Drier and Wolfrum,<sup>2</sup> Silver and Kolb,<sup>33</sup> Whyte and Phillips,<sup>4</sup> Stief *et al.*,<sup>1</sup> Andresen *et al.*,<sup>3</sup> Gordon *et al.*,<sup>34</sup> Hancock *et al.*,<sup>35</sup> Sarkisov *et al.*,<sup>36</sup> Lesclaux *et al.*,<sup>37</sup> and Hack *et al.*<sup>38</sup> The preferred temperature dependence is based on the work of Atakan *et al.*,<sup>6</sup> Silver and Kolb,<sup>33</sup> Stief *et al.*,<sup>1</sup> Lesclaux *et al.*,<sup>37</sup> and Hack *et al.*<sup>38</sup>
- (y) RRKM fit of experimental results to permit extrapolation to higher temperatures. See comment (h).
- (z) General analysis of the kinetics of thermal deNO<sub>x</sub>, the significance of the branching ratio, and its relationship to molecular properties.
- (aa) Similar, but more rigorous, RRKM treatment to that in (y). The available data could be fitted, but the profile of the branching ratio temperature dependence could not be reproduced. This point is discussed by Miller and Klippenstein.<sup>39</sup>
- (ab) Extensive review of low temperature data to derive expressions for use in atmospheric modeling. Recommendation based on the room temperature data of Hancock *et al.*,<sup>35</sup> Lesclaux *et al.*,<sup>37</sup> Sarkisov *et al.*,<sup>36</sup> Stief *et al.*,<sup>1</sup> Andresen *et al.*,<sup>3</sup> Whyte and Phillips,<sup>4</sup> Drier and Wolfrum,<sup>2</sup> Atakan *et al.*,<sup>40</sup> Wolf *et al.*,<sup>10</sup> Diau *et al.*,<sup>8</sup> and Imamura and Washida.<sup>41</sup> The temperature dependence is taken from the study of Stief *et al.*<sup>1</sup>
- (ac) Extensive review of low temperature data to derive expressions for use in atmospheric modeling. Recommend room temperature rate coefficient based on the results of Gehring *et al.*,<sup>42</sup> Lesclaux *et al.*,<sup>37</sup> Hancock *et al.*,<sup>35</sup> Sarkisov *et al.*,<sup>36</sup> Hack *et al.*,<sup>38</sup> Steif *et al.*,<sup>1</sup> Silver and Kolb,<sup>33</sup> Andresen *et al.*,<sup>3</sup> Whyte and Phillips,<sup>4</sup> Drier and Wolfrum,<sup>2</sup> Atakan *et al.*,<sup>6,40</sup> Bulatov *et al.*,<sup>5</sup> Wolf *et al.*,<sup>10</sup> and Diau *et al.*<sup>8</sup> Temperature dependence from studies of Lesclaux *et al.*,<sup>37</sup> Hack *et al.*,<sup>38</sup> Steif *et al.*,<sup>1</sup> Silver and Kolb,<sup>33</sup> Atakan *et al.*,<sup>6,40</sup> and Bulatov *et al.*<sup>5</sup> Branching ratio based on the data of Atakan *et al.*,<sup>6,40</sup> Stephens *et al.*,<sup>17</sup> and Park and Lin.<sup>12</sup>
- (ad) Results from previous studies by the authors<sup>12,19</sup> were reinterpreted using an alternative value for the rate constant of the reaction OH+NH<sub>3</sub>→NH<sub>2</sub>+H<sub>2</sub>O which plays an important role in their model. Their new values of the branching ratios derived were combined with those of Glarborg *et al.*<sup>21,25</sup> and Votsmeier *et al.*<sup>22</sup> to obtain the expression for (k<sub>3</sub>+k<sub>4</sub>)/*k* cited in the Table. The values from this expression were combined with values of the overall rate constant from the study of Park and Lin<sup>12</sup> to obtain the expressions cited for (k<sub>3</sub>+k<sub>4</sub>) and k<sub>1</sub>.

### Preferred Values

$k = 1.14 \cdot 10^{-8} T^{-1.203} \exp(106/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 200–2500 K.

$(k_3+k_4)/k = 0.7 + 3.36 \cdot 10^{-4}(T - 1600); \quad k_1/k \leq 1 - [(k_3+k_4)/k]$  over the range 600–2200 K.

### Reliability

$\Delta \log k = \pm 0.1$  over the range 200–2500 K.

$\Delta[(k_3+k_4)/k] = \pm 0.05$  over the range 600–2200 K.

### Comments on Preferred Values

This reaction is of great importance in thermal deNO<sub>x</sub>, hence the large number of measurements that have now accumulated.

Below 1000 K the rate coefficient is now reasonably well defined by the data from Refs. 1–8, 10–13 on which the preferred values are based. The older data of Gordon *et al.*,<sup>34</sup> Hancock *et al.*,<sup>35</sup> Kaskan and Hughes,<sup>43</sup> Gericke *et al.*,<sup>44</sup> and Sarkisov *et al.*,<sup>36</sup> which are not cited in the Table, also support our preferred expression, but those of Gehring *et al.*,<sup>42</sup> Kurasawa and Lesclaux,<sup>45</sup> Hack *et al.*,<sup>38</sup> Silver and Kolb,<sup>33</sup> Jeffries *et al.*,<sup>46</sup> and Gersh *et al.*<sup>47</sup> differ significantly from the recommendations.

At temperatures greater than 1000 K the data of Roose *et al.*<sup>48</sup> are very scattered and the studies of Vandooren *et al.*,<sup>9</sup> Fenimore,<sup>49</sup> Morley,<sup>50</sup> and Bian *et al.*<sup>51</sup> suggest that the rate constant shows a sharp increase with temperature at  $T \sim 1500$  K. However it is notable that the calculations of Diau and Smith,<sup>25</sup> and Miller and Klippenstein<sup>38</sup> do not reproduce this upturn in  $k$  at high temperatures and this is supported by results from the studies of Song *et al.*<sup>15,16</sup> and the more scattered data of Deppe *et al.*<sup>14</sup> The preferred values in this temperature region are based on the studies of Song *et al.*<sup>15,16</sup>

The major reaction channels are Channel (1) and those leading to OH radicals, i.e., Channel (4) leading on to Channel (3) following decomposition of the relatively unstable N<sub>2</sub>H. There is no experimental evidence for any significant contribution from other channels. The branching ratio between the radical producing and nonradical producing channels, particularly its variation with temperature, is of major importance and has been the subject of numerous studies. The results on this branching ratio,  $(k_3 + k_4)/k$  are shown in Fig. 2. It is clear that OH production begins to increase steadily at temperatures above about 600 K and this increase continues to temperatures above 2500 K. The increasing OH yield with temperature is compatible with the observed deNO<sub>x</sub> results, and the theoretical calculations<sup>25,38</sup> also predict a large increase in OH production at higher temperatures.

The branching ratios are now reasonably well defined at temperatures in the range 600–2200 K by the studies of Park and Lin,<sup>12,19,28</sup> Glarborg *et al.*,<sup>21</sup> Halbgewachs *et al.*,<sup>18</sup> Votsmeier *et al.*,<sup>22</sup> and Song *et al.*<sup>23</sup> The data of Park and Lin<sup>12,19</sup> and Halbgewachs *et al.*<sup>18</sup> originally suggested that there was a marked increase in the branching at  $T > 1200$  K but these studies have been reinterpreted by Park and Lin<sup>28</sup> to yield lower values. The expression originally derived by Votsmeier *et al.*<sup>22</sup> for the range 1340–1670 K is adopted as our preferred expression over the extended range 600–2200 K. It provides a good fit to the data over this temperature range but it should not be used outside that range, since it is clear both from the available data and from the theoretical studies, that it will predict values of  $(k_3 + k_4)/k$  too high at higher temperatures and too low at lower temperatures. At temperatures below 600 K the branching ratio,  $(k_3 + k_4)/k$ , decreases in value more slowly with decreasing temperature from a value of  $\sim 0.16$  at 600 K to  $\sim 0.1$  at 298 K.<sup>12,28</sup>

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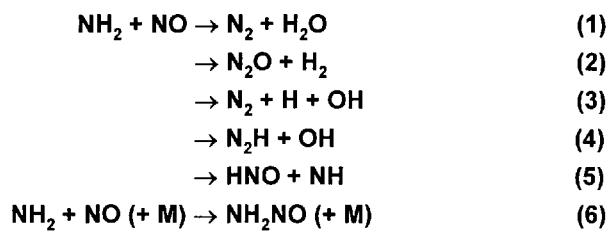
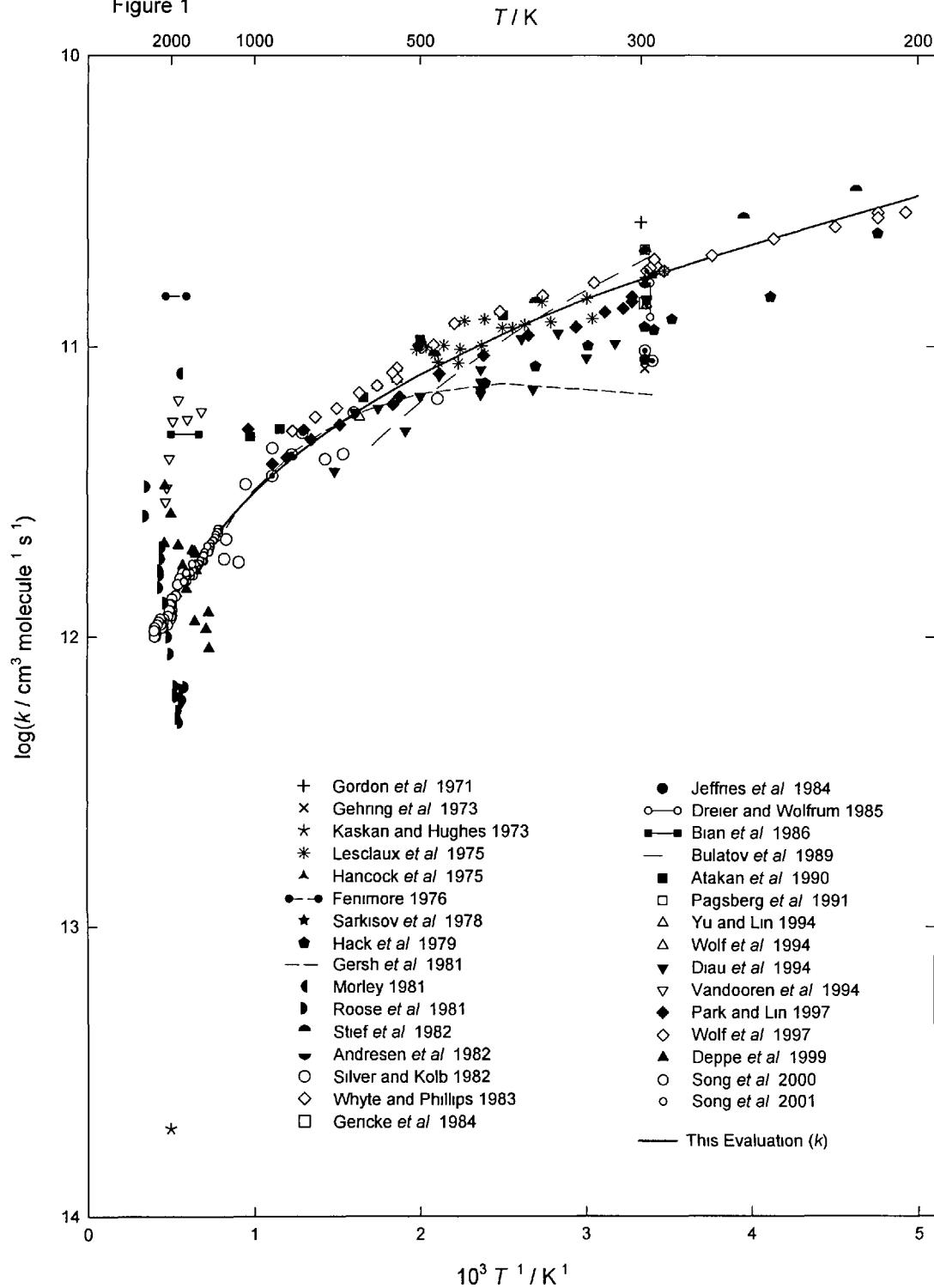


Figure 1



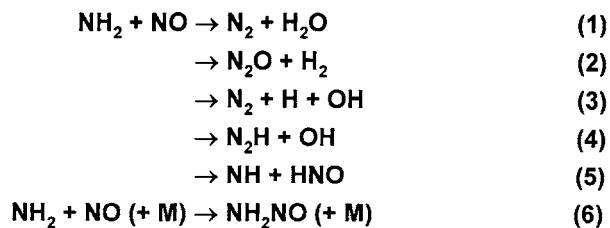
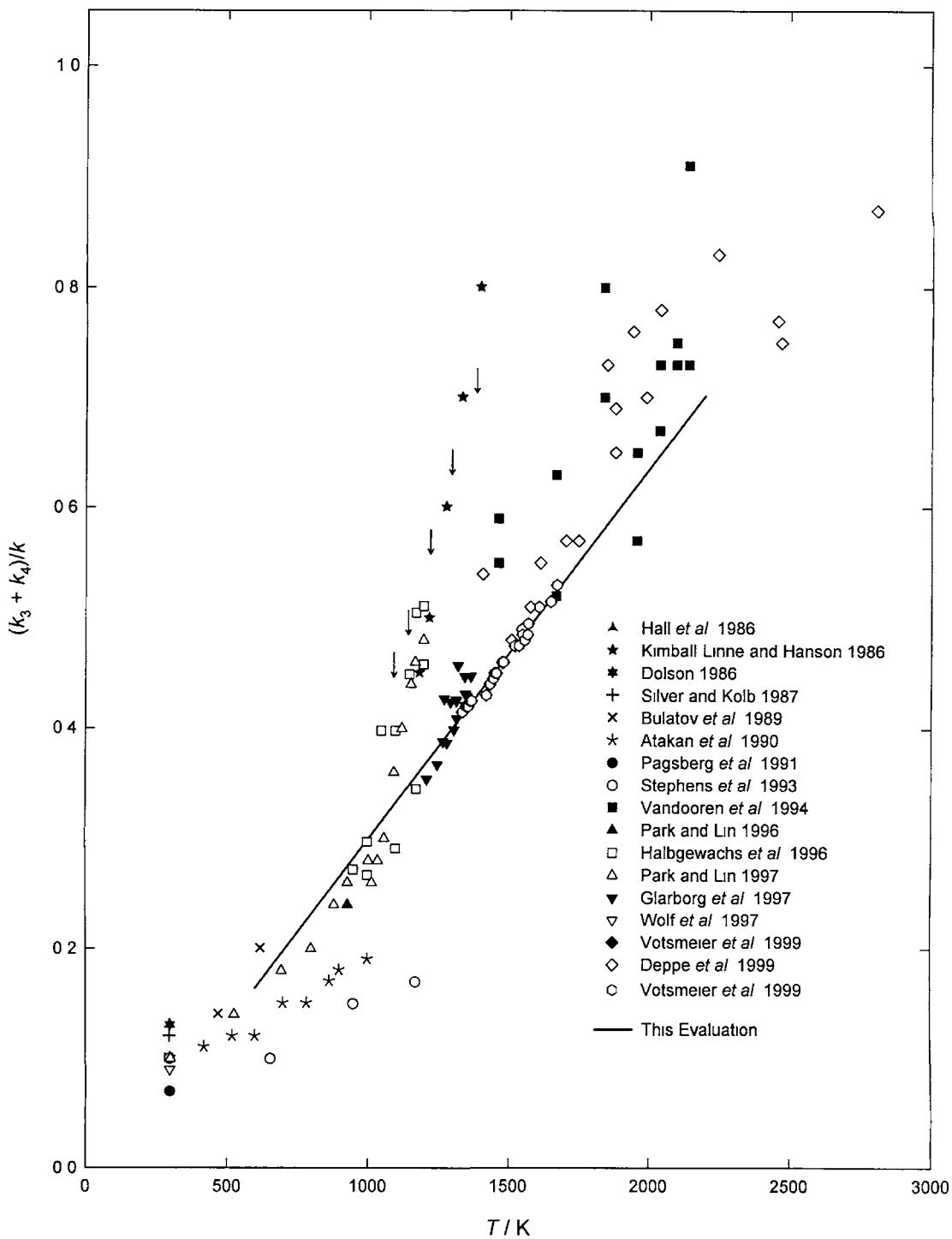
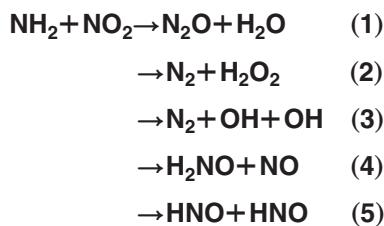


FIGURE 2



*Thermodynamic Data*

$$\begin{aligned}
 \Delta H^\circ_{298}(1) &= -382.4 \text{ kJ mol}^{-1} \\
 \Delta S^\circ_{298}(1) &= -25.8 \text{ J K}^{-1} \text{ mol}^{-1} \\
 K_c(1) &= 8.2 \cdot 10^{-3} T^{0.251} \exp(+46070/T) \\
 &(300 \leq T/\text{K} \leq 5000)
 \end{aligned}$$

$$\begin{aligned}
 \Delta H^\circ_{298}(3) &= -148.4 \text{ kJ mol}^{-1} \\
 \Delta S^\circ_{298}(3) &= 124.4 \text{ J K}^{-1} \text{ mol}^{-1} \\
 K_c(3) &= 5.7 \cdot 10^{28} T^{-0.991} \exp(+17520/T) \text{ molecule cm}^{-3} \\
 &(300 \leq T/\text{K} \leq 5000)
 \end{aligned}$$

$$\begin{aligned}
 \Delta H^\circ_{298}(5) &= 3.21 \text{ kJ mol}^{-1} \\
 \Delta S^\circ_{298}(5) &= 6.69 \text{ J K}^{-1} \text{ mol}^{-1} \\
 K_c(5) &= 2.0 T^{0.009} \exp(-374/T) \\
 &(300 \leq T/\text{K} \leq 5000)
 \end{aligned}$$

$$\begin{aligned}
 \Delta H^\circ_{298}(2) &= -358.9 \text{ kJ mol}^{-1} \\
 \Delta S^\circ_{298}(2) &= -8.50 \text{ J K}^{-1} \text{ mol}^{-1} \\
 K_c(2) &= 0.223 T^{0.075} \exp(+43180/T) \\
 &(300 \leq T/\text{K} \leq 5000)
 \end{aligned}$$

$$\begin{aligned}
 \Delta H^\circ_{298}(4) &= -77.8 \text{ kJ mol}^{-1} \\
 \Delta S^\circ_{298}(4) &= 10.19 \text{ J K}^{-1} \text{ mol}^{-1} \\
 K_c(4) &= 1.10 \cdot 10^{-4} T^{1.512} \exp(+9890/T) \\
 &(300 \leq T/\text{K} \leq 5000)
 \end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data ( $k = k_1 + k_2 + k_3 + k_4 + k_5$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
$3.2 \cdot 10^{-4} T^{-3.0}$	250–500	Hack <i>et al.</i> , 1979 <sup>1</sup>	(a)
$3.8 \cdot 10^{-8} T^{-1.30}$	298–505	Kurasawa and Lesclaux, 1979 <sup>2</sup>	(b)
$2.11 \cdot 10^{-11}$	297	Whyte and Phillips, 1983 <sup>3</sup>	(c)
$2.26 \cdot 10^{-11}$	298	Xiang, Torres, and Guillory, 1985 <sup>4</sup>	(d)
$3.38 \cdot 10^{-7} T^{-1.7}$	295–620	Bulatov <i>et al.</i> , 1989 <sup>5</sup>	(e)
$1.8 \cdot 10^{-11}$	298	Pagsberg <i>et al.</i> , 1991 <sup>6</sup>	(f)
$1.35 \cdot 10^{-11}$	298	Meunier, Pagsberg, and Sillesen, 1996 <sup>7</sup>	(g)
$1.35 \cdot 10^{-7} T^{-1.44} \exp(-135/T)$	300–910	Park and Lin, 1997 <sup>8</sup>	(h)
$9.1 \cdot 10^{-12}$	1335–1527	Song <i>et al.</i> , 2002 <sup>9</sup>	(i)
<i>Branching Ratio Measurements</i>			
$k_1/k = 0.95$	298	Hack <i>et al.</i> , 1979 <sup>1</sup>	(a)
$k_1/k = 0.59 \pm 0.03$	298	Meunier, Pagsberg, and Sillesen, 1996 <sup>7</sup>	(g)
$k_4/k = 0.40 \pm 0.05$			
$k_1/k = 0.19 \pm 0.02$	300–900	Park and Lin, 1996 <sup>10</sup>	(j)
$k_1/k = 0.14 \pm 0.02$	298	Quandt and Hershberger, 1996 <sup>11</sup>	(k)
$k_1/k = 0.24 \pm 0.04$	298	Lindholm and Hershberger, 1997 <sup>12</sup>	(l)
$k_4/k = 0.76 \pm 0.1$	298		
$k_1/k = 0.17 \pm 0.04$	1319–1493	Song <i>et al.</i> , 2002 <sup>9</sup>	(i)
<i>Reviews and Evaluations</i>			
$2.1 \cdot 10^{-12} \exp(650/T)$	250–510	NASA, 1997 <sup>13</sup>	(m)
$1.78 \cdot 10^{-6} T^{-2.0}$	250–500	IUPAC, 1997 <sup>14</sup>	(n)

**Comments**

- (a) Discharge flow study in which NH<sub>2</sub> radicals were produced by the F+NH<sub>3</sub> reaction in He carrier gas at pressures of a few mbar. [NH<sub>2</sub>] was monitored by time-resolved LIF at 598 nm. Product yields were studied in a separate flow system by mass spectrometry; 95% of the reaction appears to proceed by Channel (1).
- (b) Repetitive flash photolysis of NH<sub>3</sub>/NO<sub>2</sub>/He mixtures at total pressures in the range 4–14 mbar. [NH<sub>2</sub>] monitored by time resolved LIF at 597.7 nm.

- (c) Pulsed laser photolysis at 193 nm of NH<sub>3</sub>/NO<sub>2</sub>/He mixtures at total pressure of 2–3 mbar. [NH<sub>2</sub>] monitored by time-resolved LIF at 598 nm.
- (d) Pulsed infrared multiphoton dissociation NH<sub>3</sub>, CH<sub>3</sub>NH<sub>2</sub>, or N<sub>2</sub>H<sub>4</sub> used for NH<sub>2</sub> production in the presence of NO<sub>2</sub> and Ar at total pressures in the range 2–13 mbar. State selected NH<sub>2</sub> concentration monitored by time-resolved LIF at 533 nm. The rate constant for NH<sub>2</sub> ( $v''=1$ ) was also measured and found to be less than that for ground state NH<sub>2</sub>.
- (e) Flash photolysis of NH<sub>3</sub>/NO<sub>2</sub>/N<sub>2</sub> mixtures at total

- pressures in the range 13–860 mbar.  $[\text{NH}_2]$  monitored by time-resolved intracavity absorption.  $k$  independent of pressure in the range covered.
- (f) Pulse radiolysis, using 2 MeV electrons, of  $\text{Ar}/\text{SF}_6/\text{NH}_3/\text{NO}_2$  mixtures at a total pressure of 1 bar.  $[\text{NH}_2]$  monitored by time-resolved absorption at 597.6 nm in a multipass cell. Monitoring of transient OH absorption at 309 nm suggests only a very small contribution from Channel (3).
- (g) Technique as in (f) but a lower pressure (40 mbar) was used and  $[\text{NH}_2]$ ,  $[\text{N}_2\text{O}]$ , and  $[\text{NO}]$  were monitored by time-resolved infrared diode laser spectroscopy. Cited value of  $k$  is based on the  $[\text{NH}_2]$  kinetics. Values calculated from the growth of  $[\text{N}_2\text{O}]$  and of  $[\text{NO}]$  are in good agreement.
- (h) Pulsed laser photolysis at 193 nm of  $\text{NH}_3/\text{NO}_2/\text{He}$  mixtures at total pressures in the range 1.7–11 mbar.  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{N}_2\text{O}$ ,  $\text{NO}_2$ , and  $\text{O}_2$  were detected by quadrupole mass spectrometry. Values of  $k$  were obtained from the concentration profiles of the reactant ( $\text{NO}_2$ ) decay and from the formation of  $\text{H}_2\text{O}$  and  $\text{N}_2\text{O}$ . Substantial modeling was used to correct for effects of secondary chemistry. Branching ratios are based on the  $\text{N}_2\text{O}$  yields and the values of  $k$  measured in this study.
- (i) Reflected shock waves experiments in benzylamine ( $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2/\text{NO}_2/\text{Ar}$ ) mixtures at total pressures in the range 1.3–1.5 bar. Pyrolysis of benzylamine serves as the  $\text{NH}_2$  source.  $[\text{NH}_2]$  profiles were measured using frequency modulation absorption spectroscopy. Values of  $k$  were determined by fitting the  $[\text{NH}_2]$  profiles with a detailed mechanism. Experimental conditions were chosen to emphasize the sensitivity of the  $[\text{NH}_2]$  profiles to the  $k$  value. Branching ratios were measured by  $\text{N}_2\text{O}$  detection using IR emission near 4.5  $\mu\text{m}$ .
- (j) Technique as in (h). Branching ratios based on the  $\text{N}_2\text{O}$  yields. The value of  $k_1/k$  derived depends on the expression for  $k$  used in the modeling. Expression for  $k$  of Glarborg *et al.*<sup>15</sup> used.
- (k) Pulsed laser photolysis at 193 nm of  $\text{NH}_3/\text{NO}_2/\text{SF}_6$  mixtures at total pressures of ~1.5 mbar.  $[\text{N}_2\text{O}]$ ,  $[\text{NO}]$ , and  $[\text{H}_2\text{O}]$  were monitored by time-resolved infrared diode laser absorption spectroscopy. Large yields of NO are produced by secondary chemistry precluding determination of  $k_4/k$ .
- (l) Technique basically as in (k) but  $\text{NH}_2$  generated by photolysis of ICN at 248 nm in the presence of  $\text{NH}_3$ , leading to the fast reaction  $\text{CN} + \text{NH}_3 \rightarrow \text{HCN} + \text{NH}_2$ .
- (m) Based on the studies of Hack *et al.*,<sup>1</sup> Kurasawa and Lesclaux,<sup>2</sup> Whyte and Phillips,<sup>3</sup> and Xiang *et al.*<sup>4</sup>
- (n) Value of  $k(298\text{ K})$  is a mean of the values of Hack *et al.*,<sup>1</sup> Kurasawa and Lesclaux,<sup>2</sup> Whyte and Phillips,<sup>3</sup> Xiang *et al.*,<sup>4</sup> and Bulatov *et al.*<sup>5</sup> The temperature dependence is from the studies of Hack *et al.*,<sup>1</sup> Kurasawa and Lesclaux,<sup>2</sup> and Bulatov *et al.*<sup>5</sup>

### Preferred Values

$k = 1.38 \cdot 10^{-9} T^{-0.74} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 300–1600 K.

$k_1/k = 0.20$  over the range 300–1600 K.

### Reliability

$\Delta \log k = \pm 0.1$  at 300 K, rising to  $\pm 0.4$  at 1600 K.

$\Delta(k_1/k) = \pm 0.05$  over the range 300–1600 K.

### Comments on Preferred Values

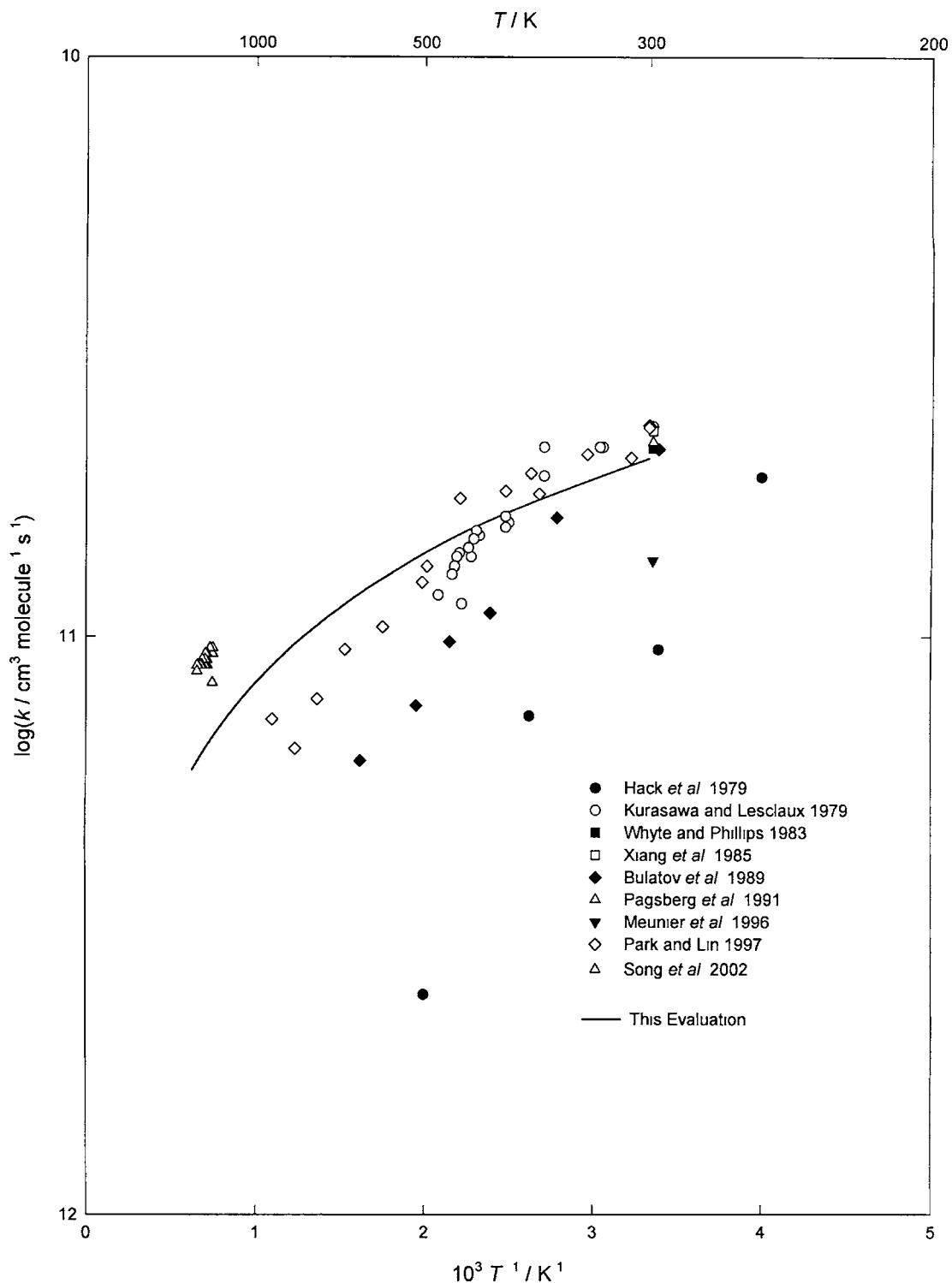
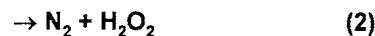
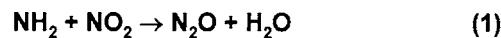
The value of  $k$  obtained by Hack *et al.*<sup>1</sup> at 298 K using a discharge flow technique is significantly lower than the values obtained in all of the other studies which used either pulsed photolysis<sup>2–5,8</sup> or pulse radiolysis.<sup>6,7</sup> This discrepancy increases at higher temperatures and it may be significant that a similar difference between discharge-flow and pulsed photolysis results has been noted for the reaction of  $\text{NH}_2$  with NO. One of the pulse radiolysis studies<sup>7</sup> also gives a value some 40% lower than the other studies<sup>2–5,7,8</sup> which, otherwise, are in excellent agreement. The preferred value of  $k$  at 298 K is  $2.2 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  based on the studies of Kurasawa and Lesclaux,<sup>2</sup> Whyte and Phillips,<sup>3</sup> Xiang *et al.*,<sup>4</sup> Bulatov *et al.*,<sup>5</sup> Pagsberg *et al.*,<sup>6</sup> and Park and Lin.<sup>8</sup>

There are also substantial differences in the temperature dependence of  $k$ . The results of Kurasawa and Lesclaux<sup>2</sup> and of Park and Lin<sup>8</sup> are in excellent agreement. However, the shock tube study of Song *et al.*<sup>9</sup> yields a  $k$  value that is higher than that obtained by the extrapolation of the Park and Lin<sup>8</sup> data. The temperature dependence of the preferred expression is based on a combination of the lower temperature data of Park and Lin<sup>8</sup> and Kurasawa and Lesclaux,<sup>2</sup> and the higher temperature data of Song *et al.*<sup>9</sup> Sufficiently large error limits are assigned to accommodate the results of Bulatov *et al.*<sup>5</sup> at high temperatures but the results of Hack *et al.*<sup>1</sup> fall outside these limits.

Theoretical treatments<sup>16</sup> of the reaction mechanism suggest that Channels (1) and (4) are the most likely and the experimental studies confirm this qualitatively. However, the quantitative agreement on the branching ratios is poor. The early study by Hack *et al.*<sup>1</sup> suggested that Channel (1) should predominate to the extent of 95% of the total reaction but more recent studies<sup>9–12</sup> suggest a much lower value with Channel (4) predominating. Glarborg *et al.*<sup>15</sup> studied the  $\text{NH}_3/\text{NO}_2$  reaction in a flow reactor over the range 850–1350 K and, from their modeling of the changes in reactant and product concentrations, concluded that Channel (1) predominates at low temperatures while Channel (4) is the more important at high temperatures. The preferred value of the branching ratio is based on the consistent results of Song *et al.*,<sup>9</sup> Park and Lin,<sup>10</sup> Quandt and Hershberger,<sup>11</sup> and Lindholm and Hershberger.<sup>12</sup> The results of Meunier *et al.*<sup>7</sup> fall well outside the preferred error limits.

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#### Thermodynamic Data

$$\begin{aligned}\Delta H^\circ_{298}(1) &= -578.1 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(1) &= -4.55 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 2.56 T^{-0.209} \exp(+69430/T) \\ &(300 \leq T/\text{K} \leq 5000)\end{aligned}$$

$$\begin{aligned}\Delta H^\circ_{298}(2) &= -388.3 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(2) &= -8.90 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 1.69 T^{-0.226} \exp(+46610/T) \\ &(300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$2.6 \cdot 10^{-11}$	298	Husain and Young, 1975 <sup>1</sup>	(a)
$4.7 \cdot 10^{-11}$	298	Becker, Brockmann, and Wiesen, 1988 <sup>2</sup>	(b)
$2.0 \cdot 10^{-10} \exp(-2010/T)$	1525–2540	Dean, Davidson, and Hanson, 1991 <sup>3</sup>	(c)
$2.5 \cdot 10^{-11}$	298	Bergeat <i>et al.</i> , 1999 <sup>4</sup>	(d)
$3.0 \cdot 10^{-10} T^{-0.32}$	15–295	Geppert <i>et al.</i> , 2000 <sup>5</sup>	(e)

#### Comments

- (a) C atoms generated in the presence of O<sub>2</sub> by repetitive flash photolysis of C<sub>3</sub>O<sub>2</sub> in a flow of He at wavelengths down to  $\sim 105$  nm. [C(<sup>3</sup>P)] monitored by optical absorption at 166 nm. The value of the rate constant obtained is significantly lower than that from earlier studies<sup>7</sup> in the same laboratory. The difference is attributed to secondary reactions produced by the higher flash energies used in the earlier “single shot” experiments.
- (b) Pulsed laser photolysis at 248 nm of slowly flowing CH<sub>2</sub>Br<sub>2</sub>/O<sub>2</sub>/He mixtures at total pressures of 2.6 mbar. [C(<sup>3</sup>P)] monitored by time-resolved two-photon LIF at 143.5 nm in the presence of a large excess of O<sub>2</sub>.
- (c) Reflected shock waves in C<sub>3</sub>O<sub>2</sub>/O<sub>2</sub>/Ar mixtures. For the kinetics experiments at  $T > 2300$  K, C atoms were formed by pyrolysis of C<sub>3</sub>O<sub>2</sub> while at  $T < 2050$  K they were produced by ArF laser photolysis of the C<sub>3</sub>O<sub>2</sub> in the shock heated gas. [C(<sup>3</sup>P)] monitored by atomic absorption spectroscopy at 156 nm.
- (d) Fast flow discharge system with C atom generated by reaction of K vapor with CCl<sub>4</sub> or CBr<sub>4</sub> in a stream of He carrier gas. [C] was monitored by resonance fluorescence at 156.11 nm or 165.72 nm in the presence of a large excess of O<sub>2</sub>. The authors suggest that the value of  $k$  obtained in this study is to be preferred to that obtained by Dorthe *et al.*<sup>6</sup> in the same laboratory because of the more direct detection method used.
- (e) Low temperatures were achieved by isentropic expansion of gas mixtures through a Laval nozzle. The mixtures consisted of the carrier gas (He, Ar, or N<sub>2</sub>) containing a small concentration of C<sub>3</sub>O<sub>2</sub> and varying amounts of O<sub>2</sub>. C(<sup>3</sup>P) atoms were produced in the flow by laser photolysis at 193 nm of the C<sub>3</sub>O<sub>2</sub>.

[C(<sup>3</sup>P<sub>J</sub>)] was monitored by time-resolved vacuum-ultraviolet laser-induced fluorescence. The results from this study were combined with those from earlier studies<sup>7,8</sup> to give the expression cited. In the earlier study the [C(<sup>3</sup>P<sub>J</sub>)] was monitored by the chemiluminescence produced by addition of a small concentration of NO<sub>2</sub> to the gas flow, which leads to the reaction C(<sup>3</sup>P<sub>J</sub>) + NO<sub>2</sub> → CO + NO, producing electronically excited NO. The results from the two studies were in good agreement.

#### Preferred Values

$k = 1.0 \cdot 10^{-10} \exp(-320/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 298–4000 K.

#### Reliability

$\Delta \log k = \pm 0.15$  at 298 K, rising to  $\pm 0.5$  at 4000 K.

#### Comments on Preferred Values

There have been a number of measurements of the rate constant of this reaction at ambient temperatures by both pulsed photolysis<sup>1,5,7–10</sup> and fast-flow<sup>4,6,11</sup> techniques. There are three studies using flash-lamp photolysis<sup>1,9,10</sup> the most recent of which gives a significantly lower value of  $k$  than the other two.<sup>9,10</sup> This later study,<sup>1</sup> which used much lower flash energies and improved detection techniques, is considered the most reliable of the three.

There are three fast flow studies.<sup>4,6,11</sup> The earliest of these<sup>11</sup> used relatively high pressures (80 mbar), with gas chromatographic product detection, and yielded only an approximate value of  $k$ . The other two studies are from the same laboratory. The more recent of the two<sup>4</sup> is considered the more reliable because of the more direct detection technique used. The pulsed laser studies<sup>2,5,7–9</sup> are in good agree-

ment but the value of  $k(298\text{ K})$  which they give ( $4.5 \cdot 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ ) is significantly higher than the most reliable of the broad-band flash photolysis studies ( $3.3 \cdot 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ ) and the fast flow studies ( $2.5 \cdot 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ ). The reason for this is not clear.

At high temperatures the only study is that of Dean *et al.*<sup>3</sup> over the range 1525–2540 K. The expression obtained for  $k$ , if extrapolated to 300 K, gives an extremely low value ( $k = 2.5 \cdot 10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  at 300 K) quite incompatible with the measured values at this temperature, but perhaps not surprising in view of the long extrapolation. It is likely that there is substantial uncertainty in the temperature coefficient derived by Dean *et al.*<sup>3</sup> although the absolute values of  $k$  may be reasonable.

To obtain the preferred expression for  $k$  we have fixed the value of  $k$  at 298 K by taking the mean of the results from Husain and Young,<sup>1</sup> Bergeat *et al.*,<sup>4</sup> and Geppert *et al.*,<sup>5</sup> and combined it with a temperature coefficient to produce an Arrhenius expression which gives values of  $k$  compatible with the high temperature results of Dean *et al.*<sup>3</sup> There is some further support for this procedure from the theoretical treatment of the reaction by Kinnersly and Murrell<sup>12</sup> whose calculated values of  $k$  give  $E/R = 130\text{ K}$  over the range 300–800 K and absolute values of  $k$  in reasonable agreement with our preferred expression.

Donovan and Husain<sup>13</sup> constructed a correlation diagram for the reaction demonstrating that there are symmetry allowed pathways to form both  $\text{O}({}^3\text{P})$  or  $\text{O}({}^1\text{D})$ . Ogryzlo *et al.*,<sup>14</sup> by monitoring the vibrational population of the CO produced, concluded that  $\text{O}({}^1\text{D})$  production was the dominant channel, and subsequent studies have supported this, but

there are no definitive measurements of the branching ratios.

There is no evidence that  $k$  is pressure dependent and Dubrin *et al.*<sup>15</sup> found no evidence for  $\text{CO}_2$  formation even in liquid oxygen. It was therefore suggested that the reaction occurs via terminal attack to give OOC and this configuration was used by Kinnersly and Murrell<sup>12</sup> as the basis of their theoretical treatment.

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#### Thermodynamic Data

$$\begin{aligned}\Delta H_{298}^{\circ}(1) &= 191.4 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ}(1) &= 6.22 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 0.644 \cdot T^{0.161} \exp(-22930/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

$$\begin{aligned}\Delta H_{298}^{\circ}(2) &= -145.6 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ}(2) &= -117.87 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 3.90 \cdot 10^{-29} T^{1.075} \exp(+17670/T) \text{ cm}^3 \text{ molecule}^{-1} \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$k_2 = 3.1 \cdot 10^{-33} [\text{Ar}]$	300	Husain and Kirsch, 1971 <sup>1</sup>	(a)
$k_1 = 7.5 \cdot 10^{-11} \exp(-22000/T)$	2720–3810	Lindackers, Burmeister, and Roth, 1990 <sup>2</sup>	(b)
$k_1 = 1.05 \cdot 10^{-10} \exp(-23160/T)$	2660–4660	Dean, Hanson, and Bowman, 1990 <sup>3</sup>	(c)
<i>Reviews and Evaluations</i>			
$k_1 = 8.69 \cdot 10^{-11} \exp(-22600/T)$	2000–5000	CEC, 1994 <sup>4</sup>	(d)

#### Comments

- (a) C atoms generated by flash photolysis of  $\text{C}_2\text{O}_3$  (at  $\lambda \approx 160 \text{ nm}$ ) were monitored by VUV resonant emission at 166 nm. Experiments conducted in 0.2–0.7 bar Ar bath gas.
- (b) The experiments were conducted behind reflected shock waves in the temperature range 2350–3290 K and at pressures of about 1.35 and 1.82 bar. Mixtures of  $\text{C}_2\text{H}_6/\text{N}_2$  and  $\text{CH}_4/\text{N}_2$  highly diluted in argon were used. The rate coefficient was directly determined from the C atom concentrations measured by the ARAS technique.
- (c) The reaction of C atoms with  $\text{N}_2$  was studied at high temperatures behind reflected shock waves. C atoms were formed by pyrolysis of dilute mixtures of  $\text{C}_3\text{O}_2$  in argon. The reaction rates were determined from measurements of C-atom and N-atom concentrations. C atoms and N atoms were detected using ARAS at 156.1 nm and 119.9 nm, respectively. Experiments were conducted within the pressure range 0.5–1 bar, with mixtures comprising, 7 ppm  $\text{C}_3\text{O}_2$  and 5%  $\text{N}_2$  in Ar, and 10 ppm  $\text{C}_3\text{O}_2$  and 4%  $\text{N}_2$  in Ar.
- (d) See Comments on Preferred Values.

#### Preferred Values

$k_1 = 8.69 \cdot 10^{-11} \exp(-22600/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 2000–5000 K.

$k_2 = 3.1 \cdot 10^{-33} [\text{Ar}] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

#### Reliability

$\Delta \log k_1 = \pm 0.15$  over the range 2000–5000 K.  
 $\Delta \log k_2 = \pm 0.5$  at 298 K.

#### Comments on Preferred Values

The only two studies of  $k_1$  employing similar shock tube techniques are in good agreement. The preferred values are obtained by taking a mean of the Arrhenius parameters of each expression. The preferred value is unchanged from our previous evaluation<sup>4</sup> and lies well within the broad range of values calculated from the equilibrium constant and indirect measurements of the reverse rate coefficient, which differ by over an order of magnitude.

The only value for  $k_2$  is that of Husain and Kirsch<sup>1</sup> determined at room temperature and low pressures, which we take as the preferred value but with large error limits until further studies are made.

A theoretical treatment of the reaction by Moskaleva and Lin<sup>5</sup> suggests that the mechanism of Channel (1) is complex passing through CNN, NCN, and *c*-NCN intermediates.

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#### Thermodynamic Data

$$\begin{aligned}\Delta H^\circ_{298}(1) &= -444.9 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(1) &= -17.9 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 0.21 T^{-0.087} \exp(+53480/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

$$\begin{aligned}\Delta H^\circ_{298}(2) &= -122.4 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(2) &= -5.05 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 0.33 T^{0.062} \exp(+14770/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2$ )

$\text{k/cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$4.8 \cdot 10^{-11}$	298	Husain and Young <sup>1</sup>	(a)
$1.6 \cdot 10^{-11}$	298	Becker, Brockmann, and Wiesen, 1988 <sup>2</sup>	(b)
$3.32 \cdot 10^{-11}$	2720–3810	Lindackers <i>et al.</i> , 1990 <sup>3</sup>	(c)
$8.0 \cdot 10^{-11}$	1550–4050	Dean, Hanson, and Bowman, 1991 <sup>4</sup>	(d)
$5.4 \cdot 10^{-11}$	298	Bergeat <i>et al.</i> , 1999 <sup>5</sup>	(e)
$3.7 \cdot 10^{-10} T^{-0.16}$	15–295	Geppert <i>et al.</i> , 2000 <sup>6</sup>	(f)
<i>Branching Ratios</i>			
$k_1/k = 0.60; k_2/k = 0.40$	2430–4040	Dean, Hanson, and Bowman, 1991 <sup>3</sup>	(c)
$k_1/k = 0.60; k_2/k = 0.40$	298	Bergeat <i>et al.</i> , 1999 <sup>5</sup>	(e)
<i>Reviews and Evaluations</i>			
$2.5 \cdot 10^{-11}$	300	CEC, 1994 <sup>7</sup>	(g)
$8.0 \cdot 10^{-11}$	1500–4050		
$k_1/k = 0.60; k_2/k = 0.40$	2400–4050		

#### Comments

- (a) C atoms generated in the presence of NO by repetitive flash photolysis of  $\text{C}_3\text{O}_2$  in a flow of He at wavelengths down to  $\sim 105$  nm.  $[\text{C}(\text{P}^3)]$  monitored by optical absorption at 166 nm. This work supersedes earlier, similar studies from the same laboratory.<sup>8</sup>
- (b) Pulsed laser photolysis at 248 nm of slowly flowing  $\text{CH}_2\text{Br}_2/\text{NO}/\text{He}$  mixtures at total pressures of 2.6 mbar.  $[\text{C}]$  monitored by time resolved two photon LiF at 143.5 nm in the presence of a large excess of NO.
- (c) Shock tube study using reflected shocks in  $\text{C}_2\text{H}_6/\text{N}_2/\text{Ar}$  mixtures at pressures in the range 1–1.8 bar. Values of  $k$  were obtained directly from the  $[\text{C}]$  profiles determined by atomic absorption spectroscopy.
- (d) Shock tube study behind reflected shock waves. C atoms produced by pyrolysis of  $\text{C}_3\text{O}_2$  in  $\text{C}_3\text{O}_2/\text{Ar}$  mixtures at temperatures in the range 2435–3737 K, by laser photolysis at 193 nm of  $\text{C}_3\text{O}_2/\text{Ar}$  mixtures in the temperature range 1576–1940 K, and by pyrolysis of  $\text{CH}_4$  over the range 3430–3737 K.  $[\text{C}]$  monitored by time resolved ARAS. Branching ratios were determined by measuring the possible products, CN, N, O, using laser absorption or ARAS. Computer modeling of a large reaction scheme showed that the  $[\text{CN}]$  profile was particularly sensitive to the branching ratio.
- (e) Fast-flow discharge system with C atom generated by reaction of K vapor with  $\text{CCl}_4$  or  $\text{CBr}_4$  in a stream of He carrier gas.  $[\text{C}]$  was monitored by resonance fluorescence at 156.11 nm or 165.72 nm in the presence of a large excess of NO. The authors suggest that the value of  $k$  obtained in this study is to be preferred to that obtained by Dorthe *et al.*<sup>9</sup> in the same laboratory because of the more direct detection method used. The atomic products of the reaction  $[\text{O}(\text{P}^3), \text{N}(\text{S}^4), \text{N}(\text{D}^2)]$  were studied by resonance fluorescence. Because of the relaxation of  $\text{N}(\text{D}^2)$  to  $\text{N}(\text{S}^4)$  it was not possible to determine the nascent branching between these two products.
- (f) Low temperatures were achieved by isentropic expansion of gas mixtures through a Laval nozzle. The mixtures consisted of the carrier gas (He, Ar, or  $\text{N}_2$ ) containing a small concentration of  $\text{C}_3\text{O}_2$  and varying amounts of NO.  $\text{C}(\text{P}^3)$  atoms were produced in the flow by laser photolysis at 193 nm of the  $\text{C}_3\text{O}_2$ .  $[\text{C}(\text{P}^3)]$  was monitored by time-resolved vacuum-ultraviolet laser-induced fluorescence. The results from this study were combined with those from an earlier study<sup>7</sup> to give the expression cited.
- (g) Based on the low temperature studies of Becker *et al.*<sup>2</sup> and Dorthe *et al.*<sup>9</sup> and on the high temperature study of Dean *et al.*<sup>4</sup>

#### Preferred Values

$$\begin{aligned}k &= 8 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ over the range } 290–4050 \text{ K.} \\ k_1/k &= 0.60; k_2/k = 0.40 \text{ over the range } 290–4050 \text{ K.}\end{aligned}$$

*Reliability*

$\Delta \log k = \pm 0.3$  over the range 290–4050 K.

$\Delta k_1/k = \Delta k_2/k = \pm 0.3$  over the range 1500–4050 K.

*Comments on Preferred Values*

There have been a number of determinations of  $k$  at 300 K<sup>1,2,5,6,8–10</sup> which range over a factor of  $\sim 10$ . Most of the studies used flash photolysis and the earlier studies<sup>8,10</sup> were probably influenced adversely by the high flash intensities which had to be used. However, considering only the more recent studies,<sup>1,2,5,6,9</sup> which include those using pulsed laser photolysis<sup>2,6</sup> and discharge flow techniques,<sup>5,9</sup> the discrepancies remain. Of these studies, that of Dorthe *et al.*<sup>9</sup> has been superseded by similar work from the same laboratory,<sup>5</sup> leaving the studies of Husain and Young,<sup>1</sup> Becker *et al.*,<sup>2</sup> Bergeat *et al.*,<sup>5</sup> and Geppert *et al.*<sup>6</sup> to consider. In all of these studies the rate constant for the C+O<sub>2</sub> reaction was also determined. The values of the ratio  $k(\text{C}+\text{O}_2)/k(\text{C}+\text{NO})$  in three of the studies<sup>1,5,6</sup> were in the range 1.9–2.9 suggesting that in these cases any differences in the absolute values of the rate constants of the two reactions was due to a systematic difference between the techniques. However, in the study of Becker *et al.*<sup>2</sup> the ratio was  $\sim 0.3$  and the absolute value obtained for  $k(\text{C}+\text{NO})$  was much lower than obtained in the other three studies. The preferred value of  $k$  at low temperatures is therefore based on the studies of Husain and Young,<sup>1</sup> Bergeat *et al.*,<sup>5</sup> and Geppert *et al.*<sup>6</sup> The values of  $k$  in these studies range over a factor of  $\sim 3$ . A potential source of this scatter might lie with the rate constant being pressure dependent but there is no obvious correlation between the values of  $k$  and the pressures used.

At high temperatures our previous evaluation<sup>7</sup> only considered the shock tube study of Dean *et al.*<sup>4</sup> There is also a similar study by Lindackers *et al.*<sup>3</sup> which gives values of  $k$  smaller than those of Dean *et al.*<sup>4</sup> by over a factor of 2. However, we continue to base the preferred value of  $k$  in the high temperature range on the value obtained by Dean *et al.*<sup>4</sup>

A value of  $k$ , independent of temperature, is taken for the preferred value over the whole temperature range with error limits which recognize the scatter in the data. Similar values for the branching ratios have been obtained by Dean *et al.*,<sup>4</sup> at high temperatures, and Bergeat *et al.*<sup>5</sup> at 298 K, which are taken as our preferred values.

Theoretical studies have investigated the kinetics at low temperatures<sup>11</sup> and over a wide temperature range<sup>12</sup> comparing their results with the experimental data. The calculations of Simonsen *et al.*<sup>12</sup> suggest that the branching ratio is relatively independent of temperature with a value of  $k_1/k \approx 0.6$  over the range 200–4500 K in accord with the experimental findings. The N atoms produced *via* Channel (1) are predicted to be N(<sup>2</sup>D)<sup>13</sup> which is supported by experiment<sup>5</sup> but some production of N(<sup>4</sup>S) is not ruled out.

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*Thermodynamic Data*

$$\Delta H^\circ_{298}(1) = -455.7 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = 0.50 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 0.130 T^{-0.267} \exp(+54660/T) \\ (300 \leqslant T/\text{K} \leqslant 5000)$$

$$\Delta H^\circ_{298}(2) = -59.2 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = -14.5 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 9.56 \cdot 10^{-4} T^{0.783} \exp(+7340/T) \\ (300 \leqslant T/\text{K} \leqslant 5000)$$

$$\Delta H^\circ_{298}(3) = -356.3 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = -40.77 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 8.79 \cdot 10^{-5} T^{0.641} \exp(+43080/T) \\ (300 \leqslant T/\text{K} \leqslant 5000)$$

See Section 3 for the origin and quality of the Thermodynamic Data.

**Rate Coefficient Data ( $k = k_1 + k_2 + k_3$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$2.6 \cdot 10^{-11}$	294	Lichtin and Lin, 1985 <sup>1</sup>	(a)
$2.4 \cdot 10^{-11}$			
$2.5 \cdot 10^{-11} T^{-0.50}$	99–297	Sims and Smith, 1988 <sup>2</sup>	(b)
$1.25 \cdot 10^{-11} \exp(204/T)$	294–761	Sims and Smith, 1988 <sup>3</sup>	(c)
$1.24 \cdot 10^{-11} \exp(196/T)$	295–775	Durant and Tully, 1989 <sup>4</sup>	(d)
$1.4 \cdot 10^{-11} \exp(220/T)$	294–1000	Atakan <i>et al.</i> , 1989 <sup>5</sup>	(e)
$1.0 \cdot 10^{-11} \exp(220/T)$	292–1565	Balla and Casleton, 1991 <sup>6</sup>	(f)
$1.7 \cdot 10^{-9} T^{-0.76} \exp(-7/T)$	26–295	Sims <i>et al.</i> , 1992 <sup>7</sup>	(g)
$9 \cdot 10^{-10} T^{-0.63}$	13–295	Sims <i>et al.</i> , 1994 <sup>8</sup>	(h)
<i>Branching Ratios</i>			
$k_1/k = 0.29$	295	Mohammed <i>et al.</i> , 1993 <sup>9</sup>	(i)
$k_1/k = 0.22$	296	Rim and Hershberger, 1999 <sup>10</sup>	(j)
$k_3/k = 0.02$			
<i>Reviews and Evaluations</i>			
$1.2 \cdot 10^{-11} \exp(210/T)$	290–4500	CEC, 1994 <sup>11</sup>	(k)
$k_1 = 1.79 \cdot 10^{-10} Z^{-1.38}$	13–3720	Hessler, 1999 <sup>12</sup>	(l)
$k_2 = 1.79 \cdot 10^{-10} Z^{-1.38} \exp(-Z^{-1}) + 4.62 \cdot 10^{-2}$ $\exp(1-Z^{-1})$ , where $Z = (1+T/21.7)$			

**Comments**

- (a) Pulsed laser photolysis of ICN/O<sub>2</sub>/Ar mixtures in a flowing system. [CN] was monitored by time resolved absorption spectroscopy at 388 nm and 619 nm, the latter giving the less precise of the two values cited.
- (b) Pulsed laser photolysis of NCNO/O<sub>2</sub>/Ar mixtures. [CN] monitored by time resolved LIF at 420 nm.
- (c) Pulsed laser photolysis at 532 nm of flowing NCNO/O<sub>2</sub>/Ar mixtures. [CN] monitored by time resolved LIF at 420 nm [CN( $v=0$ )] or 390 nm [CN( $v=1$ )].
- (d) Pulsed laser photolysis at 193 nm of flowing C<sub>2</sub>N<sub>2</sub>/O<sub>2</sub>/He or ClCN/O<sub>2</sub>/He mixtures at total pressures in the range 130–530 mbar. [CN] and [NCO] monitored by LIF.
- (e) Pulsed laser photolysis at 193 nm of flowing

C<sub>2</sub>N<sub>2</sub>/O<sub>2</sub>/N<sub>2</sub> mixtures at total pressures in the range 4–65 mbar. [CN] monitored by time resolved LIF. CN( $v=1$ ) also studied.

- (f) Pulsed laser photolysis at 193 nm of flowing C<sub>2</sub>N<sub>2</sub>/O<sub>2</sub>/Ar mixtures at total pressures in the range 6.5–65 mbar. [CN] monitored by time resolved LIF.

- (g) Pulsed laser photolysis of NCNO/O<sub>2</sub>/Ar or N<sub>2</sub> mixtures at 583 nm with gas flow cooled by passage through a supersonic nozzle. [CN] monitored by LIF.

- (h) Technique as in (g) but He used as carrier gas.

- (i) Pulsed laser photolysis at 193 nm of BrCN (or C<sub>2</sub>N<sub>2</sub>)/O<sub>2</sub>/Ar mixtures. Time resolved IR emission spectroscopy of CO( $v''$ ) was employed to study the contribution from Channel (1) to the overall reaction. IR emission signals from CO( $v''$ ) calibrated using photolysis of acetone as a CO( $v''$ ) source.

- (j) CN radicals were produced by pulsed laser photolysis of ICN at 248 nm, or of C<sub>2</sub>N<sub>2</sub> at 193 nm, in the pres-

ence of an excess of O<sub>2</sub>. The CO and CO<sub>2</sub> products were detected directly by infrared laser absorption at 2107.423 cm<sup>-1</sup> and 2337.658 cm<sup>-1</sup>, respectively, and the NCO yield was determined indirectly from the yield of N<sub>2</sub>O (detected by infrared diode laser absorption) produced on addition of an excess of NO. The branching ratio into the CO+NO channel was found to drop from a value of ~0.28 at 239 K to ~0.09 at 643 K.

- (k) Based on the data of Refs. 3–6, cited in the Table.
- (l) Expressions of the form  $k = [A/(1 + T/T_w)]^m \times \exp[(T/T_w)/(1 + T/T_w)]$ , where A, T<sub>w</sub>, and m are fitting parameters, were fitted to the experimental data to derive expressions for k<sub>1</sub> and k<sub>2</sub>.

### Preferred Values

$k = 1.2 \cdot 10^{-11} \exp(210/T)$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> over the range 200–4500 K.

$k_1/k = 0.25$  at 298 K;  $k_2/k = 1$  at  $T > 1000$  K.

### Reliability

$\Delta \log k = \pm 0.1$  at 200 K, rising to  $\pm 0.3$  at 4500 K.

$\Delta(k_1/k) = \pm 0.05$  at 298 K.

### Comments on Preferred Values

There have been many studies of the rate constant of this reaction<sup>1–8,13–30</sup> over a wide temperature range. There is excellent agreement among a number of studies on both the value of k at 298 K and on its temperature dependence at  $T < 1000$  K. The preferred expression for k is obtained by taking the mean value of E/R from the studies of Sims and Smith,<sup>3</sup> Durant and Tully,<sup>4</sup> Atakan *et al.*,<sup>5</sup> and Balla and Casleton,<sup>6</sup> and combining it with a pre-exponential factor which reproduces the mean value of k at 294–298 K from Refs. 1–8 cited in the Table. There are many fewer studies at high temperatures but the preferred expression derived from the low temperature data in this way extrapolates to give values of k within a factor of 2 of all of the available data. Values of k for this reaction have been obtained down to unusually low temperatures (13 K) and in the very low temperature regime the rate constant usually has been expressed using a T<sup>n</sup> dependence, which may be more appropriate for this type of reaction.

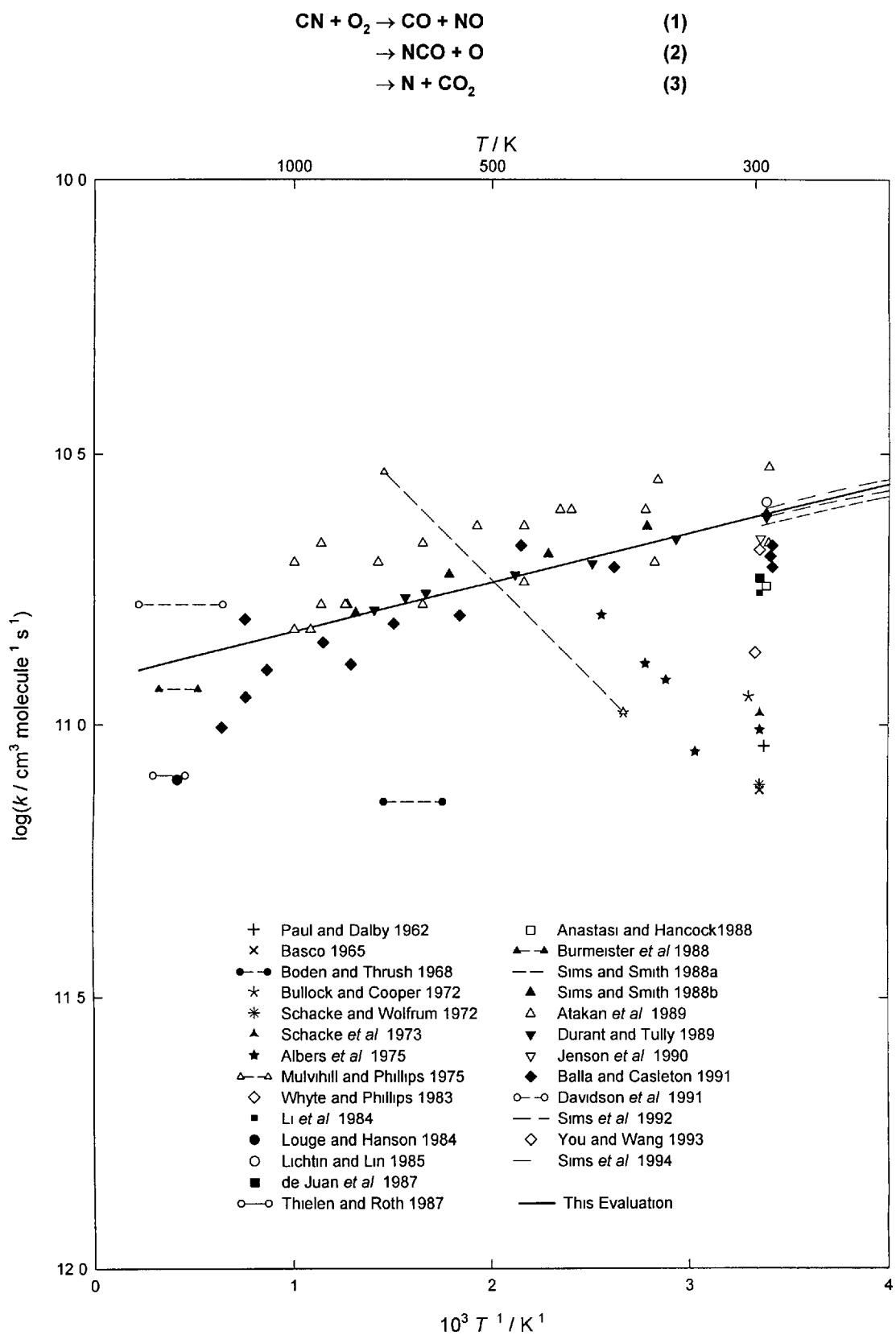
In their study of the reaction Schmatjko and Wolfrum<sup>31</sup> estimated a value of k<sub>1</sub>/k of less than 0.06 but Mohammed *et al.*<sup>9</sup> have reanalyzed these results to give a value of 0.21 in support of their own experimental value of 0.29. There is strong support for these values from the measurements of Rim and Hershberger<sup>10</sup> who obtain k<sub>1</sub>/k = 0.22 at 296 K following an earlier study<sup>32</sup> giving a less certain value of 0.23. Rim and Hershberger<sup>10</sup> also found that there was only a very small contribution from Channel (3) and that k<sub>1</sub>/k declined

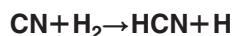
markedly with temperature. Their findings suggest that at high temperatures ( $T > 1000$  K) Channel (2) is the only important channel but Channel (1) becomes steadily more important as the temperature declines. Our recommendations for the branching ratios reflect this.

Hessler<sup>12</sup> has carried out a very careful fitting of the experimental data to functions of the form  $k = [A/(1 + T/T_w)]^m \exp[(T/T_w)/(1 + T/T_w)]$ , where A, T<sub>w</sub>, and m are fitting parameters. Expressions are derived for k<sub>1</sub> and k<sub>2</sub>. The values of k from these expressions are in excellent agreement with those recommended here for temperatures above 1000 K but diverge at lower temperatures.

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#### Thermodynamic Data

$$\begin{aligned}\Delta H_{298}^{\circ} &= -82.3 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= -16.8 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 8.2 \cdot 10^4 T^{0.718} \exp(+10200/T) \\ &\quad (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$1.4 \cdot 10^{-10}$	2700–3500	Szekeley, Hanson, and Bowman, 1983 <sup>1</sup>	(a)
$2.6 \cdot 10^{-14}$	294–300	Balla and Pasternack, 1987 <sup>2</sup>	(b)
$2.5 \cdot 10^{-14}$	298	de Juan, Smith, and Veyret, 1987 <sup>3</sup>	(c)
$3 \cdot 10^{-10} \exp(-4000/T)$	2050–2590	Natarajan and Roth, 1988 <sup>4</sup>	(d)
$2.6 \cdot 10^{-16} T^{1.6} \exp(-1340/T)$	295–768	Sims and Smith, 1988 <sup>5</sup>	(e)
$2.23 \cdot 10^{-21} T^{3.31} \exp(-756/T)$	209–740	Sun <i>et al.</i> , 1990 <sup>6</sup>	(f)
$4.9 \cdot 10^{-19} T^{2.45} \exp(-1126T)$	941–1731	Wooldridge, Hanson, and Bowman, 1996 <sup>7</sup>	(g)
$2.5 \cdot 10^{-14}$ (293 K), see Figure for other data points.	293–380	He, Tokue, and Macdonald, 1998 <sup>8</sup>	(h)
<i>Reviews and Evaluations</i>			
$8.3 \cdot 10^{-16} T^{1.51} \exp(-1531/T)$	300–3000	Tsang, 1992 <sup>9</sup>	(i)
$4 \cdot 10^{-20} T^{2.87} \exp(-820/T)$	500–3000	CEC, 1992; 1994 <sup>10</sup>	(j)

#### Comments

- (a) Shock tube study on  $\text{C}_2\text{N}_2/\text{H}_2/\text{Ar}$  mixtures at pressures in the range 270–550 mbar. [CN] monitored by time-resolved broad band absorption spectroscopy.
- (b) Pulsed laser photolysis at 193 nm of  $\text{C}_2\text{N}_2/\text{H}_2/\text{N}_2$ , He, or Ar mixtures in a static system at total pressures in the range 7–130 mbar. [CN] and [HCN] monitored by time-resolved infrared diode laser absorption.
- (c) Pulsed laser photolysis at 572 nm of  $\text{NOCN}/\text{H}_2/\text{Ar}$  mixtures at total pressures in the range 13–40 mbar. [CN] monitored by time-resolved LIF at 388 nm.
- (d) Shock tube study on  $\text{C}_2\text{N}_2/\text{H}_2/\text{Ar}$  mixtures at pressures in the range 1.8–2 bar. [H] monitored by time-resolved ARAS.
- (e) Pulsed laser photolysis at 532 nm of  $\text{NOCN}/\text{H}_2/\text{Ar}$  mixtures in a flowing system at total pressures of 66 mbar. [CN] monitored by time-resolved LIF.
- (f) Pulsed laser photolysis at 248 nm of  $\text{ICN}/\text{H}_2/\text{Ar}$  mixtures at total pressures in the range 66–660 mbar. [CN] monitored by time-resolved LIF at 388 nm.
- (g) Shock tube study of  $\text{C}_2\text{N}_2/\text{H}_2/\text{Ar}$  mixtures at total pressures near 1 bar. CN produced by pulsed laser photolysis at 193 nm and [CN] monitored by absorption at 388.444 nm. Values of  $k$  derived from steady state concentration of CN produced.
- (h) Pulsed laser photolysis at 193 nm of  $\text{C}_2\text{N}_2/\text{H}_2/\text{inert gas}$  mixtures in a flowing system at total pressures in the range 2.5–20 mbar. [CN] monitored by time-resolved diode laser near-infrared absorption at 790 nm.
- (i) Recommends the expression derived by Jacobs *et al.*<sup>11</sup>
- (j) Based on the data of Schacke *et al.*,<sup>12</sup> Li *et al.*,<sup>13</sup> Lich-

tin and Lin,<sup>14</sup> Szekeley *et al.*,<sup>1</sup> Natarajan and Roth,<sup>2</sup> de Juan *et al.*,<sup>3</sup> Balla and Pasternack,<sup>4</sup> Sims and Smith,<sup>5</sup> Atakan *et al.*,<sup>15</sup> and Sun *et al.*<sup>6</sup>

#### Preferred Values

$$k = 1.8 \cdot 10^{-19} T^{2.60} \exp(-960/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the range } 200\text{--}3500 \text{ K.}$$

#### Reliability

$$\Delta \log k = \pm 0.2 \text{ over the range } 200\text{--}3500 \text{ K.}$$

#### Comments on Preferred Values

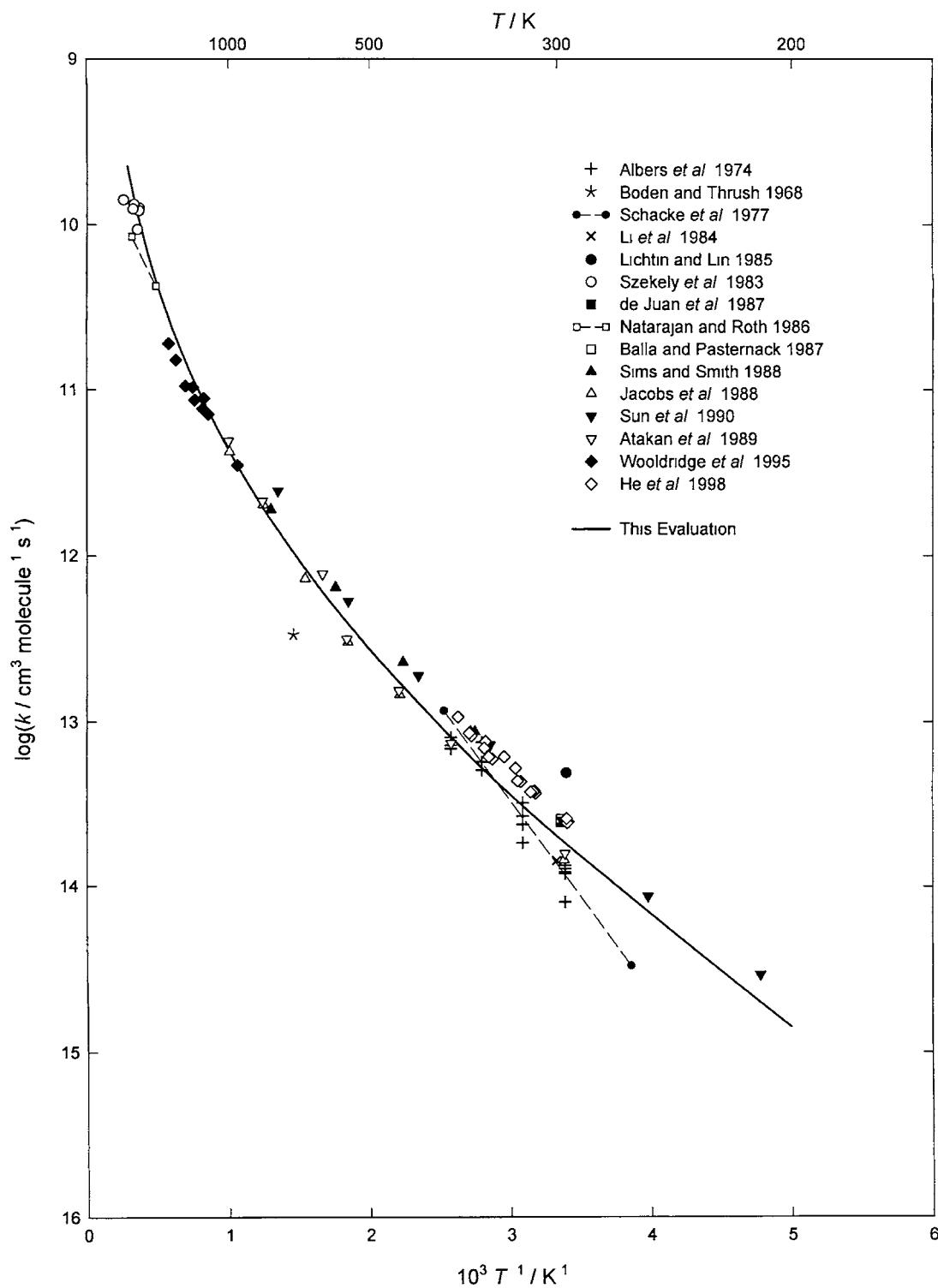
There is very good agreement among most of the studies of this reaction at temperatures above 400 K but at lower temperatures the results diverge with a difference of a factor of  $\sim 1.6$  at 300 K. At these lower temperatures our preferred values are based on the studies of He *et al.*,<sup>8</sup> Sun *et al.*,<sup>6</sup> Sims and Smith,<sup>5</sup> de Juan *et al.*,<sup>3</sup> and Balla and Pasternack<sup>2</sup> which are in excellent agreement. Most of the remaining, divergent data are older,<sup>11–17</sup> and are likely to be less reliable.

At high temperatures  $k$  is well defined over a wide temperature range by the studies of Szekeley *et al.*,<sup>1</sup> Natarajan and Roth,<sup>4</sup> and Wooldridge *et al.*<sup>7</sup>

Theoretical studies<sup>18–20</sup> of the reaction are able to reproduce the temperature dependence of  $k$  and suggest that the reaction occurs by direct abstraction rather than by adduct formation.

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#### Thermodynamic Data

$$\begin{aligned}\Delta H^{\circ}_{298}(1) &= -21.4 \text{ kJ mol}^{-1} \\ \Delta S^{\circ}_{298}(2) &= -5.89 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 1.30 \cdot 10^{-2} T^{-0.557} \exp(+2690/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

$$\begin{aligned}\Delta H^{\circ}_{298}(2) &= 15.4 \text{ kJ mol}^{-1} \\ \Delta S^{\circ}_{298}(2) &= -28.9 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 1.05 \cdot 10^{-4} T^{0.841} \exp(-1590/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$k_1 = 2.3 \cdot 10^{-12} - 3.3 \cdot 10^{-12}$	2460–2840	Szekeley, Hanson, and Bowman, 1984 <sup>1</sup>	(a)
$k_1 = 1.33 \cdot 10^{-11} \exp(-3752/T)$	588–1027	Jacobs <i>et al.</i> , 1988 <sup>2</sup>	(b)
<i>Reviews and Evaluations</i>			
$k_1 = 1.33 \cdot 10^{-11} \exp(-3755/T)$	750–2500	Tsang, 1992 <sup>3</sup>	(c)
$k_1 = 1.3 \cdot 10^{-11} \exp(-3750/T)$	500–3000	CEC, 1992; 1994 <sup>4</sup>	(c)

#### Comments

- (a) Shock tube study on  $\text{C}_2\text{N}_2/\text{H}_2\text{O}/\text{Ar}$  mixtures at total pressures in the range 0.45–0.62 bar. [CN] and [OH] were monitored by time resolved LIF behind incident shock waves near 388 nm and 306.67 nm, respectively. The [CN] and [OH] profiles were modeled by computer simulation of a detailed mechanism to obtain values of  $k$ . The data from this study were combined by the authors with data from the study of Fritz *et al.*<sup>5</sup> on the reverse reaction at lower temperatures, and with equilibrium data, to obtain the expression  $k_1 = 3.8 \cdot 10^{-11} \exp(-6700/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .
- (b) Pulsed laser photolysis at 193 nm of flowing  $\text{C}_2\text{N}_2/\text{H}_2\text{O}/\text{N}_2$  mixtures. [CN( $v=1$ )], [CN( $v=2$ )], and [OH] were monitored by time resolved LIF at 386.871, 386.887, and 306.328 nm respectively, under conditions of  $[\text{H}_2\text{O}] \geq [\text{CN}]$ .
- (c) Accepts the expression of Jacobs *et al.*,<sup>2</sup> which extrapolates well to the data of Szekeley *et al.*<sup>1</sup>

#### Preferred Values

$k = 1.3 \cdot 10^{-11} \exp(-3750/T) \text{ cm}^{-3} \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 500–3000 K.

#### Reliability

$\Delta \log k = \pm 0.3$  at 500 K, rising to  $\pm 0.5$  at 3000 K.

#### Comments on Preferred Values

There have been no studies of this reaction reported since our previous evaluations<sup>4</sup> and our preferred values are therefore unchanged.

The recommended expression is that of Jacobs *et al.*<sup>2</sup> If it is extrapolated to high temperatures it gives values of  $k_1$  in good agreement with the measurements of Szekeley *et al.*<sup>1</sup> The expression which Szekeley *et al.*<sup>1</sup> derive by combining their data with those of Fritz *et al.*<sup>5</sup> on the OH+HCN reaction [see Comment (a)] is in poor agreement with our Preferred Values.

Channel (2) has been invoked to explain some features of nitrogen containing flames<sup>6</sup> but there is no direct evidence for its occurrence.

#### References

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#### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = -862.0 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = -37.2 \text{ J K}^{-1} \text{ mol}^1$$

$$K_c(1) = 3.65 \cdot 10^{-3} T^{0.164} \exp(+103750/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(2) = -497.0 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = -25.0 \text{ J K}^{-1} \text{ mol}^1$$

$$K_c(2) = 1.08 \cdot 10^{-2} T^{0.233} \exp(+59830/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(3) = -251.2 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = 0.31 \text{ J K}^{-1} \text{ mol}^1$$

$$K_c(3) = 7.95 \cdot 10^{-2} T^{0.399} \exp(+30300/T) \\ (300 \leq T/\text{K} \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k_1 = k_2 + k_2 + k_3$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$4.0 \cdot 10^{-11} \exp(186/T)$	297–740	Wang, Yang, and Lin, 1989 <sup>1</sup>	(a)
$5.0 \cdot 10^{-11} \exp(171/T)$	298–650	Park and Hershberger, 1993 <sup>2</sup>	(b)
$7.2 \cdot 10^{-11}$	296	You and Wang, 1993 <sup>3</sup>	(c)
$2.64 \cdot 10^{-11} \exp(570/T)$	1073–1582	Wooldridge <i>et al.</i> , 1994 <sup>4</sup>	(d)
<i>Branching Ratios</i>			
$k_1/k = 0.056 \pm 0.060$	298	Park and Hershberger, 1993 <sup>2</sup>	(b)
$k_2/k = 0.076 \pm 0.032$			
$k_3/k = 0.868 \pm 0.060$			
<i>Reviews and Evaluations</i>			
$4.0 \cdot 10^{-11} \exp(186/T)$	500–2500	Tsang, 1992 <sup>5</sup>	(e)

#### Comments

- (a) Pulsed laser photolysis at 248 nm of ICN/NO<sub>2</sub>/N<sub>2</sub> mixtures at total pressures in the range 66–425 mbar. [CN] monitored by time-resolved LIF at 420 nm following excitation at ~380 nm.  $k$  found to be independent of pressure. Alternative expression given for rate constant:  $k = 10^{-4.87} T^{-1.78} \exp(-591/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .
- (b) Pulsed laser photolysis at 266 nm of ICN/NO<sub>2</sub>/SF<sub>6</sub> mixtures at total pressures of ~3 mbar. [CN], [CO], [NO], [N<sub>2</sub>O], and [CO<sub>2</sub>] were monitored by time-resolved infrared diode laser spectroscopy. Values of  $k$  derived from the [CN] profiles.
- (c) Pulsed laser photolysis at 248 nm of ICN/NO<sub>2</sub>/He mixtures at pressures in the range 68–208 mbar. [CN] monitored by time resolved LIF at 420 nm following excitation at 387.155 nm.  $k$  found to be independent of pressure.
- (d) Shock tube/pulsed laser photolysis study on C<sub>2</sub>N<sub>2</sub>/NO<sub>2</sub>/Ar mixtures at total pressures of ~1.4 bar. The mixtures were subjected to a laser pulse at 193 nm some 50  $\mu\text{s}$  after the passage of a reflected shock. [CN] and [NCO] were monitored by time-resolved absorption spectroscopy at 388.444 nm and 440.479 nm, re-

spectively. Behavior of the [NCO] profile suggests that Channel (3) is occurring at 1250 K but the branching ratio cannot be quantified.

- (e) Accepts the expression of Wang *et al.*<sup>1</sup>

#### Preferred Values

$k = 1.02 \cdot 10^{-9} T^{-0.752} \exp(-173/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 296–1600 K.

$$k_1/k = 0.06; k_2/k = 0.08; k_3/k = 0.86 \text{ at } 298 \text{ K.}$$

#### Reliability

$$\Delta \log k = \pm 0.1 \text{ at } 296 \text{ K, rising to } \pm 0.2 \text{ at } 1600 \text{ K.}$$

$$\Delta(k_1/k) = \pm 0.06; \Delta(k_2/k) = \pm 0.08; \Delta(k_3/k) = \pm 0.14 \text{ at } 298 \text{ K.}$$

#### Comments on Preferred Values

All of the measurements of the rate constant for the overall reaction are in good agreement. The results of Park and Hershberger<sup>2</sup> are systematically some 20%–25% lower than those of Wang *et al.*<sup>1</sup> but both sets of results have a very similar small temperature dependence and are consistent with the measurements at higher temperatures of Wooldridge *et al.*<sup>4</sup> The preferred expression for  $k$  is that derived by

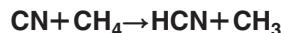
Wooldridge *et al.*<sup>4</sup> by a least squares fit to their own results together with those of Park and Hershberger,<sup>2</sup> Wang *et al.*,<sup>1</sup> and You and Wang.<sup>3</sup>

The reaction mechanism is presumed to proceed by addition followed by rapid decomposition of the complex, in accord with the observed lack of dependence of  $k$  on pressure and the small negative activation energy. The only determinations of the branching ratios are those of Park and Hershberger<sup>2</sup> which are cited in the Table. The values are given for 298 K but they also found very little change in the values up to 465 K. These values are consistent with the observation of Wang *et al.*<sup>1</sup> that Channel (3) is predominant and that of Wooldridge *et al.*<sup>4</sup> that Channel (3) is active at

1250 K. The branching ratios of Park and Hershberger<sup>2</sup> are accepted but substantial error limits are assigned until confirmatory studies are made.

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### Thermodynamic Data

$$\begin{aligned}\Delta H^\circ_{298} &= -79.0 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298} &= 7.10 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 0.415 T^{0.351} \exp(+9390/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

### Rate Coefficient Data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$5.0 \cdot 10^{-13}$	293	Schacke, Wagner, and Wolfrum, 1977 <sup>1</sup>	(a)
$5.5 \cdot 10^{-13}$	300	Li, Sayah, and Jackson, 1984 <sup>2</sup>	(b)
$5.6 \cdot 10^{-13}$	294	Sayah <i>et al.</i> , 1988 <sup>3</sup>	(c)
$2.07 \cdot 10^{-19} T^{2.64} \exp(78/T)$	294–1260	Atakan and Wolfrum, 1991 <sup>4</sup>	(d)
$1.0 \cdot 10^{-19} T^{2.64} \exp(220/T)$	292–1500	Balla <i>et al.</i> , 1991 <sup>5</sup>	(e)
$2.5 \cdot 10^{-11} \exp(-1100/T)$	296–698	Herbert, Smith, and Spencer-Smith, 1992 <sup>6</sup>	(f)
$5.73 \cdot 10^{-12} \exp(-675/T)$	160–298	Sims <i>et al.</i> , 1993 <sup>7</sup>	(g)
$5.1 \cdot 10^{-16} T^{1.53} \exp(-504/T)$	183–740	Yang <i>et al.</i> , 1993 <sup>8</sup>	(h)
<i>Reviews and Evaluations</i>			
$1.5 \cdot 10^{-19} T^{2.64} \exp(150/T)$	290–1500	CEC, 1992; 1994 <sup>9</sup>	(i)

### Comments

- (a) Flash photolysis of  $\text{CH}_4/\text{C}_2\text{N}_2/\text{He}$  mixtures at total pressures of 5–7 mbar in a flowing system.  $[\text{CN}(v=0 \text{ and } v=1)]$  monitored by time-resolved absorption spectroscopy at 388 nm. Value of  $k[\text{CN}(v=1)] = 1.1 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  obtained.
- (b) Pulsed laser photolysis of  $\text{C}_2\text{N}_2/\text{Ar}/\text{CH}_4$  mixtures.  $[\text{CN}(v=0 \text{ and } v=1)]$  monitored by LIF. A value of  $k[\text{CN}(v=1)] = 8.3 \cdot 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  obtained.
- (c) Pulsed laser photolysis at 193 nm of flowing  $\text{C}_2\text{N}_2/\text{Ar}/\text{CH}_4$  mixtures at total pressures of 6–80 mbar.  $[\text{CN}]$  monitored by time-resolved LIF.
- (d) Method as in (c). No dependence of  $k$  on pressure found in the range 2–50 mbar.
- (e) Method as in (c). Pressure range, 7–80 mbar.

- (f) Pulsed laser photolysis at 532 nm of  $\text{NCNO}/\text{CH}_4/\text{Ar}$  mixtures.  $[\text{CN}]$  monitored by time-resolved LIF. Combining their data with those of Atakan and Wolfrum,<sup>4</sup> and of Balla *et al.*,<sup>5</sup> the authors obtain the expression  $k = 1.4 \cdot 10^{-18} T^{2.3} \exp(-16/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .
- (g) Pulsed laser photolysis at 193 nm of  $\text{NCNO}/\text{CH}_4/\text{Ar}$  mixtures.  $[\text{CN}]$  monitored by time-resolved LIF.
- (h) Pulsed laser photolysis at 193 nm or 248 nm of mixtures of  $\text{CH}_4$ , Ar and the CN precursor ( $\text{BrCN}$ ,  $\text{ICN}$ , or  $\text{C}_2\text{N}_2$ ).  $[\text{CN}]$  monitored by time-resolved LIF at 388 nm.
- (i) Based on the expressions derived by Atakan and Wolfrum,<sup>4</sup> and Balla *et al.*<sup>5</sup>

### Preferred Values

$$k = [6.2 \cdot 10^{-12} \exp(-735/T) + 2.20 \cdot 10^{-10} \exp(-3100/T)] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the range } 160\text{--}1500 \text{ K.}$$

*Reliability*

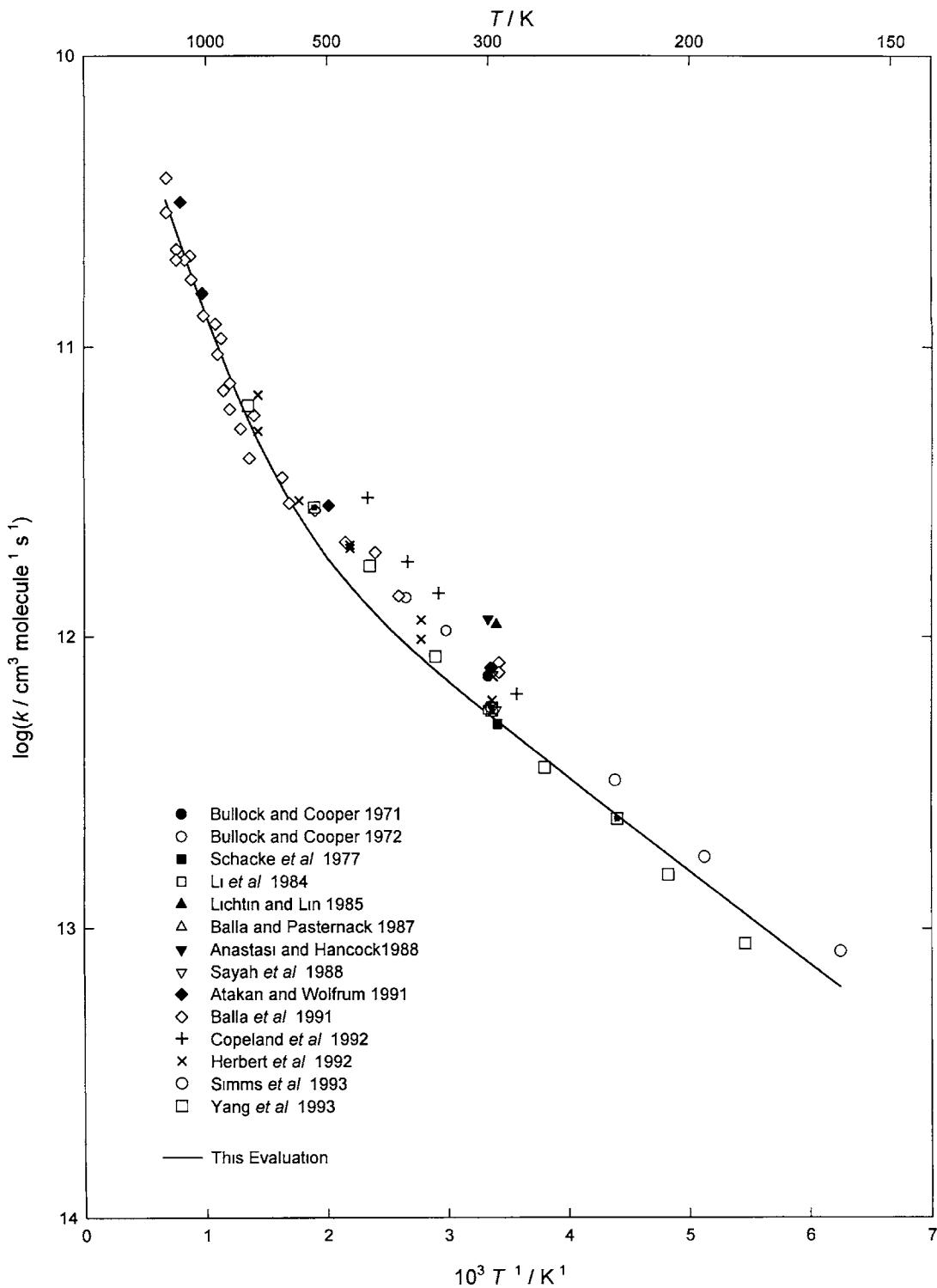
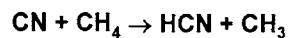
$\Delta \log k = \pm 0.1$  at 300 K, rising to  $\pm 0.15$  at 1500 K and 160 K.

*Comments on Preferred Values*

The rate constant for this reaction seems well defined at high temperatures by the data of Atakan and Wolfrum<sup>4</sup> and Balla *et al.*<sup>5</sup> and at lower temperatures by the data of Schacke *et al.*,<sup>1</sup> Li *et al.*,<sup>2</sup> Sayah *et al.*,<sup>3</sup> Herbert *et al.*,<sup>6</sup> Sims *et al.*,<sup>7</sup> and Yang *et al.*<sup>8</sup> The preferred expression for  $k$  is based on these studies. There are several other studies<sup>10–15</sup> in quite good agreement.

**References**

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**NCO(+M)→CO+N(+M)***Thermodynamic Data*

$$\begin{aligned}\Delta H_{298}^{\circ} &= 235.1 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= 118.6 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 2.64 \cdot 10^{28} T^{-1.171} \exp(-28520/T) \text{ molecule cm}^{-3} \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$3.65 \cdot 10^{-10} \exp(-27200/T) \text{ (M=Ar)}$	2370–3050	Mertens and Hanson, 1996 <sup>1</sup>	(a)
<i>Reviews and Evaluations</i>			
$1.5 \cdot 10^{-9} \exp(-23500/T) \text{ (M=Ar)}$	1450–2600	CEC, 1992; 1994 <sup>2</sup>	(b)
$0.19 T^{-1.95} \exp(30160/T) \text{ (M=N}_2\text{)}$	1800–2500	Tsang 1992 <sup>3</sup>	(c)
$0.21 T^{-1.91} \exp(-30114/T) \text{ (M=CO}_2\text{)}$			

**Comments**

- (a) Shock tube study using dilute mixtures of HNCO in Ar at total pressures in the range 0.69–1.17 bar. [NCO] monitored by time-resolved cw laser absorption at 440 nm.
- (b) Based on the studies of Higashihara *et al.*<sup>4</sup> and Louge and Hanson.<sup>5</sup>
- (c) Based on the data of Higashihara *et al.*<sup>4</sup> and Louge and Hanson<sup>5</sup> for M=Ar. Expressions for N<sub>2</sub> and CO<sub>2</sub> as the collision partners were derived from the expression for M=Ar using RRKM calculation and assumption that collision efficiencies are analogous to those found in N<sub>2</sub>O decomposition.

**Preferred Values**

$$k = 3.7 \cdot 10^{-10} \exp(-27200/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad \text{for M=Ar over the range 2000–3100 K.}$$

*Reliability*

$$\Delta \log k_0 = \pm 0.2 \text{ for M=Ar over the range 2000–3100 K.}$$

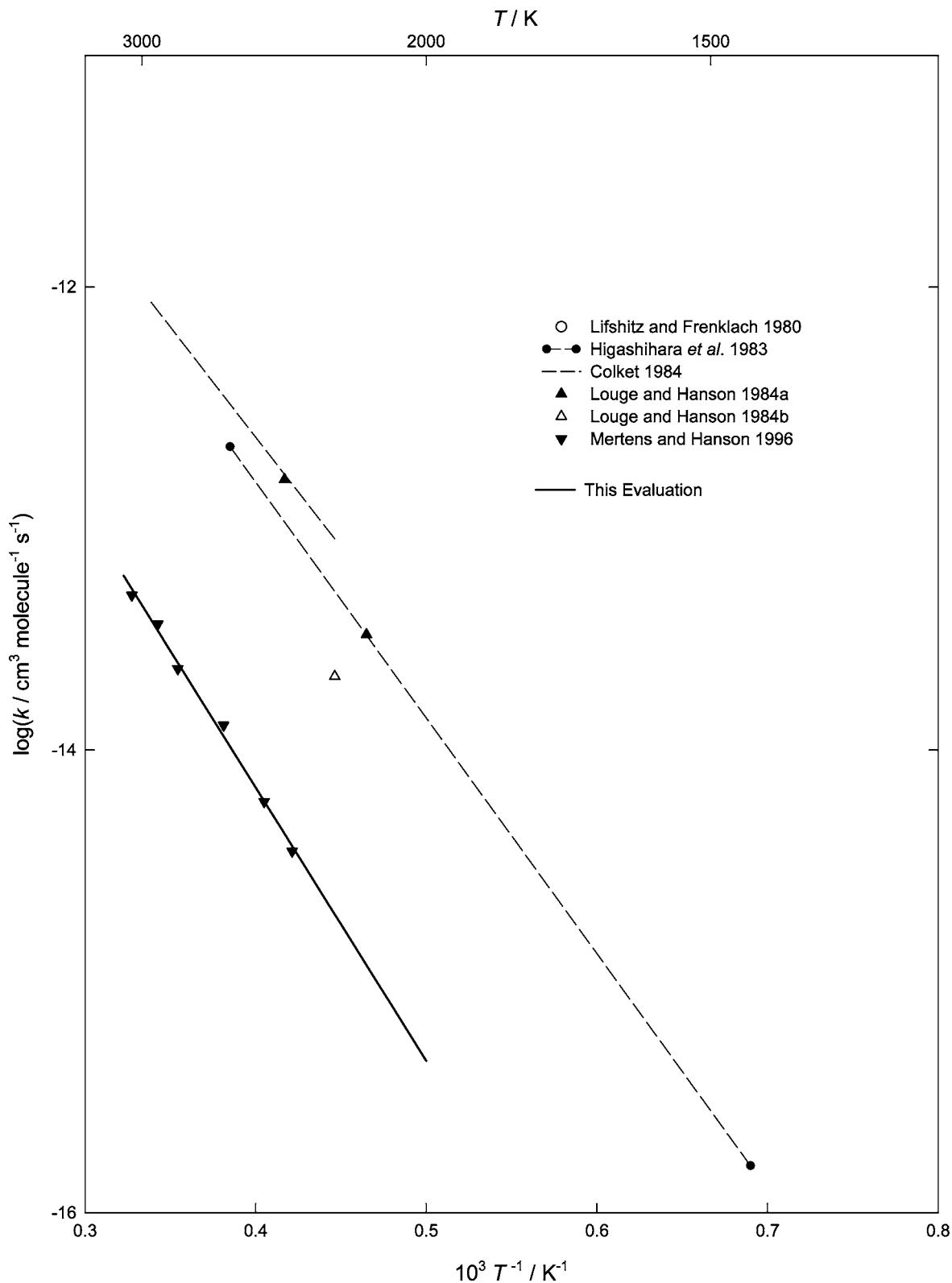
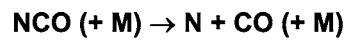
*Comments on Preferred Values*

The preferred expression is that derived in the study by Mertens and Hanson.<sup>1</sup> This work supersedes the previous

studies from the same laboratory by Louge and Hanson<sup>5,8</sup> and gives significantly lower values of  $k$  than all of the earlier studies on which our previous recommendations were based.<sup>4–8</sup> Most of the earlier work was based on C<sub>2</sub>N<sub>2</sub> decomposition and involved a number of uncertainties as reflected in the substantial error limits assigned to our previous recommendations. The more recent work,<sup>1</sup> which uses HNCO decomposition, incorporates new values for the NCO absorption coefficient and newer kinetic data in the computer simulation, and seems much more soundly based.

**References**

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#### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = -610.82 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = -37.54 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 4.58 \cdot 10^{-2} T^{-0.235} \exp(+73450/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(2) = -245.77 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = -25.35 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 1.36 \cdot 10^{-1} T^{-0.166} \exp(+29530/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(3) = -78.67 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = 107.31 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 2.16 \cdot 10^{28} T^{-1.269} \exp(+9190/T) \text{ molecule cm}^{-3} \\ (300 \leq K \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2 + k_3$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$1.69 \cdot 10^{-11} \exp(197/T)$	294–538	Perry, 1985 <sup>1</sup>	(a)
$3.4 \cdot 10^{-11}$	295	Hancock and McKendrick, 1986 <sup>2</sup>	(b)
$5.0 \cdot 10^{-7} T^{-1.53} \exp(-260/T)$	294–1260	Atakan and Wolfrum, 1991 <sup>3</sup>	(c)
$2.9 \cdot 10^{-12}$	2380–2660	Mertens <i>et al.</i> , 1992 <sup>4</sup>	(d)
$k_2 = 3.3 \cdot 10^{-11}$	298	Jones and Wang, 1993 <sup>5</sup>	(e)
$3.3 \cdot 10^{-11}$	298	Wategaonkar and Setser, 1993 <sup>6</sup>	(f)
$1.7 \cdot 10^{-5} T^{-2.01} \exp(-470/T)$	293–836	Juang, Lee, and Wang, 1995 <sup>7</sup>	(g)
$1.45 \cdot 10^{-5} T^{-1.98} \exp(-449/T)$	290–1098	Becker <i>et al.</i> , 1997 <sup>8</sup>	(h)
<i>Branching Ratios</i>			
$k_1/k = 0.65$	298	Becker, Kurtenbach, and Wiesen, 1992 <sup>9</sup>	(i)
$k_2/k = 0.35$			
$k_1/k = 0.56$	296–623	Cooper, Park, and Hershberger, 1993 <sup>10</sup>	(j)
$k_2/k = 0.44$			
$k_2/k = 0.3–0.5$	1098–1443	Flatness and Kramlich, 1996 <sup>11</sup>	(k)
<i>Reviews and Evaluations</i>			
$2.3 \cdot 10^{-6} T^{-1.73} \exp(-380/T)$	290–3000	CEC, 1994 <sup>12</sup>	(l)

#### Comments

- (a) Flow system, NCO produced by pulsed laser photolysis of HNCO/Ar/NO mixtures. Decay of NCO monitored using laser induced fluorescence at 416.8 nm.
- (b) NCO produced by infrared multi-photon dissociation of phenyl isocyanate. Decay of NCO in large excess of NO monitored by laser induced fluorescence at 438.48 nm. This work supersedes earlier, similar studies in which vibrational excitation of NCO may have influenced the results.
- (c) Pulsed laser photolysis of  $(\text{CN})_2/\text{O}_2/\text{NO}$  mixtures at 193 nm. NCO produced by rapid reaction of photolytically generated CN with  $\text{O}_2$ .  $[\text{NCO}]$  monitored by LIF.
- (d) Shock tube study of HNCO/ $\text{N}_2\text{O}/\text{Ar}$  mixtures. NCO monitored by absorption at 440.79 nm.  $k$  derived by fitting NCO profile to a 25 step reaction scheme.  $[\text{NCO}]$  profile shown to be sensitive to value of  $k$ .
- (e) NCO was produced by multiphoton dissociation of

phenylisocyanate and detected by CARS spectroscopy. Results are based on assumed mechanism.  $\text{N}_2$  was not detected, thus eliminating Channels (1) and (3) from consideration. Results are probably of limited reliability.

- (f) NCO generated by the reaction of F with HNCO in a discharge flow reactor and detected by LiF. Pressure of Ar in the 0–10 mbar range.
- (g) NCO generated by laser photolysis of ICN and BrCN to produce CN followed by rapid reaction with  $\text{O}_2$  and  $\text{NO}_2$  at a pressure of 133 mbar He. NCO concentration determined by laser induced fluorescence.
- (h) NCO radicals generated by pulsed excimer laser photolysis of CINCO and detected by LiF at 438.6 nm. NCO was reacted with NO in excess at 27 mbar pressure of Ar.
- (i) NCO generated by the photolysis of CINCO in a static reactor at 254 nm. Concentration of products determined by FTIR. Reaction pressure was 133 mbar in Ar

bath gas. N<sub>2</sub>O and CO concentrations found to be equal, thus eliminating the possibility of contributions from Channel (3). Fitting of CO<sub>2</sub> concentration profile leads to value for contributions from Channel (1). Sum of contributions from all channels equal to 1.

- (j) NCO generated by the laser photolysis of ICN at 266 nm or BrNCO at 266 nm, and reaction of CN with O<sub>2</sub>. Concentration of products determined by infrared diode laser absorption. Pressures of 3–5 mbar SF<sub>6</sub>. These results supersede those of Cooper and Hershberger 1992.<sup>13</sup>
- (k) Stirred reactor experiment with 1% HCN injected into an almost dry, hot stream, generated from CO combustion in dry air containing NO (0.5%–1%) in nitrogen at atmospheric pressure. N<sub>2</sub>O yield is compared with modeling results to obtain  $k_2/k$ .
- (l) See Comments on Preferred Value.

### Preferred Values

$k = 2.3 \cdot 10^{-6} T^{-1.73} \exp(-380/T)$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> over the range 300–2700 K.

$k_1/k = 5.2 T^{-0.35} \exp(-61.3/T)$  over the range 300–2700 K.

$k_2/k = 0.142 T^{0.20} \exp(-20.5/T)$  over the range 300–2700 K.

$k_3 \ll k_1$  and  $k_2$  over the range 300–2700 K.

### Reliability

$\Delta \log k = \pm 0.15$  at 300 K, increasing to  $\pm 0.3$  at 2700 K.

$\Delta(k_1/k) = \pm 0.1$  at 300 K, increasing to  $^{+0.3}_{-0.1}$  at 2700 K.

$\Delta(k_2/k) = \pm 0.1$  at 300 K, increasing to  $^{+0.1}_{-0.3}$  at 2700 K.

### Comments on Preferred Values

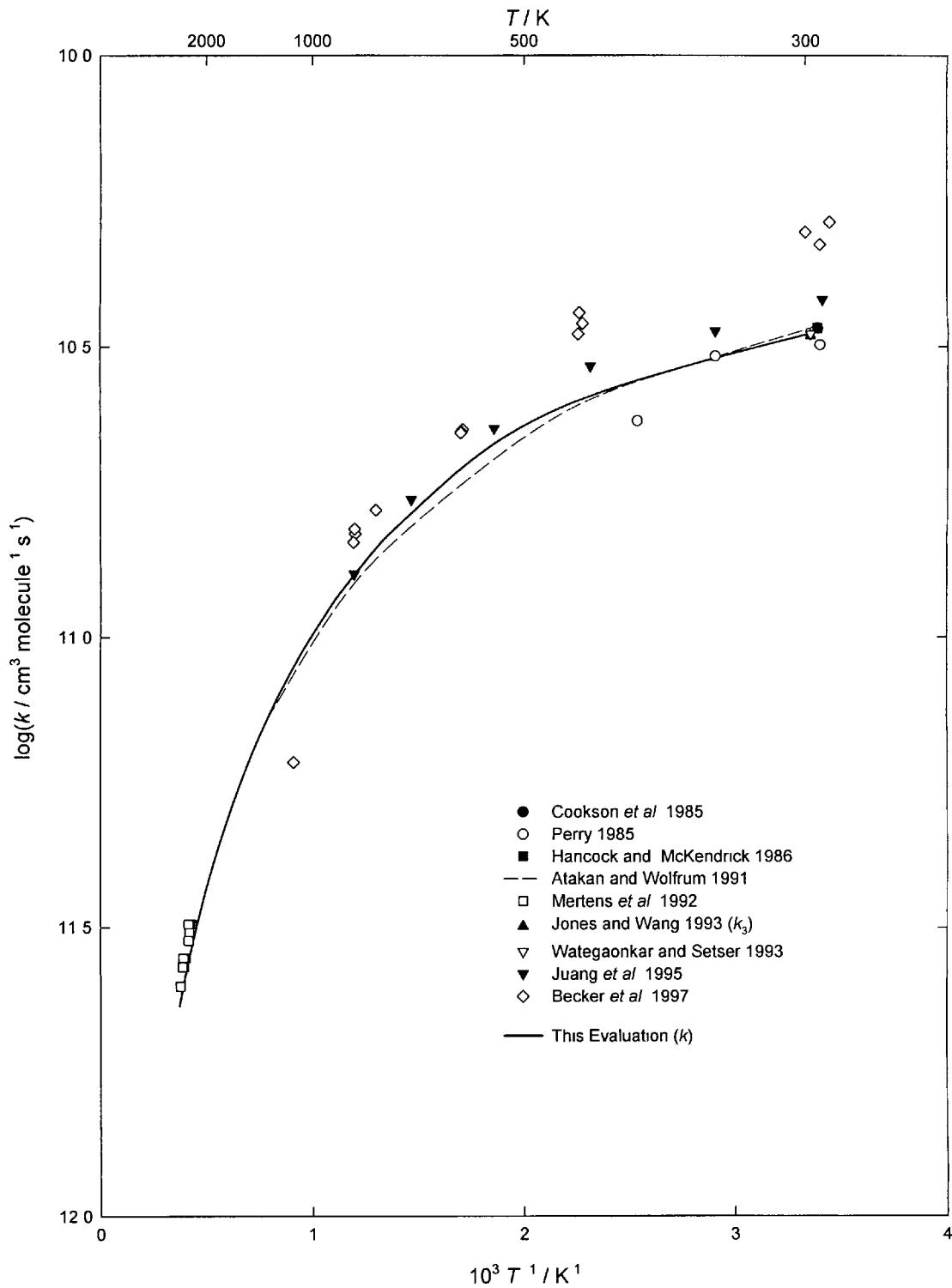
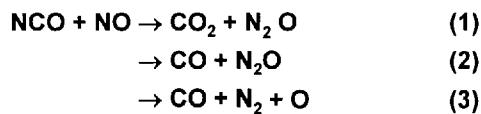
The preferred values for the overall rate coefficient, which are unchanged from those in our previous evaluation, CEC, 1994,<sup>12</sup> were based on the studies of Perry,<sup>1</sup> Hancock and McKendrick,<sup>2</sup> Atakan and Wolfrum,<sup>3</sup> and Mertens *et al.*<sup>4</sup> As can be seen in the accompanying figure, the more recent measurements are completely consistent with this expression.

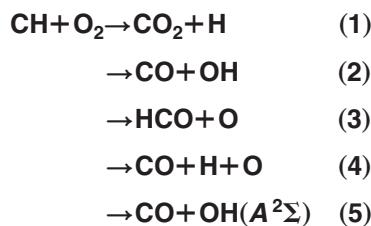
There is now more information on the branching ratios. The results of Cooper and Hershberger<sup>13</sup> are superseded by

the study of Cooper *et al.*<sup>10</sup> which includes a more detailed treatment of the secondary chemistry. Cooper *et al.*<sup>10</sup> find that over the temperature range 296–623 K Channel (3) contributes <10% to the overall reaction and is probably unimportant, and that the other two channels are probably equally important. RRKM calculations by Lin *et al.*<sup>14</sup> based on BAC-MP4 calculations of the potential energy surface, in which the barriers have been scaled to reproduce the room temperature experimental results, yield temperature dependent branching ratios of Channels (1) and (2), with Channel (3) unimportant over the range 300–5000 K, in good agreement with the observations of Cooper *et al.*<sup>10</sup> and with the finding of Hancock and McKendrick<sup>2,15</sup> that no NO+O chemiluminescence was observable in their experiments. In a more recent study Zhu and Lin<sup>16</sup> have recalculated the rate constants  $k$ ,  $k_1$ , and  $k_2$  using energies and structures predicted by high level molecular orbital methods. The expression for  $k$  obtained is in excellent agreement with the expression recommended here and also agrees with the limited data on the branching ratios. In the absence of extensive experimental data for the branching ratios, we therefore provisionally accept the expressions given by Zhu and Lin,<sup>16</sup> with substantial error limits.

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*Thermodynamic Data*

$$\begin{aligned}
 \Delta H_{298}^{\circ}(1) &= -772.0 \text{ kJ mol}^{-1} \\
 \Delta S_{298}^{\circ}(1) &= -59.7 \text{ J K}^{-1} \text{ mol}^{-1} \\
 K_c(1) &= 8.42 \cdot 10^{-6} T^{-0.656} \exp(+93080/T) \\
 &\quad (300 \leq T/\text{K} \leq 5000)
 \end{aligned}$$

$$\begin{aligned}
 \Delta H_{298}^{\circ}(3) &= -304.1 \text{ kJ mol}^{-1} \\
 \Delta S_{298}^{\circ}(3) &= -2.69 \text{ J K}^{-1} \text{ mol}^{-1} \\
 K_c(3) &= 0.846 T^{-0.026} \exp(+36580/T) \\
 &\quad (300 \leq T/\text{K} \leq 5000)
 \end{aligned}$$

$$\begin{aligned}
 \Delta H_{298}^{\circ}(5) &= -279.8 \text{ kJ mol}^{-1} \\
 \Delta S_{298}^{\circ}(5) &= -5.83 \text{ J K}^{-1} \text{ mol}^{-1} \\
 K_c(5) &= 6.28 \cdot 10^{-4} T^{0.890} \exp(+34180/T) \\
 &\quad (300 \leq T/\text{K} \leq 5000)
 \end{aligned}$$

$$\begin{aligned}
 \Delta H_{298}^{\circ}(2) &= -669.9 \text{ kJ mol}^{-1} \\
 \Delta S_{298}^{\circ}(2) &= -6.79 \text{ J K}^{-1} \text{ mol}^{-1} \\
 K_c(2) &= 17.8 T^{-0.507} \exp(+80310/T) \\
 &\quad (300 \leq T/\text{K} \leq 5000)
 \end{aligned}$$

$$\begin{aligned}
 \Delta H_{298}^{\circ}(4) &= -239.8 \text{ kJ mol}^{-1} \\
 \Delta S_{298}^{\circ}(4) &= 85.1 \text{ J K}^{-1} \text{ mol}^{-1} \\
 K_c(4) &= 5.79 \cdot 10^{24} T^{-0.378} \exp(+28820/T) \text{ molecule cm}^{-3} \\
 &\quad (300 \leq T/\text{K} \leq 5000)
 \end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data ( $k = k_1 + k_2 + k_3 + k_4 + k_5$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$3.3 \cdot 10^{-11}$	298	Messing, Sadowsky, and Filseth, 1979 <sup>1</sup>	(a)
$5.9 \cdot 10^{-11}$	298	Butler <i>et al.</i> , 1980, 1981 <sup>2,3</sup>	(b)
$5.4 \cdot 10^{-11}$	297–676	Berman <i>et al.</i> , 1982 <sup>4</sup>	(c)
$2.3 \cdot 10^{-11}$	290	Anderson, Freedman, and Kolb, 1987 <sup>5</sup>	(d)
$5.1 \cdot 10^{-11}$	297	Becker <i>et al.</i> , 1989 <sup>6</sup>	(e)
$3.5 \cdot 10^{-11}$	297	Okada <i>et al.</i> , 1993 <sup>7</sup>	(f)
$3.26 \cdot 10^{-11}$	298	Mehlmann <i>et al.</i> , 1996 <sup>8</sup>	(g)
$3.82 \cdot 10^{-11}$	298–708	Bocherel <i>et al.</i> , 1996 <sup>9</sup>	(h)
$5.6 \cdot 10^{-10} T^{-0.48}$	13–295		
$1.64 \cdot 10^{-10} T^{0.22}$	293–720	Taatjes, 1996 <sup>10</sup>	(i)
$1.25 \cdot 10^{-10}$	2600–3500	Markus, Roth, and Just, 1996 <sup>11</sup>	(j)
$1.62 \cdot 10^{-10}$	2200–2600	Röhrig <i>et al.</i> , 1997 <sup>12</sup>	(k)
$3.6 \cdot 10^{-11}$	298	Bergeat <i>et al.</i> , 2002 <sup>13</sup>	(l)
<i>Reviews and Evaluations</i>			
$5.5 \cdot 10^{-11}$	300–2000	CEC, 1992; 1994 <sup>14</sup>	(m)

**Comments**

- (a) Multiphoton dissociation of  $\text{CH}_3\text{NH}_2$ ; [CH] monitored by LIF and  $[\text{OH}(\text{A}^2\Sigma^+)]$  by chemiluminescence.  $k$  found to be pressure independent in the range 13–40 mbar Ar.
- (b) Multiphoton dissociation of  $\text{CH}_3\text{Br}$  at 193 nm; [CH] monitored by LIF near 430 nm at a total pressure of 132 mbar Ar.
- (c) Multiphoton dissociation of  $\text{CH}_3\text{Br}$  at 266 nm; [CH] monitored by LIF at 429.8 nm at a total pressure of 132 mbar Ar. No significant temperature dependence of  $k$  found.
- (d) Fast flow reactor in which CH was produced by sequential Br atom abstraction from  $\text{CHBr}_3$  by alkali

metal atoms (Na or K). [CH] and [OH] were monitored by LIF at a total pressure of 2.6 mbar He/Ar.

- (e) Pulsed excimer laser photolysis at 248 nm of  $\text{CH}_2\text{Br}_2$  or  $\text{CHClBr}_2$  in Ar/O<sub>2</sub> mixtures. Relative [CH] monitored by LIF at a total pressure of 2.6 mbar.
- (f) Pulsed excimer laser photolysis at 193 nm of  $\text{CHBr}_3$  in Ar/O<sub>2</sub> mixtures. Relative [CH] monitored by LIF. No pressure dependence of  $k$  observed over the range 6.6–39 mbar.
- (g) Pulsed laser photolysis at 248 nm of  $\text{CHBr}_3$  in Ar/O<sub>2</sub> mixtures. Relative [CH] monitored by LIF. Values of  $k$  were determined for the  $v=0$  and  $v=1$  states at a total pressure of 26 mbar. Value cited in the Table is for  $v=0$ ; for  $v=1$ ,  $k=4.13 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

- (h) Pulsed laser photolysis at 266 nm of CHBr<sub>3</sub> in Ar/O<sub>2</sub> mixtures. Relative [CH] monitored by LIF. A total pressure of 39 mbar was used in the measurements in the range 298–708 K.
- (i) Pulsed laser photolysis at 248 nm of CHBr<sub>3</sub> in He/O<sub>2</sub> mixtures. [OH] monitored by chemiluminescence. Measurements at 293 K show *k* to be independent of pressure over the range 65–460 mbar.
- (j) Shock tube study using reflected shocks in C<sub>2</sub>H<sub>6</sub>/Ar mixtures. [CH] monitored by tunable laser absorption following perturbation of the system by addition of O<sub>2</sub> at a total pressure of 1 bar. *k* derived by computer simulation using a detailed reaction mechanism.
- (k) Shock tube study using reflected shocks in C<sub>2</sub>H<sub>6</sub>/O<sub>2</sub>/Ar mixtures. [CH] profiles determined by cw laser absorption at 431.131 nm. Detailed mechanism used to fit [CH] profiles and hence derive values of *k*.
- (l) Fast flow system using He carrier gas at 2.6 mbar total pressure and CH production by reaction of K atoms with CHBr<sub>3</sub>. The [CH] was monitored by LIF in the presence of a large excess of O<sub>2</sub> to give values of *k*. Atomic H and O production were monitored by resonance fluorescence at 121.6 nm and 130.4 nm, respectively. CHO production was studied by LIF and the chemiluminescence spectrum from the OH produced was analyzed. The OH chemiluminescence could be used to follow the reaction progress and yielded a rate constant in good agreement with that from the [CH] decay.
- (m) Values of Berman *et al.*<sup>4</sup> adopted.

### Preferred Values

$k = 4 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 290–800 K.

$k = 1.4 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 2200–3500 K.

### Reliability

$\Delta \log k = \pm 0.3$  at 290 K, rising to  $\pm 0.5$  at 800 K.

$\Delta \log k = \pm 0.3$  over the range 2200–3500 K.

### Comments on Preferred Values

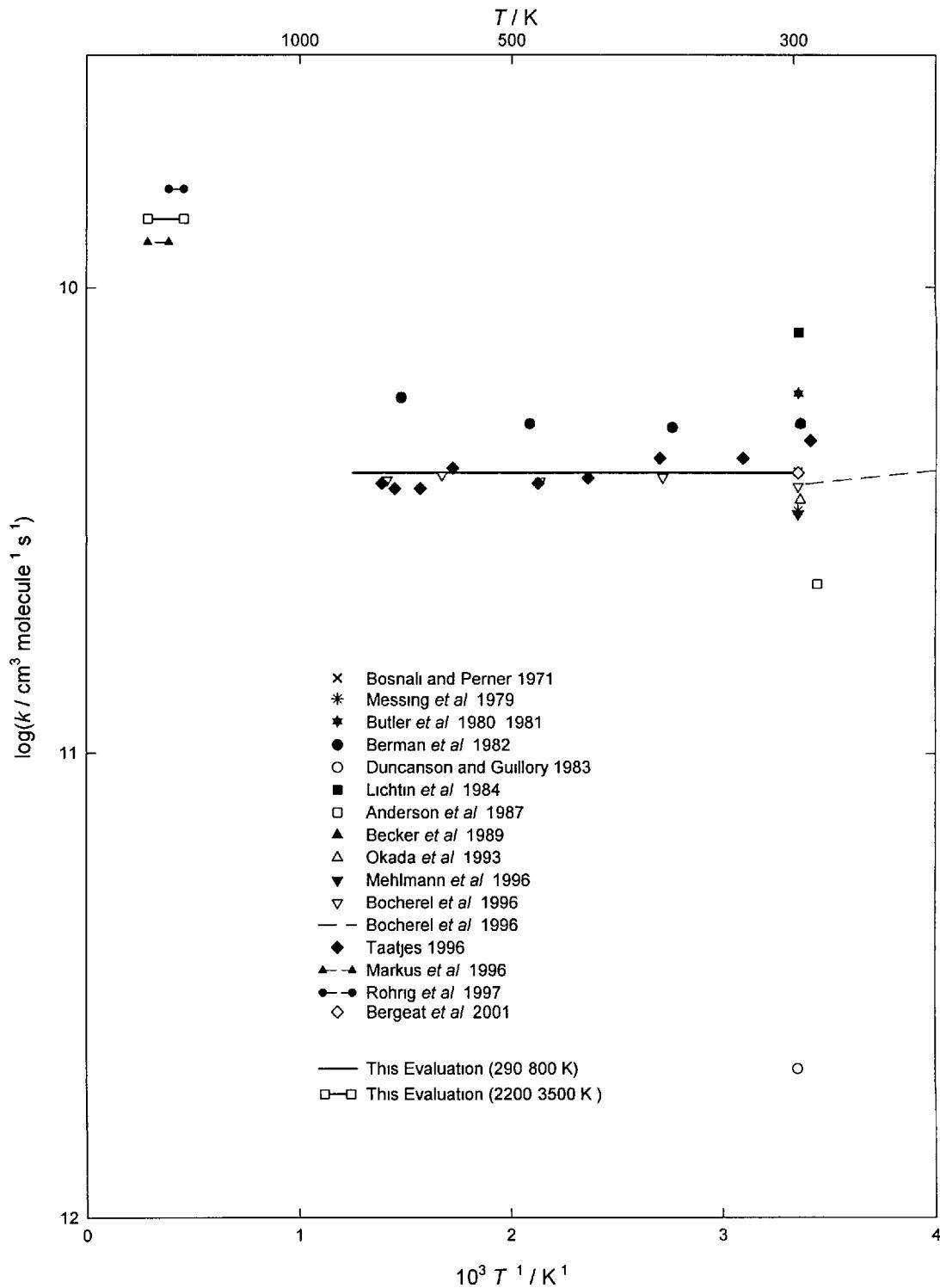
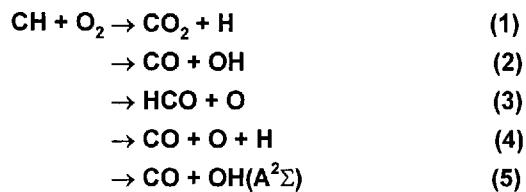
The values of *k* obtained at 298 K vary by more than a factor of 2 despite virtually identical techniques having been used in several cases. The mean value of the studies listed gives a value at 298 K of  $4.0 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . There is also a study by Bosnali and Perner<sup>15</sup> which gives an upper limit consistent with this mean value, a rather high value from Lichtin *et al.*,<sup>16</sup> and a value reported by Duncanson and Guillory<sup>17</sup> which is an order of magnitude lower than other measurements and which is discounted. Studies of the temperature dependence of *k* in the low temperature region suggest zero or a small negative temperature dependence in the range 298–708 K.

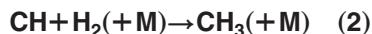
There are now two studies at higher temperatures, those of Markus *et al.*<sup>11</sup> and Röhrig *et al.*<sup>12</sup> at 2600–3500 K and 2200–2600 K, respectively, which are in good agreement but which give values of *k* approximately a factor of 3 greater than the value at 298 K. This may imply a change in reaction mechanism as temperature increases but studies are needed between 700 K and 2000 K before conclusions can be drawn. Our recommendations for high temperatures are limited to the temperature range of these two shock tube studies.<sup>11,12</sup>

There are a number of exothermic reaction channels available. The reaction mechanism is believed to be one of addition followed by very rapid decomposition of the adduct to products<sup>7</sup> but studies of the pressure dependence of *k* provide no evidence for stabilization of the adduct up to the highest pressures used (460 mbar in the low temperature region). Lin<sup>18</sup> observed vibrationally excited CO and CO<sub>2</sub> to be formed at room temperature. OH(A<sup>2Σ<sup>+</sup></sup>) is also known to be formed,<sup>1,13,16</sup> and its chemiluminescence has been used to monitor the kinetics of the reaction. Okada *et al.*<sup>7</sup> estimated the OH yield to be 20%. Bergeat *et al.*<sup>13</sup> were able to measure relative branching ratios for O and H production and also carried out *ab initio* calculations to estimate the branching ratios. Their experimental and theoretical results were consistent with the ratios  $k_1:k_2:k_3:k_4 = 0.3:0.2:0.2:0.3$ . These estimates probably offer the best current guide to the branching ratios until reliable experimental data become available.

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#### Thermodynamic Data

$$\begin{aligned}\Delta H_{298}^{\circ}(1) &= 11.96 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ}(1) &= -4.02 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 0.337 T^{0.061} \exp(-1360/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

$$\begin{aligned}\Delta H_{298}^{\circ}(2) &= -450.0 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ}(2) &= -119.6 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 9.84 \cdot 10^{-28} T^{0.488} \exp(+54280/T) \text{ cm}^3 \text{ molecule}^{-1} \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$1.7 \cdot 10^{-11}$	298	Bosnali and Perner, 1971 <sup>1</sup>	(a)
$2.3 \cdot 10^{-11}$	298	Butler <i>et al.</i> , 1979, <sup>2</sup> 1980 <sup>3</sup>	(b)
$k_2 = 2.4 \cdot 10^{-12} \exp(520/T)$	159–300	Berman and Lin, 1984 <sup>4</sup>	(c)
$k_1 = 3.6 \cdot 10^{-10} \exp(-1960/T)$	400–660		
$k_1 = 2.4 \cdot 10^{-10} \exp(-1760/T)$	372–675	Zabarnick, Fleming, and Lin, 1986 <sup>5</sup>	(d)
$1.4 \cdot 10^{-11}$	297		
$5.8 \cdot 10^{-13}$	298	Böhland, Temps, and Wagner, 1987 <sup>6</sup>	(e)
$6.3 \cdot 10^{-13}$	290	Anderson, Freedman, and Kolb, 1987 <sup>7</sup>	(f)
$2.0 \cdot 10^{-12}$	297	Becker <i>et al.</i> , 1989 <sup>8</sup>	(g)
$5.99 \cdot 10^{-14} \exp(736/T)$	207–298	Becker, Kurtenbach, and Wiesen, 1991 <sup>9</sup>	(h)
$3.75 \cdot 10^{-10} \exp(-1662/T)$	327–397		
$2.3 \cdot 10^{-10} \exp(-1650/T)$	362–466	McIlroy and Tully, 1993 <sup>10</sup>	(i)
$3.1 \cdot 10^{-10} \exp(-1650/T)$	484–744	Brownword <i>et al.</i> , 1997 <sup>11</sup>	(j)
$k_2^0[\text{Ar}] = [\text{Ar}]4.7 \cdot 10^{-26} T^{-1.6}$	53–484		
$k_2^\infty = 2.5 \cdot 10^{-10} T^{0.08}$			
$k_2^0[\text{He}] = [\text{He}]1.5 \cdot 10^{-30} T^{-2.6}$	185–800	Fulle and Hippler, 1997 <sup>12</sup>	(k)
$k_2^\infty = 8.5 \cdot 10^{-11} T^{0.15}$			
$F_{c,2} = 0.48 + 0.25 \exp(-T/300)$			
<i>Reviews and Evaluations</i>			
$2.4 \cdot 10^{-10} \exp(-1760/T)$	300–1000	CEC, 1992, 1994 <sup>13</sup>	(l)

#### Comments

- (a) Pulse radiolysis of  $\text{CH}_4/\text{H}_2$  mixtures at pressures in the range 15–270 mbar. [CH] monitored by absorption spectroscopy at 314.4 nm.
- (b) CH generated by pulsed multiphoton dissociation of  $\text{CHBr}_3$  at 193 nm and monitored by LIF at 429.8 nm. Total pressures, 40–130 mbar Ar.
- (c) Pulsed multiphoton dissociation of  $\text{CHBr}_3$  at 266 nm and monitored by LIF at 429.8 nm at a total pressure of 130 mbar Ar. Pressure dependence of  $k$  studied at 297 K over the range 33–790 mbar;  $k$  increases with increase in pressure.
- (d) Technique as in (c).  $k_1$  determined by measuring total rate at and subtracting Channel (2) contribution, obtained from Ref. 4.
- (e) Fast flow reactor in which CH radicals were produced by excimer laser photolysis at 193 nm of  $\text{CH}_2\text{CO}$ . [CH] and  $[\text{CH}_2]$  monitored by laser magnetic resonance, absolute [H] by ARAS. Rate constant attributed to Channel (1). Total pressure range, 2.2–2.8 mbar He.
- (f) Fast flow reactor in which CH radicals were produced by reaction of  $\text{CH}_3\text{Br}$  with an excess of alkali-metal

- (g) CH generated by pulsed excimer laser photolysis at 248 nm of  $\text{CH}_2\text{Br}_2$  in a bath gas of Argon; at a total pressure of 3.4 mbar. Relative [CH] monitored by LIF.
- (h) CH generated pulsed excimer laser photolysis at 248 nm of  $\text{CHClBr}_2$  in a bath gas of Argon. Relative [CH] monitored by LIF. A total pressure of 5.3 mbar was used for experiments in which the temperature was varied over the range 207–397 K and pressures in the range 2.6–778 mbar for experiments at 298 K. The reaction exhibited a negative pressure dependence at 298 K.
- (i) CH produced by pulsed excimer laser photolysis at 248 nm of  $\text{CHBr}_3$  or  $\text{CHClBr}_2$  in a bath gas of He. Relative [CH] monitored by LIF.  $k$  determined as a function of temperature (240–470 K) at 11 mbar and 987 mbar total pressure and as a function of pressure (10.5 mbar–0.99 bar) at 294 K. The reaction exhibits a negative pressure dependence at 294 K and a complex temperature dependence in the pressure range 10.7 mbar–1 bar. At low pressures and high temperatures the contribution of Channel (2) is small and the expression for  $k_1$

cited in the Table could be derived under such conditions. RRKM-master equation calculations were applied to the data on  $k$  obtained under conditions where Channel (1) was dominant (high pressures and low temperatures) to derive values of  $k_2^\infty$  ranging from  $9.15 \cdot 10^{-11}$  at 240 K to  $6.11 \cdot 10^{-11}$  at 470 K.

- (j) CH produced by pulsed laser photolysis at 266 nm from  $\text{CHBr}_3$  in a bath gas of Ar.  $[\text{CH}(v=0)]$  and  $[\text{CH}(v=1)]$  monitored by LIF. Heated cells were used for the temperature range 86–744 K and cryogenically cooled cells (CRESU technique) for the range 13–295 K. Values of  $k$  for  $\text{CH}(v=0)$  were determined over the range 53–744 K and for  $\text{CH}(v=1)$  over the range 23–584 K. The pressure dependence was studied over the range 5.3–530 mbar in the heated cells and 0.37–5.9 mbar in the cryogenically cooled experiments. The rate constant exhibits a complex  $T$  and  $P$  dependence. The tabulated value of  $k_2^\infty$  is derived from the quenching rate of  $\text{CH}(v=1)$  which is considered to be a more reliable source than values derived by from the  $\text{CH}(v=0)$  reaction rates.
- (k) CH produced by excimer laser photolysis at 248 nm of  $\text{CHBr}_3$  in a bath gas of He over a range of total pressures of 1–160 bar. Relative  $[\text{CH}]$  monitored by LIF. In the data analysis the low pressure data of Zabarnick *et al.*<sup>5</sup> are assumed for  $k_1$  and values of  $k_1^0$  and  $k_1^\infty$  are derived by fitting using Troe formalism (see Introduction)
- (l) Based on the data of Zabarnik *et al.*<sup>5</sup>

### Preferred Values

$k_1 = 2.9 \cdot 10^{-10} \exp(-1670/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 200–1000 K.

$k_2^0 = 4.7 \cdot 10^{-26} T^{-1.6} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  for M=Ar over the range 200–1000 K.

$k_2^\infty = 8.5 \cdot 10^{-11} T^{0.15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 200–1000 K.

$F_{c,2} = 0.48 + 0.25 \exp(-T/300)$  for M=Ar over the temperature range 200–1000 K.

### Reliability

$\Delta \log k_1 = \pm 0.3$  over the range 200–1000 K.

$\Delta \log k_2^0 = \pm 0.3$  for M=Ar over the range 200–1000 K.

$\Delta \log k_2^\infty = \pm 0.3$  over the range 200–1000 K.

$\Delta F_{c,2} = \pm 0.1$  for M=Ar over the range 200–1000 K.

### Comments on Preferred Values

The third body combination, Channel (2), is important at low temperatures and high pressures giving rise to a pressure

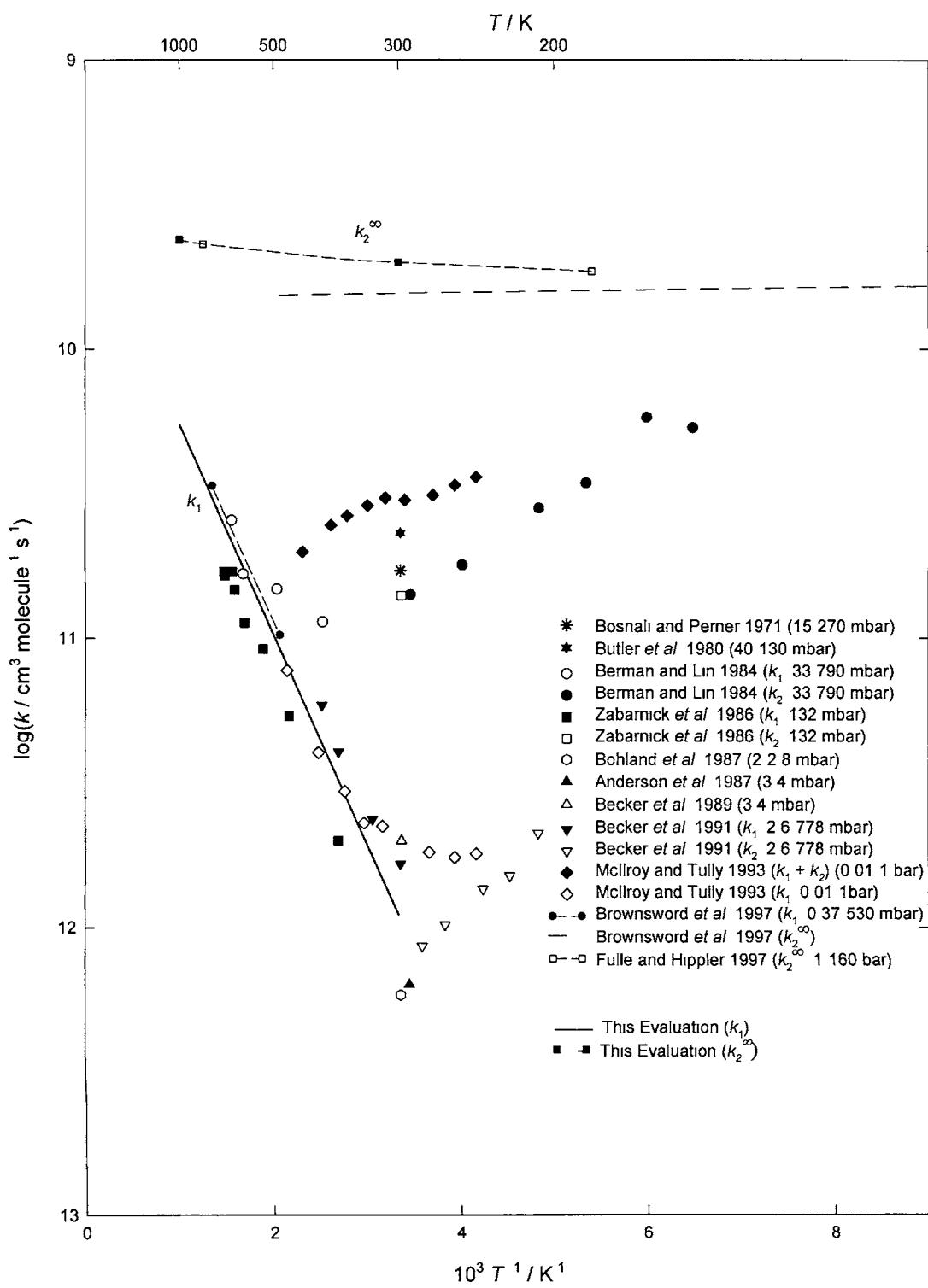
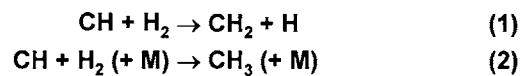
dependent overall rate constant in many of the studies of this reaction. A recent study by Fulle and Hippler,<sup>12</sup> covering a wide range of temperature (185–800 K) and pressure (1–160 bar), and another by Brownsword *et al.*,<sup>11</sup> at lower temperatures, have done much to clarify the relative importance of the two reaction channels.

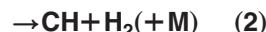
There have been a number of studies in which conditions of sufficiently high temperature and/or low pressure have been used to enable the contribution of Channel (1) to be isolated from that of Channel (2) and hence to yield reliable values of  $k_1$ . The preferred expression for  $k_1$  is a fit to the high temperature, low pressure data of Becker *et al.*,<sup>9</sup> McIlroy and Tully,<sup>10</sup> Brownsword *et al.*,<sup>11</sup> Berman and Lin,<sup>4</sup> and Zabarnick *et al.*<sup>5</sup> which are in good agreement. The single temperature studies of Bosnali and Perner,<sup>1</sup> Butler *et al.*,<sup>2,3</sup> Böhland *et al.*,<sup>6</sup> Anderson *et al.*,<sup>7</sup> Becker *et al.*<sup>8</sup> and Braun *et al.*<sup>14</sup> also support this expression. It should be noted that  $k_1$  may also be pressure dependent.

Both Fulle and Hippler<sup>12</sup> and Brownsword *et al.*<sup>11</sup> have derived rate parameters for  $k_2$  by fitting their pressure and temperature dependent data to expressions of the type devised by Troe and his coworkers (see Introduction, Section 2.4). Fulle and Hippler<sup>12</sup> used the data of Zabarnick *et al.*<sup>5</sup> for  $k_1$  to combine with their own data to obtain  $k_2$  but Brownsword *et al.*<sup>11</sup> obtained values of both  $k_1$  and  $k_2$  from their own data. The two studies agree well and are the basis for our recommended expressions for  $k_2$ . The study of McIlroy and Tully<sup>10</sup> also gives a value of  $k_2^\infty$  within the error limits of our recommendations.

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*Thermodynamic Data*

$$\Delta H^\circ_{298}(1) = 461.5 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = 115.5 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 3.43 \cdot 10^{26} T^{-0.427} \exp(-55580/T) \text{ molecule cm}^{-3}$$

(300 ≤ T/K ≤ 5000)

$$\Delta H^\circ_{298}(2) = 449.6 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = 119.6 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 1.02 \cdot 10^{27} T^{-0.488} \exp(-54230/T) \text{ molecule cm}^{-3}$$

(300 ≤ T/K ≤ 5000)

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data ( $k = k_1 + k_2$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$k_1 = 1.0 \cdot 10^{-8} \exp(-44900/T)$	1700–2300	Bhaskaran, Frank, and Just, 1979 <sup>1</sup>	(a)
$k_1 = 3.23 \cdot 10^{-8} \exp(-46100/T)$	2150–2850	Roth, Barner, and Löhr, 1979 <sup>2</sup>	(b)
$k_1 = 3.2 \cdot 10^{-8} \exp(-46000/T)$	2100–3800	Markus, Woiki, and Roth, 1992 <sup>3</sup>	(c)
$k_2 = 1.15 \cdot 10^{-9} \exp(-41500/T)$	2500–3800	Dean and Hanson, 1992 <sup>4</sup>	(d)
$k_2 = 8.3 \cdot 10^{-9} \exp(-42800/T)$	1224–2520	Lim and Michael, 1994 <sup>5</sup>	(e)
$k_1 = 4.7 \cdot 10^{-9} \exp(-42500/T)$	2200–2600	Röhrig <i>et al.</i> , 1997 <sup>6</sup>	(f)
$k_2 = 1.7 \cdot 10^{-8} \exp(-42900/T)$	2000–4000	Eng <i>et al.</i> , 2001 <sup>7</sup>	(g)
See Comment (g)			
<i>Reviews and Evaluations</i>			
$k_1 = 1.7 \cdot 10^{-8} \exp(-45600/T)$	1500–3000	Warnatz, 1984 <sup>8</sup>	(h)
$k_1 = 1.7 \cdot 10^{-8} \exp(-45600/T)$	1500–3000	CEC, 1992, 1994 <sup>9</sup>	(i)

**Comments**

- (a) Shock-tube study of  $\text{C}_2\text{H}_6/\text{O}_2$  mixtures with direct detection of H and O by atomic resonance absorption spectrometry.
- (b) Shock-tube study of  $\text{C}_2\text{H}_6/\text{Ar}$  mixtures with direct measurement of time dependent [H]. Pressures ~1.5 bar.
- (c) Shock tube study on  $\text{C}_2\text{H}_6/\text{Ar}$  mixtures using reflected shock waves at pressures in the range 1.1–1.8 bar. [H] was monitored by ARAS at 121.6 nm and [CH] by ring dye laser absorption spectroscopy at 431.131 nm. Values of  $k$  were determined from the initial slopes of the absorption profiles but in a later study Markus and Roth<sup>10</sup> found the initial slopes of their [CH] profiles to be pressure dependent.
- (d) Shock tube study on  $\text{C}_2\text{H}_6/\text{Ar}$  or  $\text{CH}_4/\text{Ar}$  mixtures using reflected shock waves at pressure of 0.5–1.3 bar. [CH] was monitored by narrow-linewidth laser absorption at 431 nm and [C] by ARAS at 156.1 nm. Values of  $k$  were derived by fitting the [CH] and [C] profiles using a detailed mechanism. Kiefer and Kumaran<sup>11</sup> later showed that the profiles could be fitted using different values of  $k_1$  and  $k_2$ . The expression  $k_2 = 3.3 \cdot 10^{-8} \exp(-45600/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was chosen to account for the rapid rise in the [CH] and [C].
- (e) Shock tube study on  $\text{CH}_3/\text{Kr}$  mixtures using reflected shock waves at pressure below 1 bar. [H] was moni-

tored by ARAS at 121.6 nm. Values of  $k$  were determined by fitting the [H] profiles using a detailed mechanism.

- (f) Shock tube study on  $\text{C}_2\text{H}_6/\text{O}_2/\text{Ar}$  mixtures using reflected shocks at pressures of 1.1 or 1.2 bar. [CH] was monitored by narrow-linewidth laser absorption at 431.131 nm. Values of  $k$  were obtained by fitting the [CH] profiles using a detailed mechanism.
- (g) Shock tube study on  $\text{CH}_2\text{N}_2\text{CH}_3/\text{Ar}$  or  $(\text{CH}_3)_2\text{CO}/\text{Ar}$  mixtures using incident and reflected shocks at pressures in the range 0.1–4.8 bar. [H] was monitored by ARAS at 121.6 nm. Values of  $k$  were obtained from the initial slopes of the [H] profiles. The H atom signal was calibrated using  $\text{H}_2/\text{N}_2\text{O}$  system to generate known concentrations of H atoms. The branching ratios, which were determined from the initial concentration of  $\text{CH}_3$  precursor and the [H] generated, were found to be pressure dependent indicating that the reaction is still in its “fall-off” region. Arrhenius expressions for  $k$  were not derived—the paper should be consulted for values of  $k$ . The system was modeled using master equation and statistical unimolecular rate theories.
- (h) Based on data of Bhaskaran *et al.*<sup>1</sup> and Roth *et al.*<sup>2</sup>
- (i) Recommendation of Warnatz.<sup>8</sup>

**Preferred Values**

$k_1 = 1.7 \cdot 10^{-8} \exp(-45600/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 1500–3500 K.

$k_2 = 1.1 \cdot 10^{-8} \exp(-42800/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 1500–3500 K.

### Reliability

$\Delta \log k_1 = \pm 0.5$  over the range 1500–3500 K.  
 $\Delta \log k_2 = \pm 0.5$  over the range 1500–3500 K.

### Comments on Preferred Values

The preferred expression for  $k_2$  is based on the studies of Dean and Hanson,<sup>4</sup> Markus *et al.*,<sup>3</sup> and Röhrig *et al.*<sup>6</sup> There are some uncertainties associated with the experiments of Dean and Hanson<sup>4</sup> and Markus *et al.*<sup>3</sup> (see Comments) but the study of Röhrig *et al.*<sup>6</sup> appears to be reliable. The expression recommended is also very close to the expression derived by Fulle and Hippler<sup>12</sup> from their study of the reverse reaction [ $k_2 = 8.3 \cdot 10^{-9} \exp(-42800/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ]. The approximate expression obtained by Markus *et al.*<sup>13</sup> is also in reasonable agreement.

The preferred expression for  $k_1$  is based on the studies of Bhaskaran *et al.*,<sup>1</sup> Roth *et al.*,<sup>2</sup> Markus *et al.*,<sup>3</sup> Lim and Michael,<sup>5</sup> and Eng *et al.*<sup>7</sup> all of which are in good agreement. Its derivation has also been influenced by the values of the branching ratios obtained by Eng *et al.*<sup>7</sup>

There is little direct experimental information on the branching ratios. Markus *et al.*<sup>3</sup> determined both  $k_1$  and  $k_2$  in a single study but there are uncertainties associated with pressure effects in their measurements [Comment (c)]. Dean and Hanson<sup>4</sup> required values of both  $k_1$  and  $k_2$  to model their measurements but the results were not particularly sensitive

to  $k_1$ . The most reliable study appears to be that of Eng *et al.*<sup>7</sup> who found the branching ratio ( $k_1/k_2$ ) to be almost temperature independent over the range 2500–3100 but to be strongly pressure dependent, increasing from 0.3 to 0.7 in going from ~0.1 to 2 bar at 2750 K. Their modeling of the reaction suggests that at 1 bar and 2000 K Channel (2) predominates while by 3000 K Channel (1) has become dominant. Our preferred expressions give values of the branching ratios approximating to those obtained by Eng *et al.*<sup>7</sup> at pressures above 1 bar.

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## CH+H<sub>2</sub>O→Products

### Rate Coefficient Data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$4.5 \cdot 10^{-11}$	298	Bosnali and Perner, 1971 <sup>1</sup>	(a)
$9.5 \cdot 10^{-12} \exp(380/T)$	298–669	Zabarnick, Fleming, and Lin, 1988 <sup>2</sup>	(b)
$5.09 \cdot 10^{-8} T^{-1.42}$	291–723	Blitz <i>et al.</i> , 1999 <sup>3</sup>	(c)
<i>Reviews and Evaluations</i>			
$9.5 \cdot 10^{-12} \exp(380/T)$	300–1000	CEC, 1992; 1994 <sup>4</sup>	(d)

### Comments

- Pulse radiolysis of CH<sub>4</sub>/H<sub>2</sub>O mixtures at a total pressure of 20 mbar. [CH] monitored by absorption spectroscopy at 314.4 nm.
- Multiphoton dissociation of CH<sub>3</sub>Br at 266 nm; [CH] monitored by laser induced fluorescence at 429.8 nm in an excess of H<sub>2</sub>O at total pressures in the range 25–400 mbar (bath gas, Ar). No pressure dependence of  $k$  observed.
- Pulsed laser photolysis at 248 nm of CHBr<sub>3</sub>/H<sub>2</sub>O/He mixtures. [CH] was monitored by time-resolved LIF at

~390 nm or ~430 nm under conditions of H<sub>2</sub>O in large excess over CH. Values of  $k$  were independent of total pressure in the range 26–260 mbar. The reactions of CH( $v=1$ ) and CD( $v=0,1,2$ ) with H<sub>2</sub>O and D<sub>2</sub>O were also studied.

(d) Accepts the expression of Zabarnick *et al.*<sup>2</sup>

### Preferred Values

$k = 7.6 \cdot 10^{-8} T^{-1.42} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 290–1000 K.

*Reliability*

$\Delta \log k = \pm 0.5$  at 290 K, rising to  $\pm 1.0$  at 1000 K.

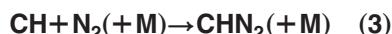
*Comments on Preferred Values*

All of the available data are cited in the Table. Although the studies of Zabarnick *et al.*<sup>2</sup> and Blitz *et al.*<sup>3</sup> are in reasonable agreement with regard to the temperature dependence of  $k$  the absolute values in the two studies differ by approximately a factor of 2, while the value of  $k$  (298 K) obtained by Bosnali and Perner<sup>1</sup> is nearly a factor of 3 larger than that of Blitz *et al.*<sup>3</sup> Blitz *et al.*<sup>3</sup> have suggested that the differences may be due largely to the difficulty in determining the H<sub>2</sub>O concentration because of its strong propensity to adsorb on vessel walls. In that respect their technique appears to be the most reliable of the studies. However, the preferred expression for  $k$  is obtained by combining the tem-

perature dependence found by Blitz *et al.*<sup>3</sup> with an  $A$  factor based on the mean value of  $k$  (298 K) from the three cited studies.<sup>1–3</sup> There is some evidence from the modeling of low pressure stoichiometric CH<sub>4</sub>/O<sub>2</sub>/N<sub>2</sub> flames<sup>5</sup> that at high temperatures the rate constant may be higher than predicted by these recommendations, but within the error limits suggested.

**References**

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*Thermodynamic Data*

$$\Delta H^\circ_{298}(1) = 11.4 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = -19.5 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 1.97 \cdot 10^{-3} T^{0.553} \exp(-1154/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(2) = 122.3 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = -32.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 6.73 \cdot 10^{-6} T^{1.212} \exp(-14380/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(3) = -101.5 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = -124.6 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 1.56 \cdot 10^{-30} T^{1.448} \exp(+12430/T) \text{ cm}^3 \text{ molecule}^{-1} \\ (300 \leq T/\text{K} \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data ( $k = k_1 + k_2 + k_3$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$9.3 \cdot 10^{-13}$ at 132 mbar Ar	300	Butler <i>et al.</i> , 1980 <sup>1</sup>	(a)
$k_3^\infty = 6.3 \cdot 10^{-13}$	300	Wagel <i>et al.</i> , 1982 <sup>2</sup>	(b)
$k_3^\infty [\text{N}_2 + \text{Ar}] = [\text{N}_2 + \text{Ar}] 2.6 \cdot 10^{-31}$	300		
$1.7 \cdot 10^{-14} \exp(975/T)$ at 130 mbar Ar	297–675	Berman and Lin, 1983 <sup>3</sup>	(c)
$k_3^\infty = 2 \cdot 10^{-11}$			
$k_3^\infty [\text{N}_2 + \text{Ar}] = 2.8 \cdot 10^{-31} [\text{N}_2 + \text{Ar}]$			
$7.1 \cdot 10^{-14}$ at 13 mbar Ar	300	Duncanson and Guillory, 1983 <sup>4</sup>	(d)
$8.0 \cdot 10^{-14}$ at 2.6 mbar Ar	300	Becker, Englehardt, and Wiesen, 1989 <sup>5</sup>	(e)
$1.0 \cdot 10^{-12} \exp(-7000/T)$	2632–2859	Lindackers, Burmeister, and Roth, 1990 <sup>6</sup>	(f)
$7.3 \cdot 10^{-12} \exp(-11060/T)$	2500–3820	Dean, Hanson, and Bowman, 1990 <sup>7</sup>	(g)
$k_3 = 2.58 \cdot 10^{-15} \exp(1150/T)$ at 26 mbar Ar	301–894	Becker <i>et al.</i> , 1992 <sup>8</sup>	(h)
$44.0 T^{-5.3} \exp(-664.6/T)$ at 130 mbar (Ar+N <sub>2</sub> )	298–1075	Medhurst, Garland, and Nelson, 1993 <sup>9</sup>	(i)
$k_3^\infty = 1.9 \cdot 10^{-12} \exp(433/T)$	298–750	Becker, Geiger, and Wiesen, 1995 <sup>10</sup>	(j)
$k_3^\infty [\text{N}_2 + \text{Ar}] = 1.1 \cdot 10^{-21} T^{-3.5} \exp(-770/T) [\text{N}_2 + \text{Ar}]$			
$1.38 \cdot 10^{-13}$ at 26 mbar Ar	297	Mehlman <i>et al.</i> , 1996 <sup>11</sup>	(k)
$3.01 \cdot 10^{-13}$ at 66 mbar Ar	297		
$4.96 \cdot 10^{-14}$ at 26 mbar Ar	359		
$k_3^\infty [\text{Ar}] = 8.34 \cdot 10^{-26} T^{-2.3} [\text{Ar}]$	202–584	Brownword <i>et al.</i> , 1996 <sup>12</sup>	(l)
$k_3^\infty = 9.6 \cdot 10^{-11} T^{-0.15}$	200–500	Fulle and Hippler, 1996 <sup>13</sup>	(m)
$k_3^\infty [\text{Ar}] = 3.9 \cdot 10^{-25} T^{-2.6} [\text{Ar}]$			

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
$k_3 \cdot [He] = 7.8 \cdot 10^{-25} T^{-2.8} [He]$ $F_{2,c} = \exp(-T/660) + \exp(-1080/T)$ for M=He $k_3 \cdot [Ar] = 4.4 \cdot 10^{-26} T^{-2.2} [Ar]$	52–584	Le Picard <i>et al.</i> , 1998 <sup>14</sup>	(n)
<i>Reviews and Evaluations</i> $2.6 \cdot 10^{-12} \exp(-9030/T)$ for $p < 1 \text{ bar}$	2000–4000	CEC, 1994 <sup>15</sup>	(o)

### Comments

- (a) Pulsed laser photolysis at 193 nm of slowly flowing mixtures of  $\text{CHBr}_3/\text{Ar}/\text{N}_2$ . CH produced by multiphoton absorption by the  $\text{CHBr}_3$  and [CH] monitored by LIF near 430 nm.  $k$  was shown to be pressure dependent. The value cited is at 132 mbar Ar; other values are  $5.6 \cdot 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (79 mbar) and  $4.9 \cdot 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (39 mbar).
- (b) CH produced by pulsed  $\text{CO}_2$  laser multiphoton dissociation of  $\text{CH}_3\text{NH}_2$ ,  $\text{CH}_3\text{CN}$ , or  $c\text{-C}_3\text{H}_6$ . [CH] monitored by time-resolved LIF. Slowly flowing mixtures of the source gas and  $\text{N}_2$  in Ar carrier gas were studied at pressures in the range 1.3–105 mbar. Values of  $k_0$  and  $k_\infty$  were derived using a simple Lindemann model.
- (c) Pulsed laser photolysis at 266 nm of slowly flowing mixtures of  $\text{CHBr}_3/\text{N}_2/\text{Ar}$ . [CH] monitored by time resolved LIF at 429.8 nm. Total pressures were varied over the range 33–1036 mbar at 297 K, and the temperature was varied over the range 297–675 K at a constant pressure of 132 mbar. No significant difference was found between the collision efficiencies of  $\text{N}_2$  and Ar.
- (d) CH produced by pulsed  $\text{CO}_2$  laser multiphoton dissociation of  $\text{CH}_3\text{OH}$  in  $\text{N}_2/\text{Ar}$  mixtures. [CH] monitored by time resolved LIF at 430 nm. Value of  $k$  for relaxation of  $\text{CH}(v=1)$  at 300 K was also determined.
- (e) Pulsed laser photolysis at 248 nm of slowly flowing  $\text{CH}_2\text{Br}_2/\text{N}_2/\text{Ar}$  and  $\text{CHClBr}_2/\text{N}_2/\text{Ar}$  mixtures at a total pressure of 2.6 mbar. [CH] monitored by time-resolved LIF at 430 nm.
- (f) Study of reflected shock waves in  $\text{C}_2\text{H}_6/\text{N}_2/\text{Ar}$  mixtures at pressures in the range 1.5–1.79 bar. Studies carried out on  $\text{N}_2$  free mixtures, with the [C] and [H] profiles being measured by ARAS, were used to characterize the mechanism of  $\text{C}_2\text{H}_6$  pyrolysis under these conditions. In studies with  $\text{N}_2$  present, [N] profiles were measured by ARAS and the profiles were fitted by computer simulation to a detailed mechanism to derive values of  $k$ .
- (g) Shock tube studies on  $\text{CH}_4/\text{N}_2/\text{Ar}$  and  $\text{C}_2\text{H}_6/\text{N}_2/\text{Ar}$  mixtures at pressures in the range 0.62–1.02 bar. [CH] monitored by time resolved LIF at 431.131 nm and in some experiments [N] was monitored by time-resolved ARAS. Values of  $k$  were obtained by fitting the [CH] profiles using computer simulation of a detailed mechanism. The fitting was shown to be sensitive to  $k$ .
- (h) Technique as in (e) but measurements carried out at 26
- (i) Pulsed laser photolysis of  $\text{CHClBr}_2/\text{N}_2/\text{Ar}$  mixtures in a high temperature flow reactor at pressures in the range 13–263 mbar. [CH] monitored by time resolved LIF near 387 nm.  $k$  was studied as a function of temperature at 131 mbar total pressure and as a function of pressure at 298 K and 750 K.
- (j) Technique as in (e). Values of  $k$  were determined as a function of temperature at pressures of 26 mbar, 131 mbar, and 816 mbar, and as a function of pressure at temperatures of 298 K, 410 K, 561 K, and 750 K. No significant difference was found between the collision efficiencies of  $\text{N}_2$  and Ar. Values of  $k_0$ ,  $k_\infty$ , and  $F_c$  were obtained by fitting the data to Troe expressions. Values of  $F_c$  obtained were 0.60 (298 K), 0.47 (410 K), 0.34 (561 K), and 0.25 (750 K).
- (k) Pulsed laser photolysis at 248 nm of  $\text{CHBr}_3/\text{N}_2/\text{Ar}$  mixtures. [CH] was monitored by time-resolved LIF at 431.5 nm. Values of  $k$  for the relaxation of  $\text{CH}(v=1)$  at 296 K were also determined.
- (l) Pulsed laser photolysis at 266 nm of slowly flowing  $\text{CHBr}_3/\text{N}_2/\text{Ar}$  mixtures. [CH] monitored by time-resolved LIF using excitation at ~430 nm and detection at ~490 nm. Values of  $k$  were determined as a function of pressure in the range 5–520 mbar at temperatures of 202 K, 294 K, 364 K, 484 K, and 584 K. No significant difference was found between the collision efficiencies of  $\text{N}_2$  and Ar. Values of  $k_0$ , and  $k_\infty$  were derived by a global fit of the data using the Troe formalism. There is a degree of uncertainty in the expression derived for  $k_\infty$  because of the relatively long extrapolation to high pressures and only the expression for  $k_0$  is cited.
- (m) Pulsed laser photolysis at 248 nm of slowly flowing  $\text{CHBr}_3$  (or  $\text{CHClBr}_2$ )/ $\text{N}_2/\text{He}$  mixtures. [CH] was monitored by time resolved LIF using excitation at 429.19 nm and detection at 431.5 nm. Values of  $k$  were determined as a function of pressure using pressures in the range 1–150 bar at temperatures of 200 K, 250 K, 300 K, 400 K, and 500 K. The equilibrium constant for Channel (2) was determined over the range 542–715 K. The data were fitted using the Troe formalism to obtain values of  $k_0$ ,  $k_\infty$ , and  $F_c$ .
- (n) Low temperature study using isentropic expansion of gas through a Laval nozzle (CRESU technique) to

achieve temperatures of 52–54 K. Flows of CHBr<sub>3</sub>/N<sub>2</sub>/Ar mixtures were subjected to pulsed laser photolysis at 266 nm and the [CH] was monitored by time resolved LIF using excitation at 430 nm and detection at 490 nm. Values of  $k$  were obtained at 52–54 K as a function of pressure at Ar densities over the range (5–82) · 10<sup>17</sup> molecule cm<sup>-3</sup>. The values obtained in this study were combined with data from the earlier study of Brownsword *et al.*<sup>12</sup> to obtain the expression for  $k_3^{\circ}$  via a global fitting procedure. The same experimental results are reported in Le Picard and Canosa.<sup>16</sup>

- (o) Based on the high temperature data of Dean *et al.*<sup>7</sup> and Lindackers *et al.*<sup>6</sup>

### Preferred Values

$$(k_1 + k_2) = 6.0 \cdot 10^{-12} \exp(-11060/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the range } 1000\text{--}4000 \text{ K.}$$

$$k_3^{\circ} = 9.6 \cdot 10^{-11} T^{-0.15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the range } 200\text{--}1000 \text{ K.}$$

$$k_3^{\circ} = 4.4 \cdot 10^{-26} T^{-2.2} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \text{ for M=Ar, N}_2 \text{ over the range } 50\text{--}1000 \text{ K.}$$

$$F_{3,c} = \exp(-T/660) + \exp(-1080/T) \text{ for M=Ar, N}_2 \text{ over the range } 200\text{--}500 \text{ K.}$$

### Reliability

$\Delta \log(k_1 + k_2) = \pm 0.3$  over the range 2500–4000 K, rising to  $\pm 0.7$  at 1000 K.

$\Delta \log k_3^{\circ} = \pm 0.3$  over the range 200–1000 K.

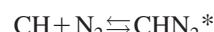
$\Delta \log k_3^{\circ} = \pm 0.2$  for M=Ar, N<sub>2</sub> over the range 50–1000 K.

$\Delta F_{3,c} = \pm 0.1$  for M=Ar, N<sub>2</sub> over the range 200–1000 K.

### Comments on Preferred Values

This reaction is believed to be the initial step in the formation of “prompt” NO in hydrocarbon combustion and, consequently, its kinetics have been the subject of many studies.

At low temperatures the rate constant is pressure dependent, with a negative temperature coefficient at constant pressure, but at sufficiently high temperatures ( $T > \sim 1100\text{--}1200$  K) the rate constant has a positive temperature coefficient and appears to be independent of pressure. At low temperatures the mechanism proposed is:



All of the low temperature data are cited in the Table<sup>1–5,8–14</sup> apart from the two earliest studies.<sup>17,18</sup> When analyzed using models accounting adequately for the temperature and pressure dependence of  $k_2$ , the data are in reasonable agreement. All of the low temperature measurements have been carried out in the “fall off” region of  $k_2$  and extrapolation is required to obtain values of the high and low pressure limiting rate constants. The most recent studies have used the methods developed by Troe and his collaborators.

Only in the study of Fulle and Hippler<sup>13</sup> were sufficiently high pressures used for a reliable extrapolation to be made to obtain  $k_3^{\circ}$ . Their value of  $4.1 \cdot 10^{11}$  at 300 K receives support from measurement of the rate constant for collisional relaxation of CH( $v=1$ ) by N<sub>2</sub> which is expected to correspond to  $k_3^{\circ}$ . Values at room temperature of  $3.0 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,  $3.7 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , and  $3.0 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  have been obtained by Herbert *et al.*,<sup>19</sup> Mehlmann *et al.*,<sup>11</sup> and Duncanson and Guillory,<sup>4</sup> respectively. The first two of these studies provide good support for Fulle and Hippler’s expression<sup>13</sup> for  $k_3^{\circ}$  which is adopted as our preferred expression together with their expression for  $F_{3,c}$ .

A number of expressions have been derived for  $k_3^{\circ}$ . Most of the measurements used Ar as the bath gas but a number of studies<sup>3,11,12</sup> have shown that there is no significant difference between the collision efficiencies of N<sub>2</sub> and Ar. The most recent studies are those of Becker *et al.*,<sup>10</sup> Brownsword *et al.*,<sup>12</sup> Fulle and Hippler,<sup>13</sup> and Le Picard *et al.*<sup>14</sup> giving expressions which agree well at temperatures close to 300 K but diverge at higher and lower temperatures. In the study of Le Picard *et al.*<sup>14</sup> measurements of  $k_3$  were made at 52–54 K. The expression of Becker *et al.*<sup>10</sup> is incompatible with these results and that of Fulle and Hippler<sup>13</sup> gives rather high values at these temperatures. Le Picard *et al.*<sup>14</sup> combined their results with the higher temperature data of Brownsword *et al.*<sup>12</sup> to derive an expression for  $k_3^{\circ}$  which provides the best available fit to all of the low temperature data and which we adopt as our preferred expression.

Thermal dissociation of the adduct back to reactants becomes significant at temperatures above 500 K and Fulle and Hippler<sup>13</sup> were able to study the establishment of equilibrium between CHN<sub>2</sub> and CH+N<sub>2</sub>. Equilibrium constants were determined for the range 542–715 K and a value of the enthalpy of formation of CHN<sub>2</sub> was derived. Values of  $k$  were obtained by Medhurst *et al.*<sup>9</sup> in this temperature region, but they did not consider the redissociation of the adduct in interpreting their data, and Becker *et al.*<sup>8</sup> also published results at these temperatures but later indicated that they were in error.<sup>10</sup>

It has usually been accepted that at high temperatures Channel (1) predominates with the decomposition of the initially formed HCNN to HCN+N becoming more important than the stabilization reaction and, in accord with that, N atom production has been observed in the reaction.<sup>6,7</sup> However this view has recently been challenged by Moskaleva and Lin.<sup>20</sup> They have carried out *ab initio* molecular orbital and multichannel RRKM calculations on the possible reaction paths open to the HCNN and come to the conclusion that NCN+H formation is favored. They suggest that the N atoms observed are formed by subsequent reactions of the NCN. Using the NCN+H decomposition pathway and a detailed mechanism for the subsequent reactions, they have remodeled the results from the two shock tube studies of Dean *et al.*<sup>7</sup> and Lindackers *et al.*<sup>6</sup> They obtained good agreement with the [CH] profiles observed by Dean *et al.*,<sup>7</sup> but the agreement with the [N] profiles observed by Lindackers

*et al.*<sup>6</sup> was only marginally acceptable. However it is clear that there is still considerable uncertainty on the predominant pathway at high temperatures and until this feature of the reaction is clarified by further studies we limit our recommendation to values of ( $k_1 + k_2$ ). The recommended expression for ( $k_1 + k_2$ ) is based on the shock tube studies of Lindackers *et al.*<sup>6</sup> and Dean *et al.*<sup>7</sup> both of which were interpreted originally as yielding values of  $k_1$  but which we now assign to ( $k_1 + k_2$ ). The values of ( $k_1 + k_2$ ) in the temperature range where these studies overlap are in good agreement but the values of  $E/R$  from the two studies differ substantially. Since the study of Lindackers *et al.*<sup>6</sup> covered only a small temperature range the value of  $E/R$  from the study of Dean *et al.*<sup>7</sup> is preferred. The preferred expression for ( $k_1 + k_2$ ) is obtained by combining this value of  $E/R$  with a pre-exponential factor based on the values of ( $k_1 + k_2$ ) in the overlap region of the two studies. There are also two flame studies<sup>21,22</sup> which are not cited in the Table. They give higher values of  $k_1$  and rather lower values of  $E/R$  than the shock tube studies which are more direct in their determination of  $k_1$  and are preferred. As well as that of Moskaleva and Lin<sup>20</sup> the reaction has also been the subject of a number of other recent theoretical studies.<sup>23–25</sup> Only the high temperature data are given in the Arrhenius plot.

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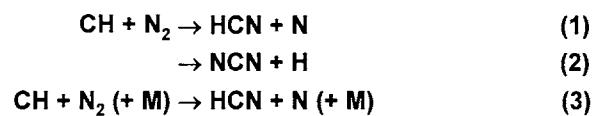
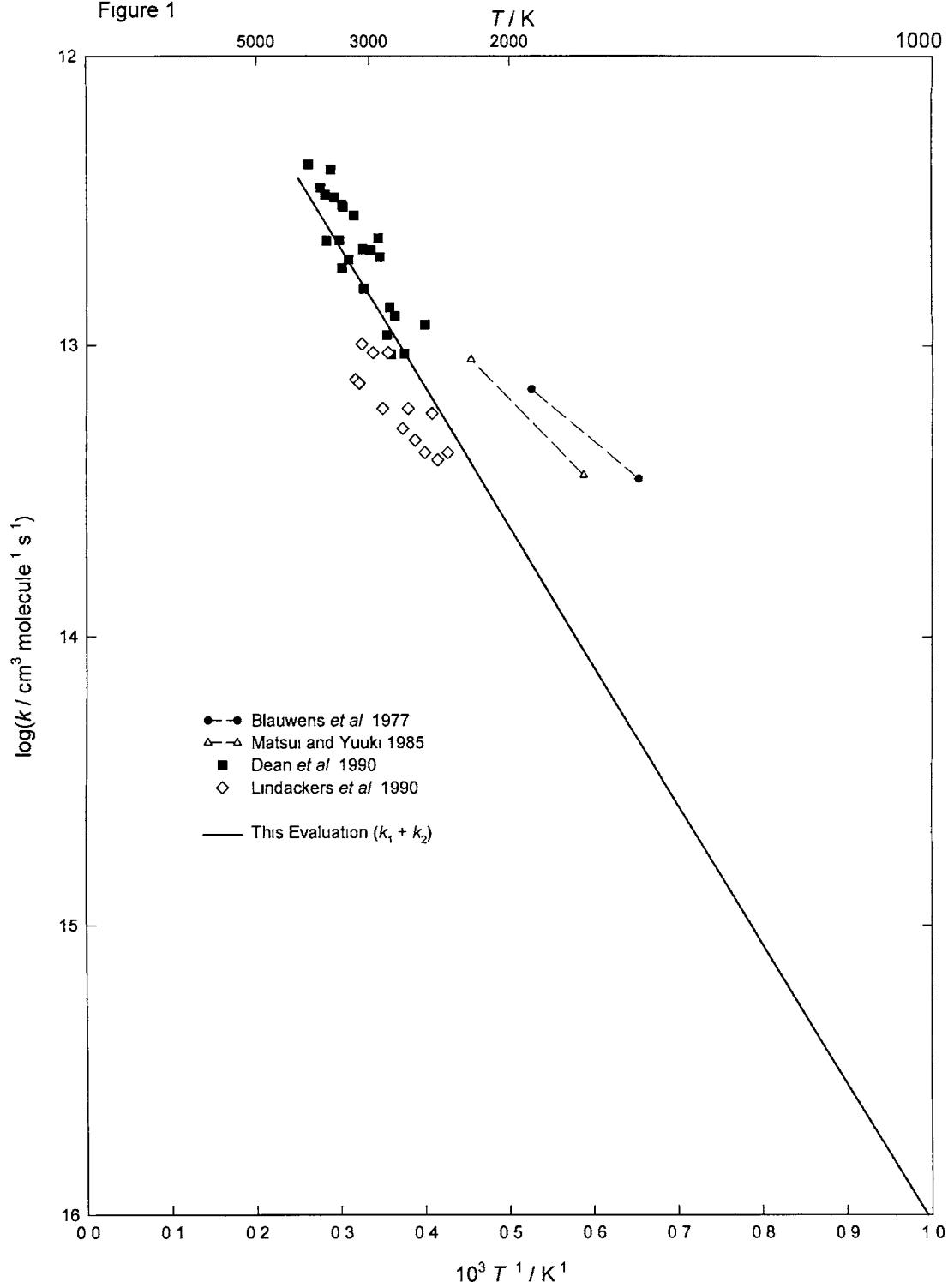


Figure 1



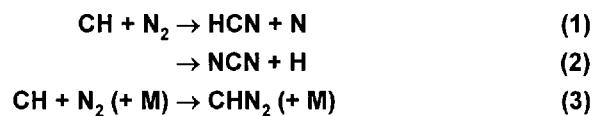
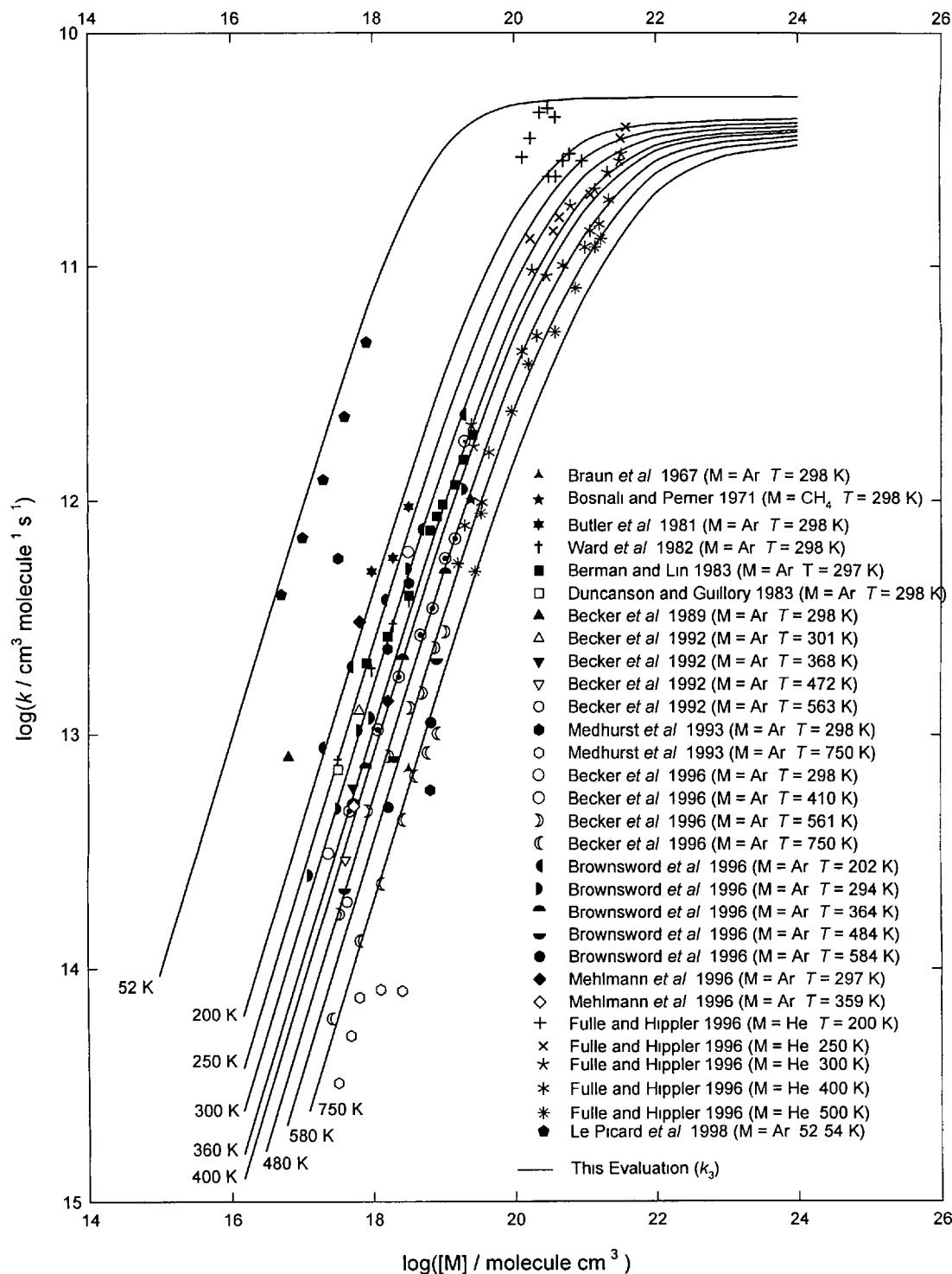
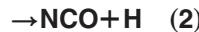


Figure 2





#### Thermodynamic Data

$$\Delta H^{\circ}_{298}(1) = -440.7 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298}(1) = -14.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 1.60 T^{-0.314} \exp(+52860/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^{\circ}_{298}(2) = -341.7 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298}(2) = -46.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 7.73 \cdot 10^{-6} T^{0.909} \exp(+41380/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^{\circ}_{298}(3) = -302.4 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298}(3) = -30.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 1.02 \cdot 10^{-3} T^{0.455} \exp(+36550/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^{\circ}_{298}(4) = -214.3 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298}(4) = -7.29 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(4) = 2.33 T^{-0.240} \exp(+25650/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^{\circ}_{298}(5) = -170.9 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298}(5) = -16.06 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(5) = 7.16 \cdot 10^{-2} T^{0.085} \exp(+20620/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^{\circ}_{298}(6) = -62.7 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298}(6) = -40.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(6) = 2.06 \cdot 10^{-4} T^{1.512} \exp(+7520/T) \\ (300 \leq T/\text{K} \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2 + k_3 + k_4 + k_5 + k_6$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$1.9 \cdot 10^{-10}$	297–676	Berman <i>et al.</i> , 1982 <sup>1</sup>	(a)
$2.0 \cdot 10^{-10}$	298	Wagel <i>et al.</i> , 1982 <sup>2</sup>	(b)
$2.5 \cdot 10^{-10}$	298	Lichtin <i>et al.</i> , 1983; <sup>3</sup> 1984 <sup>4</sup>	(c)
$1.66 \cdot 10^{-10}$	2570–3790	Dean <i>et al.</i> , 1991 <sup>5</sup>	(d)
$1.87 \cdot 10^{-10}$	298–1311	Becker <i>et al.</i> , 1993 <sup>6</sup>	(e)
$1.6 \cdot 10^{-10}$	297	Okada <i>et al.</i> , 1993 <sup>7</sup>	(f)
$1.85 \cdot 10^{-10}$	298	Mehlmann <i>et al.</i> , 1996 <sup>8</sup>	(g)
$3.48 \cdot 10^{-10} T^{-0.13}$	13–708	Bocherel <i>et al.</i> , 1996 <sup>9</sup>	(h)
$1.9 \cdot 10^{-10}$	298	Bergeat <i>et al.</i> , 1998 <sup>10</sup>	(i)
$2.0 \cdot 10^{-10}$	298	Geiger, Wiesen, and Becker, 1999 <sup>11</sup>	(j)
$1.4 \cdot 10^{-10}$			
<i>Branching Ratio Measurements</i>			
$k_1/k < 0.1$	2390–3350	Dean <i>et al.</i> , 1991 <sup>5</sup>	(d)
$k_4/k < 0.3$	2570–3790		
$k_1/k = 0.15$	297	Okada <i>et al.</i> , 1993 <sup>7</sup>	(f)
$k_4/k = 0.002$			
$k_3/(k_2+k_3+k_5+k_6) = 0.72$	300	Bergeat <i>et al.</i> , 1998 <sup>10</sup>	(i)
$(k_2+k_6)/(k_2+k_3+k_5+k_6) = 0.21$			
$k_5/(k_2+k_3+k_5+k_6) = 0.07$			
<i>Reviews and Evaluations</i>			
$2.0 \cdot 10^{-10}$	300–4000	CEC, 1994 <sup>12</sup>	(k)

#### Comments

- (a) Pulsed laser photolysis at 266 nm of slowly flowing CHBr<sub>3</sub>/Ar/NO mixtures at total pressures of 130 mbar. [CH] monitored by time-resolved LIF at ~430 nm.
- (b) Pulsed laser photolysis study in which CH radicals were produced by multiphoton dissociation (CO<sub>2</sub> laser) of CH<sub>3</sub>NH<sub>2</sub>, CH<sub>3</sub>CN, or *c*-C<sub>3</sub>H<sub>6</sub> in slowly flowing

mixtures with NO and Ar at total pressures of ~7 mbar. [CH] monitored by time-resolved LIF.

- (c) Pulsed laser photolysis at 266 nm of slowly flowing CHBr<sub>3</sub>/NO/Ar mixtures at total pressures of 28 mbar. Emission spectra of CH and of NH were recorded. Relative [NH] monitored by means of time-resolved emission at 336.2 nm.

- (d) Shock tube study. Pyrolysis of  $\text{C}_2\text{H}_6/\text{NO}/\text{Ar}$  or  $\text{CH}_4/\text{NO}/\text{Ar}$  mixtures.  $\text{CH}$ ,  $\text{NH}$ , and  $\text{OH}$  were detected by narrow-linewidth laser absorption.  $[\text{CH}]$  profiles in the presence and absence of  $\text{NO}$  were compared and used to derive  $k$  by fitting with a detailed reaction mechanism. Upper limits to  $k_1/k$  and  $k_4/k$  were derived from the  $[\text{NH}]$  and  $[\text{OH}]$  measurements. Authors conclude that Channel (3) is the major reaction route.
- (e) Pulsed laser photolysis at 248 nm of  $\text{CHClBr}_2/\text{NO}/\text{Ar}$  mixtures at pressures of 5 mbar.  $[\text{CH}]$  monitored by time-resolved LIF at 431.4 nm.
- (f) Pulsed laser photolysis study in which the  $\text{CH}$  radicals were produced by 193 nm laser photolysis of  $\text{CHBr}_3$  or  $(\text{CH}_3)\text{CO}$  in flowing  $\text{NO}/\text{Ar}$  mixtures.  $[\text{CH}]$  monitored by time resolved LIF at 430 nm. The reaction products  $\text{NH}$ ,  $\text{OH}$ ,  $\text{CN}$ , and  $\text{NCO}$  were also detected by LIF. Interpretation of measured product yields is complicated by possibility of fast secondary reactions. Thus different values are obtained for  $k_4/k$  depending on the product ( $\text{CN}$  or  $\text{OH}$ ) measured. The value cited is based on  $\text{CN}$  detection.  $\text{OH}$  detection gives  $k_4/k=0.2$  but there are other  $\text{OH}$  sources which may contribute. On the basis of a theoretical treatment the authors conclude that Channel (5) is likely to be dominant.
- (g) Technique as in (e) but total pressures of  $\sim 26$  mbar.
- (h) Two experimental techniques were used covering the temperature ranges 13–295 K and 298–708 K. The low temperatures were achieved using the CRESU technique (isentropic expansion of a gas through a Laval nozzle) and the high temperature experiments were carried out in a conventionally heated cell. In both sets of experiments the  $\text{CH}$  radicals were produced by multiphoton dissociation with 266 nm radiation of  $\text{CHBr}_3$  in a carrier gas of  $\text{He}$ ,  $\text{Ar}$ , or  $\text{N}_2$ .  $[\text{CH}]$  was monitored by time-resolved LIF.
- (i) Fast flow system in which  $\text{CH}$  radicals were produced by reaction of potassium atoms with  $\text{CHBr}_3$  in  $\text{He}$  carrier gas at a pressure of  $\sim 2.6$  mbar. LIF excitation at 431 nm, 590 nm, and 388 nm was used to probe for  $\text{CH}$ ,  $\text{CHBr}$ , and  $\text{CN}$ . Chemiluminescence from the reaction was collected and dispersed over the range 195–850 nm and  $\text{N}$ ,  $\text{H}$ , and  $\text{O}$  atoms were detected by resonance fluorescence at 120.00 nm, 121.57 nm, and 130.35 nm respectively. In all cases time resolved signals were obtained. The value of  $k$  cited is from monitoring the  $[\text{CH}]$  but  $\text{NH}$  and  $\text{NCO}$  chemiluminescence signals also gave similar values indicating that these radicals were not produced by secondary chemistry.  $\text{CN}$  could not be detected by LIF and only a very weak chemiluminescence signal was found suggesting that the contribution of Channel (4) is negligible.
- (j) Pulsed laser photolysis at 248 nm of  $\text{CHClBr}_2/\text{NO}/\text{Ar}$  mixtures. The radical products were monitored by time-resolved LIF. The excitation spectra of  $\text{NH}$ ,  $\text{CN}$ ,  $\text{NCO}$ , and  $\text{C}_2$  were recorded and their relative concentrations were monitored at 336.0 nm, 387.1 nm, 438.6 nm, and 516.5 nm, respectively. The two values of  $k$

cited were obtained by analysis of the relative concentration versus time profiles of the  $\text{NH}$  and  $\text{CN}$ . A similar analysis of the  $\text{NCO}$  profile gave a much smaller value of  $k$  ( $4.4 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) suggesting that  $\text{NCO}$  is not a primary product.

- (k) Based on the data of Refs. 1–5 and the data of Butler *et al.*<sup>13,14</sup>

### Preferred Values

$k = 1.9 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 200–4000 K.

$k_1/k = 0.08$ ;  $k_2/k = 0.13$ ;  $k_3/k = 0.69$ ;  $k_4/k = 0.01$ ;  $k_5/k = 0.06$ ;  $k_6/k = 0.03$  over the range 200–4000 K.

### Reliability

$\Delta \log k = \pm 0.15$  at 200 K rising to  $\pm 0.3$  at 4000 K.  
 $\Delta(k_1/k) = (\Delta k_2/k) = \Delta(k_5/k) = \pm 0.05$ ;  $\Delta(k_3/k) = \pm 0.15$ ;  
 $\Delta(k_4/k) = \pm 0.01$ ;  $\Delta(k_6/k) = \pm 0.02$  over the range 200–4000 K.

### Comments on Preferred Values

The measurements of  $k$  at temperatures in the region of 300 K are in excellent agreement. The mean value from the studies cited<sup>1–4,6–11</sup> is taken as the preferred value. As well as these data earlier studies by Butler *et al.*<sup>13,14</sup> give a value of  $k$  barely outside the error limits assigned. Data at higher<sup>5</sup> and lower temperatures<sup>9</sup> are consistent with an extremely small temperature coefficient for  $k$ , the data over the whole temperature range (13–4000 K) scattering by no more than  $\pm 25\%$ . A recent theoretical treatment<sup>14</sup> also suggests little change in  $k$  with temperature in the range 300–2000 K.

There is still considerable uncertainty over the branching ratios. Geiger *et al.*<sup>11</sup> have observed the production of  $\text{NH}$ ,  $\text{CN}$ , and  $\text{NCO}$  radicals in the  $\text{CH} + \text{NO}$  reaction. The kinetics of their production showed that  $\text{NH}$  and  $\text{CN}$  were primary products but the source of the  $\text{NCO}$  was not clear and they were not able to determine branching ratios. The data of Bergeat *et al.*<sup>10</sup> provide the most direct experimental information and their results are supported strongly by the theoretical study of Marchand *et al.*<sup>15</sup> who obtained values in very close agreement. This theoretical study<sup>15</sup> also gave values for the branching ratios for the  $\text{CD} + \text{NO}$  reaction which agree reasonably well with the measured values of Lambrecht and Hershberger.<sup>16</sup> The study of Bergeat *et al.*<sup>10</sup> provides quantitative data for the channels leading to production of atoms and more qualitative data on those leading to radical products. Combining their own data with the theoretical values of Marchand *et al.*<sup>15</sup> they derive the branching ratios which we have adopted as the preferred values. These values are compatible with the upper limits of Dean *et al.*<sup>5</sup> and, within the error limits, with the estimates of Okada *et al.*<sup>7</sup> The calculations of Marchand *et al.*<sup>15</sup> suggest that the branching ratios change only slightly with temperature up to 2000 K. It should also be noted that the exothermicity of

Channel (5) is sufficient to dissociate the CHO so that this channel may involve contributions from the formation of N + H + CO. The contributions from channels leading to HNC + O and HOC + N are considered to be very small.

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### Thermodynamic Data

$$\begin{aligned}\Delta H^\circ_{298}(1) &= 115.2 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(1) &= -32.95 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 4.44 \cdot 10^6 T^{1.243} \exp(-13480/T) \\ (300 \leq T/K \leq 5000) \end{aligned}$$

$$\begin{aligned}\Delta H^\circ_{298}(2) &= -310.5 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(2) &= -135.1 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 1.03 \cdot 10^{-12} T^{1.292} \exp(+37590/T) \text{ cm}^3 \text{ molecule}^{-1} \\ (300 \leq T/K \leq 5000) \end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

### Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$4.6 \cdot 10^{-13} \exp(861/T)$	297–676	Berman <i>et al.</i> , 1982 <sup>1</sup>	(a)
$2.7 \cdot 10^{-13}$	294	Anderson <i>et al.</i> , 1989 <sup>2</sup>	(b)
$3.07 \cdot 10^{-13}$	2900–3500	Markus and Roth, 1992 <sup>3</sup>	(c)
$k_2^0[\text{Ar}] = [\text{Ar}] 6.3 \cdot 10^{-24} T^{-2.5}$	202–584	Brownsword <i>et al.</i> , 1996 <sup>4</sup>	(d)
$k_2^\infty = 1.3 \cdot 10^{-11}$		Mehlmann <i>et al.</i> , 1996 <sup>5</sup>	(e)
$k_2^0[\text{Ar}] = [\text{Ar}] 4.2 \cdot 10^{-30}$	298		
$k_2^0[\text{He}] = [\text{He}] 3.9 \cdot 10^{-30}$			
$k_2^\infty = 5.9 \cdot 10^{-11}$			
$6.0 \cdot 10^{-6} T^{-2.4}$	293–650	Taatjes, 1997 <sup>6,7</sup>	(f)
$k_2^0[\text{He}] = [\text{He}] 2.4 \cdot 10^{-30}$			
$k_2^\infty = 1.66 \cdot 10^{-9} T^{-0.4}$	300–800	Fulle, Hippel, and Striebel, 1998 <sup>8</sup>	(g)
<i>Reviews and Evaluations</i>			
$4.6 \cdot 10^{-13} \exp(861/T)$	300–1000	CEC, 1992; 1994 <sup>9</sup>	(h)

### Comments

- (a) Pulsed laser photolysis of CHBr<sub>3</sub>/CO/Ar mixtures at 266 nm and total pressure of 133 mbar. [CH] monitored by time resolved LIF at 429.8 nm.  $k$  was found to increase by a factor of 3 as the pressure of the bath gas (Ar) was increased from 66 mbar to 850 mbar at a temperature of 298 K. At the lowest pressures used in this study the rate constant is close to its low pressure limit.
- (b) Fast flow system operating at  $\sim 2.6$  mbar pressure. Iso-
- (c) Shock tube study on CH<sub>4</sub>/Ar and CH<sub>4</sub>/CO/Ar mixtures. Time-resolved [CH] measurements made by laser absorption at 432.1311 nm.  $k$  values derived by fitting [CH] profile.
- (d) Pulsed laser photolysis of CHBr<sub>3</sub>/CO/Ar mixtures at

topic exchange of carbon studied by monitoring isotopic variants of CH by LIF. Results combined with those of Butler *et al.*<sup>11</sup> and Berman *et al.*<sup>1</sup> to derive the values  $k_2^0 = 4.9 \cdot 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ ,  $k_2^\infty = 1.1 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,  $F_c$  of 0.55, and  $N = 3.25$ .

(e) Shock tube study on CH<sub>4</sub>/Ar and CH<sub>4</sub>/CO/Ar mixtures. Time-resolved [CH] measurements made by laser absorption at 432.1311 nm.  $k$  values derived by fitting [CH] profile.

(f) Pulsed laser photolysis of CHBr<sub>3</sub>/CO/Ar mixtures at

- 266 nm and total pressures in the range 5.3–530 mbar. [CH] monitored by LIF at 490 nm. High and low pressure limiting rate constants derived by global fit of data obtained at pressures >13 mbar using calculated values of  $F_c$ . Value of  $k_2^\infty$  not expected to be very accurate because the measurements are taken far from the high pressure limit.
- (e) Pulsed laser photolysis of  $\text{CHBr}_3/\text{CO}/\text{Ar}$  (or He) mixtures at 248 nm and at total pressures in the range 13–133 mbar. [CH] monitored by LIF at 431.5 nm. High and low pressure limiting rate constants obtained by fitting data using Troe formalism and an assumed value of  $F_c$  of 0.7. Value of  $k = 1.1 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for quenching of  $\text{CO}(v=1)$  at 298 K obtained.
- (f) Pulsed laser photolysis of  $\text{CHBr}_3/\text{CO}/\text{He}$  mixtures at 248 nm and pressures in the range 16.5–658 mbar. [CH] monitored by LIF using a cw laser operating in the 429 nm region and capable of resolving the isotopic variants of the CH. Reaction rates for  $^{12}\text{CH}$  and  $^{12}\text{CD}$  measured. The value of  $k$  cited in the Table is for 133 mbar total pressure. Expression for  $k_2^\infty$  and value of  $k_2^\infty = 3.7 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  obtained by a fit to the data using Troe formalism and an assumed  $F_c$  of 0.6. The expressions quoted in Ref. 6 are corrected in Ref. 7.
- (g) Pulsed laser photolysis of  $\text{CHBr}_3/\text{CO}/\text{He}$  mixtures at 248 nm and pressures in the range 4–160 bar. [CH] monitored by saturated LIF at 431.5 nm. In the analysis of the results a low pressure limiting value of  $k_2^\infty = 4.1 \cdot 10^{-30} (T/298)^{-1.9} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  for  $M = \text{Ar}$  was assumed based on the value obtained by Brownsword *et al.*<sup>4</sup> but with a slightly modified temperature dependence which gives a better fit to the data at the higher temperatures used. The results were fitted using Troe formalism with calculated values of  $F_c$  in the range from 0.68 (300 K) to 0.56 (800 K).
- (h) Accepts the expression of Berman *et al.*<sup>1</sup>

### Preferred Values

$k_1 = 3.1 \cdot 10^{-13}$  over the range 2500–3500 K.  
 $k_2^\infty = 6.3 \cdot 10^{-24} T^{-2.5} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  for  $M = \text{Ar}$  over the range 200–1000 K.

$k_2^\infty = 1.7 \cdot 10^{-9} T^{-0.4} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 200–1000 K.

$F_c = 0.6$  for  $M = \text{Ar}$  over the range 200–1000 K.

### Reliability

$\Delta \log k_1 = \pm 0.3$  over the range 2500–3500 K.  
 $\Delta \log k_2^\infty = \pm 0.3$  for  $M = \text{Ar}$  over the range 200–1000 K.  
 $\Delta \log k_2^\infty = \pm 0.3$  over the range 200–1000 K.  
 $\Delta F_c = \pm 0.1$  for  $M = \text{Ar}$  over the range 200–1000 K.

### Comments on Preferred Values

At low temperatures the rate constant is pressure dependent and Channel (2) is considered to predominate. There are

now a number of studies of the pressure dependence at temperatures in the range 200–800 K from which parameters defining the “fall-off” behaviour of  $k_2$  have been derived.<sup>1,2,4–8</sup>

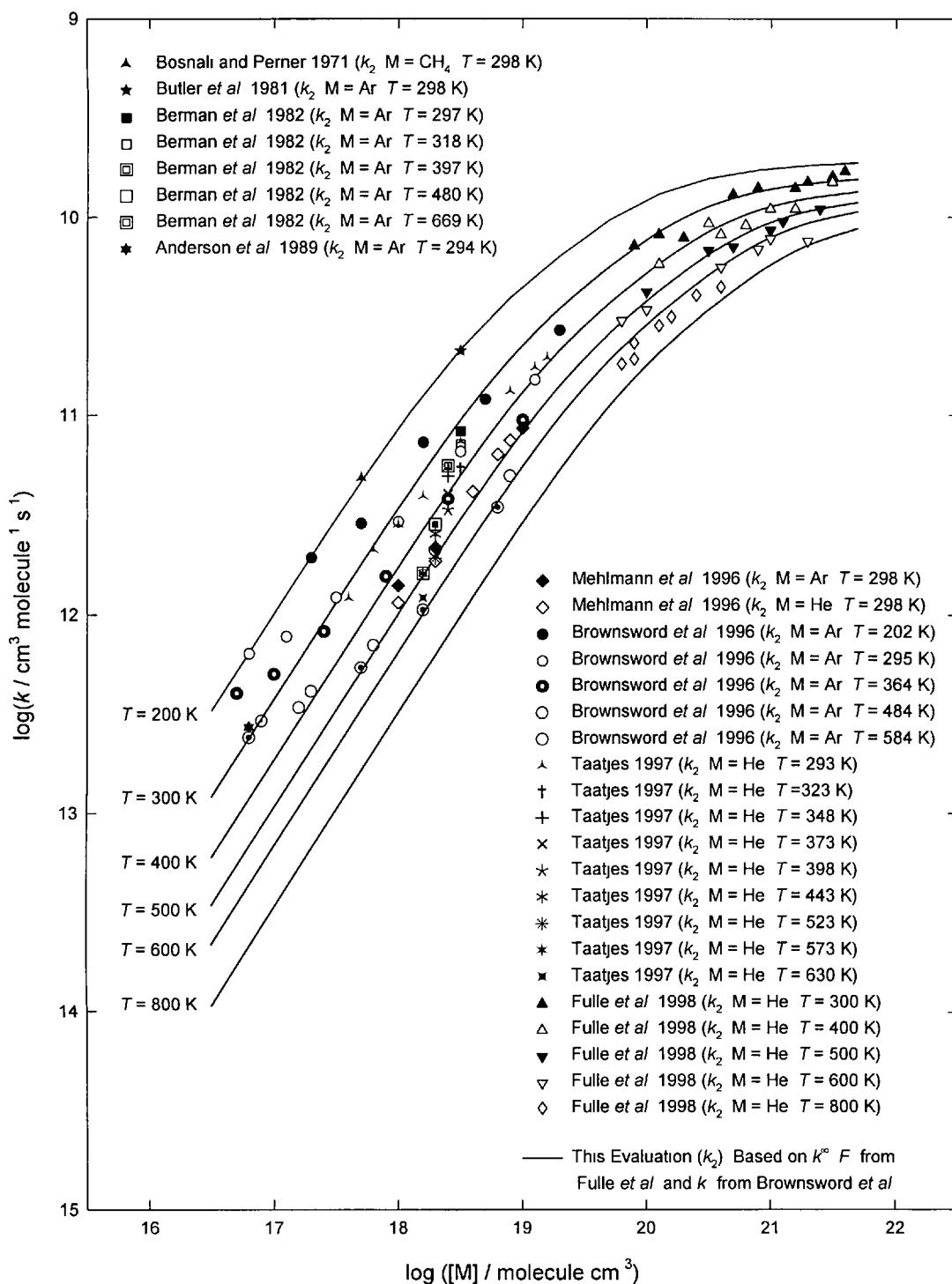
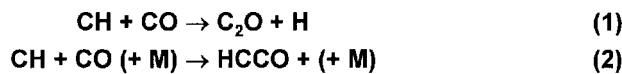
All of the data in the studies cited in the Table are in good agreement, as is that in the older study by Bosnali and Perner,<sup>10</sup> and only the results of Butler *et al.*<sup>11</sup> seem unacceptably low. The preferred expression for  $k_2^\infty$  is that of Brownsword *et al.*<sup>4</sup> which is based on a global fit to data covering substantial ranges of temperature and pressure and with which values derived from other studies are in reasonable agreement.

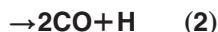
The only study at sufficiently high pressures to give a reasonably short extrapolation to  $k_2^\infty$  is that of Fulle *et al.*<sup>8</sup> Their expression for  $k_2^\infty$  is accepted and, since they used the low pressure data of Brownsword *et al.*<sup>4</sup> in their extrapolation procedure, our recommended high and low pressure limits should be compatible. Furthermore the expression for  $k_2^\infty$  given by Fulle *et al.*<sup>8</sup> is in good agreement with values of rate constant for relaxation of  $\text{CO}(v=1)$ <sup>5,12</sup> which is believed to be an alternative route to the high pressure limiting value of the rate constant. Fulle *et al.*<sup>7</sup> found values of  $F_c$  in the range 0.56 (800 K) to 0.68 (300 K). Our preferred value is taken in the middle of this range.

It has been suggested<sup>4</sup> that Channel (1) may make a small contribution to the overall reaction at low temperatures. However, this proposal was based on the impression that Channel (1) is close to thermoneutral, as suggested by older thermodynamic data. More recent measurements of the enthalpy of formation of  $\text{C}_2\text{O}$  suggest that Channel (1) is substantially endothermic, as given in the thermodynamic data at the head of this data sheet. On this basis Fulle *et al.*<sup>8</sup> derive the expression  $k_1 = 2.6 \cdot 10^{-11} \exp(-14160/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , which they obtain by assigning  $E_a = \Delta H^\circ_{298}(1)$  and combining it with an  $A$  factor to give the value of  $k$  obtained by Markus and Roth<sup>3</sup> at 2900–3500 K, assumed to be due solely to Channel (1). Confirmatory thermodynamic data and studies of  $k$  at high temperatures are desirable but, provisionally, the value of  $k_1$  obtained by Markus and Roth is recommended for use at high temperatures.

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- <sup>10</sup> M. W. Bosnali and D. Perner, Z. Naturforsch. A **26**, 1768 (1971).
- <sup>11</sup> J. E. Butler, J. W. Fleming, L. P. Goss, and M. C. Lin, Chem. Phys. **56**, 355 (1981).
- <sup>12</sup> L. B. Herbert, I. R. Sims, I. W. M. Smith, D. W. A. Stewart, A. C. Symonds, A. Canosa, and B. R. Rowe, J. Phys. Chem. **100**, 14928 (1996).





#### Thermodynamic Data

$$\begin{aligned}\Delta H^0_{298}(1) &= -271.4 \text{ kJ mol}^{-1} \\ \Delta S^0_{298}(1) &= 22.98 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_e(1) &= 3.43 \cdot 10^3 T^{-0.753} \exp(+32310/T) \\ &(300 \leq T/\text{K} \leq 5000)\end{aligned}$$

$$\begin{aligned}\Delta H^0_{298}(2) &= 363.2 \text{ kJ mol}^{-1} \\ \Delta S^0_{298}(2) &= 21.78 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_e(2) &= 8.4 \cdot 10^{22} T^{0.941} \exp(-43750/T) \text{ molecule cm}^{-3} \\ &(300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$1.9 \cdot 10^{-12}$	298	Butler <i>et al.</i> , 1981 <sup>1</sup>	(a)
$5.7 \cdot 10^{-12} \exp(-345/T)$	297–676	Berman <i>et al.</i> , 1982 <sup>2</sup>	(b)
$3.15 \cdot 10^{-10} \exp(-7950/T)$	2500–3500	Markus, Roth, and Just, 1995 <sup>3</sup>	(c)
$4.5 \cdot 10^{-7} T^{-2.17} + 2.34 \cdot 10^{-11} \exp(-1495/T)$	296–873	Mehlmann <i>et al.</i> , 1996 <sup>4</sup>	(d)
<i>Reviews and Evaluations</i>			
$5.7 \cdot 10^{-12} \exp(-345/T)$	300–1000	CEC, 1992; 1994 <sup>5</sup>	(e)

#### Comments

- (a) Multiphoton dissociation of CHBr<sub>3</sub> at 193 nm; [CH] monitored by LIF at 429.8 nm in the presence of an excess of CO<sub>2</sub> at a total pressure of 132 mbar Ar.
- (b) Technique and conditions as in (a) but 266 nm laser radiation used.
- (c) Shock tube study using reflected shocks in C<sub>2</sub>H<sub>6</sub>/Ar mixtures at a total pressure of 1 bar. [CH] monitored by tuneable laser absorption at 431.13 nm. Perturbation of the [CH] profile by addition of CO<sub>2</sub> observed and fitted to a detailed reaction mechanism by numerical simulation.
- (d) Pulsed laser photolysis of CHBr<sub>3</sub> at 248 nm used to produce CH in Ar/CO<sub>2</sub> mixtures. [CH] (in the  $v=0$  and  $v=1$  states) monitored by LIF. Different rates of removal were inferred for the two vibrational states. The expression tabulated is for CH ( $v=0$ ). The rate constant was found to be independent of pressure over the range 6.6–105 mbar.
- (e) Expression of Berman *et al.*<sup>2</sup> adopted.

#### Comments on Preferred Values

The data at 298 K from the studies of Butler *et al.*,<sup>1</sup> Berman *et al.*,<sup>2</sup> and Mehlman *et al.*,<sup>4</sup> are in excellent agreement. However the two studies of the temperature dependence of  $k$  in this temperature region differ significantly. Berman *et al.*<sup>2</sup> obtain a small negative value for  $E/R$  whereas Mehlman *et al.*<sup>3</sup> observe a complex dependence of  $k$  on temperature with  $k$  decreasing slightly as the temperature is increased from 298 K, going through a minimum at  $\sim 450$  K, and rising rapidly beyond that up to the high temperature limit of their study (873 K). This suggests a change in the reaction mechanism in the 450 K region possibly, relating to the initial formation of an adduct.

The expression obtained by Mehlman *et al.*<sup>3</sup> extrapolates reasonably well to the high temperature results of Markus *et al.*<sup>4</sup> However, the minimum observed by Mehlman *et al.*<sup>3</sup> remains to be confirmed and the preferred expression therefore is a fit to the data of Markus *et al.*,<sup>4</sup> Butler *et al.*,<sup>1</sup> and Berman *et al.*<sup>2</sup> Substantial error limits are suggested until more information is available on the pressure and temperature dependence of  $k$ . There is no information on the relative importance of the product channels.

#### References

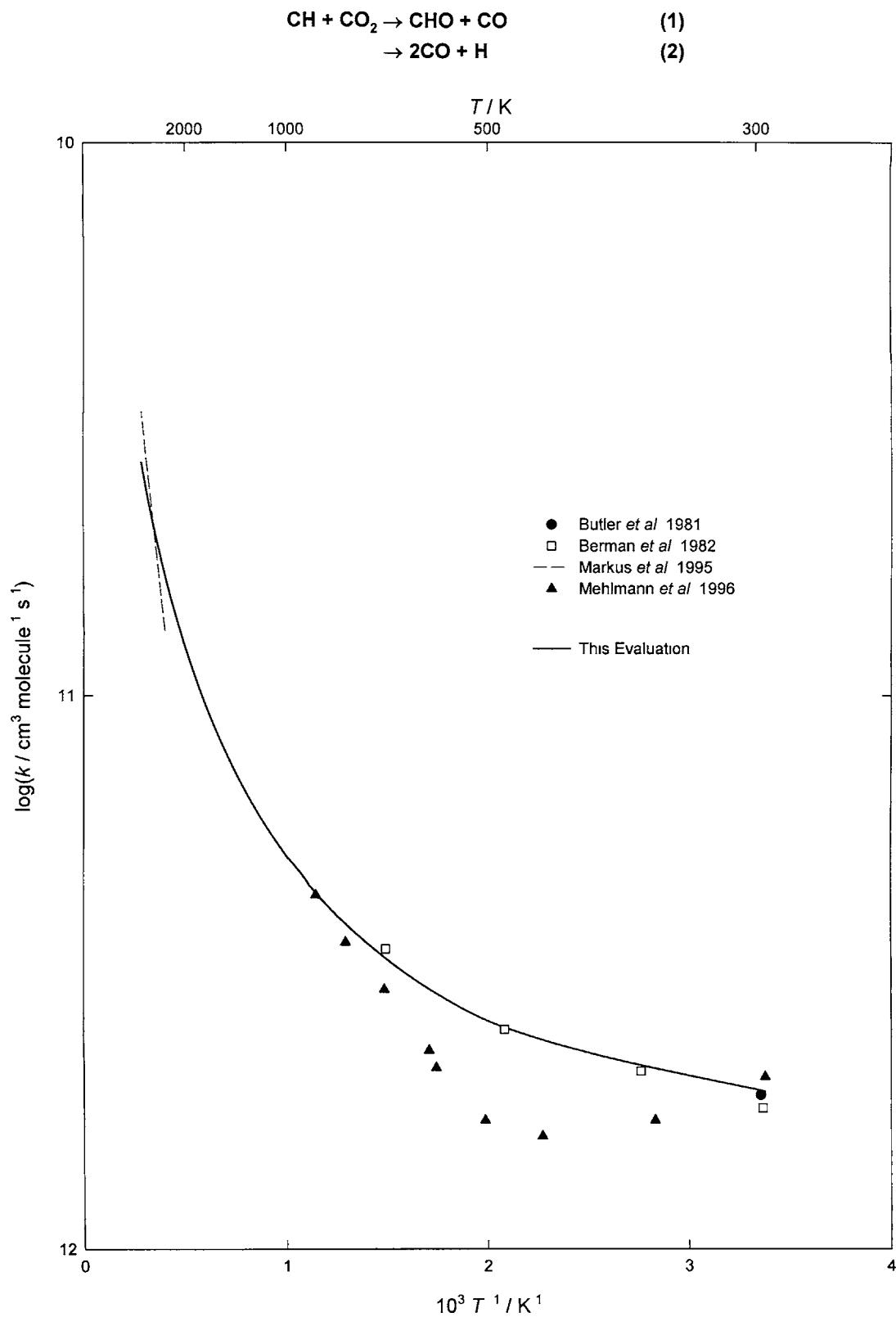
- <sup>1</sup>J. E. Butler, J. W. Fleming, L. P. Goss, and M. C. Lin, Chem. Phys. **56**, 355 (1981).
- <sup>2</sup>M. R. Berman, J. W. Fleming, A. B. Harvey, and M. C. Lin, 19th Symp. (Int.) Combustion, 1982, p. 73.
- <sup>3</sup>M. W. Markus, P. Roth, and Th. Just, Int. J. Chem. Kinet. **28**, 171 (1996).
- <sup>4</sup>C. Mehlmann, M. J. Frost, D. E. Heard, B. J. Orr, and P. F. Nelson, J. Chem. Soc. Faraday Trans. **92**, 2335 (1996).
- <sup>5</sup>CEC, 1992; Supplement I, 1994 (see references in Introduction).

#### Preferred Values

$k = 1.06 \cdot 10^{-16} T^{1.51} \exp(360/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 296–3500 K.

#### Reliability

$\Delta \log k = \pm 0.15$  at 296 K, rising to  $\pm 0.3$  at 3500 K.





*Thermodynamic Data*

$$\begin{aligned}\Delta H^\circ(1) &= -251.1 \text{ kJ mol}^{-1} \\ \Delta S^\circ(1) &= -35.21 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 7.49 \cdot 10^{-5} T^{0.928} \exp(+30520/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

$$\begin{aligned}\Delta H^\circ(2) &= 15.3 \text{ J K}^{-1} \text{ mol}^{-1} \\ \Delta S^\circ(2) &= 19.86 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 1.39 \cdot 10^2 T^{-0.283} \exp(-2130/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data ( $k = k_1 + k_2$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$1.0 \cdot 10^{-10}$	298	Butler <i>et al.</i> , 1981 <sup>1</sup>	(a)
$5.0 \cdot 10^{-11} \exp(200/T)$	167–652	Berman and Lin, 1983 <sup>2</sup>	(b)
$3.96 \cdot 10^{-8} T^{1.04} \exp(-36.1/T)$	23–295	Canosa <i>et al.</i> , 1997 <sup>3</sup>	(c)
$6.5 \cdot 10^{-10} T^{-0.4}$	290–697	Thiesemann, MacNamara, and Taatjes, 1997 <sup>4</sup>	(d)
$1.53 \cdot 10^{-8} T^{-0.9}$	290–772	Blitz <i>et al.</i> , 1997 <sup>5</sup>	(e)
<i>Reviews and Evaluations</i>			
$5.0 \cdot 10^{-11} \exp(200/T)$ .	200–700	CEC, 1992; 1994 <sup>6</sup>	(f)

**Comments**

- (a) CH generated by pulsed laser multiphoton dissociation of  $\text{CHBr}_3$  at 193 nm in Ar at a total pressure of 132 mbar. [CH] monitored by LIF at 429.8 nm.
- (b) CH generated by pulsed multiphoton dissociation of  $\text{CHBr}_3$  at 266 nm in Ar at total pressures in the range 33–260 mbar. [CH] monitored by LIF at 429.8 nm.  $k$  found to be independent of pressure over the range studied.
- (c) CH generated by pulsed multiphoton dissociation of  $\text{CHBr}_3$  at 248 or 266 nm in a variety of carrier gases (He, Ar, N<sub>2</sub>) at total gas densities in the range  $(0.57\text{--}40) \cdot 10^{16} \text{ molecule cm}^{-3}$ . [CH] monitored by off resonance LIF, exciting at  $\sim 430$  nm and detecting at  $\sim 490$  nm.
- (d) CH generated by pulsed laser photolysis of  $\text{CHBr}_3$  in He at total pressures in the range 20–400 mbar. [CH] monitored by cw LIF at 430 nm. The reactions CD +  $\text{CH}_4$  and CH+CD<sub>4</sub> were also studied and isotope effects determined.
- (e) CH generate by pulsed laser photolysis of  $\text{CHBr}_3$  at 193 nm in Ar at total pressures in the range 66–400 mbar. [CH] monitored by pulsed LIF at 431.5 nm. The analogous reactions involving CD and CD<sub>4</sub> were also studied.
- (f) Accepts the expression of Berman and Lin.<sup>2</sup>

**Preferred Values**

$k = 2.2 \cdot 10^{-8} T^{-0.94} \exp(-29/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$   
over the range 160–750 K.

*Reliability*

$\Delta \log k = \pm 0.2$  over the range 160–750 K.

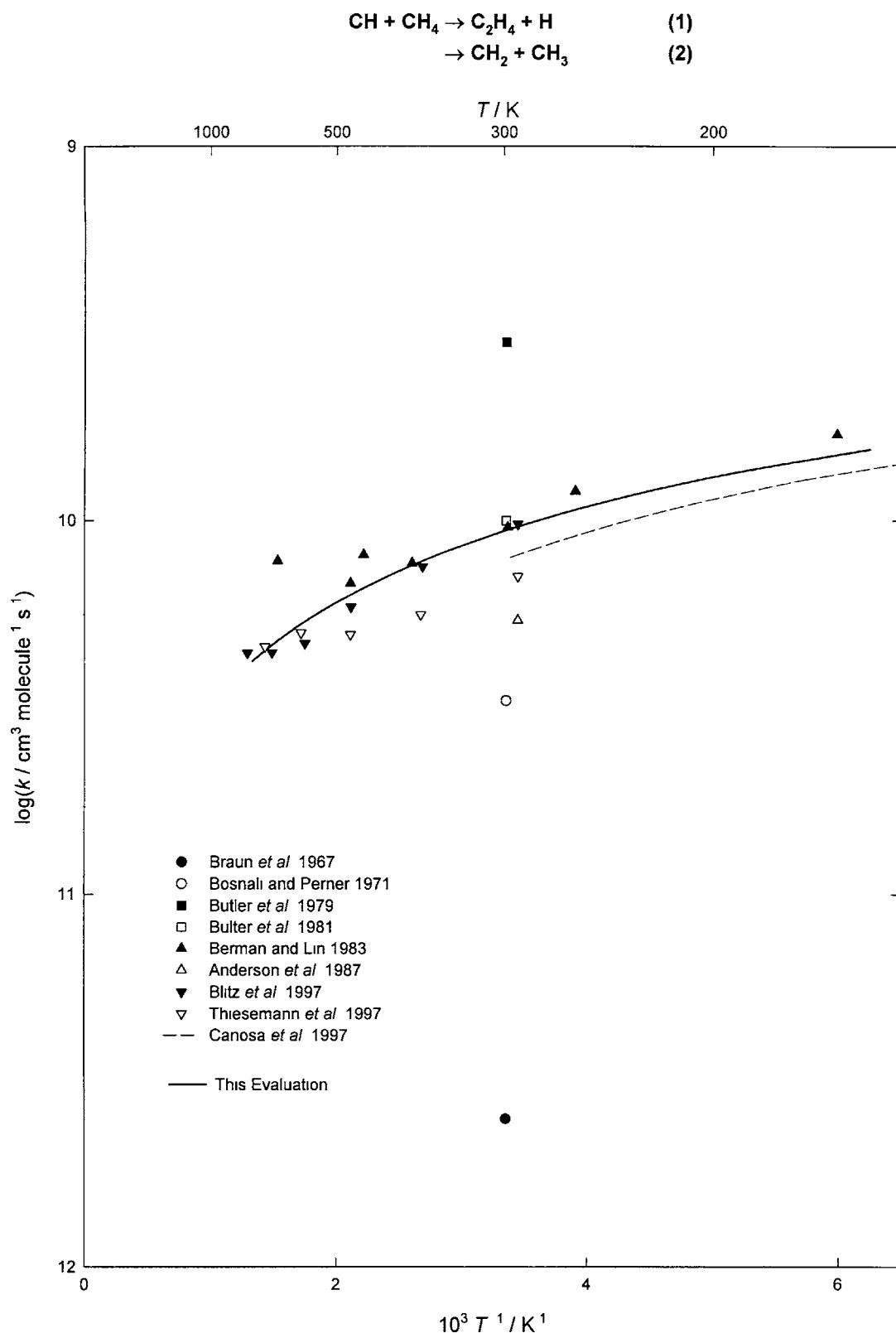
*Comments on Preferred Values*

Since our previous evaluations<sup>6</sup> there have been three studies<sup>3–5</sup> in good agreement with the results of Berman and Lin<sup>2</sup> on which our previous recommendations were based. The preferred expression is a fit to the data from the five studies cited in the Table which are considered the most reliable. The older studies of Braun *et al.*,<sup>7</sup> Bosnali and Perner,<sup>8</sup> and Butler *et al.*<sup>9</sup> and the more recent fast flow reactor study of Anderson *et al.*<sup>10</sup> are not used in deriving the preferred expression.

There is no direct experimental evidence on the channel branching ratios. The general view<sup>2–5</sup> is that the reaction mechanism involves a barrierless association, or insertion, followed by rapid dissociation of the intermediate so formed. The likely products are H+ $\text{C}_2\text{H}_4$ , Channel (1), since stabilization of the adduct is expected to be insignificant under all but the most extreme conditions.<sup>5</sup>

**References**

- <sup>1</sup>J. E. Butler, J. W. Fleming, L. P. Goss, and M. C. Lin, Chem. Phys. **56**, 355 (1981).
- <sup>2</sup>M. R. Berman and M. C. Lin, Chem. Phys. **82**, 435 (1983).
- <sup>3</sup>A. Canosa, I. R. Sims, D. Travers, I. W. M. Smith, and B. R. Rowe, Astronom. Astrophys. **323**, 644 (1997).
- <sup>4</sup>H. Thiesemann, J. MacNamara, and C. A. Taatjes, J. Phys. Chem. **101**, 1881 (1997).
- <sup>5</sup>M. A. Blitz, D. G. Johnson, M. Pesa, S. H. Robertson, and P. W. Seakins, J. Chem. Soc. Faraday Trans. **93**, 1473 (1997).
- <sup>6</sup>CEC, 1992; Supplement I, 1994 (see references in Introduction).
- <sup>7</sup>W. Braun, J. R. McNesby, and A. M. Bass, J. Chem. Phys. **46**, 2071 (1967).
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- <sup>9</sup>J. E. Butler, L. P. Goss, M. C. Lin, and J. W. Hudgens, Chem. Phys. Lett. **63**, 104 (1979).
- <sup>10</sup>S. M. Anderson, A. Freedman, and C. E. Kolb, J. Phys. Chem. **91**, 6272 (1987).



**CH+HCHO→Products****Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$1.6 \cdot 10^{-10} \exp(260/T)$	297–670	Zabarnick, Fleming, and Lin, 1990 <sup>1</sup>	(a)
<i>Reviews and Evaluations</i>			
$1.6 \cdot 10^{-10} \exp(260/T)$	300–700	CEC, 1992; 1994 <sup>2</sup>	(b)

**Comments**

- (a) Multiphoton dissociation of CHBr<sub>3</sub> at 266 nm; [CH] monitored by laser induced fluorescence at 429.8 nm. Total pressure 25–400 mbar Ar. Rate constant found to be independent of total pressure.  
 (b) Accepts the expression of Zabarnick *et al.*<sup>1</sup>

**Reliability**

$\Delta \log k = \pm 1$  over the range 300–700 K.

**Comments on Preferred Values**

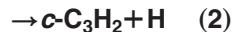
The only available experimental measurement is accepted but with wide error limits. The preferred values are unchanged from our previous evaluations.<sup>2</sup>

**Preferred Values**

$k = 1.6 \cdot 10^{-10} \exp(260/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 300–700 K.

**References**

- <sup>1</sup>S. Zabarnick, J. W. Fleming, and M. C. Lin, 21st Symp. (Int.) Combustion, 1988, p. 713.  
<sup>2</sup>CEC, 1992; Supplement I, 1994 (see references in Introduction).

**Thermodynamic Data**

$$\begin{aligned}\Delta H^\circ(1) &= 44.4 \text{ kJ mol}^{-1} \\ \Delta S^\circ(1) &= -14.69 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 6.82 \cdot 10^{-3} T^{0.502} \exp(-5240/T) \\ (300 \leq T/K \leq 5000)\end{aligned}$$

$$\begin{aligned}\Delta H^\circ(2) &= -129.7 \text{ kJ mol}^{-1} \\ \Delta S^\circ(2) &= -33.03 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 5.27 \cdot 10^{-3} T^{0.147} \exp(+15730/T) \\ (300 \leq T/K \leq 5000)\end{aligned}$$

$$\begin{aligned}\Delta H^\circ(3) &= 148.6 \text{ kJ mol}^{-1} \\ \Delta S^\circ(3) &= -8.36 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(3) &= 4.83 \cdot 10^{-3} T^{0.746} \exp(-17870/T) \\ (300 \leq T/K \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data ( $k = k_1 + k_2 + k_3$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$3.5 \cdot 10^{-10} \exp(61/T)$	171–657	Berman <i>et al.</i> , 1982 <sup>1</sup>	(a)
$1.6 \cdot 10^{-9} T^{-0.23} \exp(-16/T)$	23–295	Canosa <i>et al.</i> , 1997 <sup>2</sup>	(b)
$1.0 \cdot 10^{-9} T^{-0.2}$	288–710	Thiesemann, MacNamara, and Taatjes, 1997 <sup>3</sup>	(c)
<i>Reviews and Evaluations</i>			
$3.5 \cdot 10^{-10} \exp(61/T)$	200–700	CEC, 1992; 1994 <sup>4</sup>	(d)

## Comments

- (a) Pulsed multiphoton dissociation of  $\text{CHBr}_3/\text{C}_2\text{H}_2$  mixtures at 266 nm at a total pressure of 130 mbar Ar.  $[\text{CH}]$  monitored by LIF at 429.8 nm
- (b) Pulsed multiphoton dissociation of  $\text{CHBr}_3/\text{C}_2\text{H}_2$  mixtures at 266 or 248 nm in a flow of He, Ar, or  $\text{N}_2$  carrier gas.  $[\text{CH}]$  monitored by LIF at  $\sim 490$  nm. Rate constant found to be independent of pressure.
- (c) Pulsed laser photolysis of  $\text{CHBr}_3/\text{C}_2\text{H}_2$  mixtures at total pressures in the range 10–530 mbar He.  $[\text{CH}]$  monitored by LIF using a cw laser operating at 430 nm. Rate constant found to be independent of pressure in the range 130–530 mbar. Reasons for anomalous behavior at lower pressures unclear.
- (d) Accepts the expression of Berman *et al.*<sup>2</sup>

## Preferred Values

$$k = 3.1 \cdot 10^{-10} \exp(61/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the range } 200\text{--}700 \text{ K.}$$

### Reliability

$\Delta \log k = \pm 0.3$  over the range 200–700 K.

### Comments on Preferred Values

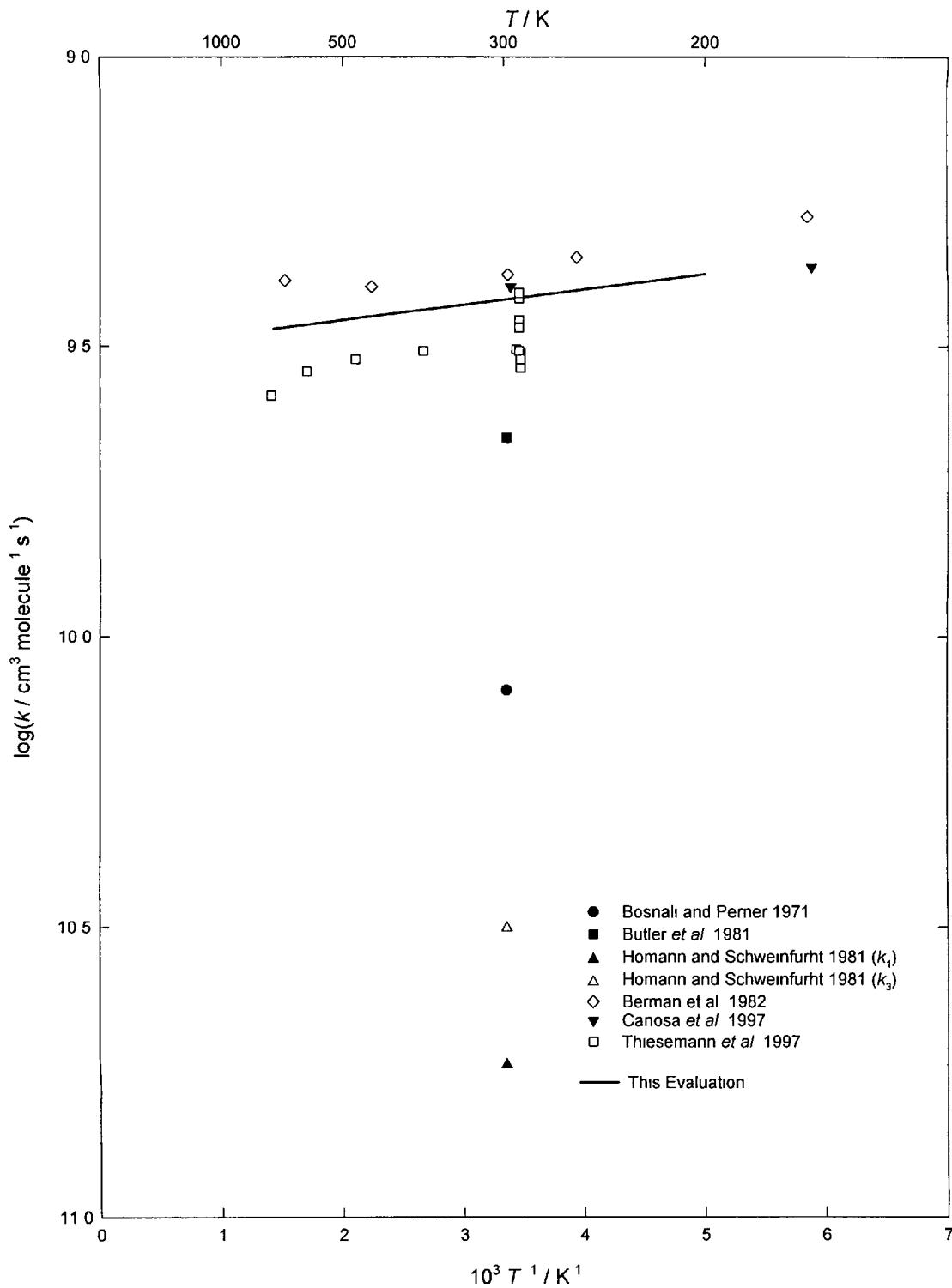
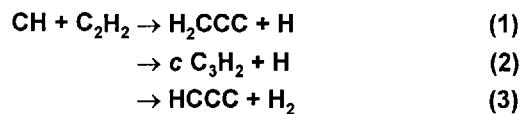
The studies of Berman *et al.*,<sup>1</sup> Canosa *et al.*,<sup>2</sup> and Thiesemann *et al.*<sup>3</sup> are in very good agreement over the temperature range where the three studies overlap both in terms of the values of  $k$  and the temperature dependence. In the preferred expression for  $k$  the temperature dependence obtained by Berman *et al.*<sup>1</sup> is accepted and combined with a pre-exponential factor adjusted to give the mean value of  $k$  at 298 K from the studies of Berman *et al.*,<sup>1</sup> Canosa *et al.*,<sup>2</sup> and Thiesemann *et al.*<sup>3</sup> A more complex temperature dependence is observed at very low temperatures ( $T < 100$  K) by Canosa *et al.*<sup>2</sup> The earlier result of Butler *et al.*<sup>5</sup> at 298 K is in reasonable agreement but that of Bosnali and Perner<sup>6</sup> appears to be unacceptably low.

The reaction mechanism has been discussed by Berman *et al.*<sup>1,7</sup> and Canosa *et al.*<sup>2</sup> and has been the subject of theoretical studies by Walch,<sup>8</sup> Guadagnini *et al.*,<sup>9</sup> and Vereecken and Peeters.<sup>10</sup> The very high value of the rate constant and its independence of pressure suggests an addition or insertion process followed by rapid decomposition of the intermediate

so formed. The calculations show that only under the most extreme conditions will any stabilization of the initially formed intermediate occur and for all practical purposes rearrangement and fragmentation products will be formed. Guadagnini *et al.*<sup>9</sup> find that  $\text{H}_2\text{CCC} + \text{H}$  is the main product with negligible amounts of  $\text{HCCCH} + \text{H}$  and no cyc- $\text{C}_3\text{H}_2$ . In the more extensive theoretical study of Vereecken and Peeters,<sup>10</sup> they find that at pressures up to several atmospheres the main products are  $\text{HCCCH} + \text{H}$ ,  $c\text{-C}_3\text{H}_2 + \text{H}$ , and  $\text{C}_3\text{H} + \text{H}_2$ , e.g., under typical combustion conditions (1500 K and 1 bar pressure), the main products are  $\text{HCCCH} + \text{H}$  ( $\sim 80\%$ ) and cyc- $\text{C}_3\text{H}_2 + \text{H}$  ( $\sim 10\%$ ), together with small contributions from  $\text{C}_3\text{H} + \text{H}_2$ . There are two experimental studies of the branching ratios. In a discharge flow study at 600 K on the  $\text{C}_2\text{H}_2/\text{O}/\text{H}$  system in which a number of products and intermediates were monitored by mass spectrometry, Boullart *et al.*<sup>11</sup> obtained values of 85% and 15% for the channels leading to  $\text{C}_3\text{H}_2 + \text{H}$  and  $\text{C}_3\text{H} + \text{H}_2$ , respectively, in reasonable agreement with the calculated values of Vereecken and Peeters.<sup>10</sup> Using pulsed laser photolysis of  $\text{CHBr}_3/\text{C}_2\text{H}_2$  mixtures at 295 K and LIF detection of H atoms, McKee *et al.*<sup>12</sup> measured the H atom yield relative to that from the  $\text{CH} + \text{CH}_4$  reaction. They obtained a yield of  $1.07 \pm 0.17$  which is compatible with the values of Boullart *et al.*<sup>11</sup> within the error limits of the two studies. The calculations of Vereecken and Peeters<sup>10</sup> appear currently to offer the best guide to the products and branching ratios.

## References

- <sup>1</sup> M. R. Berman, J. W. Fleming, A. B. Harvey, and M. C. Lin, Chem. Phys. **73**, 27 (1982).
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- <sup>3</sup> H. Thiesemann, J. MacNamara, and C. A. Taatjes, J. Phys. Chem. **101**, 1881 (1997)
- <sup>4</sup> CEC, 1992; Supplement I, 1994 (see references in Introduction).
- <sup>5</sup> J. E. Butler, J. W. Fleming, L. P. Goss, and M. C. Lin, Chem. Phys. **56**, 355 (1981)
- <sup>6</sup> M. W. Bosnali and D. Perner, Z. Naturforsch. A **26**, 1768 (1971).
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- <sup>12</sup> K. McKee, M. A. Blitz, M. J. Pilling, H.-B. Qian, A. Taylor, and P. W. Seakins, J. Phys. Chem. A **107**, 5710 (2003).



**CH+C<sub>2</sub>H<sub>4</sub>→Products****Rate Coefficient Data**

<i>k/cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup></i>	<i>T/K</i>	References	Comments
<i>Rate Coefficient Measurements</i>			
$2.2 \cdot 10^{-10} \exp(173/T)$	160–652	Berman <i>et al.</i> , 1982 <sup>1</sup>	(a)
$7.8 \cdot 10^{-9} T^{-0.546} \exp(-29/T)$	23–295	Canosa <i>et al.</i> , 1997 <sup>2</sup>	(b)
<i>Reviews and Evaluations</i>			
$2.2 \cdot 10^{-10} \exp(173/T)$	200–700	CEC, 1992; 1994 <sup>3</sup>	(c)

**Comments**

- (a) Pulsed multiphoton dissociation of CHBr<sub>3</sub> at 266 nm in a bath gas of Ar at a total pressure of 130 mbar. [CH] monitored by LIF at 429.8 nm.
- (b) Pulsed laser photolysis of CHBr<sub>3</sub>/C<sub>2</sub>H<sub>4</sub> mixtures at 248 nm or 266 nm in a flow of He, Ar, or N<sub>2</sub> carrier gas. [CH] monitored by LIF at ~490 nm. Rate constant independent of pressure.
- (c) Accepts the expression of Berman *et al.*<sup>1</sup>

**Preferred Values**

$k = 2.2 \cdot 10^{-10} \exp(173/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 200–700 K.

**Reliability**

$\Delta \log k = \pm 0.5$  over the range 200–700 K.

**Comments on Preferred Values**

The most recent study, that of Canosa *et al.*,<sup>2</sup> is in reasonable agreement with the recommendations of our previous evaluation<sup>3</sup> which were based on the data of Berman *et al.*<sup>1</sup> The preferred expression for *k* is therefore unchanged but the

error limits are slightly reduced. The value of *k* obtained by Butler *et al.*<sup>4</sup> at 298 K also supports the present recommendation, but that of Bosnali and Perner<sup>5</sup> is rather low.

The only information on product formation comes from a study of McKee *et al.*<sup>6</sup> who used pulsed laser photolysis of CHBr<sub>3</sub>/C<sub>2</sub>H<sub>4</sub> mixtures at 295 K and LIF detection of H atoms, to measure an H atom yield relative to that from the CH+CH<sub>4</sub> reaction of  $1.14 \pm 0.12$ . It is suggested that the only other product is likely to be allene. McKee *et al.*<sup>6</sup> show that this result is compatible with previous theoretical and related photochemical studies with the reaction proceeding by addition and formation of an allyl radical intermediate.

**References**

- <sup>1</sup> M. R. Berman, J. W. Fleming, A. B. Harvey, and M. C. Lin, Chem. Phys. **73**, 27 (1982).
- <sup>2</sup> A. Canosa, I. R. Sims, I. W. M. Smith, and B. R. Rowe, Astron. Astrophys. **323**, 644 (1997).
- <sup>3</sup> CEC, 1992; Supplement I, 1994 (see references in Introduction).
- <sup>4</sup> J. E. Butler, J. W. Fleming, L. P. Goss, and M. C. Lin, Chem. Phys. **56**, 355 (1981).
- <sup>5</sup> M. W. Bosnali and D. Perner, Z. Naturforsch. A **26**, 1768 (1971).
- <sup>6</sup> K. McKee, M. A. Blitz, M. J. Pilling, H.-B. Qian, A. Taylor, and P. W. Seakins, J. Phys. Chem. A **107**, 5710 (2003).

**CH+C<sub>2</sub>H<sub>6</sub>→Products****Rate Coefficient Data**

<i>k/cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup></i>	<i>T/K</i>	Reference	Comments
<i>Rate Coefficient Measurements</i>			
4.0·10 <sup>-10</sup>	298	Butler <i>et al.</i> , 1981 <sup>1</sup>	(a)
1.8·10 <sup>-10</sup> exp(132/T)	162–650	Berman and Lin, 1983 <sup>2</sup>	(b)
<i>Reviews and Evaluations</i>			
1.8·10 <sup>-10</sup> exp(132/T)	200–700	CEC 1992; 1994 <sup>3</sup>	(c)

**Comments**

- (a) Multiphoton dissociation of CHBr<sub>3</sub> at 193 nm; [CH] monitored by laser-induced fluorescence at 429.8 nm. Total pressure 132 mbar Ar.
- (b) Multiphoton dissociation of CHBr<sub>3</sub> at 266 nm; [CH] monitored by laser-induced fluorescence at 429.8 nm. Total pressure 132 mbar Ar. Estimate also given for *k*(CH+C<sub>3</sub>H<sub>8</sub>), based on the observed linear dependence of *k* on the number of C-H bonds in the molecule reacting with CH.
- (c) Accepts the expression of Berman and Lin.<sup>2</sup>

**Preferred Values**

$$k = 1.8 \cdot 10^{-10} \exp(132/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the range } 200\text{--}700 \text{ K.}$$

**Reliability**

$\Delta \log k = \pm 0.5$  over the range 200–700 K.

**Comments on Preferred Values**

The available data are in reasonable agreement but until they are confirmed wide error limits are suggested. The preferred values are unchanged from our previous evaluations.<sup>3</sup> The only information on product formation comes from a study of McKee *et al.*<sup>4</sup> who used pulsed laser photolysis of CHBr<sub>3</sub>/C<sub>2</sub>H<sub>6</sub> mixtures at 295 K and LIF detection of H atoms, to measure an H atom yield relative to that from the CH+CH<sub>4</sub> reaction, of 0.22±0.09. It has been proposed that the reaction proceeds by insertion of the CH followed by rapid decomposition of the excited alkyl radical intermediate produced.<sup>2,4</sup> Calculations of McKee *et al.*<sup>4</sup> suggest that this mechanism is compatible with their yield of 0.22 for formation of C<sub>3</sub>H<sub>6</sub>+H, with the other main products being CH<sub>3</sub>+C<sub>2</sub>H<sub>4</sub>.

**References**

- <sup>1</sup>J. E. Butler, J. W. Fleming, L. P. Goss, and M. C. Lin, Chem. Phys. **56**, 355 (1981).
- <sup>2</sup>M. R. Berman and M. C. Lin, Chem. Phys. **82**, 435 (1983).
- <sup>3</sup>CEC, 1992; Supplement I, 1994 (see references in Introduction).
- <sup>4</sup>K. McKee, M. A. Blitz, M. J. Pilling, H.-B. Qian, A. Taylor, and P. W. Seakins, J. Phys. Chem. (in press).

**CH+CH<sub>3</sub>CCH→Products****Rate Coefficient Data**

<i>k/cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup></i>	<i>T/K</i>	Reference	Comments
<i>Rate Coefficient Measurements</i>			
4.6·10 <sup>-10</sup>	298	Butler <i>et al.</i> , 1981 <sup>1</sup>	(a)

**Comments**

- (a) Multiphoton dissociation of CHBr<sub>3</sub> at 193 nm; [CH] monitored by laser-induced fluorescence at 429.8 nm. Total pressure 132 mbar Ar.

**Preferred Values**

No recommendation.

**Comments on Preferred Values**

No recommendation is made. The only available measurement was made using an ArF laser operating at 193 nm to

dissociate CH<sub>3</sub>Br<sub>3</sub> as the CH source. Work in the same laboratory<sup>2,3</sup> suggests that such excimer laser studies may be suspect owing to possible absorption by the accompanying unsaturated compound and subsequent photochemical reactions.

**References**

- <sup>1</sup>J. E. Butler, J. W. Fleming, L. P. Goss, and M. C. Lin, Chem. Phys. **56**, 355 (1981).
- <sup>2</sup>M. R. Berman, J. W. Fleming, A. B. Harvey, and M. C. Lin, Chem. Phys. **73**, 27 (1982).
- <sup>3</sup>M. R. Berman and M. C. Lin, Chem. Phys. **82**, 435 (1983).

**CH+C<sub>3</sub>H<sub>8</sub>→Products****Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$1.4 \cdot 10^{-10}$	298	Bosnali and Perner, 1971 <sup>1</sup>	(a)
$3.7 \cdot 10^{-10}$	298	Berman and Lin, 1983 <sup>2</sup>	(b)
$1.9 \cdot 10^{-10} \exp(240/T)$	298–689	Zabarnick, Fleming, and Lin, 1987 <sup>3</sup>	(c)
<i>Reviews and Evaluations</i>			
$1.9 \cdot 10^{-10} \exp(240/T)$	300–700	CEC, 1992; 1994 <sup>4</sup>	(d)

**Comments**

- (a) Pulse radiolysis of CH<sub>4</sub>/C<sub>3</sub>H<sub>8</sub> mixtures at 20 mbar pressure; [CH] monitored by absorption at 314.4 nm.
- (b) Multiphoton dissociation of CHBr<sub>3</sub> at 266 nm; [CH] monitored by laser-induced fluorescence at 429.8 nm. Total pressure 132 mbar Ar. Estimate of  $k(\text{CH} + \text{C}_3\text{H}_8)$  also given based on the observed linear dependence of  $k$  on the number of C-H bonds in the molecule reacting with CH.
- (c) Multiphoton dissociation of CHBr<sub>3</sub> at 266 nm; [CH] monitored by laser-induced fluorescence at 429.8 nm. Total pressure 25–400 mbar Ar. Rates independent of total pressure.
- (d) Accepts the expression of Zabarnick *et al.*<sup>3</sup>

**Preferred Values**

$k = 1.9 \cdot 10^{-10} \exp(240/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 298–700 K.

**Reliability**

$\Delta \log k = \pm 0.5$  over the range 298–700 K.

**Comments on Preferred Values**

The preferred values, which are unchanged from our previous evaluations,<sup>4</sup> are based on the two most recent studies,<sup>2,3</sup> which are in good agreement, but wide error limits are suggested. It has been proposed that the reaction proceeds by insertion of the CH followed by rapid decomposition of the excited alkyl radical so produced.<sup>2,3</sup>

**References**

- <sup>1</sup> M. W. Bosnali and D. Perner, Z. Naturforsch. A **26**, 1768 (1971).
- <sup>2</sup> M. R. Berman and M. C. Lin, Chem. Phys. **82**, 435 (1983).
- <sup>3</sup> S. Zabarnick, J. W. Fleming, and M. C. Lin, Chem. Phys. **112**, 409 (1987).
- <sup>4</sup> CEC, 1992; Supplement I, 1994 (see references in Introduction).

**CH+n-C<sub>4</sub>H<sub>10</sub>→Products****Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$1.3 \cdot 10^{-10}$	298	Bosnali and Perner, 1971 <sup>1</sup>	(a)
$5.8 \cdot 10^{-10}$	298	Butler <i>et al.</i> , 1981 <sup>2</sup>	(b)
$4.4 \cdot 10^{-10} \exp(28/T)$	257–653	Berman and Lin, 1983 <sup>3</sup>	(c)
<i>Reviews and Evaluations</i>			
$4.4 \cdot 10^{-10} \exp(28/T)$	250–700	CEC, 1992; 1994 <sup>4</sup>	(d)

**Comments**

- (a) Pulse radiolysis of CH<sub>4</sub>/n-C<sub>4</sub>H<sub>10</sub> mixtures at 20 mbar pressure; [CH] monitored by absorption spectroscopy at 314.4 nm.
- (b) Multiphoton dissociation of CHBr<sub>3</sub> at 193 nm; [CH] monitored by laser-induced fluorescence at 429.8 nm. The total pressure was 132 mbar Ar.

- (c) Multiphoton dissociation of CHBr<sub>3</sub> at 266 nm; [CH] monitored by laser-induced fluorescence at 429.8 nm. Total pressure 132 mbar Ar. Estimate of  $k(\text{CH} + \text{C}_3\text{H}_8)$  also given based on the observed linear dependence of  $k$  on the number of C-H bonds in the molecule reacting with CH.
- (d) Accepts the expression of Berman and Lin.<sup>3</sup>

### Preferred Values

$k = 4.4 \cdot 10^{-10} \exp(28/T)$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> over the range 250–700 K.

### Reliability

$\Delta \log k = \pm 0.5$  over the range 250–700 K.

### Comments on Preferred Values

The preferred values are unchanged from our previous evaluations,<sup>4</sup> and are based on the two most recent studies,<sup>2,3</sup>

which are in reasonable agreement, but wide error limits are suggested. It has been proposed that the reaction proceeds by insertion of the CH followed by rapid decomposition of the excited alkyl radical so produced.<sup>3</sup>

### References

- <sup>1</sup> M. W. Bosnali and D. Perner, Z. Naturforsch. A **26**, 1768 (1971).
- <sup>2</sup> J. E. Butler, J. W. Fleming, L. P. Goss, and M. C. Lin, Chem. Phys. **56**, 355 (1981).
- <sup>3</sup> M. R. Berman and M. C. Lin, Chem. Phys. **82**, 435 (1983).
- <sup>4</sup> CEC, 1992; Supplement I, 1994 (see references in Introduction).

## CH + *i*-C<sub>4</sub>H<sub>10</sub> → Products

### Rate Coefficient Data

$k/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$2.0 \cdot 10^{-10} \exp(240/T)$	298–689	Zabarnick, Fleming, and Lin, 1987 <sup>1</sup>	(a)
<i>Reviews and Evaluations</i>			
$2.0 \cdot 10^{-10} \exp(240/T)$	300–700	CEC, 1992; 1994 <sup>2</sup>	(b)

### Comments

- (a) Multiphoton dissociation of CHBr<sub>3</sub> at 266 nm; [CH] monitored by laser-induced fluorescence at 429.8 nm. Total pressure 25–400 mbar Ar. Rate constant independent of total pressure.
- (b) Accepts the expression of Zabarnick *et al.*<sup>1</sup>

### Reliability

$\Delta \log k = \pm 0.7$  over the range 298–700 K.

### Comments on Preferred Values

The only available experimental measurements of  $k$  are accepted but with wide error limits. The preferred values are unchanged from our previous evaluations. It has been proposed that the reaction proceeds by insertion of the CH followed by rapid decomposition of the excited alkyl radical so produced.<sup>1,3</sup>

### References

- <sup>1</sup> S. Zabarnick, J. W. Fleming, and M. C. Lin, Chem. Phys. **112**, 409 (1987).
- <sup>2</sup> CEC, 1992; Supplement I, 1994 (see references in Introduction).
- <sup>3</sup> M. R. Berman and M. C. Lin, Chem. Phys. **82**, 435 (1983).

### Preferred Values

$k = 2.0 \cdot 10^{-10} \exp(240/T)$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> over the range 298–700 K.

## CH + *neo*-C<sub>5</sub>H<sub>12</sub> → Products

### Rate Coefficient Data

$k/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$1.6 \cdot 10^{-10} \exp(340/T)$	298–689	Zabarnick, Fleming, and Lin, 1987 <sup>1</sup>	(a)
<i>Reviews and Evaluations</i>			
$1.6 \cdot 10^{-10} \exp(340/T)$	300–700	CEC, 1992; 1994 <sup>2</sup>	(b)

### Comments

- (a) Multiphoton dissociation of CHBr<sub>3</sub> at 266 nm; [CH] monitored by laser-induced fluorescence at 429.8 nm. Total pressure 25–400 mbar Ar. Rate constant independent of total pressure.
- (b) Accepts the expression of Zabarnick *et al.*<sup>1</sup>

### Preferred Values

$$k = 1.6 \cdot 10^{-10} \exp(340/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the range } 298\text{--}700 \text{ K.}$$

### Reliability

$$\Delta \log k = \pm 0.7 \text{ over the range } 298\text{--}700 \text{ K.}$$

### Comments on Preferred Values

The only available experimental measurements of  $k$  are accepted but with wide error limits. The preferred values are unchanged from our previous evaluations.<sup>2</sup> It has been proposed that the reaction proceeds by insertion of the CH followed by rapid decomposition of the excited alkyl radical so produced.<sup>1,3</sup>

### References

- <sup>1</sup> S. Zabarnick, J. W. Fleming, and M. C. Lin, Chem. Phys. **112**, 409 (1987).  
<sup>2</sup> CEC, 1993; Supplement I, 1994 (see references in Introduction).  
<sup>3</sup> M. R. Berman and M. C. Lin, Chem. Phys. **82**, 435 (1983).



### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = 326.3 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = 93.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 6.74 \cdot 10^{24} T^{0.235} \exp(-39261/T) \text{ molecule cm}^{-3} \\ (300 \leqslant T/\text{K} \leqslant 5000)$$

$$\Delta H^\circ_{298}(2) = 424.0 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = 102.6 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 1.815 \cdot 10^{24} T^{0.091} \exp(-50836/T) \text{ molecule cm}^{-3} \\ (300 \leqslant T/\text{K} \leqslant 5000)$$

$$\Delta H^\circ_{298}(3) = 37.91 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = -6.18 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 4.95 \cdot 10^{-1} T^{-0.004} \exp(-4570/T) \\ (300 \leqslant T/\text{K} \leqslant 4000)$$

See Section 3 for the origin source of the Thermodynamic Data.

### Rate Coefficient Data ( $k = k_1 + k_2 + k_3$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$k_1 = 2.2 \cdot 10^{-10} \exp(-29700/T)$	2500–3800	Dean and Hanson, 1992 <sup>1</sup>	(a)
$k_2 = 7 \cdot 10^{-9} \exp(-41800/T)$	2200–3400	Markus, Tereza, and Roth, 1994 <sup>2</sup>	(b)
$k_1 = 2.5 \cdot 10^{-10} \exp(-32200/T)$	1700–3500	Zaslonsko, Smirnov, and Tereza, 1994 <sup>3</sup>	(c)
$k_1 = 1.1 \cdot 10^{-9} \exp(-34700/T)$	1900–2700	Bauerle, Klatt, and Wagner, 1995 <sup>4</sup>	(d)
$k_2 = 8.4 \cdot 10^{-9} \exp(-42800/T)$			
$k_2 = 9 \cdot 10^{-9} \exp(-45100/T)$			
<i>Reviews and Evaluations</i>			
$< 1 \cdot 10^{-16}$	298	Laufer, 1981; <sup>5</sup> Tsang and Hampson, 1986 <sup>6</sup>	(e)

### Comments

- (a) Shock tube study of C<sub>1</sub> hydrocarbon radical decomposition based on pyrolysis of dilute ethane or methane in argon. Analysis based on fits to [C] and [CH] profiles, using a 35-reaction mechanism. [CH] was detected by narrow line laser absorption and [C] by ARAS. Channel (1) was needed to account for the rapid rise in [C] which could not be explained by sequential H-atom

abstraction from CH<sub>i</sub> species. The [CH] profile was more sensitive to CH<sub>3</sub> decomposition at short times, but the profile could not be modeled without Channel (2).

- (b) Shock tube study using reflected shock waves in ketene/Ar mixtures over the pressure range 0.7–2.4 bar. [CH] was monitored by laser absorption at 432.1 nm and [C] and [H] were monitored by ARAS.  $k_1$  was

derived by fitting the [C] profiles using a detailed mechanism. No evidence was found for the occurrence of Channel (2).

- (c) Shock tube study of methane and of ethane decomposition;  $[\text{CH}_3]$  monitored by absorption spectroscopy. A reanalysis of data in Refs. 1 and 2, using an 85 reaction scheme, is included.
- (d) Shock tube study of methylene recombination and decomposition in an argon diluent using ketene as the radical source. The decomposition measurements were made at high densities ( $5 \cdot 10^{18} \text{ cm}^{-3}$ ) and at low ketene concentrations, which was varied over a 7-fold range.  $[\text{H}]$  was monitored by ARAS and the system simulated using a 21 reaction scheme.  $k_1$  was fixed at the value from Ref. 2 and it was assumed that CH decomposes rapidly into C+H.
- (e) Upper limit derived by Laufer from study of Laufer and Bass.<sup>7</sup> This limit is also recommended by Tsang and Hampson.<sup>6</sup>

### Preferred Values

$k_1 = 5.0 \cdot 10^{-10} \exp(-32600/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 1700–4000 K.

$k_2 = 1.56 \cdot 10^{-8} \exp(-44880/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 1700–4000 K.

### Reliability

$\Delta \log k_1 = \pm 0.7$  at 1700 K, falling to  $\pm 0.4$  at 4000 K.

$\Delta \log k_2 = \pm 0.7$  at 1700 K, falling to  $\pm 0.4$  at 4000 K.

### Comments on Preferred Values

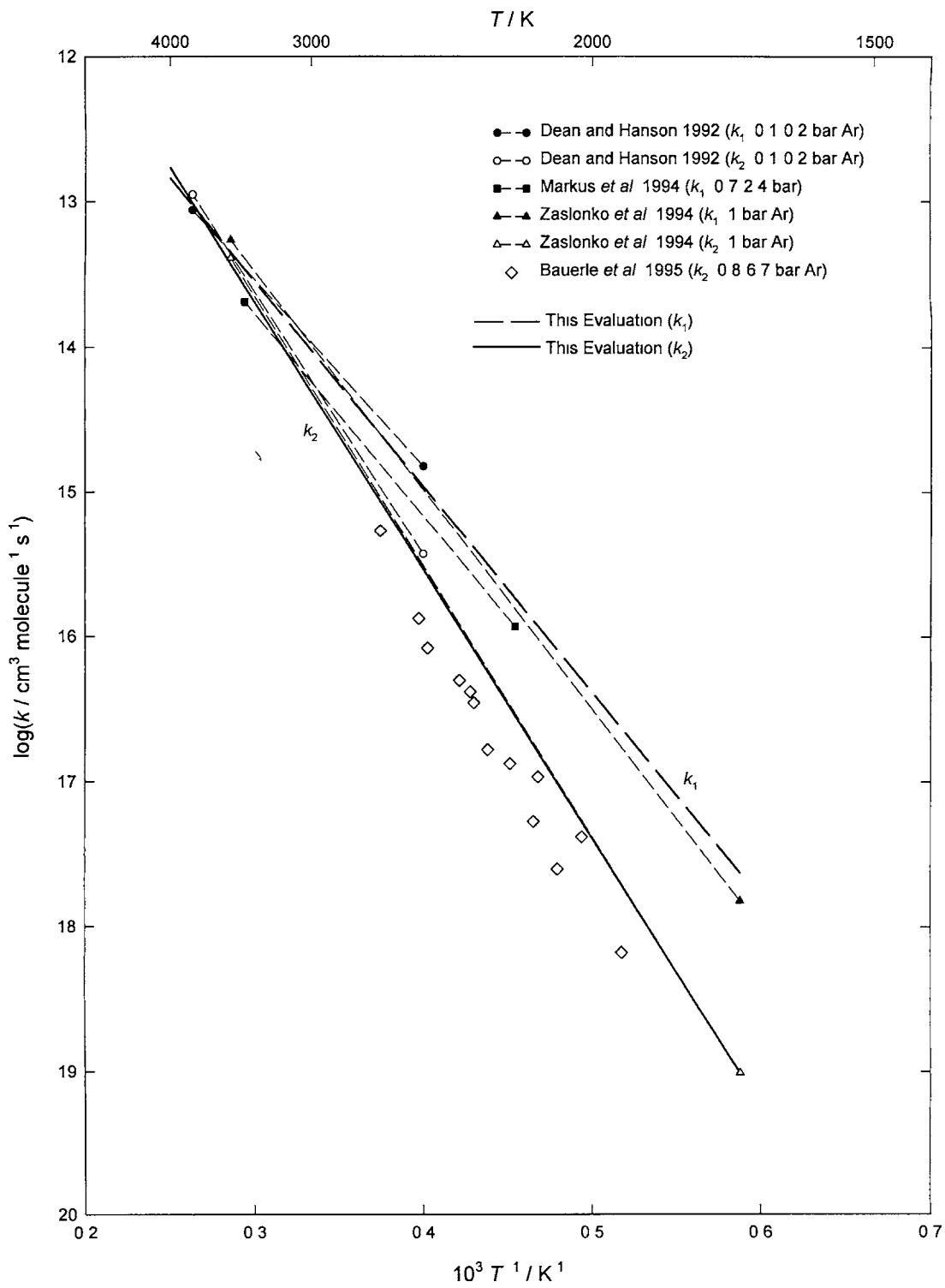
References 1, 2, and 4 all use monitoring of species formed in reactions (1) and (2), whereas in Ref. 3,  $[\text{CH}_3]$  is monitored, which is the precursor to  $\text{CH}_2$  in the system studied. The systems are complex, but there is very good agree-

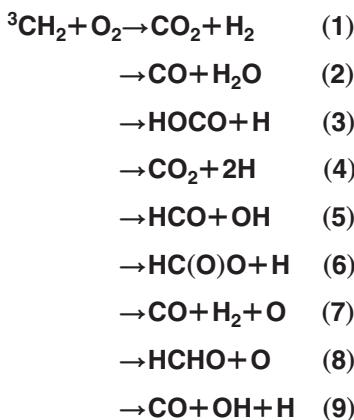
ment between the different measurements. Both channels correlate, with conserved spin, with  $^3\text{CH}_2$ ;  $^1\text{CH}_2$  only correlates with  $\text{CH} + \text{H}$  in a spin conserved reaction. The experiments were conducted under conditions where it was not feasible to distinguish between the two electronic states of methylene. At 2000 K, under the conditions of Ref. 4, the equilibration time for the two states is  $< 1 \mu\text{s}$ , with about 5% of the methylene present in the excited singlet state, rising to 15% at 4000 K. The rate constants, therefore, refer to the total concentration of methylene (both spin states), which, within the accuracy of the rate constants, is close to the triplet concentration. The rate parameters for  $k_1$  are chosen to fit the data from Refs. 1–3 and those for  $k_2$  are based on the results from Refs. 1, 3, and 4.

In addition to decomposition,  $^3\text{CH}_2$  is also collisionally activated to  $^1\text{CH}_2$  [Channel (3)]. The rate coefficient for this process is given by  $k_{-3} K_3$ , where  $k_{-3}$  is the rate coefficient for collisional deactivation (see  $^1\text{CH} + \text{M}$  data sheet) and  $K_3$  is the equilibrium constant given above. For the reactive gases,  $k_3$  is calculated explicitly in the appropriate tables (see relevant data sheets). While the fractional concentration of  $^1\text{CH}_2$  in an equilibrated mixture is small, it is the more reactive spin state, and reaction via activation to the singlet species should be considered as a potentially significant mechanism.

### References

- <sup>1</sup>A. J. Dean and R. K. Hanson, Int. J. Chem. Kinet. **24**, 517 (1992).
- <sup>2</sup>M. W. Markus, A. M. Tereza, and P. Roth, 25th Symp. (Int.) Combustion, 1994, p. 705.
- <sup>3</sup>I. S. Zaslonsko, V. N. Smirnov and A. M. Tereza, Kinet. Catal. **35**, 5 (1994).
- <sup>4</sup>S. Bauerle, M. Klatt, and H. Gg. Wagner, Ber. Bunsenges. Phys. Chem. **99**, 870 (1995).
- <sup>5</sup>A. H. Laufer, Rev. Chem. Intermed. **4**, 225 (1981).
- <sup>6</sup>W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data **15**, 1087 (1981).
- <sup>7</sup>A. H. Laufer and A. M. Bass, Combust. Flame **32**, 215 (1978).



*Thermodynamic Data*

$$\Delta H^\circ_{298}(1) = -783.9 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = -55.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 2.5 \cdot 10^{-5} T^{0.595} \exp(+94430/T)$$

(300 ≤  $T/\text{K}$  ≤ 5000)

$$\Delta H^\circ_{298}(3) = -389.4 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = -33.70 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 1.60 \cdot 10^{-5} T^{1.024} \exp(+47180/T)$$

(300 ≤  $T/\text{K}$  ≤ 5000)

$$\Delta H^\circ_{298}(5) = -305.8 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(5) = 8.02 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(5) = 4.4 T^{-0.056} \exp(+36720/T)$$

(300 ≤  $T/\text{K}$  ≤ 5000)

$$\Delta H^\circ_{298}(7) = -251.8 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(7) = 89.14 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(7) = 1.31 \cdot 10^{25} T^{-0.407} \exp(+30210/T) \text{ molecule cm}^{-3}$$

(300 ≤  $T/\text{K}$  ≤ 5000)

$$\Delta H^\circ_{298}(9) = -245.9 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(9) = 95.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(9) = 3.22 \cdot 10^{25} T^{-0.416} \exp(+29480/T) \text{ molecule cm}^{-3}$$

(300 ≤  $T/\text{K}$  ≤ 5000)

$$\Delta H^\circ_{298}(2) = -742.7 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = -13.67 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 3.33 T^{-0.406} \exp(+89170/T)$$

(300 ≤  $T/\text{K}$  ≤ 5000)

$$\Delta H^\circ_{298}(4) = -348.0 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(4) = 42.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(4) = 1.52 \cdot 10^{19} T^{0.746} \exp(+44240/T) \text{ molecule cm}^{-3}$$

(300 ≤  $T/\text{K}$  ≤ 5000)

$$\Delta H^\circ_{298}(6) = -323.0 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(6) = -45.69 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(6) = 1.38 \cdot 10^{-4} T^{0.526} \exp(+38960/T)$$

(300 ≤  $T/\text{K}$  ≤ 5000)

$$\Delta H^\circ_{298}(8) = -249.8 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(8) = -20.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(8) = 9.8 \cdot 10^{-3} T^{0.282} \exp(+30190/T)$$

(300 ≤  $T/\text{K}$  ≤ 5000)

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data ( $k = k_1 + k_2 + k_3 + k_4 + k_5 + k_6 + k_7 + k_8 + k_9$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$3.3 \cdot 10^{-12}$	296	Böhland <i>et al.</i> , 1984 <sup>1</sup>	(a)
$3.24 \cdot 10^{-12}$	293	Darwin <i>et al.</i> , 1989 <sup>2</sup>	(b)
$8.3 \cdot 10^{-13}$	1000–1700	Dombrowsky <i>et al.</i> , 1992 <sup>3</sup>	(c)
$1.45 \cdot 10^{-11} \exp(-505/T)$	233–433	Bley <i>et al.</i> , 1992 <sup>4</sup>	(d)
$5.45 \cdot 10^{-2} T^{-3.3} \exp(-1443/T)$	1012–1751	Dombrowsky and Wagner, 1992 <sup>5</sup>	(e)
$3.0 \cdot 10^{-12}$	298	Alvarez and Moore, 1994 <sup>6</sup>	(f)
<i>Reviews and Evaluations</i>			
$4.1 \cdot 10^{-11} \exp(-750/T)$	300–1000	CEC, 1992; 1994 <sup>7</sup>	(g)

**Comments**

- (a) Discharge flow study.  ${}^3\text{CH}_2$  radicals were produced by passage of a discharge through a  $\text{CH}_2\text{CO}/\text{He}$  mixture or by means of the  $\text{O} + \text{CH}_2\text{CO}$  reaction.  $[{}^3\text{CH}_2]$  was monitored by LMR.

- (b) Pulsed laser photolysis at 351 nm of  $\text{CH}_2\text{CO}/\text{O}_2$  mixtures.  $[{}^3\text{CH}_2]$  monitored by cw diode laser absorption at  $883.3 \text{ cm}^{-1}$ .
- (c) Shock tube study using incident shocks in  $\text{CH}_2\text{N}_2/\text{O}_2/\text{Ar}$  mixtures.  $[\text{O}]$  and  $[\text{H}]$  were monitored by ARAS. Rate constants were derived by fitting O and

- H atom profiles using a detailed mechanism. Branching ratios found for the O and H producing channels were  $0.08 \pm 0.04$  and  $0.10 \pm 0.04$ , respectively.
- (d) Discharge flow study in which  ${}^3\text{CH}_2$  radicals were produced by titration of O atoms with  $\text{CH}_2\text{CO}$  and reacted with an excess of  $\text{O}_2$ .  $[{}^3\text{CH}_2]$  and  $[\text{OH}]$  were monitored by LMR;  $[\text{O}]$  and  $[\text{H}]$  were monitored by ESR. Upper limits for the branching ratios for O atom, H atom, and OH formation obtained were 0.10, 0.20, and 0.30, respectively.
  - (e) Shock tube study using incident shocks in  $\text{CH}_2\text{N}_2/\text{O}_2/\text{Ar}/\text{He}$  mixtures at pressures of  $\sim 1$  bar.  $[\text{CO}]$  and  $[\text{CO}_2]$  were monitored by time-resolved infrared emission at  $4.76 \mu\text{m}$  and  $4.26 \mu\text{m}$ , respectively.  $[\text{OH}]$  was monitored by cw laser absorption. Values of  $k$  were obtained by fitting the measured product profiles using a detailed mechanism. The data on H and O atom production from an earlier study<sup>3</sup> were also used in the simulation. It was found that three quarters of the reactions leads to stable products. The main product is CO with a CO:CO<sub>2</sub> ratio of  $\sim 4$ .
  - (f) Pulsed laser photolysis at 351 nm of  $\text{CH}_2\text{CO}/\text{O}_2/\text{Ar}$  mixtures.  $[\text{CO}]$ ,  $[\text{CO}_2]$ , and  $[\text{HCHO}]$  were monitored by infrared diode laser absorption.  ${}^{13}\text{C}$  labeling was used to elucidate some aspects of the mechanism. Measured product yields for CO, CO<sub>2</sub>, and  $\text{CH}_2\text{O}$  were 0.34, 0.40, and 0.16, respectively. Indirect evidence suggests an OH yield of 0.30.
  - (g) Value of  $k$  of Böhland *et al.*<sup>1</sup> combined with the temperature dependence of Vinckier and Debruyne.<sup>8</sup>

### Preferred Values

$k = 3.0 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 250–1700 K.

### Reliability

$\Delta \log k = \pm 0.3$  at 250 K, rising to  $\pm 0.7$  at 1700 K.

### Comments on Preferred Values

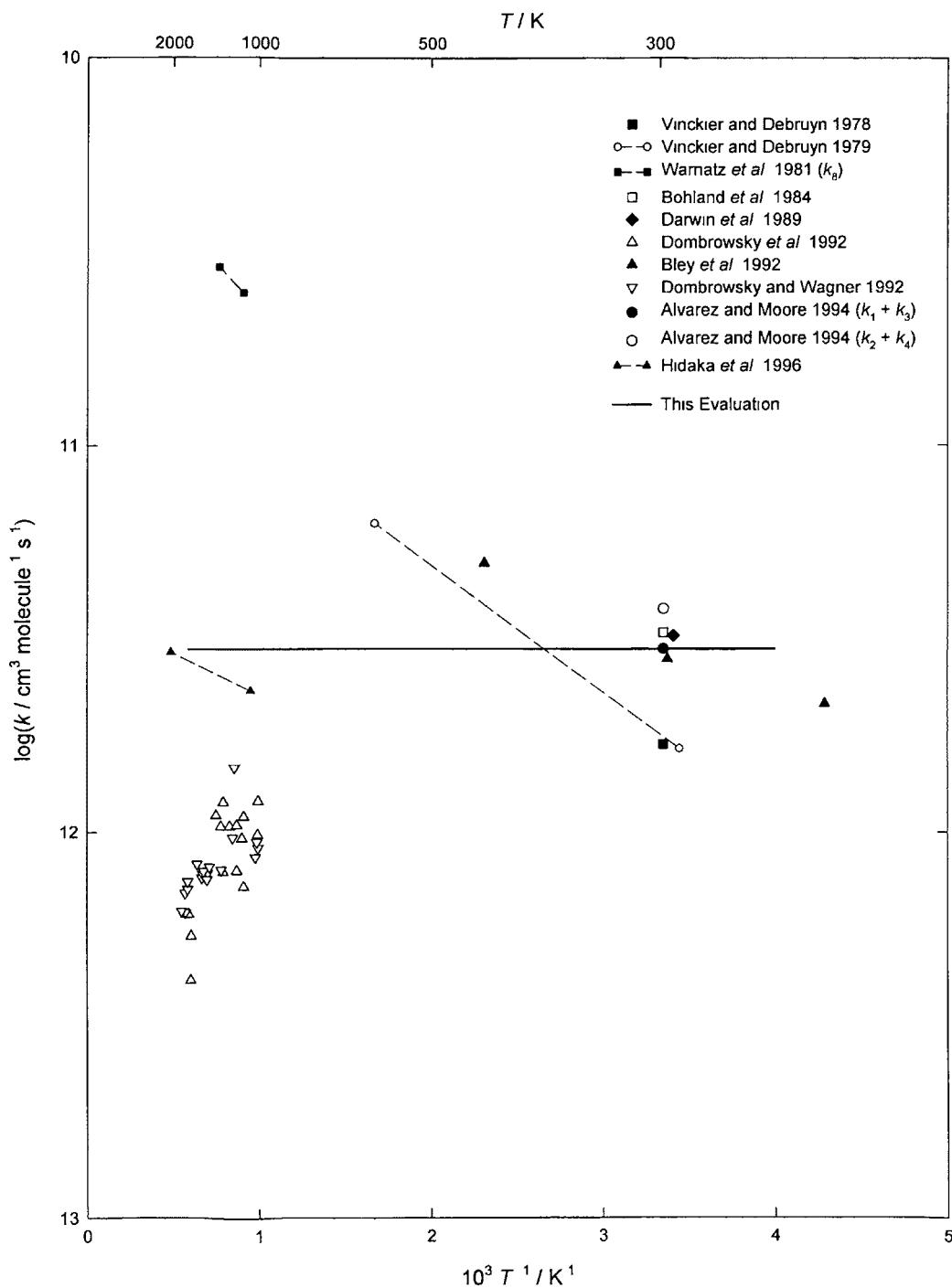
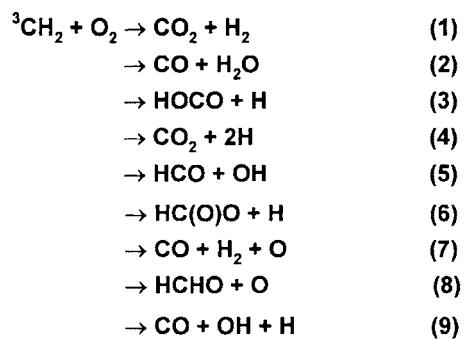
There are a number of studies at low temperatures which give values of  $k$  in good agreement,<sup>1,2,4,6</sup> with a mean value of  $k$  at 298 K of  $3.3 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . There are also measurements of the temperature dependence of  $k$  in this temperature region<sup>4,8,9</sup> which are in reasonable agreement.

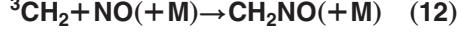
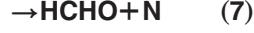
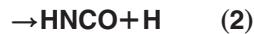
The values of  $k$  at high temperatures are much less certain. Of the studies carried out at temperatures above 1000 K<sup>3,5,10–12</sup> those of Dombrowsky *et al.*<sup>3</sup> and Dombrowsky and Wagner<sup>5</sup> appear to be the most reliable. The values of the rate constant that are obtained are approximately an order of magnitude smaller than predicted by extrapolation of the expressions for  $k$  found in the low temperatures measurements.<sup>4,8</sup> Significantly different values of  $E/R$  are also obtained at low and high temperatures. Details of the reaction mechanism that may give rise to this are unclear. Because of these uncertainties we take as the preferred values a temperature independent value of  $k$  with error limits which encompass the high and low temperature data.

Measurements of the branching ratios also differ between the high and low temperature studies. The measurements of Alvarez and Moore<sup>6</sup> at 296 K and those of Dombrowsky *et al.*<sup>3</sup> and Dombrowsky and Wagner<sup>5</sup> at temperatures of 1000–1700 K are in agreement that the major reaction channels are those leading to stable products (CO,CO<sub>2</sub>) but the low temperature measurements give a ratio of CO to CO<sub>2</sub> of 0.85 while the high temperature studies give a value of  $\sim 4$ . The low temperature value is supported by a similar result obtained by Rowland<sup>13</sup> from a static photolysis-end product study, but at this stage we make no recommendations for the branching ratios.

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#### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = -401.7 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = -13.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 0.569 T^{-0.157} \exp(+48280/T) \\ (300 \leqslant T/\text{K} \leqslant 5000)$$

$$\Delta H^\circ_{298}(3) = -353.7 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = -42.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 2.29 \cdot 10^{-5} T^{0.848} \exp(+42740/T) \\ (300 \leqslant T/\text{K} \leqslant 5000)$$

$$\Delta H^\circ_{298}(5) = -287.1 \text{ kJ mol}$$

$$\Delta S^\circ_{298}(5) = -14.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(5) = 0.434 T^{-0.140} \exp(+34520/T) \\ (300 \leqslant T/\text{K} \leqslant 5000)$$

$$\Delta H^\circ_{298}(7) = -116.6 \text{ kJ mol}$$

$$\Delta S^\circ_{298}(7) = -33.6 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(7) = 3.18 \cdot 10^{-4} T^{0.506} \exp(+14380/T) \\ (300 \leqslant T/\text{K} \leqslant 5000)$$

$$\Delta H^\circ_{298}(9) = -81.1 \text{ kJ mol}$$

$$\Delta S^\circ_{298}(9) = -0.06 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(9) = 0.422 T^{0.129} \exp(+9790/T) \\ (300 \leqslant T/\text{K} \leqslant 5000)$$

$$\Delta H^\circ_{298}(11) = 8.7 \text{ kJ mol}$$

$$\Delta S^\circ_{298}(11) = -20.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(11) = 3.52 \cdot 10^{-4} T^{0.762} \exp(-680/T) \\ (300 \leqslant T/\text{K} \leqslant 4000)$$

$$\Delta H^\circ_{298}(2) = -378.7 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = -52.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 8.7 \cdot 10^{-7} T^{1.135} \exp(+45910/T) \\ (300 \leqslant T/\text{K} \leqslant 4000)$$

$$\Delta H^\circ_{298}(4) = -308.5 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(4) = -20.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(4) = 5.64 \cdot 10^{-3} T^{0.417} \exp(+37210/T) \\ (300 \leqslant T/\text{K} \leqslant 5000)$$

$$\Delta H^\circ_{298}(6) = -271.7 \text{ kJ mol}$$

$$\Delta S^\circ_{298}(6) = -43.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(6) = 1.0 \cdot 10^{-4} T^{-0.60} \exp(+32860/T) \\ (300 \leqslant T/\text{K} \leqslant 4000)$$

$$\Delta H^\circ_{298}(8) = -89.7 \text{ kJ mol}$$

$$\Delta S^\circ_{298}(8) = -65.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(8) = 4.37 \cdot 10^{-9} T^{1.67} \exp(+11330/T) \\ (300 \leqslant T/\text{K} \leqslant 4000)$$

$$\Delta H^\circ_{298}(10) = -73.7 \text{ kJ mol}$$

$$\Delta S^\circ_{298}(10) = -36.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(10) = 6.1 \cdot 10^{-4} T^{0.506} \exp(+8880/T) \\ (300 \leqslant T/\text{K} \leqslant 5000)$$

$$\Delta H^\circ_{298}(12) = -307.3 \text{ kJ mol}$$

$$\Delta S^\circ_{298}(12) = -155.6 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(12) = 1.06 \cdot 10^{-33} T^{1.880} \exp(+37550/T) \text{ cm}^3 \text{ molecule}^{-1} \\ (300 \leqslant T/\text{K} \leqslant 5000)$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2 + k_3 + k_4 + k_5 + k_6 + k_7 + k_8 + k_9 + k_{10} + k_{11} + k_{12}$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$2.3 \cdot 10^{-12} \exp(554/T)$	293–588	Vinckier and DeBruyn, 1979 <sup>1</sup>	(a)
$2.9 \cdot 10^{-11}$	293	Darwin <i>et al.</i> , 1989 <sup>2</sup>	(b)
$3.7 \cdot 10^{-11}$	296	Seidler <i>et al.</i> , 1989 <sup>3</sup>	(c)
$5.8 \cdot 10^{-12} \exp(438/T)$	294–1025	Atakan <i>et al.</i> , 1992 <sup>4</sup>	(d)
$1.7 \cdot 10^{-12}$	1100–2500	Bauerle, Klatt, and Wagner, 1995 <sup>5</sup>	(e)

$k/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$	T/K	Reference	Comments
<i>Branching Ratios</i>			
$k_4/k < 0.1$	300	Atakan <i>et al.</i> , 1992 <sup>4</sup>	(d)
$k_4/k = 0.63$	1000		
$k_4/k = 0.12$	1000	Bauerle, Klatt, and Wagner, 1995 <sup>5</sup>	(e)
$k_4/k = 0.25$	2000		
$k_4/k = 0.11$	298	Fikri, Meyer, and Temps, 2002 <sup>6</sup>	(f)
$k_8/k = 0.89$			

### Comments

- (a) Fast flow discharge study. Steady state concentration of  $\text{CH}_2$  established by  $\text{O} + \text{C}_2\text{H}_2$  reaction. Addition of NO perturbs steady state by competing for  $\text{CH}_2$ , mainly via the  $\text{O} + \text{CH}_2$  reaction.  $[\text{CH}_2]$  monitored by molecular beam mass-spectrometry.  $k(\text{O} + \text{CH}_2) = 1 \cdot 3 \cdot 10^{-10} \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$  used throughout the temperature range. Total pressure  $2 \cdot 9 \text{ mbar}$ , mainly He.
- (b) Pulsed laser photolysis at 351 nm of ketene/NO/He mixtures.  $[\text{CH}_2]$  monitored by infrared laser absorption at  $883.288 \text{ cm}^{-1}$  in a large excess of NO. Pressures not specified.
- (c) Discharge flow system.  $\text{CH}_2$  produced either by laser photolysis of  $\text{CH}_2\text{CO}$  at 193 nm or by  $\text{O} + \text{CH}_2\text{CO}$  reaction.  $[\text{CH}_2]$  monitored by far infrared laser magnetic resonance spectroscopy. Carrier gas, He, at pressures in the range 1.8–3.9 mbar.
- (d) Kinetics studies used pulsed laser photolysis at 193 nm of ketene/ $\text{N}_2$ /NO mixtures at total pressures in the range 7.7–56 mbar to generate  $\text{CH}_2$  in a large excess of NO.  $[\text{OH}]$  product [Channel (4)] monitored by laser induced fluorescence.  
Reaction product studies used laser photolysis at 308 nm of ketene/ $\text{N}_2$ /NO mixtures at pressures in the range 3–15 mbar with molecular beam mass-spectrometric detection of products. No CN or CNO were detectable. Some evidence for  $\text{CH}_2\text{NO}$  formation was found. OH yield calibrated relative to  $\text{CH}_2$  to give branching ratios for OH production of  $0.63 \pm 0.25$  at 1025 K but less than 0.1 at 294 K.  
Kinetics results were analyzed in terms of formation of  $\text{CH}_2\text{NO}$  followed by its unimolecular decay via a number of channels. The tabulated rate constant is identified as that for formation of the complex. The rate constant for OH formation from the  $\text{CH}_2\text{NO}$  was found to be dependent on pressure and ketene concentration.
- (e)  $\text{CH}_2$  generated using incident shock waves in ketene/NO/Ar or  $\text{CH}_2\text{N}_2$ /NO/Ar mixtures.  $[\text{H}]$  and  $[\text{O}]$  monitored by atomic resonance absorption spectroscopy and  $[\text{OH}]$  by laser absorption spectroscopy at 308.4 nm. Pressures in the range 280–2015 mbar were used. Fitting of the measured concentration profiles to a substantial reaction scheme gave values of overall  $k$  and rate constants for H and OH production.
- (f) Photolysis of  $\text{CH}_2\text{CO}/\text{NO}$  mixtures at 313 nm in a bath gas of He (100 mbar) or Ar (570 mbar). Yields deter-

mined by FTIR analysis of reactants ( $\text{H}_2\text{CCO}$ , NO) and products ( $\text{CO}$ ,  $\text{C}_2\text{H}_4$ , HCNO, HCN,  $\text{N}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ). The system was modeled using a detailed mechanism. Extensive theoretical calculations were carried out using *ab initio* and density functional methods. The experimental results agree with those from an earlier, preliminary study<sup>7</sup> using the same technique.

### Preferred Values

$k = 5.6 \cdot 10^{-12} \exp(500/T) \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$  over the range 290–1000 K.  
 $k_4/k = 0.10$ ;  $k_8/k = 0.90$  over the range 290–1000 K.

### Reliability

$\Delta \log k = \pm 0.4$  at 290 K, rising to  $\pm 0.7$  at 1000 K.  
 $\Delta(k_4/k) = \Delta(k_8/k) = \pm 0.05$  over the range 290–1000 K.

### Comments on Preferred Values

The most recent studies<sup>2–4</sup> at ambient temperatures give values of  $k$  in good agreement. The mean of the values of Darwin *et al.*,<sup>2</sup> Seidler *et al.*,<sup>3</sup> and Atakan *et al.*<sup>4</sup> is adopted as the value of  $k$  at 298 K. Earlier studies,<sup>1,8,9</sup> using less direct methods and dependent on an understanding of the secondary chemistry in the systems used, gave much lower values of  $k$ .

The only two studies of the temperature dependence of  $k$ <sup>1,4</sup> agree on a small negative dependence with increase in temperature. A mean of the values of  $E/R$  obtained by Vinckier and Debruyn<sup>1</sup> and Atakan *et al.*,<sup>4</sup> is adopted and combined with the value of  $k$  at 298 K to give the preferred expression for  $k$ . Pilling and Robertson<sup>9</sup> and Atakan *et al.*<sup>4</sup> have obtained evidence suggesting that the rate constant may be pressure dependent which adds to the uncertainty in making recommendations for this reaction. Wide error limits on  $k$  are therefore suggested.

There is also a value of  $k$  obtained at temperatures in the range 1100–2500 K from a shock tube study<sup>5</sup> aimed primarily at investigating product channels. It is lower by a factor of 2 than is given by extrapolation of our preferred expression but the study was carried out at much higher pressures than those on which our recommendations are based.

Measurements of the branching ratios are made difficult by the number of channels available, the reactivity of some of the product species with their propensity to initiate secondary chemistry, and the possible pressure dependence of

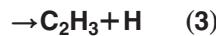
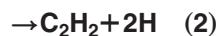
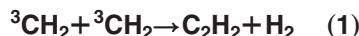
product yields. Using FTIR spectroscopy Grussdorf *et al.*<sup>7</sup> identified the major stable products at ambient temperatures and pressures as HCNO and HCN [Channels (8) and (4), respectively] together with a number of others products derived from the reactions of the H and OH produced concurrently. These findings were confirmed in a subsequent, more detailed study<sup>6</sup> using similar methods. It was also found that there was no systematic effect of changing pressures, which suggested that the  $^3\text{CH}_2$  and any  $^1\text{CH}_2$  present give the same products. A theoretical treatment of the system<sup>6</sup> using *ab initio* and density functional methods gave results in good agreement with the experiments and suggested that (i) stabilization of the initially formed  $\text{H}_2\text{CNO}$  is negligible up to pressures of  $> 1$  bar, (ii) at ambient pressures, and at temperatures up to 2000 K, Channel (8) is dominant with  $k_8/k \approx 0.94$  and that Channel (4) makes a small contribution with  $k_4/k$  in the range 0.015–0.05.

Some of the intermediate radicals have also been detected and some attempts have been made to determine their yields. Su *et al.*<sup>10</sup> observed the production of CO, HCO, HOCH, OH, and NH<sub>2</sub> from both  $^3\text{CH}_2$  and  $^1\text{CH}_2$  in their FTIR study but yields could not be determined and there was some difficulty in attributing these products to specific channels. The preliminary study of Seidler *et al.*<sup>3</sup> suggested that neither OH nor H were main products in contrast to the implications from measurements on the stable products.<sup>6,7</sup> Atakan *et al.*<sup>4</sup> find an OH radical yield of  $< 0.1$  at 300 K which rises to 0.63 at 1000 K, but in a shock tube study Bauerle *et al.*<sup>5</sup> obtain an OH yield of 0.12 at 1000 K rising to 0.25 at 2000

K. The pressures used in the shock tube work were much higher, which may be relevant, but, overall, studies on atom and radical production are not sufficiently definitive for any conclusions to be drawn from them. The measurements of stable product yields by Grussdorf *et al.*<sup>7</sup> and Fikri *et al.*,<sup>6</sup> supported by the theoretical treatments of the reaction,<sup>10–12</sup> seem to represent the best guide to the major reaction channels and are the basis of our recommendations for the branching ratios.

## References

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### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = -552.6 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = -58.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 1.78 \cdot 10^{-7} T^{1.271} \exp(+66844/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(2) = -116.7 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = 40.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 1.08 \cdot 10^{17} T^{2.422} \exp(+14653/T) \text{ molecule cm}^{-3} \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(3) = -263.1 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = -41.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 2.63 \cdot 10^{-7} T^{1.422} \exp(+32247/T) \\ (300 \leq T/\text{K} \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

### Rate Coefficient Data ( $k = k_1 + k_2 + k_3$ )

$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$5.3 \cdot 10^{-11}$	298	Braun, Bass, and Pilling, 1970 <sup>1</sup>	(a)
$k_1 = 1.7 \cdot 10^{-10}$	2000–2800	Frank, Bhaskaran, and Just, 1987 <sup>2</sup>	(b)
$k_1 = 2.6 \cdot 10^{-9} \exp(-6010/T)$	1100–2700	Bauerle <i>et al.</i> , 1995 <sup>3</sup>	(c)
$k_2 = 3.3 \cdot 10^{-10} \exp(-5530/T)$			

$k/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$	T/K	Reference	Comments
<i>Branching Ratios</i>			
$k_2/k \geq 0.9$	298	Becerra <i>et al.</i> , 1987 <sup>4</sup>	(d)
<i>Reviews and Evaluations</i>			
$2.0 \cdot 10^{-10} \exp(-400/T)$	300–3000	CEC, 1992; 1994 <sup>5</sup>	(e)
$k_2/k = 0.9$			

### Comments

- (a) VUV flash photolysis of ketene; time dependence of  $[{}^3\text{CH}_2]$  and the  $[\text{C}_2\text{H}_2]$  product were monitored by VUV absorption spectroscopy.
- (b) Thermal decomposition of ketene behind reflected shocks.  $[\text{H}]$  and  $[\text{CO}]$  were monitored by absorption spectroscopy.
- (c) Shock tube study.  $\text{CH}_2$  was generated by the decomposition of ketene and of diazomethane.  $[\text{H}]$  was monitored by ARAS. The data were analyzed using a 21-reaction scheme and great care was taken to assess the effects of the major reactions on the results. The  $[\text{H}]$  profile was sensitive to ketene dissociation but not to diazomethane, which decomposes much more rapidly. The results for the two precursors are in good agreement. A sensitivity analysis shows that the  $[\text{H}]$  profile is primarily dependent on  $k_1$  and  $k_2$ . Under the experimental conditions no information can be obtained on Channel (3) because of the rapid decomposition of  $\text{C}_2\text{H}_3$ .
- (d) Reanalysis of earlier work based on excimer laser photolysis of ketene at 308 nm. The source of molecular hydrogen is now identified as  ${}^3\text{CH}_2 + \text{H}$ , implying that (2) is the more likely dominant channel.
- (e) Based on the data of Braun *et al.*<sup>1</sup> and Frank *et al.*<sup>2</sup>

### Preferred Values

$k = 3.0 \cdot 10^{-9} \exp(-6000/T) \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$  over the range 1000–3000 K.

### Reliability

$\Delta \log k = \pm 0.5$  over the range 1000–3000 K.

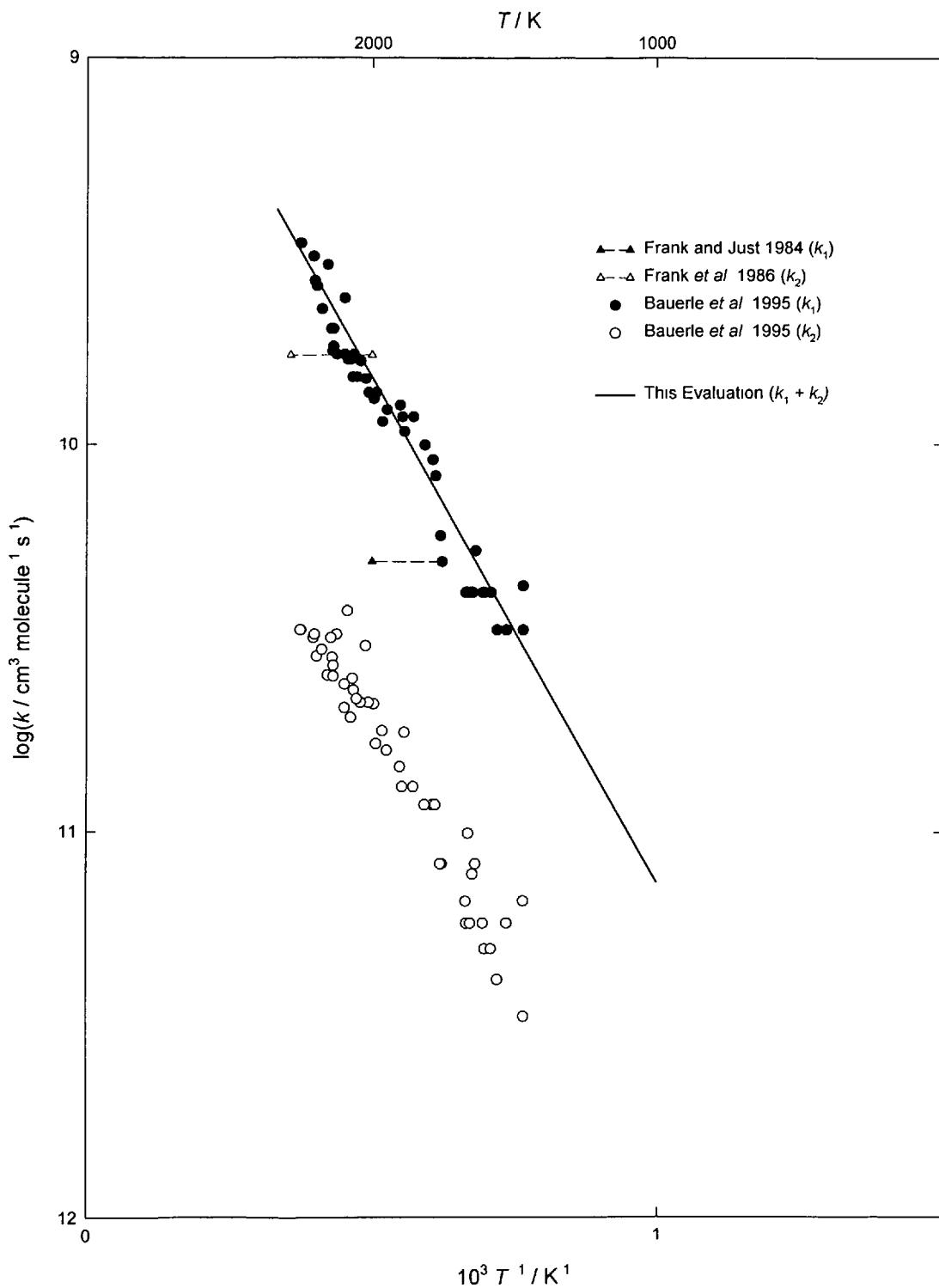
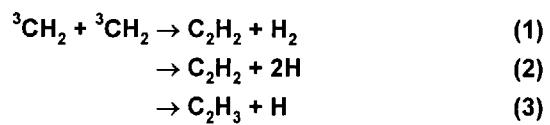
### Comments on Preferred Values

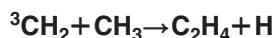
At high temperatures there are two studies, those of Frank *et al.*<sup>2</sup> and of Bauerle *et al.*<sup>3</sup> which are in reasonable agreement on the value of the overall rate constant but differ in their assignment of the branching ratios. The study of Bauerle *et al.*<sup>3</sup> suggests that Channel (1) is the dominant channel whereas that of Frank *et al.*<sup>3</sup> favors Channel (2). The low temperature study of Becerra *et al.*<sup>4</sup> also favors Channel (2), giving a value of  $k_2/k \geq 0.9$ . There is no information on Channel (3). At this stage only an overall rate constant is recommended based on the studies of Bauerle *et al.*<sup>3</sup> and Frank *et al.*<sup>2</sup> and limited to temperatures above 1000 K, with substantial error limits assigned until confirmatory studies are available.

The only value of  $k$  available at lower temperatures is from the study of Braun *et al.*<sup>1</sup> at 298 K. The value obtained is larger than the values of  $k_1$  and  $k_2$  obtained by Bauerle *et al.*<sup>3</sup> at 1100 K which may imply that the reaction mechanism involves addition followed by competition between stabilization of the adduct and decomposition by Channels (1)–(3), but further studies are clearly necessary and no recommendations are made for the low temperature region.

### References

- <sup>1</sup> W. Braun, A. M. Bass, and M. J. Pilling, *J. Chem. Phys.* **52**, 5131 (1970).
- <sup>2</sup> P. Frank, K. A. Bhaskaran, and Th. Just, *J. Phys. Chem.* **90**, 2226 (1986).
- <sup>3</sup> S. Bauerle, M. Klatt, and H. Gg. Wagner, *Ber. Bunsenges. Phys. Chem.* **99**, 870 (1995).
- <sup>4</sup> R. Becerra, C. E. Canosa-Mas, H. M. Frey, and R. Walsh, *J. Chem. Soc. Faraday Trans. 2* **83**, 435 (1987).
- <sup>5</sup> CEC, 1992; Supplement I, 1994 (see references in Introduction).





#### Thermodynamic Data

$$\begin{aligned}\Delta H_{298}^{\circ} &= -266.4 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= -55.08 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 1.45 \cdot 10^{-7} T^{1.236} \exp(+32690/T) \\ &\quad (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the origin and quality of the Thermodynamic Data.

#### Rate Coefficient Data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$5 \cdot 10^{-11}$	298	Pilling and Robertson, 1975 <sup>1</sup>	(a)
$1.0 \cdot 10^{-10}$	298	Laufer and Bass, 1975 <sup>2</sup>	(b)
$3 \cdot 10^{-11}$	1800–2700	Olson and Gardiner, 1978 <sup>3</sup>	(c)
$3 \cdot 10^{-11}$	1700–2200	Bhaskaran <i>et al.</i> , 1979 <sup>4</sup>	(d)
$(7-10) \cdot 10^{-11}$	1320–2300	Frank and Braun-Unkhoff, 1987 <sup>5</sup>	(e)
$1.1 \cdot 10^{-10}$	298	Deters <i>et al.</i> , 1998 <sup>6</sup>	(f)
$1.7 \cdot 10^{-11}$	1350–2400	Hidaka <i>et al.</i> , 2000 <sup>7</sup>	(g)
$2.1 \cdot 10^{-10}$	298	Wang and Fockenberg, 2001 <sup>8</sup>	(h)
<i>Reviews and Evaluations</i>			
$7 \cdot 10^{-11}$	298	Laufer, 1981 <sup>9</sup>	(i)
$7 \cdot 10^{-11}$	300–2500	Warnatz, 1984; <sup>10</sup> Tsang and Hampson, 1986 <sup>11</sup>	(j)
$7 \cdot 10^{-11}$	300–3000	CEC, 1992; 1994 <sup>12</sup>	(k)

#### Comments

- (a) Flash photolysis of mixtures of ketene and azomethane in Ar with end product analysis by GC. Total pressure, 260 mbar. Product formation simulated by numerical integration of a detailed mechanism. The value of  $k$  is sensitive to value chosen for  $k(\text{CH}_3 + \text{CH}_3)$  ( $4.2 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ).
  - (b) Flash photolysis of mixtures of ketene and azomethane in Ar with end product analysis by GC. Total pressures in the range 66–920 mbar. Product formation simulated by numerical integration of a detailed mechanism. Rate coefficient sensitive to value chosen for  $k(\text{CH}_3 + \text{CH}_3)$  ( $9.5 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ).
  - (c) IR absorption study of fuel rich  $\text{CH}_4/\text{O}_2/\text{Ar}$  mixtures behind incident shock waves. Simulation of product yields by numerical integration used to obtain values of  $k$ .
  - (d) Atomic resonance absorption study of [H] in reflected shock waves.
  - (e) Atomic resonance absorption study of [H] in reflected shock waves using a range of  $\text{CH}_3$  precursors (azomethane, methyl iodide, ethane) to obtain data over a wide range of temperatures.
  - (f) Discharge flow study at a total pressure of 1.33 mbar.  $\text{CH}_3$  and  $\text{CH}_2$  were generated by reactions of F atoms with  $\text{CH}_4$  and  $\text{CH}_3$ , respectively. Far infrared LMR was used to monitor  $[\text{CH}_2]$  directly, and  $[\text{CH}_3]$  indirectly by detection of the NO produced by the reaction of the  $\text{CH}_3$  with added  $\text{NO}_2$ . Computer simulations were carried out to investigate side reactions.
  - (g) Shock tube study on the pyrolysis and oxidation of
- $\text{CH}_4$  using a range of  $\text{CH}_4/\text{O}_2/\text{H}_2/\text{Ar}$  mixtures at pressures in the range 1.5–4.5 bar. Two shock tubes were used. The first had facilities for time-resolved and single pulse product analysis studies. IR emissions at  $3.48 \mu\text{m}$ ,  $4.24 \mu\text{m}$ , and  $2.56 \mu\text{m}$  were monitored and reactants and products could be sampled and analyzed by GC. The second shock tube was equipped for laser absorption at  $3.39 \mu\text{m}$  and IR emission studies behind reflected shocks. The measured profiles were simulated using a detailed mechanism. Error limits of a factor of 2 are suggested by the authors.
- (h) Pulsed laser photolysis at 193 nm of  $\text{CH}_3\text{OCH}_3/\text{He}$  mixtures at 1.3 mbar total pressure. The photolysis pulse produced  $\text{CH}_3$  radicals some of which are dissociated in the same pulse to give  $\text{CH}_2$  radicals. Concentrations of reactants and products were monitored by time-resolved photoionization mass spectrometry.
- (i) Based on a reanalysis of Refs. 1 and 2.
- (j) Value of Warnatz<sup>9</sup> based on Refs. 1–4; Tsang and Hampson<sup>11</sup> accept the evaluation of Laufer.<sup>8</sup>
- (k) Based on a reanalysis of Refs. 1 and 2, using the high temperature data to infer temperature independence of  $k$ .

#### Preferred Values

$$k = 1.2 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the range } 298-3000 \text{ K.}$$

#### Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K, rising to } \pm 0.7 \text{ at } 3000 \text{ K.}$$

*Comments on Preferred Values*

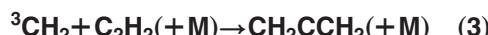
There is considerable scatter on the data at 298 K. The rate data of Refs. 1 and 2, which were derived from very similar studies, need correction for the value of the rate constant for the methyl radical recombination used in the simulations. Taking  $k(\text{CH}_3 + \text{CH}_3) = 6 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (this evaluation) at 298 K at the pressures employed, increases the rate constant in Refs. 1 to  $6 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and decreases that in Refs. 2 to  $8 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . In the experiments of Deters *et al.*<sup>6</sup> and of Wang and Fockenberg<sup>8</sup> values of both  $k$  and  $k(\text{CH}_3 + \text{CH}_3)$  were derived from the experimental data. The conditions were very similar ( $\sim 1.3$  mbar He) but the values of  $k$  and of  $k(\text{CH}_3 + \text{CH}_3)$  derived were both substantially different in the two studies. However, the ratios  $k/k(\text{CH} + \text{CH}_3)$  from the two studies only differ by about 25%. The source of this systematic difference is not clear. Provisionally, the preferred value of  $k$  is taken as the mean of the values from the low temperature studies of Laufer and Bass,<sup>1</sup> Pilling and Robertson,<sup>2</sup> Deters *et al.*,<sup>6</sup> and Wang and Fockenberg.<sup>8</sup>

The reaction is presumed to proceed via an ethyl radical adduct. A significant temperature dependence for  $k$  is therefore not expected, which is supported by the results from the

shock tube studies.<sup>3–5,7</sup> If anything they suggest a very small negative temperature dependence, but the scatter on the results at high temperatures is large and, provisionally, a temperature independent  $k$  is recommended with substantial error limits.

**References**

- <sup>1</sup> A. H. Laufer and A. M. Bass, J. Phys. Chem. **78**, 1344 (1974).
- <sup>2</sup> M. J. Pilling and J. A. Robertson, J. Chem. Soc. Faraday Trans. 1 **73**, 968 (1977).
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- <sup>4</sup> K. Bhaskharan, P. Frank, and Th. Just, 12th Int. Symp. on Shock Tubes and Waves, 1979.
- <sup>5</sup> P. Frank and M. Braun-Unkhoff, 16th Int. Symp. on Shock Tubes and Waves, 1987.
- <sup>6</sup> R. Deters, M. Otting, H. Gg. Wagner, F. Temps, and S. Dóbé, Ber. Bunsenges. Phys. Chem. **102**, 978 (1998).
- <sup>7</sup> Y. Hidaka, K. Sato, Y. Henmi, H. Tanaka, and K. Inami, Combust. Flame **118**, 340 (2000).
- <sup>8</sup> B. Wang and C. Fockenberg, J. Phys. Chem. A **105**, 8449 (2001).
- <sup>9</sup> A. H. Laufer, Rev. Chem. Intermed. **4**, 225 (1981).
- <sup>10</sup> J. Warnatz, in *Combustion Chemistry*, edited by W. C. Gardiner (Springer, New York, 1984).
- <sup>11</sup> W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data **15**, 1087 (1986).
- <sup>12</sup> CEC, 1992; Supplement I, 1994 (see references in Introduction).

*Thermodynamic Data*

$$\begin{aligned}\Delta H^\circ_{298}(1) &= -59.62 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(1) &= -27.91 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 3.41 \cdot 10^{-5} T^{1.022} \exp(+7496/T) \\ (300 \leqslant T/\text{K} \leqslant 4000)\end{aligned}$$

$$\begin{aligned}\Delta H^\circ_{298}(3) &= -428.1 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(3) &= -152.4 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(3) &= 2.96 \cdot 10^{-32} T^{1.415} \exp(+52000/T) \text{ cm}^3 \text{ molecule}^{-1} \\ (300 \leqslant T/\text{K} \leqslant 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

$$\begin{aligned}\Delta H^\circ_{298}(2) &= 37.91 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(2) &= -6.18 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 0.495 T^{-0.004} \exp(-4570/T) \\ (300 \leqslant T/\text{K} \leqslant 4000)\end{aligned}$$

$$\begin{aligned}\Delta H^\circ_{298}(4) &= -433.7 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(4) &= -147.5 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(4) &= 1.02 \cdot 10^{-31} T^{1.328} \exp(+52630/T) \text{ cm}^3 \text{ molecule}^{-1} \\ (300 \leqslant T/\text{K} \leqslant 5000)\end{aligned}$$

**Rate Coefficient Data ( $k = k_1 + k_2 + k_3 + k_4$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$2.0 \cdot 10^{-11} \exp(-3330/T)$	296–728	Böhland, Temps, and Wagner, 1986 <sup>1</sup>	(a)
$7.0 \cdot 10^{-12} \exp(-3330/T)$	1100–2000	Hidaka <i>et al.</i> , 1996 <sup>2</sup>	(b)
<i>Reviews and Evaluations</i>			
$2.0 \cdot 10^{-11} \exp(-3330/T)$	300–1000	CEC, 1992; 1994 <sup>3</sup>	(c)

### Comments

- (a) Flow tube study, with  ${}^3\text{CH}_2$  generated from a discharge through, or flash photolysis of,  $\text{CH}_2\text{CO}$ .  $[{}^3\text{CH}_2]$  monitored by LMR.
- (b) Pyrolysis and oxidation of acetylene in reflected shocks. Concentration of  $\text{CO}_2$  monitored by IR emission, those of hydrocarbons by GC, and of polyacetylenes by mass spectrometry. In the mechanism, the formation of  $\text{CO}_2$  and the decay of  $\text{C}_2\text{H}_2$  depend on the competition between the reactions of  ${}^3\text{CH}_2$  with  $\text{C}_2\text{H}_2$  and  $\text{O}_2$ . The latter rate constant was assumed to be  $4 \cdot 10^{-12} \exp(-500/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , which is slightly greater than the values measured by Dombrowsky and Wagner<sup>4</sup> in this temperature range. The temperature dependence of  $k$  was taken from Ref. 3 and the  $A$  factor adjusted. The products were ascribed to the adduct,  $\text{C}_3\text{H}_4$ .
- (c) Accepts the expression of Böhland *et al.*<sup>1</sup>

### Preferred Values

$k = 2.0 \cdot 10^{-11} \exp(-3330/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 296–2000 K.

$k_2 = 5.5 \cdot 10^{-9} T^{-0.90} \exp(-4570/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 296–1000 K.

### Reliability

$\Delta \log k = \pm 0.3$  at 296 K, rising to  $\pm 0.6$  at 2000 K.

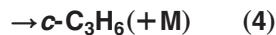
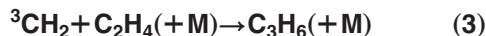
$\Delta \log k_2 = \pm 0.6$  over the range 296–1000 K.

### Comments on Preferred Values

Early indirect measurements<sup>5–8</sup> gave high values for  $k$ , but the careful work of Canosa-Mas *et al.*<sup>9,10</sup> demonstrated the deficiencies in the mechanistic interpretations on which they were based, and it is now widely accepted that the reaction is slow at room temperature. The only direct experiments to give absolute rate constants are those of Böhland *et al.*<sup>1</sup> and their Arrhenius parameters are recommended. The measurements of Hidaka *et al.*<sup>2</sup> are less direct, but support the recommended rate parameters, with increased uncertainty, over a wider temperature range. Most references cite (3) and (4) as the major channels, although that to  $\text{H} + \text{C}_3\text{H}_3$  is 60.6 kJ mol<sup>-1</sup> exothermic and predominates in the reaction of  ${}^1\text{CH}_2$ . Activation to the singlet becomes a significant channel at higher temperatures. The recommended value for  $k_2$  has been obtained from data on the reverse reaction (see data sheet for  $\text{CH}_2 + \text{M}$ ) and the thermodynamic data.

### References

- <sup>1</sup>T. Böhland, F. Temps, and H. Gg. Wagner, 21st Symp. (Int.) Combustion, 1986, p. 841.
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- <sup>4</sup>Ch. Dombrowsky and H. Gg. Wagner, Ber. Bunsenges. Phys. Chem. **96**, 1048 (1992).
- <sup>5</sup>A. H. Laufer and A. M. Bass, J. Phys. Chem. **78**, 1344 (1974).
- <sup>6</sup>M. J. Pilling and J. A. Robertson, J. Chem. Soc. Faraday Trans. 1 **73**, 968 (1977).
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- <sup>9</sup>C. E. Canosa-Mas, H. M. Frey, and R. Walsh, J. Chem. Soc. Faraday Trans. 2 **80**, 861 (1984).
- <sup>10</sup>C. E. Canosa-Mas, H. M. Frey, and R. Walsh, J. Chem. Soc. Faraday Trans. 2 **81**, 283 (1985).



#### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = -54.18 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = -39.95 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 1.72 \cdot 10^{-10} T^{2.398} \exp(+7795/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(3) = -422.8 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = -147.52 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(4) = 7.71 \cdot 10^{-33} T^{1.731} \exp(+51410/T) \text{ cm}^3 \text{ molecule}^{-1} \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(2) = 37.91 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = -6.18 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 0.495 T^{-0.004} \exp(-4570/T) \\ (300 \leq T/\text{K} \leq 4000)$$

$$\Delta H^\circ_{298}(4) = -389.3 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(4) = -176.61 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(4) = 2.25 \cdot 10^{-35} T^{2.011} \exp(+47610/T) \text{ cm}^3 \text{ molecule}^{-1} \\ (300 \leq T/\text{K} \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2 + k_3 + k_4$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$5.3 \cdot 10^{-12} \exp(-2660/T)$	296–728	Böhland, Temps, and Wagner, 1986; <sup>1</sup> Kraus <i>et al.</i> , 1993 <sup>2</sup>	(a)
<i>Reviews and Evaluations</i>			
$5.3 \cdot 10^{-12} \exp(-2660/T)$	300–1000	CEC, 1992; 1994 <sup>3</sup>	(b)

#### Comments

- (a) Discharge flow study with  ${}^3\text{CH}_2$  monitored by LMR and generated from O+CH<sub>2</sub>CO and by 308 nm laser flash photolysis of CH<sub>2</sub>CO. A correction was made for reaction proceeding via activation to the singlet. This analysis is expanded in Ref. 2. The overall rate constant for deactivation+reaction of the singlet was taken as  $2.3 \cdot 10^{-10} (T/296)^{-0.82} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , with a  $T$  independent efficiency for the deactivation channel of 0.2.
- (b) Accepts the expression of Böhland *et al.*<sup>1</sup>

#### Preferred Values

$k = 5.3 \cdot 10^{-12} \exp(-2660/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 296–1000 K.

$k_2 = 9.4 \cdot 10^{-12} \exp(-4290/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 296–1000 K.

#### Reliability

$\Delta \log k = \pm 0.3$  over the range 296–1000 K.

$\Delta \log k_2 = \pm 0.5$  over the range 296–1000 K.

#### Comments on Preferred Values

The rate coefficients were measured by Böhland *et al.*<sup>1</sup> over the pressure range 0.52–7.5 mbar and were found to be independent of pressure. RRKM calculations<sup>1</sup> demonstrate that the energized triplet adduct decomposes under these conditions via Channel (1), while at higher pressures propene is formed, with cyclopropane predominating at the high pressure limit. End product analysis studies by Rowland *et al.*<sup>4</sup> showed that propene is the major product in excess ethene in the pressure range 13–230 mbar. Note also that, at a given pressure, the yields of propene and cyclopropene will decrease as the temperature increases. The expression for  $k_2$  was obtained from the equilibrium constant and the expression for  $k_{-2}$  (see data sheet for  ${}^1\text{CH}_2 + \text{M}$ ).

#### References

- <sup>1</sup> T. Böhland, F. Temps, and H. Gg. Wagner, Ber. Bunsenges. Phys. Chem. **90**, 468 (1986).
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- <sup>4</sup> F. S. Rowland, P. S-T. Lee, D. C. Montague, and R. L. Russell, Discuss Faraday Soc. **53**, 111 (1972).

*Thermodynamic Data*

$$\begin{aligned}\Delta H^\circ_{298} &= -37.91 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298} &= 6.18 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 2.02 \cdot T^{0.004} \exp(+4570/T) \\ &\quad (300 \leq T/\text{K} \leq 4000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data ( $k$  is the overall rate coefficient,  $k_M$  is the rate coefficient for  ${}^1\text{CH}_2 + \text{M} \rightarrow {}^3\text{CH}_2 + \text{M}$ )**

M	$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>				
He	$k_M = k = 3.1 \cdot 10^{-12}$	298	Ashfold <i>et al.</i> , 1981 <sup>1</sup>	(a)
	$k_M = k = 3.5 \cdot 10^{-12}$	295	Langford, Petek, and Moore, 1983 <sup>2</sup>	(b)
	$k_M = k = 1.0 \cdot 10^{-11} \exp(-380/T)$	210–475	Wagener, 1990 <sup>3</sup>	(c)
Ar	$k_M = k = 5.8 \cdot 10^{-12}$	298	Ashfold <i>et al.</i> , 1981 <sup>1</sup>	(a)
	$k_M = k = 6.0 \cdot 10^{-12}$	295	Langford, Petek, and Moore, 1983 <sup>2</sup>	(b)
	$k_M = k = 3.0 \cdot 10^{-14} T^{0.93}$	295–859	Hancock and Heal, 1992 <sup>4</sup>	(d)
N <sub>2</sub>	$k_M = k = 8.8 \cdot 10^{-12}$	298	Ashfold <i>et al.</i> , 1981 <sup>1</sup>	(a)
	$k_M = k = 1.1 \cdot 10^{-11}$	295	Langford, Petek, and Moore, 1983 <sup>2</sup>	(b)
	$k_M = k = 2.4 \cdot 10^{-14} T^{1.0}$	210–475	Wagener, 1990 <sup>3</sup>	(c)
	$k_M = k = 2.1 \cdot 10^{-11} \exp(-217/T)$	298–462	Hayes <i>et al.</i> , 1996 <sup>5</sup>	(e)
H <sub>2</sub>	$1.0 \cdot 10^{-10}$	200–2000	This evaluation	(f)
	$k_M/k = 0.1$	298		
O <sub>2</sub>	$5.2 \cdot 10^{-11}$	300–1000	This evaluation	(g)
	$k_M/k = 1.0$	295		
H <sub>2</sub> O	$2.2 \cdot 10^{-10}$	298	Hack, Wagner and Wilms, 1988 <sup>6</sup>	(h)
	$k_M/k = 0.25$			
	$9.1 \cdot 10^{-11} \exp(217/T)$	298–462	Hayes <i>et al.</i> , 1996 <sup>5</sup>	(e)
CO <sub>2</sub>	$3.3 \cdot 10^{-11}$	298	Koch <i>et al.</i> , 1990 <sup>7</sup>	(i)
	$k_M/k = 0.67$			
CH <sub>4</sub>	$3.1 \cdot 10^{-11} \exp(250/T)$	200–1000	This evaluation	(j)
	$k_M/k = 0.1$	298		
C <sub>2</sub> H <sub>2</sub>	$5.6 \cdot 10^{-8} T^{-0.9}$	296–1000	This evaluation	(k)
	$k_M/k = 0.2$	298		
C <sub>2</sub> H <sub>4</sub>	$9.4 \cdot 10^{-11} \exp(280/T)$	210–1000	This evaluation	(l)
	$k_M/k = 0.2$	295		

**Comments**

- (a)  ${}^1\text{CH}_2$  produced by IRMPD of acetic anhydride and detected by time-resolved LIF.
- (b) Pulsed excimer laser photolysis of ketene at 308 nm with time-resolved dye laser absorption spectroscopy.
- (c) Pulsed excimer laser photolysis of ketene at 308 nm.  $[{}^1\text{CH}_2]$  monitored by time-resolved LIF near 589 nm.
- (d) Pulsed excimer laser photolysis of ketene at 308 nm and time-resolved dye laser absorption of  $[{}^1\text{CH}_2]$  at 590.5 nm.
- (e) Pulsed excimer laser photolysis of ketene at 308 nm and time-resolved LIF of  $[{}^1\text{CH}_2]$ .
- (f) See  ${}^1\text{CH}_2 + \text{H}_2$  data sheet.
- (g) See  ${}^1\text{CH}_2 + \text{O}_2$  data sheet.
- (h) Pulsed excimer laser photolysis of ketene at 308 nm and time-resolved laser induced fluorescence. The OH

product ( ${}^1\text{CH}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_3 + \text{OH}$ ) was detected by LIF and calibrated against the signal from  $\text{NO}_2 + \text{excess H}$  in a discharge flow system. The excimer laser energy was measured and the absorbed energy calculated from the known absorption cross section of  $\text{CH}_2\text{CO}$  at 308 nm. The yield of OH was shown to be  $>50\%$  and it was assumed that the balance occurred by collision induced intersystem crossing with a yield of  $0.25 \pm 0.25$ . At higher pressures, stabilization of the methanol adduct will become significant.

- (i) Pulsed excimer laser photolysis of ketene at 308 nm and time-resolved LIF of  $[{}^1\text{CH}_2]$  near 590 nm. Yield of  ${}^3\text{CH}_2$  determined by LMR.
- (j) See  ${}^1\text{CH}_2 + \text{CH}_4$  data sheet.
- (k) See  ${}^1\text{CH}_2 + \text{C}_2\text{H}_2$  data sheet.
- (l) See  ${}^1\text{CH}_2 + \text{C}_2\text{H}_4$  data sheet.

## Preferred Values

M	$k_M/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$	T/K	$\Delta \log k$	$\Delta(k_M/k)$
He	$1.1 \cdot 10^{-11} \exp(-380/T)$	200–1000	±0.2 over the range 200–300 K, increasing to ±0.4 at 1000 K	
Ar	$3.0 \cdot 10^{-14} T^{0.93}$	200–1000	±0.2	
N <sub>2</sub>	$2.0 \cdot 10^{-11} \exp(-237/T)$	200–1000	±0.2 at 200 K, rising to ±0.3 at 1000 K	
H <sub>2</sub>	$1.0 \cdot 10^{-11}$	200–1000		$^{+0.3}_{-0.1}$ at 300 K, rising to $^{+0.5}_{-0.1}$ at 200 K and 1000 K
O <sub>2</sub>	$5.2 \cdot 10^{-11}$	300–1000		$^{+0.0}_{-0.3}$ at 300 K, rising to $^{+0.0}_{-0.5}$ at 1000 K
H <sub>2</sub> O	$2.5 \cdot 10^{-11} \exp(217/T)$	300–1000		±0.3 at 300 K, rising to $^{+0.5}_{-0.3}$ at 1000 K
CO <sub>2</sub>	$2.2 \cdot 10^{-11}$	300–1000		±0.3 at 300 K, rising to $^{+0.3}_{-0.6}$ at 1000 K
CH <sub>4</sub>	$3.1 \cdot 10^{-12} \exp(250/T)$	200–1200		$^{+0.3}_{-0.1}$ at 300 K, rising to $^{+0.5}_{-0.1}$ at 200 K and 1200 K
C <sub>2</sub> H <sub>2</sub>	$1.1 \cdot 10^{-8} T^{-0.9}$	200–1000		$^{+0.3}_{-0.2}$ at 300 K, rising to $^{+0.6}_{-0.2}$ at 200 K and 1000 K
C <sub>2</sub> H <sub>4</sub>	$1.9 \cdot 10^{-11} \exp(280/T)$	200–1000		±0.2 at 300 K, rising to $^{+0.5}_{-0.2}$ at 200 K and 1000 K

## Comments on Preferred Values

There is quite good agreement between the room temperature measurements for He, Ar, and N<sub>2</sub>. The limited investigations of temperature dependence show that the rate coefficients increase with increase in temperature. The mechanism of collisional transfer from the singlet to the triplet state of methylene with nonreactive gases is relatively well understood and has been investigated experimentally and discussed in some detail by Hancock and Heal<sup>4</sup> and by Bley and Temps.<sup>8</sup> The process is known as *collision induced intersystem crossing* (CIISC) and proceeds via a small number of rotational states in the singlet electronic state that have mixed singlet/triplet character. The purpose of the collisions is to transfer CH<sub>2</sub> from unperturbed to perturbed states by rotational energy transfer. As the temperature increases, the number of perturbed states that are significantly populated increases, increasing the rate of transfer to such states and the overall rate coefficient for CIISC.

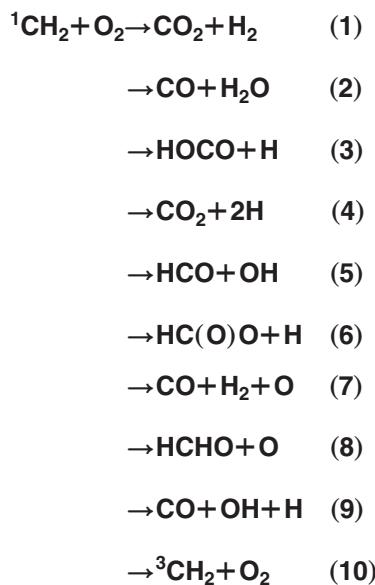
The situation is more complex for reactive gases. With the exception of H<sub>2</sub>O and CO<sub>2</sub>, the data in the above tables are taken from the appropriate analysis of the overall rate coefficient in this evaluation. For H<sub>2</sub>O, there has been a single analysis, while for CO<sub>2</sub> the temperature dependence of the overall rate coefficient has been taken from the work of Hayes *et al.*,<sup>5</sup> while the triplet yield at room temperature has been taken from Koch *et al.*<sup>7</sup> For all of the reactive partners, the yield of triplet has been measured at room temperature only. If the same CIISC mechanism as for inert gases applies then, since the rate coefficients for the reactive gases are either invariant or decrease as the temperature rises, it would be expected that the fractional yield of the triplet would increase. However, it is unlikely that the same mechanism applies. For O<sub>2</sub>, for example, the process is spin allowed, be-

cause of the triplet spin character of O<sub>2</sub>. For the other species, the potential energy surface is strongly attractive and new mechanisms for transfer between the two surfaces may become feasible, with different temperature dependences. Measurements of the temperature dependence of the triplet yield are needed for such collision partners. For the present, we have assumed that the yield of triplet does not change with *T* and have adopted large error limits.

Rate coefficients for transfer from the triplet to the singlet may be calculated via the equilibrium constant. Reactivation to the more reactive singlet may be an important mechanism for removal of the triplet at higher temperatures, especially for species with which it reacts only slowly, such as H<sub>2</sub> and CH<sub>4</sub>. At 300 K, the equilibrium constant (the reciprocal of that given in the table above) is  $1.2 \cdot 10^{-7}$  at 300 K and  $5 \cdot 10^{-3}$  at 1000 K. Thus, even for C<sub>2</sub>H<sub>2</sub>, the effective rate constant for reaction via the singlet,  $1.1 \cdot 10^{-13} \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ , is comparable with that for direct reaction of the triplet,  $3.7 \cdot 10^{-13} \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ .

## References

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*Thermodynamic Data*

$$\Delta H^\circ_{298}(1) = -783.9 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = -55.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 2.5 \cdot 10^{-5} T^{0.595} \exp(+94430/T)$$

(300 ≤  $T/\text{K}$  ≤ 5000)

$$\Delta H^\circ_{298}(3) = -427.33 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = -27.52 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 3.01 \cdot 10^{-5} T^{1.037} \exp(+51750/T)$$

(300 ≤  $T/\text{K}$  ≤ 5000)

$$\Delta H^\circ_{298}(5) = -343.7 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(5) = 14.20 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(5) = 8.28 T^{-0.043} \exp(+41290/T)$$

(300 ≤  $T/\text{K}$  ≤ 5000)

$$\Delta H^\circ_{298}(7) = -289.7 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(7) = 95.32 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(7) = 2.47 \cdot 10^{25} T^{-0.394} \exp(+34780/T) \text{ molecule cm}^{-3}$$

(300 ≤  $T/\text{K}$  ≤ 5000)

$$\Delta H^\circ_{298}(9) = -245.7 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(9) = 95.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(9) = 3.22 \cdot 10^{25} T^{-0.416} \exp(+29450/T) \text{ molecule cm}^{-3}$$

(300 ≤  $T/\text{K}$  ≤ 5000)

$$\Delta H^\circ_{298}(2) = -742.7 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = -13.67 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 3.33 T^{-0.406} \exp(+89170/T)$$

(300 ≤  $T/\text{K}$  ≤ 5000)

$$\Delta H^\circ_{298}(4) = -348.0 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(4) = 42.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(4) = 1.52 \cdot 10^{19} T^{0.746} \exp(+44240/T) \text{ molecule cm}^{-3}$$

(300 ≤  $T/\text{K}$  ≤ 5000)

$$\Delta H^\circ_{298}(6) = -361.0 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(6) = -39.51 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(6) = 2.59 \cdot 10^{-4} T^{0.540} \exp(+43540/T)$$

(300 ≤  $T/\text{K}$  ≤ 5000)

$$\Delta H^\circ_{298}(8) = -249.8 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(8) = -20.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(8) = 9.8 \cdot 10^{-3} T^{0.282} \exp(+30190/T)$$

(300 ≤  $T/\text{K}$  ≤ 5000)

$$\Delta H^\circ_{298}(10) = -37.91 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(10) = 6.18 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(10) = 2.02 \cdot T^{0.004} \exp(+4570/T)$$

(300 ≤  $T/\text{K}$  ≤ 4000)

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data ( $k = k_1 + k_2 + k_3 + k_4 + k_5 + k_6 + k_7 + k_8 + k_9 + k_{10}$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$3.0 \cdot 10^{-11}$	298	Ashfold <i>et al.</i> , 1981 <sup>1</sup>	(a)
$7.4 \cdot 10^{-11}$	295	Langford, Petek, and Moore, 1983 <sup>2</sup>	(b)
<i>Branching Ratios</i>			
$k_{10}/k = 1.0$	295	Blitz <i>et al.</i> , 2003 <sup>3</sup>	(c)
$k_{10}/k = 1.0$	295	Hancock and Haverd, 2003 <sup>4</sup>	(d)
<i>Reviews and Evaluations</i>			
$5.2 \cdot 10^{-11}$	300–1000	Tsang and Hampson, 1986 <sup>5</sup>	(e)
$5.2 \cdot 10^{-11}$	300–1000	CEC, 1992; 1994 <sup>6</sup>	(e)

### Comments

- (a)  ${}^1\text{CH}_2$  radicals were produced by IRMPD of acetic anhydride/ $\text{H}_2$  mixtures and monitored by LIF.
- (b) Pulsed excimer laser photolysis of ketene/ $\text{H}_2$  mixtures at 308 nm with time-resolved dye laser absorption spectroscopy at  $\sim 600$  nm used to monitor  $[{}^1\text{CH}_2]$ .
- (c) Pulsed laser photolysis of ketene/ $\text{O}_2$  mixtures at 308 nm.  $[\text{H}]$  was monitored by vacuum ultraviolet LIF. The growth of the H atom signal was a factor of  $>10$  slower than expected for formation from  ${}^1\text{CH}_2 + \text{O}_2$  but was compatible with formation from the triplet following deactivation of the singlet to the triplet by  $\text{O}_2$ . This observation does not eliminate other reaction channels, which do not form H, but, when taken together with the results of Hancock and Haverd,<sup>4</sup> it strongly supports unit yield of Channel (10).
- (d) Pulsed laser photolysis of ketene/ $\text{O}_2$  mixtures at 308 nm (producing mainly singlet methylene) and at 351 nm (producing only triplet methylene), with detection of vibrationally excited  $\text{CO}_2$  and  $\text{HCHO}$  by infrared chemiluminescence. The rate of formation of vibrationally excited  $\text{CO}_2$  and  $\text{HCHO}$  was independent of photolysis wavelength and at a rate compatible with formation from  ${}^3\text{CH}_2 + \text{O}_2$ . Addition of Ar, which deactivates the singlet to the triplet, had a minimal effect on the IR emission.
- (e) Based on Refs. 1 and 2.

### Preferred Values

$k = k_{10} = 5.2 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 300–1000 K.

### Reliability

$\Delta \log k = \pm 0.3$  at 300 K, rising to  $\pm 0.5$  at 1000 K.

### Comments on Preferred Values

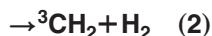
The kinetics of this reaction are much less well characterized than a number of other reactions involving  ${}^1\text{CH}_2$ . No temperature dependent investigation has been conducted and the two room temperature measurements differ significantly. It has been suggested that there might be a precursor dependence connected with reaction of vibrationally excited  ${}^1\text{CH}_2$

but IRMPD<sup>1</sup> forms products with little vibrational energy. The excess energy at 308 nm in the dissociation of  $\text{CH}_2\text{CO}$  to form  ${}^1\text{CH}_2 + \text{CO}$  is only  $23 \text{ kJ mol}^{-1}$ , which corresponds to  $\sim 2000 \text{ cm}^{-1}$ , so that any vibrational excitation in methylene will be limited.

There has been no direct investigation of the products of the reaction. Su *et al.*<sup>7</sup> determined the infrared emission spectra from reaction with oxygen of both singlet and triplet methylene following laser photolysis of ketene. They found little difference in the spectra of CO and  $\text{CO}_2$ , but with some indication of slightly higher vibrational excitation for both species formed from the singlet. They also observed emission from vibrationally excited  $\text{H}_2\text{CO}$  for both methylene species, but from excited water only in the case of the triplet. In  ${}^{14}\text{CH}_2\text{CO}$  tracer studies Rowland *et al.*<sup>8</sup> found similar relative product yields for both  ${}^1\text{CH}_2$  and  ${}^3\text{CH}_2 + \text{O}_2$  and argued that this might indicate that the main mechanism of reaction of  ${}^1\text{CH}_2 + \text{O}_2$  is deactivation to  ${}^3\text{CH}_2$ . The results of Blitz *et al.*<sup>3</sup> and of Hancock and Haverd<sup>4</sup> were obtained from experiments that are more direct than any of the other investigations and form the basis of our recommendations. Hancock and Haverd<sup>4</sup> used much lower ketene concentrations than Su *et al.*<sup>7</sup> and it is possible that there was some interference from the  ${}^1\text{CH}_2 + \text{CH}_2\text{CO}$  reaction in the latter measurements. Ashfold *et al.*<sup>1</sup> have argued that, since the rate coefficient for total removal of  ${}^1\text{CH}_2$ ,  $k$ , is three times larger than would be expected for deactivation to the triplet, a chemical mechanism predominates. However, the high value for  $k_{10}$  may arise from a different mechanism for collision induced intersystem crossing from that found for inert gases, relating to the triplet spin character of  $\text{O}_2$ .

### References

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#### Thermodynamic Data

$$\begin{aligned}\Delta H^\circ_{298}(1) &= -63.93 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(1) &= -10.74 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 4.19 \cdot 10^{-3} T^{0.563} \exp(+7996/T) \\ &\quad (300 \leq T/\text{K} \leq 4000)\end{aligned}$$

$$\begin{aligned}\Delta H^\circ_{298}(2) &= -37.91 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(2) &= 6.18 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 2.02 T^{0.004} \exp(+4570/T) \\ &\quad (300 \leq T/\text{K} \leq 4000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$1.3 \cdot 10^{-10}$	298	Ashfold <i>et al.</i> , 1981 <sup>1</sup>	(a)
$1.1 \cdot 10^{-10}$	298	Langford, Petek, and Moore, 1983 <sup>2</sup>	(b)
$7.0 \cdot 10^{-11} \exp(160/T)$	210–475	Wagener, 1990 <sup>3</sup>	(c)
$1.0 \cdot 10^{-10}$	295–859	Hancock and Heal, 1992 <sup>4</sup>	(d)
$k_1 = 2.2 \cdot 10^{-10}$	1850–2100	Davidson <i>et al.</i> , 1995 <sup>5</sup>	(e)
<i>Branching Ratios</i>			
$k_1/k > 0.8$	298	Braun, Bass, and Pilling, 1970 <sup>6</sup>	(f)
$k_2/k = 0.1$	298	Blitz, Pilling, and Seakins, 2001 <sup>7</sup>	(g)
<i>Reviews and Evaluations</i>			
$1.2 \cdot 10^{-10}$	298	Tsang and Hampson, 1986 <sup>8</sup>	(h)
$1.2 \cdot 10^{-10}$	300–1000	CEC, 1992; 1994 <sup>9</sup>	(h)

#### Comments

- (a)  ${}^1\text{CH}_2$  radicals were produced by IRMPD of acetic anhydride/ $\text{H}_2$  mixtures and detected by LIF.
- (b) Pulsed excimer laser photolysis of ketene/ $\text{H}_2$  mixtures at 308 nm with time resolved dye laser absorption spectroscopy at  $\sim 600$  nm used to monitor  $[{}^1\text{CH}_2]$ .
- (c) Pulsed laser photolysis of ketene/ $\text{H}_2$ /He mixtures at 308 nm.  $[{}^1\text{CH}_2]$  monitored by time resolved LIF near 589 nm. On the basis of the measured temperature dependence of physical quenching rate constants, in the same study, the author suggests that Channel (4) will increase in relative importance with increase in temperature and become comparable to removal by chemical reaction at  $\sim 1000$  K.
- (d) Pulsed laser photolysis at 308 nm of ketene/ $\text{H}_2$  mixtures.  $[{}^1\text{CH}_2]$  was monitored by time-resolved dye laser absorption at 590.5 nm.
- (e) Shock tube study of methyl iodide/argon and ethane/argon mixtures. Studies on the methyl iodide/argon mixtures covered the temperature range 1860–2275 K and pressure range 1.7–2.2 bar. Studies on the ethane/argon mixtures covered the temperature range 2188–2360 K and pressure range 1.6–1.8 bar.  $[\text{CH}_3]$  was monitored by time-resolved narrow line laser absorp-

tion at 216.615 nm and a detailed mechanism was used to simulate the  $[\text{CH}_3]$  profile. The cited value of  $k$  gave a good fit in the range 1850–2100 K.

- (f) Flash photolysis of ketene/ $\text{H}_2$  mixtures. VUV absorption spectroscopy used to monitor both  $[{}^3\text{CH}_2]$  and  $[\text{CH}_3]$ .
- (g) Pulsed laser photolysis at 308 nm of ketene/ $\text{H}_2$ /NO mixtures. Quenching of  ${}^1\text{CH}_2$  produces  ${}^3\text{CH}_2$  which subsequently reacts with NO to produce OH. The OH was monitored by time-resolved LIF at 307.93 nm. The values of  $k$  were derived by fitting the limited reaction scheme involved to the OH profiles.
- (h) Based on Refs. 1 and 2.

#### Preferred Values

$k = 1.0 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 200–2100 K.

$k_2/k = 0.1$  over the range 200–1000 K.

#### Reliability

$\Delta \log k = \pm 0.1$  at 300 K, rising to  $\pm 0.3$  at 200 K and 2100 K.

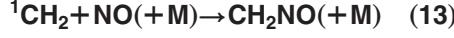
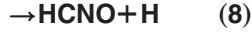
$\Delta(k_2/k) = {}^{+0.3}_{-0.1}$  at 300 K, rising to  ${}^{+0.5}_{-0.1}$  at 200 K and 1000 K.

*Comments on Preferred Values*

There is excellent agreement between all four measurements of  $k$  at room temperature.<sup>1–4</sup> Hancock and Heal<sup>4</sup> provide the most extensive data set. A slightly higher value is obtained at high temperatures by Davidson *et al.*<sup>5</sup> suggesting a small positive temperature dependence of  $k$  in contrast to the slight negative  $T$  dependence observed by Wagener.<sup>3</sup> These differences are probably within the scatter of all of the measurements and a temperature independent value is recommended. The high efficiency of Channel (1), observed experimentally by Braun *et al.*<sup>6</sup> and by Blitz *et al.*,<sup>7</sup> is also supported by estimates of the deactivation rate coefficient based on a Parmenter-Seaver analysis.<sup>10</sup>

**References**

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*Thermodynamic Data*

$$\Delta H^\circ_{298}(1) = -439.6 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = -7.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 1.15 \cdot 10^{-0.153} \exp(+52850/T) \\ (300 \leqslant T/\text{K} \leqslant 5000)$$

$$\Delta H^\circ_{298}(3) = -391.6 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = -36.6 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 4.63 \cdot 10^{-5} \cdot T^{0.852} \exp(+47310/T) \\ (300 \leqslant T/\text{K} \leqslant 5000)$$

$$\Delta H^\circ_{298}(5) = -325.0 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(5) = -8.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(5) = 0.877 \cdot T^{-0.136} \exp(+39090/T) \\ (300 \leqslant T/\text{K} \leqslant 5000)$$

$$\Delta H^\circ_{298}(7) = -154.5 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(7) = -27.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(7) = 6.42 \cdot 10^{-4} \cdot T^{0.510} \exp(+18950/T) \\ (300 \leqslant T/\text{K} \leqslant 5000)$$

$$\Delta H^\circ_{298}(2) = -416.6 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = -46.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 1.76 \cdot 10^{-6} \cdot T^{1.139} \exp(+50480/T) \\ (300 \leqslant T/\text{K} \leqslant 4000)$$

$$\Delta H^\circ_{298}(4) = -346.4 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(4) = -13.91 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(4) = 1.14 \cdot 10^{-2} \cdot T^{0.421} \exp(+41710/T) \\ (300 \leqslant T/\text{K} \leqslant 5000)$$

$$\Delta H^\circ_{298}(6) = -309.6 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(6) = -36.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(6) = 2.02 \cdot 10^{-4} \cdot T^{-0.604} \exp(+37430/T) \\ (300 \leqslant T/\text{K} \leqslant 4000)$$

$$\Delta H^\circ_{298}(8) = -127.6 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(8) = -59.6 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(8) = 8.74 \cdot 10^{-9} \cdot T^{1.674} \exp(+15900/T) \\ (300 \leqslant T/\text{K} \leqslant 4000)$$

$$\begin{aligned}\Delta H_{298}^{\circ}(9) &= -119.0 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ}(9) &= 6.1 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(9) &= 0.852 T^{0.133} \exp(+14360/T) \\ (300 \leq T/\text{K} \leq 5000) &\end{aligned}$$

$$\begin{aligned}\Delta H_{298}^{\circ}(11) &= -22.1 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ}(11) &= -14.0 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(11) &= 7.11 \cdot 10^{-4} T^{0.766} \exp(+3030/T) \\ (300 \leq T/\text{K} \leq 4000) &\end{aligned}$$

$$\begin{aligned}\Delta H_{298}^{\circ}(13) &= -345.2 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ}(13) &= -149.4 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(13) &= 2.16 \cdot 10^{-33} T^{1.884} \exp(+42120/T) \text{ cm}^3 \text{ molecule}^{-1} \\ (300 \leq T/\text{K} \leq 5000) &\end{aligned}$$

$$\begin{aligned}\Delta H_{298}^{\circ}(10) &= -111.6 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ}(10) &= -30.2 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(10) &= 1.23 \cdot 10^{-3} T^{0.510} \exp(+13450/T) \\ (300 \leq T/\text{K} \leq 5000) &\end{aligned}$$

$$\begin{aligned}\Delta H_{298}^{\circ}(12) &= -37.91 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ}(12) &= 6.18 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(12) &= 2.02 T^{0.004} \exp(+4570/T) \\ (300 \leq T/\text{K} \leq 4000) &\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

### Rate Coefficient Data ( $k = k_1 + k_2 + k_3 + k_4 + k_5 + k_6 + k_7 + k_8 + k_9 + k_{10} + k_{11} + k_{12} + k_{13}$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$1.6 \cdot 10^{-10}$	293	Langford, Petek, and Moore, 1983 <sup>1</sup>	(a)
$1.6 \cdot 10^{-10}$	296–645	Hancock and Heal, 1992 <sup>2</sup>	(b)

### Comments

- (a) Excimer laser flash photolysis of ketene at 308 nm with [ ${}^1\text{CH}_2$ ] monitored by time-resolved dye laser absorption spectroscopy.
- (b) Excimer laser flash photolysis at 308 nm with [ ${}^1\text{CH}_2$ ] monitored by time-resolved dye laser absorption at 590.5 nm.

### Preferred Values

$k = 1.6 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 293–1000 K.

### Reliability

$\Delta \log k = \pm 0.2$  at 293 K, rising to  $\pm 0.3$  at 1000 K.

### Comments on Preferred Values

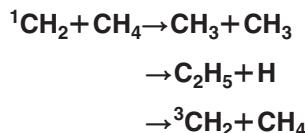
There is excellent agreement at room temperature between the two direct measurements, and the experiments of Hancock and Heal<sup>2</sup> show clearly the lack of any temperature dependence in the rate coefficient.

Information on the branching ratios is less secure. Su *et al.*<sup>3</sup> used time resolved FTIR and observed  $\text{NH}_2$ , CO, and HOCH, supporting the involvement of Channels (1) and (6).

The time resolution of their system was  $3 \mu\text{s}$  and the  $1/e$  time of the reaction at their experimental pressure of NO (0.7 mbar) was  $\sim 0.6 \mu\text{s}$ , so that they were unable to observe the rate of formation of the products to confirm their direct production from  ${}^1\text{CH}_2$ . There remains the possibility, therefore, that the mechanism involves initial formation of the triplet and subsequent reaction to form the observed products. Su *et al.*<sup>3</sup> argued against this conclusion, and in favor of direct product formation, on the basis of differences in the observed product spectra at short times from the singlet and triplet reactions. Their discrete Fourier transform (DFT) calculations of the potential energy surface are in broad agreement with their experimental results and show initial formation of  $\text{CH}_2\text{NO}$ , on a barrierless surface, followed by isomerization over low barriers to form the observed products. More detailed calculations have also been performed on this surface<sup>4,5</sup> providing broadly similar conclusions.

### References

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- <sup>5</sup>W. A. Shapley and G. B. Bacska, *J. Phys. Chem. A* **103**, 4514 (1999).

*Thermodynamic Data*

$$\begin{aligned}
 \Delta H^\circ_{298}(1) &= -60.6 \text{ kJ mol}^{-1} \\
 \Delta S^\circ_{298}(1) &= 13.1 \text{ J K}^{-1} \text{ mol}^{-1} \\
 K_c(1) &= 1.48 T^{0.240} \exp(+7220/T) \\
 &(300 \leq T/\text{K} \leq 5000)
 \end{aligned}$$

$$\begin{aligned}
 \Delta H^\circ_{298}(3) &= -37.91 \text{ kJ mol}^{-1} \\
 \Delta S^\circ_{298}(3) &= 6.18 \text{ J K}^{-1} \text{ mol}^{-1} \\
 K_c(3) &= 2.02 \cdot T^{0.004} \exp(+4570/T) \\
 &(300 \leq T/\text{K} \leq 5000)
 \end{aligned}$$

$$\begin{aligned}
 \Delta H^\circ_{298}(2) &= -14.5 \text{ kJ mol}^{-1} \\
 \Delta S^\circ_{298}(2) &= -13.1 \text{ J K}^{-1} \text{ mol}^{-1} \\
 K_c(2) &= 2.72 \cdot 10^{-5} T^{1.302} \exp(+2200/T) \\
 &(300 \leq T/\text{K} \leq 5000)
 \end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data ( $k = k_1 + k_2 + k_3$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$7.3 \cdot 10^{-11}$	298	Ashfold <i>et al.</i> , 1981 <sup>1</sup>	(a)
$7.0 \cdot 10^{-11}$	295	Langford, Petek, and Moore, 1983 <sup>2</sup>	(b)
$2.6 \cdot 10^{-11} \exp(287/T)$	210–475	Wagener, 1990 <sup>3</sup>	(c)
$3.2 \cdot 10^{-11} \exp(265/T)$	298–462	Hayes <i>et al.</i> , 1996 <sup>4</sup>	(d)
<i>Branching Ratios</i>			
$k_3/k = 0.17$	296	Böhland, Temps, and Wagner, 1985 <sup>5</sup>	(e)
$k_3/k = 0.10$	296	Bley and Temps, 1993 <sup>6</sup>	(f)
<i>Reviews and Evaluations</i>			
$5.2 \cdot 10^{-11}$	298	Tsang and Hampson, 1986 <sup>7</sup>	(g)

**Comments**

- (a)  ${}^1\text{CH}_2$  radicals were produced by IRMPD of acetic anhydride/H<sub>2</sub> mixtures and detected by LIF.
- (b) Pulsed excimer laser photolysis of ketene/H<sub>2</sub> mixtures at 308 nm, with  $[{}^1\text{CH}_2]$  monitored by time-resolved dye laser absorption spectroscopy at  $\sim 600$  nm.
- (c) Excimer laser photolysis of ketene at 308 nm.  $[{}^1\text{CH}_2]$  monitored by time-resolved LIF near 591 nm.
- (d) Pulsed laser photolysis of ketene at 308 nm.  $[{}^1\text{CH}_2]$  monitored by time-resolved LIF near 589 nm. On the basis of the measured temperature dependence of physical quenching rate constants, in the same study, the author suggests that Channel (3) will increase in relative importance with increase in temperature and become comparable to removal by chemical reaction at  $\sim 1000$  K (see discussion on  ${}^1\text{CH}_2 + \text{M}$ ).
- (e) Excimer laser flash photolysis of ketene at 308 nm, with detection of  $[{}^3\text{CH}_2]$  by LMR. It is assumed that there is zero yield of triplet CH<sub>2</sub> at 308 nm.
- (f) Analysis of collision induced intersystem crossing in methylene. Reinterpreted the results of Böhland *et al.*<sup>5</sup> with the latest measurements of the quantum yield for the triplet at 308 nm of 0.1. The temperature dependence was calculated assuming the same temperature dependence for Channel (3) as found for N<sub>2</sub>.
- (g) Based on Refs. 1 and 2.

**Preferred Values**

$k = 3.1 \cdot 10^{-11} \exp(250/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 200–1200 K.

$(k_1 + k_2)/k = 0.9$ ;  $k_3/k = 0.1$  over the range 200–1200 K.

*Reliability*

$\Delta \log k = \pm 0.1$  at 300 K, rising to  $\pm 0.3$  at 200 K and 1200 K.

$\Delta(k_3/k) = {}^{+0.3}_{-0.1}$  at 300 K, rising to  ${}^{+0.5}_{-0.1}$  at 200 K and 1200 K.

*Comments on Preferred Values*

There is excellent agreement between all four measurements of  $k$  at room temperature,<sup>1–4</sup> with satisfactory agreement between the two measurements of the temperature dependence<sup>3,4</sup> over the limited range studied. The recommended values are based on all of the measurements cited in the Table.

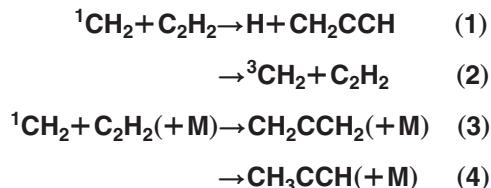
The reaction proceeds by insertion into a C-H bond to form energized C<sub>2</sub>H<sub>6</sub>. It is likely that the most exothermic Channel, (1), will predominate. Stabilization to form C<sub>2</sub>H<sub>6</sub> is unlikely except at very high pressures.

The efficiency of Channel (3) is based on the room temperature measurements of Böhland *et al.*<sup>5</sup> Bley and Temps<sup>6</sup> suggested the same temperature dependence as the found for

$\text{N}_2$ , where the rate coefficient increases roughly linearly with temperature. This overall positive temperature dependence for Channel (3), coupled with the negative temperature dependence of the overall rate coefficient, would mean that physical quenching became increasingly important with increasing temperature. It is not clear, however, that the same process for collisionally inducing intersystem crossing occurs on reactive potential energy surfaces (see data sheet on  ${}^1\text{CH}_2 + \text{M}$ ). In the absence of direct experimental measurements, the yield of Channel (3) is only quoted at room temperature.

## References

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- <sup>4</sup>F. Hayes, W. D. Lawrence, W. S. Staker, and K. D. King, J. Phys. Chem. **100**, 11314 (1996).
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- <sup>7</sup>W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data **15**, 1087 (1986).



### Thermodynamic Data

$$\begin{aligned}\Delta H^\circ_{298}(1) &= -97.53 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(1) &= -21.73 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 4.48 \cdot 10^{-5} T^{1.082} \exp(+12100/T) \\ (300 \leq T/\text{K} \leq 4000) \end{aligned}$$

$$\begin{aligned}\Delta H^\circ_{298}(3) &= -466.0 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(3) &= -146.2 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(3) &= 1.13 \cdot 10^{-31} T^{1.336} \exp(+56510/T) \text{ cm}^3 \text{ molecule}^{-1} \\ (300 \leq T/\text{K} \leq 4000) \end{aligned}$$

$$\begin{aligned}\Delta H^\circ_{298}(2) &= -37.91 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(2) &= 6.18 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 2.02 T^{0.004} \exp(+4570/T) \\ (300 \leq T/\text{K} \leq 4000) \end{aligned}$$

$$\begin{aligned}\Delta H^\circ_{298}(4) &= -471.6 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(4) &= -141.3 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(4) &= 4.06 \cdot 10^{-32} T^{1.245} \exp(+57140/T) \text{ cm}^3 \text{ molecule}^{-1} \\ (300 \leq T/\text{K} \leq 4000) \end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

### Rate Coefficient Data ( $k = k_1 + k_2 + k_3 + k_4$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$3.7 \cdot 10^{-10}$	298	Hack <i>et al.</i> , 1988 <sup>1</sup>	(a)
$2.9 \cdot 10^{-10}$	298	Hayes <i>et al.</i> , 1995 <sup>2</sup>	(b)
$k_1 = 3.5 \cdot 10^{-10}$	298	Adamson <i>et al.</i> , 1996 <sup>3</sup>	(c)
$5.1 \cdot 10^{-8} T^{-0.9}$	205–773	Blitz <i>et al.</i> , 2000 <sup>4</sup>	(d)
<i>Branching Ratios</i>			
$k_2/k = 0.22$	298	Hack <i>et al.</i> , 1988 <sup>1</sup>	(a)
<i>Reviews and Evaluations</i>			
$3.7 \cdot 10^{-10}$	300–1000	CEC, 1992; 1994 <sup>5</sup>	(e)
$k_2/k = 0.22$			

### Comments

- (a) Laser flash photolysis of ketene at 308 nm,  ${}^1\text{CH}_2$  detected by LIF. Production of  ${}^3\text{CH}_2$  [Channel (4)] detected by LMR.
- (b) Pulsed laser photolysis of ketene/ $\text{C}_2\text{H}_2$  mixtures at 308 nm.  $[{}^1\text{CH}_2]$  monitored by laser absorption at 590.7 nm.
- (c) The rate constant was measured relative to the rate constants for forming  $\text{CH}_3$  from  ${}^1\text{CH}_2 + \text{H}_2$  and  $\text{CH}_4$ .  ${}^1\text{CH}_2$  was generated from the 308 nm photolysis of

ketene and relative methyl and propargyl radical concentrations were measured by IR absorption over a range of  $[\text{H}_2]:[\text{CH}_4]:[\text{C}_2\text{H}_2]$  ratios at total pressures in the range 18.8–21.6 mbar.

- (d) Pulsed laser photolysis of  $\text{CH}_2\text{CO}/\text{C}_2\text{H}_2$  mixture at 308 nm.  $[{}^1\text{CH}]$  monitored by laser induced fluorescence at  $\sim 655$  nm. Modeling study carried out to assess the extent of stabilization of the adduct as a function of temperature and pressure.
- (e) Accepts the value of Hack *et al.*<sup>1</sup>

### Preferred Values

$k = 5.6 \cdot 10^{-8} T^{-0.9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 200–1000 K.

$k_1/k = 0.8$ ,  $k_2/k = 0.2$  over the range 200–1000 K.

### Reliability

$\Delta \log k = \pm 0.2$  at 200 K, rising to  $\pm 0.4$  at 1000 K.

$\Delta(k_2/k) = {}^{+0.3}_{-0.2}$  at 300 K, rising to  ${}^{+0.6}_{-0.2}$  at 200 K and 1000 K.

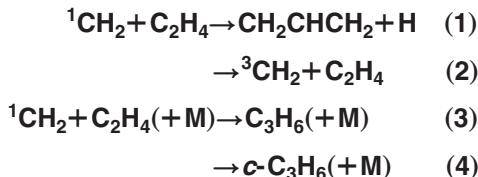
### Comments on Preferred Values

There is good agreement between the three direct determinations at room temperature.<sup>1,2,4</sup> The less direct studies of Canosa-Mas *et al.*,<sup>6,7</sup> based on product analysis, give a value of  $2.1 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 295 K, also in good agreement with the direct measurements. The preferred expression for  $k$  is based on the three direct studies and the temperature dependence obtained by Blitz *et al.*<sup>4</sup> Product analysis and modeling<sup>4,6,7</sup> show that the reaction involves initial formation of energized cyclopropene which can rapidly isomerize to form energized allene and methyl acetylene. The work of Adamson *et al.*,<sup>3</sup> who directly measured  $k_3$  and found a value close to that of the overall rate coefficient, suggests that, at the pressures investigated ( $\sim 20$  mbar), stabilization of  $\text{C}_3\text{H}_4^*$  and its isomerization products is unimportant and the sole reactive channel is formation of H

+  $\text{C}_3\text{H}_3$ . The *ab initio* and RRKM calculations of Guadagnini *et al.*<sup>8</sup> for Channel (1) also give values of  $k_1$  close to the experimental values of  $k$  and suggest a small negative temperature coefficient for  $k_1$ . Blitz *et al.*<sup>4</sup> have modeled the reaction to study the extent of stabilization of the adduct as a function of temperature and pressure. They conclude that at a temperature of  $\sim 1500$  K stabilization becomes significant at pressures in excess of 10 atm and, under the conditions pertaining in engines, the yields of stabilized products (allene, propyne) will need to be considered. For the branching ratio the room temperature value for  $k_2/k$  of Hack *et al.*<sup>1</sup> has been adopted; there are no data on its temperature dependence.

### References

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- <sup>2</sup> F. Hayes, G. J. Gutsche, W. D. Lawrence, W. S. Staker, and K. D. King, Combust. Flame **100**, 653 (1995).
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- <sup>5</sup> CEC, 1992; Supplement I, 1994 (see references in Introduction).
- <sup>6</sup> C. E. Canosa-Mas, H. M. Frey, and R. Walsh, J. Chem. Soc. Faraday Trans. 2 **81**, 283 (1983).
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### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = -92.1 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = -30.13 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 8.11 \cdot 10^{-7} T^{1.357} \exp(+11930/T) \quad (300 \leq T/\text{K} \leq 4000)$$

$$\Delta H^\circ_{298}(3) = -460.8 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = -141.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 3.19 \cdot 10^{-32} T^{0.643} \exp(+55910/T) \text{ cm}^3 \text{ molecule}^{-1} \quad (300 \leq T/\text{K} \leq 4000)$$

$$\Delta H^\circ_{298}(2) = -37.91 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = 6.18 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 2.02 T^{0.004} \exp(+4570/T) \quad (300 \leq T/\text{K} \leq 4000)$$

$$\Delta H^\circ_{298}(4) = -427.3 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(4) = -166.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(4) = 6.27 \cdot 10^{-27} T^{1.563} \exp(+52340/T) \text{ cm}^3 \text{ molecule}^{-1} \quad (300 \leq T/\text{K} \leq 4000)$$

See Section 3 for the source of the Thermodynamic Data.

### Rate Coefficient Data ( $k = k_1 + k_2 + k_3 + k_4$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$1.5 \cdot 10^{-10}$	295	Langford, Petek, and Moore, 1983 <sup>1</sup>	(a)
$2.1 \cdot 10^{-10}$	295	Canosa-Mas, Frey, and Walsh, 1985 <sup>2</sup>	(b)
$2.3 \cdot 10^{-10}$	298	Hack <i>et al.</i> , 1989 <sup>3</sup>	(c)
$1.0 \cdot 10^{-10} \exp(250/T)$	210–475	Wagener, 1990 <sup>4</sup>	(d)
$8.8 \cdot 10^{-11} \exp(310/T)$	298–462	Hayes <i>et al.</i> , 1996 <sup>5</sup>	(e)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Branching Ratios</i>			
$k_2/k=0.13$	295	Böhland, Temps, and Wagner, 1985 <sup>6</sup>	(f)
$k_2/k=0.2$	295	Hack <i>et al.</i> , 1989 <sup>3</sup>	(c)
<i>Reviews and Evaluations</i>			
$1.5 \cdot 10^{-10}$	300–2500	Tsang and Hampson, 1986 <sup>7</sup>	(g)
$2.0 \cdot 10^{-11}$	300–1000	CEC, 1994 <sup>8</sup>	(h)
$k_2/k=0.2$			

### Comments

- (a) Pulsed excimer laser photolysis of ketene at 308 nm with time resolved detection of  ${}^1\text{CH}_2$  by cw dye laser absorption at 610 nm.
- (b) Pulsed excimer laser photolysis of ketene at 308 nm with stable product detection by GC. The total pressure was 530 mbar. The product distribution was simulated by numerical integration. It was assumed that the rate coefficients for reaction of  ${}^1\text{CH}_2$  with  $\text{C}_2\text{H}_4$  and  $\text{CH}_2\text{CO}$  are the same; this assumption has been justified by subsequent measurements (e.g., Ref. 5).
- (c) Pulsed excimer laser photolysis of ketene at 308 nm.  $[{}^1\text{CH}_2]$  was monitored by LIF and  $[{}^3\text{CH}_2]$  by LMR.
- (d) Pulsed laser photolysis of ketene/ $\text{C}_2\text{H}_4$ /He mixtures at 308 nm.  $[{}^1\text{CH}_2]$  was monitored by time-resolved LIF near 589 nm. The author suggests that, on the basis of these results and those of others, Channel (2) will increase in importance as temperature increases and will predominate at temperature of  $\sim 1000$  K and above.
- (e) Excimer laser flash photolysis of ketene/ $\text{C}_2\text{H}_4$  mixtures at 308 nm.  $[{}^1\text{CH}_2]$  was monitored by time resolved laser absorption at 590.7 nm.
- (f) Excimer laser flash photolysis of ketene/ $\text{C}_2\text{H}_4$  mixtures at 308 nm.  $[{}^3\text{CH}_2]$  was monitored by LMR. A zero quantum yield of  ${}^3\text{CH}_2$  at 308 nm was assumed. Thus the value for  $k_2/k$  represents an upper limit.
- (g) Accepts the value of Langford *et al.*<sup>1</sup>
- (h) Value of  $k$  based on the data of Langford *et al.*<sup>1</sup> and Hack *et al.*<sup>3</sup> the value of  $k_2/k$  is that of Hack *et al.*<sup>3</sup>

### Preferred Values

$k = 9.4 \cdot 10^{-11} \exp(280/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 210–1000 K.

$k_2/k=0.2$  over the range 210–1000 K.

### Reliability

$\Delta \log k = \pm 0.1$  at 210 K, rising to  $\pm 0.3$  at 1000 K.

$\Delta(k_2/k) = \pm 0.2$  at 300 K, rising to  $^{+0.5}_{-0.2}$  at 210 K and 1000 K.

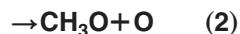
### Comments on Preferred Values

The measurements at room temperature show good consistency and Refs. 4 and 5 demonstrate that  $k$  has only a weak negative  $T$  dependence. The preferred expression for  $k$  is based on these two studies.<sup>4,5</sup>

The observed negative temperature dependence is in agreement with the *ab initio* calculations of Reuter *et al.*<sup>9</sup> which show that the reaction occurs on an attractive potential energy surface, with no maximum. The initial approach is asymmetric, but leads to formation of cyclopropane, which is sufficiently energized to isomerize to give propene. Under the conditions of the experiments of Canosa-Mas *et al.*,<sup>2</sup> (295 K, 526 mbar) cyclopropane is not a significant product, suggesting that it can be ignored under higher temperature combustion conditions. There is no direct evidence for the occurrence of Channel (1) although it could be expected to become important at higher temperatures and low pressures. Hack *et al.*<sup>3</sup> used a similar technique to Böhland *et al.*<sup>6</sup> to determine  $k_2/k$  but with an improved method of data analysis; the value of Hack *et al.*<sup>3</sup> has been adopted. Wagener<sup>4</sup> has argued that  $k_2/k$  increases with temperature, based on an analysis of the deactivation mechanism.

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#### Thermodynamic Data

$$\begin{aligned}\Delta H_{298}^0(1) &= -215.6 \text{ kJ mol}^{-1} \\ \Delta S_{298}^0(1) &= 3.39 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 4.4 T^{-0.167} \exp(+25920/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

$$\begin{aligned}\Delta H_{298}^0(2) &= 120.0 \text{ kJ mol}^{-1} \\ \Delta S_{298}^0(2) &= -8.66 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 2.52 \cdot 10^{-3} T^{0.703} \exp(-14170/T) \\ (200 \leq T/\text{K} \leq 6000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$k_1 = 3.1 \cdot 10^{-12} \exp(-10224/T)$	1000–2500	Yu, Wang, and Frenklach, 1995 <sup>1</sup>	(a)
$k_2 = 4.9 \cdot 10^{-11} \exp(-15340/T)$			
$k_2 = 3.9 \cdot 10^{-11} \exp(-16858/T)$	1600–2100	Michael, Kumaran, and Su, 1999 <sup>2</sup>	(b)
$k_2 = 2.66 \cdot 10^{-11} \exp(-15813/T)$	1575–1822	Hwang <i>et al.</i> , 1999 <sup>3</sup>	(c)
<i>Reviews and Evaluations</i>			
$k_2 = 3.3 \cdot 10^{-6} T^{-1.57} \exp(-14710/T)$	300–2500	Tsang and Hampson, 1986 <sup>4</sup>	(d)
$k_1 = 5.5 \cdot 10^{-13} \exp(-4500/T)$	1000–2500	CEC, 1992; 1994 <sup>5</sup>	(e)
$k_2 = 2.2 \cdot 10^{-10} \exp(-15800/T)$	300–2500		

#### Comments

- (a) Shock tube study on fuel-lean  $\text{CH}_4/\text{O}_2/\text{He}$  mixtures at pressures in the range 1.45–2.42 bar and temperatures in the range 1550–2200 K. [OH] and [CO] were monitored by time-resolved absorption behind reflected shock waves at 310.123 nm for OH and at the  $2 \rightarrow 1$  P(10) transition in CO. The expression for  $k_1$  was obtained by theoretical calculations using the barrier height of the exit channel to form  $\text{HCHO} + \text{OH}$  as an adjustable parameter while numerically fitting an average of the experimental values for  $k_1$  of Baldwin and Golden<sup>22</sup> and of Grela *et al.*<sup>23</sup> The expression for  $k_2$  was obtained by using this expression for  $k_1$  and modeling the CO and OH experimental profiles using the GRI-Mech 1.2 mechanism.
- (b) Shock tube study on  $\text{CH}_3\text{I}/\text{O}_2/\text{He}$  mixtures at pressures in the range 0.3–0.6 bar. [O] profiles were measured behind reflected shock waves by time resolved ARAS. Values of  $k$  were derived by computer fitting using a detailed mechanism but the initial  $\text{CH}_3$  concentration was sufficiently small for a good degree of isolation of the reaction to be achieved.
- (c) Shock tube study on fuel-lean  $\text{CH}_4/\text{O}_2/\text{Ar}$  mixtures at pressures in the range 2.1–4.8 bar.  $[\text{CH}_3]$  and [OH] profiles were obtained behind reflected shock waves by time resolved absorption at 214 nm and 310 nm, respectively. Values of  $k$  were derived by modeling using the GRI-MECH 2.11 mechanism.
- (d) Based on the data of Hsu *et al.*<sup>10</sup> and Bhaskaran *et al.*<sup>9</sup>
- (e) The expression for  $k_1$  is based on the data of Saito

*et al.*<sup>11</sup> and unpublished results of Fraak and Zellner and that for  $k_2$  on the data of Hsu *et al.*<sup>10</sup> and Saito *et al.*<sup>11</sup>

#### Preferred Values

$k_1 \leq 3.7 \cdot 10^{-12} \exp(-11140/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 1000–2500 K.

$k_2 = 3.5 \cdot 10^{-11} \exp(-16340/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 1000–2500 K.

See Note added in proof.

#### Reliability

$\Delta \log k_2 = \pm 0.7$  at 1000 K, falling to  $\pm 0.2$  at 2500 K.

#### Comments on Preferred Values

Only the data for Channels (1) and (2) are considered on this data sheet. The data for the addition channel, forming  $\text{CH}_3\text{O}_2$ , which is the predominant channel at low temperatures, are evaluated on the data sheet which follows the present one.

Both Channels (1) and (2) have been the subject of a number of experimental<sup>1–3,6–24</sup> and theoretical<sup>1,22,25–29</sup> studies. There is a degree of agreement amongst the experimental data for Channel (2) which, apart from the very high values of Hsu *et al.*<sup>10</sup> and Saito *et al.*<sup>11</sup> scatter over a factor of  $\sim 3$ , but those for Channel (1) differ by more than an order of magnitude. In the experimental studies it has proved difficult to find conditions which “isolate” the channels from each other, and from the secondary chemistry, which affects the results significantly in all of the systems studied. There are also important differences in the methods used to analyze the results.

For  $k_2$ , the experimental data from the three most recent shock tube studies,<sup>1–3</sup> cited in the Table, are in excellent agreement, but in analyzing the data different corrections were used in deriving the temperatures induced by the shock wave and there were important differences in the secondary chemistry used to model the systems. Consequently the expression derived by Yu *et al.*<sup>1</sup> gives values of  $k_2$  approximately a factor of 3 higher than those of Michael *et al.*<sup>2</sup> and of Hwang *et al.*<sup>3</sup> These differences have been discussed by the authors.<sup>30–32</sup> Michael *et al.*<sup>2</sup> used a very sensitive detection system for O atoms enabling them to work at low initial CH<sub>3</sub> concentrations and hence to minimize effects of secondary chemistry. The study of Hwang *et al.*,<sup>3</sup> in which CH<sub>3</sub> and OH concentrations were monitored, agrees to within ~30% with that of Michael *et al.*<sup>2</sup> Our preferred expression for  $k_2$  is based on these two studies.<sup>1,2</sup>

The data for Channel (1) tend to fall into two groups, one group<sup>11,15–20</sup> having values about an order of magnitude greater than the other.<sup>9,11,14,22–24,34</sup> The high values were obtained from systems in which the data analysis assumed that Channel (1) was dominant. This is now known not to be so and Yu *et al.*<sup>1</sup> reanalyzed much of the data from the high value studies to show that it could be reconciled with the low values of  $k_1$  from their expression, cited in the Table. Yu *et al.*<sup>1</sup> obtained their expression for  $k_1$  by fitting a theoretical model to the data of Baldwin and Golden<sup>22</sup> and Grela *et al.*<sup>23</sup> This expression overlaps with data in most of the low value studies but it has a value of  $E/R$  much higher than found in all but one of the other studies. Furthermore, Michael *et al.*,<sup>2</sup> in their study of the reaction, could find no significant contribution from Channel (1) over the range 1600–2100 K and Hwang *et al.*<sup>3</sup> also found that their results could be interpreted using a very low (but not zero) value for  $k_1$ . We conclude therefore that the status of the experimental data on  $k_1$  remains very uncertain. Zhu *et al.*<sup>33</sup> have carried out *ab initio* MO and variational transition theory calculations to derive expressions for the rate constants of the three reaction channels. The results suggest that at 1 bar, adduct formation is dominant below ~1200 K, giving way to Channel (1), which then predominates up to temperatures close to 2500 K, with Channel (2) being dominant above that, in conflict with the most recent experimental findings.<sup>2,3</sup> Further studies are clearly needed and as an interim measure we have derived an expression for  $k_1$  by combining the branching ratios calculated by Zhu *et al.*<sup>33</sup> with the preferred expression for  $k_2$  and recommend that this expression be taken as giving upper limits to  $k_1$ .

#### Note added in proof:

Since the data-sheet was prepared new data on the importance of Channel (1) has been provided through the shock tube measurements of Herbon *et al.* [Herbon *et al.*, Proc. Comb. Inst. **30**, 955 (2005)] and Srinivasan *et al.* [J. Chem. Phys. (in press)].

Herbon *et al.* used narrow wavelength laser absorption to measure relative OH concentrations in shocked CH<sub>3</sub>I/O<sub>2</sub>/He mixtures. From the rise time of the OH signal, they determined the overall rate coefficient  $k$ . They then used ARAS to

measure absolute oxygen atom concentrations and hence the yield of Channel (2). From these measurements the rate coefficient expressions for the two channels, over the temperature range 1590–2430 K derived were:

$$k_1 = 1.14 \cdot 10^{-22} T^{2.86} \exp(-4916/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

$$k_1 = 1.01 \cdot 10^{-16} T^{1.54} \exp(-14005/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

Srinivasan *et al.* also used absorption spectroscopy with a resonance lamp and multipass configuration. CH<sub>3</sub>I was used as the radical source and they reanalysed their results on Channel (2) from their oxygen atom experiments which used ARAS.<sup>2</sup> A numerical iterative fitting procedure was used to determine rate constants for both channels, guided by sensitivity analysis. In contrast to their investigation,<sup>2</sup> they found that Channel (1) has the larger rate coefficient over the whole temperature range of their experiments. They found:

$$k_1 = 8.36 \cdot 10^{-13} \exp(-6395/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad \text{over the range } 1303\text{--}2272 \text{ K.}$$

$$k_1 = 4.47 \cdot 10^{-16} T^{1.54} \exp(-12572/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad \text{over the range } 1665\text{--}2109 \text{ K.}$$

The results for  $k_1$  from the two studies are in excellent agreement at high temperatures and differ by a factor of  $\sqrt{2}$  at 1600 K. The direct nature of the measurements and the good agreement allows evaluated rate expression for  $k_1$ , superseding our previous recommendations to be proposed as:

$$k_1 = 1.1 \cdot 10^{-12} \exp(-7094/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad \text{over the range } 1000\text{--}2500 \text{ K.}$$

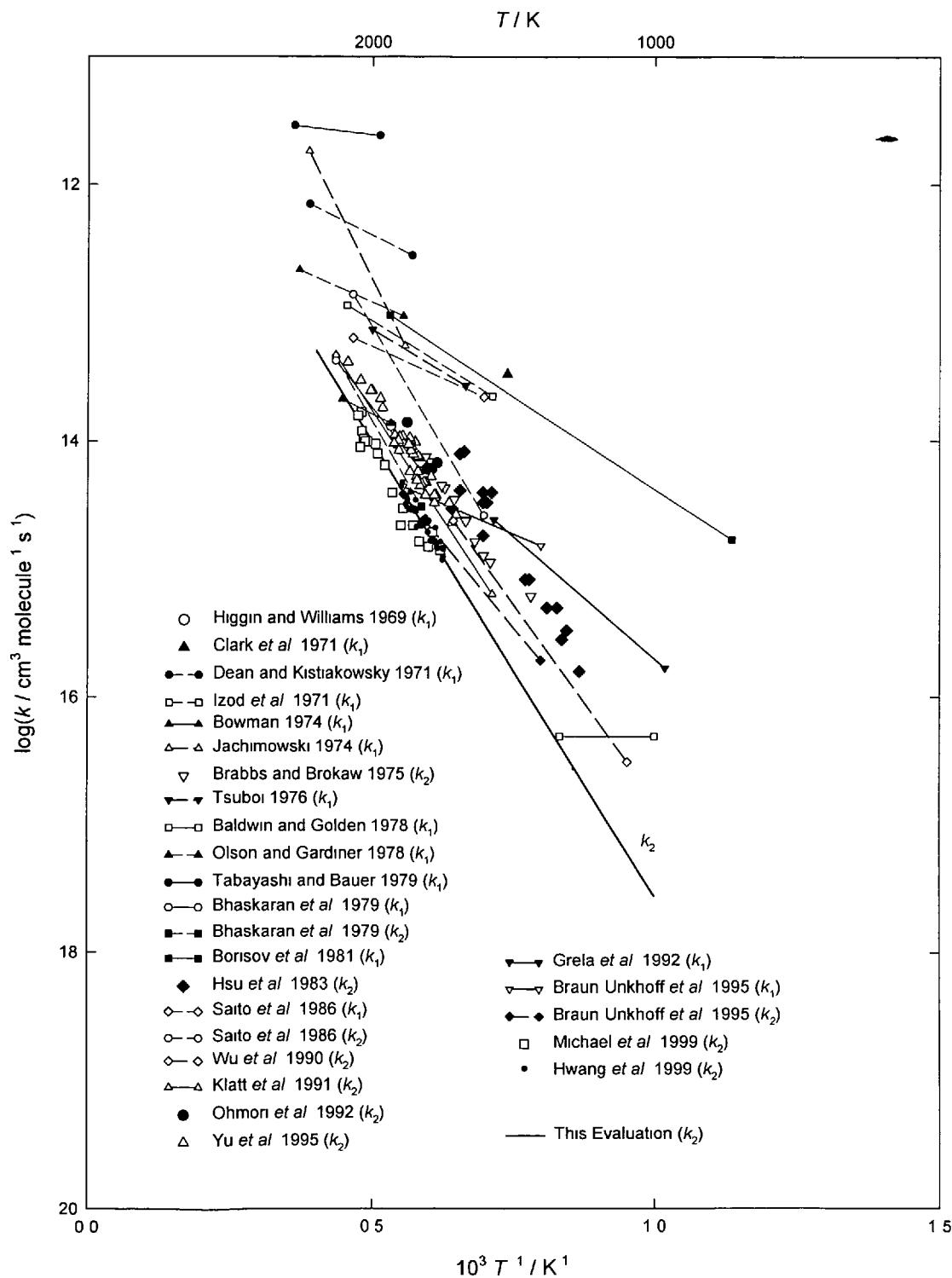
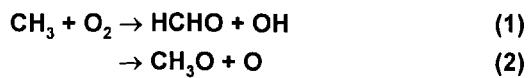
with  $\Delta \log k = \pm 0.7$  at 1000 K, falling to  $\pm 1.0$  at 2500 K.

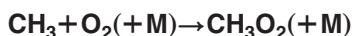
Both sets of measurements of  $k_2$  are in good agreement with our previously recommended expression, with a maximum difference of 40%. Our recommended expression for  $k_2$  is therefore unchanged but the uncertainty at lower temperatures can be reduced. We suggest  $\Delta \log k = \pm 0.3$  at 1000 K, falling to  $\pm 0.15$  at 2500 K.

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*Thermodynamic Data*

$$\Delta H_{298}^{\circ} = -126.3 \text{ kJ mol}^{-1}$$

$$\Delta S_{298}^{\circ} = -129.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c = 1.13 \cdot 10^{-30} T^{1.314} \exp(+15600T) \text{ cm}^3 \text{ molecule}^{-1}$$

(300 ≤ T/K ≤ 5000)

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	[M]/molecule cm <sup>-3</sup>	Reference	Comments
<i>Rate Coefficient Measurements</i>				
<i>Low Pressure Range</i>				
$3.4 \cdot 10^{-31} [\text{He}]$	295	$(0.2-2.2) \cdot 10^{17}$ (He)	Plumb and Ryan, 1982 <sup>1</sup>	(a)
$4.8 \cdot 10^{-31} [\text{Ar}]$	298	$(1.7-19) \cdot 10^{16}$ (Ar)	Selzer and Bayes, 1983 <sup>2</sup>	(b)
$8.0 \cdot 10^{-32} \exp(560/T) [\text{Ar}]$	230–568	$(6-30) \cdot 10^{16}$ (Ar)	Pratt and Wood, 1984 <sup>3</sup>	(c)
$4.8 \cdot 10^{-31} [\text{Ar}]$	298	$(1.0-15) \cdot 10^{18}$ (Ar)	Pilling and Smith, 1985 <sup>4</sup>	(d)
$7.0 \cdot 10^{-31} [\text{Ar}]$	298	$(5.4-2500) \cdot 10^{18}$ (Ar)	Cobos <i>et al.</i> , 1985 <sup>5</sup>	(e)
$8.0 \cdot 10^{-31} [\text{N}_2]$		$(5.4-3600) \cdot 10^{18}$ (N <sub>2</sub> )		
$1.5 \cdot 10^{-22} T^{-3.3} [\text{Ar}]$	334–582	$(0.5-15) \cdot 10^{18}$ (Ar)	Keiffer, Pilling, and Smith, 1987 <sup>6</sup>	(f)
$7.86 \cdot 10^{-22} T^{-3.64} [\text{N}_2]$	264–370	$(1-3600) \cdot 10^{17}$ (N <sub>2</sub> )	Kaiser, 1993 <sup>7</sup>	(g)
<i>High Pressure Range</i>				
$1.1 \cdot 10^{-12}$	298	$(1.0-15) \cdot 10^{18}$ (Ar)	Pilling and Smith, 1985 <sup>4</sup>	(d)
$2.2 \cdot 10^{-12}$	298	$(6.0-3600) \cdot 10^{18}$ (Ar)	Cobos <i>et al.</i> , 1985 <sup>5</sup>	(e)
$1.3 \cdot 10^{-15} T^{1.2}$	334–582	$(0.5-15) \cdot 10^{18}$ (Ar)	Keiffer, Pilling, and Smith, 1987 <sup>6</sup>	(f)
$1.4 \cdot 10^{-15} T^{1.2}$	264–370	$(1-3600) \cdot 10^{17}$ (N <sub>2</sub> )	Kaiser, 1993 <sup>7</sup>	(g)
<i>Reviews and Evaluations</i>				
$k_0[\text{Ar}] = 1.5 \cdot 10^{-22} T^{-3.3} [\text{Ar}]$	300–800		CEC, 1992; 1994 <sup>8</sup>	(h)
$k_0[\text{N}_2] = 1.6 \cdot 10^{-22} T^{-3.3} [\text{N}_2]$	300–800			
$k_\infty = 1.3 \cdot 10^{-15} T^{1.2}$				
$F_c = 0.466-1.30 \cdot 10^{-4} T$				
$k_0[\text{Air}] = 1.2 \cdot 10^{-23} T^{-3.0} [\text{Air}]$	200–300		NASA, 1997 <sup>9</sup>	(i)
$k_\infty = 2.9 \cdot 10^{-8} T^{-1.7}$				
$F_c = 0.6$				
$k_0[\text{N}_2] = 1.49 \cdot 10^{-22} T^{-3.3} [\text{N}_2]$	200–300		IUPAC, 1999 <sup>10</sup>	(j)
$k_\infty = 3.4 \cdot 10^{-15} T^{1.1}$				
$F_c(\text{N}_2) = 0.27$				

**Comments**

- (a) Discharge flow study in which CH<sub>3</sub> was generated by the reaction F+CH<sub>4</sub>. The decay of [CH<sub>3</sub>] an excess of O<sub>2</sub> was monitored by time resolved mass spectrometry.  $k_0$  was obtained by extrapolation using the values  $k_\infty = 2 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $F_c = 0.51$ .
- (b) Pulsed laser photolysis at 193 nm of CH<sub>3</sub>NO<sub>2</sub>/O<sub>2</sub>/bath gas (He, Ar, N<sub>2</sub>) mixtures. [CH<sub>3</sub>] monitored by time resolved photoionization mass spectrometry. Relative collisional efficiencies Ar:N<sub>2</sub>:O<sub>2</sub>:He were determined as 1.0:1.1:1.1:1.9.
- (c) Discharge flow study in which CH<sub>3</sub> radicals were generated by the H+C<sub>2</sub>H<sub>4</sub> reaction. Product yields were analyzed by gas chromatography.  $k_0$  was obtained by extrapolation using the same parameters as Plumb and Ryan [see Comment (a)].
- (d) Pulsed laser photolysis at 193 nm of CH<sub>3</sub>N<sub>2</sub>/O<sub>2</sub>/Ar mixtures with [CH<sub>3</sub>] monitored by absorption spectroscopy. Earlier flash photolysis studies on the same

system were demonstrated to be in error because of neglect of the effects of the CH<sub>3</sub>+CH<sub>3</sub>O<sub>2</sub> reaction. The technique used was devised to eliminate contributions from this reaction.

(e) Pulsed laser photolysis at 193 nm of CH<sub>3</sub>N<sub>2</sub>/O<sub>2</sub>/bath gas (N<sub>2</sub>, Ar) mixtures in a high pressure cell. [CH<sub>3</sub>] was monitored by time-resolved absorption spectroscopy.

(f) Technique as in Comment (d) but acetone used as the photolytic source of CH<sub>3</sub> radicals.

(g) Relative rate study in which the rate constants for the reactions CH<sub>3</sub>+O<sub>2</sub>+M and CH<sub>3</sub>+NO+M were determined relative to that of the CH<sub>3</sub>+Cl<sub>2</sub> reaction. CH<sub>4</sub>/Cl<sub>2</sub>/O<sub>2</sub>/bath gas (N<sub>2</sub>, SF<sub>6</sub>, He) mixtures were irradiated with a broad band light source and after irradiation the products were analyzed for CH<sub>4</sub> loss and CH<sub>3</sub>Cl formation by gas chromatography. Values of  $k/k(\text{CH}_3+\text{Cl}_2)$  were obtained by fitting the yields to a detailed mechanism. Using  $k(\text{CH}_3+\text{Cl}_2) = 3.95 \cdot 10^{-12} \exp(-64/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  values of  $k$

were obtained for N<sub>2</sub> diluent over the range 4–14000 mbar at 297 K, 26–2000 mbar at 370 K, and 53–1450 mbar at 370 K. More limited pressure ranges were studied for He, Ar, and SF<sub>6</sub>.

- (h) Based on the data of Selzer and Bayes,<sup>2</sup> Pilling and Smith,<sup>4</sup> and Keiffer *et al.*<sup>6</sup>
- (i) The low pressure limit is taken from Selzer and Bayes<sup>2</sup> and the high pressure limit is based on the study of Cobos *et al.*<sup>5</sup> with the temperature dependence estimated. The  $F_c$  of 0.6 is estimated.
- (j) Based on the data of Cobos *et al.*,<sup>5</sup> Keiffer *et al.*,<sup>6</sup> and Kaiser<sup>7</sup> together with calculated values of  $F_c$ .<sup>11</sup>

### Preferred Values

$k_0 = 1.5 \cdot 10^{-22} T^{-3.3} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  for M=Ar over the range 300–800 K.

$k_0 = 1.6 \cdot 10^{-22} T^{-3.3} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  for M=N<sub>2</sub> over the range 300–800 K.

$k_\infty = 1.3 \cdot 10^{-15} T^{1.2} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 300–800 K.

$F_c = 0.466 - 1.30 \cdot 10^{-4} T$  for M=Ar, N<sub>2</sub> over the range 300–800 K.

### Reliability

$\Delta \log k = \pm 0.3$  for M=Ar, N<sub>2</sub> over the temperature range 300–800 K and the pressure range 0.5–2000 mbar.

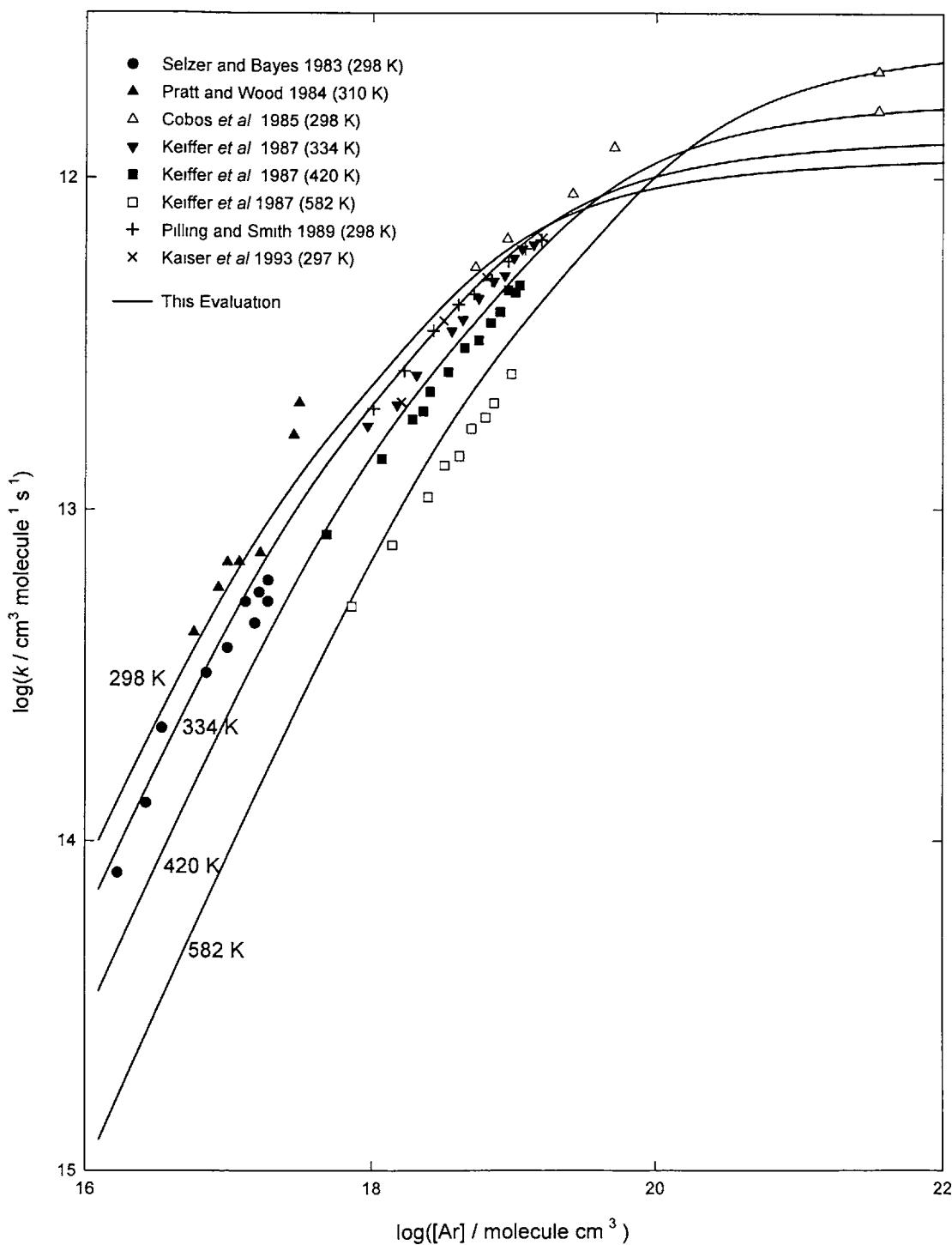
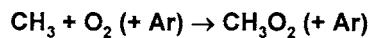
### Comments on Preferred Values

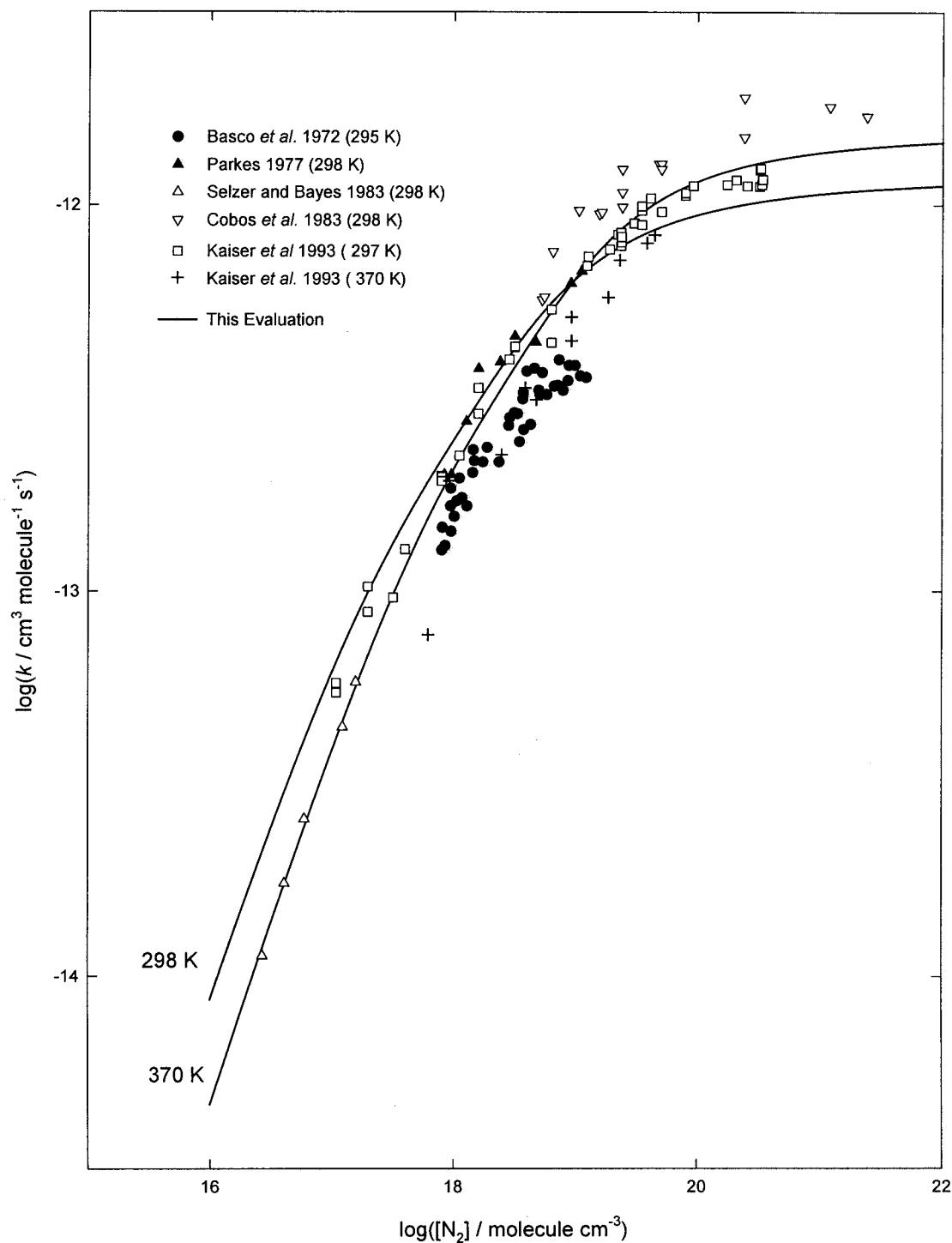
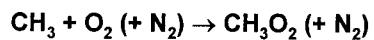
All of the studies of this reaction since 1980 are cited in the Table. There are also a number of earlier studies<sup>12–27</sup> which are not used in the evaluation. Since our previous evaluations<sup>8</sup> there has been one study, that of Kaiser,<sup>7</sup> which has given expressions for  $k_0$ ,  $k_\infty$ , and  $F_c$  in good agreement with our previously recommended expressions which are unchanged. They are based on the data of Selzer and Bayes,<sup>2</sup> Pilling and Smith,<sup>4</sup> and Keiffer *et al.*<sup>6</sup> but the results of Pratt and Wood<sup>3</sup> and Kaiser<sup>7</sup> are in good agreement. The IUPAC

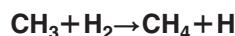
values for  $k_\infty$ , which gives slightly higher values of  $k$  than our recommendations, were also derived from the same data but used a calculated value of  $F_c=0.27$  based on the results of Cobos *et al.*<sup>5</sup> Our preferred parameters for  $k$  do not reproduce the high pressure data of Cobos *et al.*<sup>5</sup> to better than a factor of  $\sim 2$  suggesting that they may be less satisfactory at very high pressures.

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*Thermodynamic Data*

$$\begin{aligned}\Delta H_{298}^{\circ} &= -3.77 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= -23.9 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 1.97 \cdot 10^{-3} T^{0.368} \exp(+815/T) \\ &\quad (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$3.10^{-15}$	825	Gowenlock, Polanyi, and Warhurst, 1953 <sup>1</sup>	(a)
$7.0 \cdot 10^{-13} \exp(-2240/T)$	372–480	Gesser and Steacie, 1956 <sup>2</sup>	(b)
$6.8 \cdot 10^{-16}$	780	Benson and Jain, 1959 <sup>3</sup>	(c)
$1.07 \cdot 10^{-12} \exp(-5320/T)$	399–645	Shapiro and Weston, 1972 <sup>4</sup>	(d)
$7.6 \cdot 10^{-14}$	1340	Clark and Dove, 1973 <sup>5</sup>	(e)
$1.32 \cdot 10^{-18} T^2 \exp(-4810/T)$	372–1370	Kobrinsky and Pacey, 1974 <sup>6</sup>	(f)
$8.32 \cdot 10^{-13} \exp(-5290/T)$	584–671	Marshall and Shahkar, 1981 <sup>7</sup>	(g)
$3.3 \cdot 10^{-11} \exp(-7200/T)$	1066–2166	Möller, Mozzhukhin, and Wagner, 1986 <sup>8</sup>	(h)
$3.5 \cdot 10^{-11} \exp(-7780/T)$	1250–1950	Baeck <i>et al.</i> , 1995 <sup>9</sup>	(i)
$1.45 \cdot 10^{-11} \exp(-6810/T)$	646–1104	Knyazev <i>et al.</i> , 1996 <sup>10</sup>	(j)
$1.90 \cdot 10^{-10} \exp(-10814/T)$	1269–1806	Sutherland, Su, and Michael, 2001 <sup>11</sup>	(k)
<i>Reviews and Evaluations</i>			
$1 \cdot 14 \cdot 10^{-20} T^{2.74} \exp(-4740/T)$	300–2500	CEC, 1992; 1994 <sup>12</sup>	(l)

**Comments**

- (a) Pyrolysis of  $(\text{CH}_3)_2\text{Hg}$  in a flow system with  $\text{H}_2$  carrier gas. End product analyses of  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  by low-temperature distillation.  $k/k^{1/2}(\text{CH}_3 + \text{CH}_3) = 4.10^{-10} \text{ cm}^{3/2} \text{ molecule}^{-1/2} \text{ s}^{-1/2}$  determined at 825 K. The cited value of  $k$  is based on  $k(\text{CH}_3 + \text{CH}_3) = 6.0 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 825 K.
- (b) Steady-state photolysis of  $\text{CH}_2\text{CO}$  in the presence of  $\text{H}_2$ . End product analyses of  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  by low-temperature distillation.  $k/k^{1/2}(\text{CH}_3 + \text{CH}_3) = 9.12 \cdot 10^{-8} \exp(-2240/T) \text{ cm}^{3/2} \text{ molecule}^{-1/2} \text{ s}^{-1/2}$  determined over the temperature range 372–480 K. The cited value of  $k$  based on  $k(\text{CH}_3 + \text{CH}_3) = 6.0 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , independent of temperature.
- (c) Study of the effect of  $\text{H}_2$  on the rate of pyrolysis of  $(\text{CH}_3)_2\text{O}$  in a static reaction vessel determined by pressure measurements.
- (d) Steady-state photolysis of  $(\text{CH}_3)_2\text{CO}$  in the presence of  $\text{H}_2/\text{D}_2$  mixtures with analyses of  $\text{CH}_4/\text{CH}_3\text{D}$  by mass spectrometry.  $k/k(\text{CH}_3 + \text{D}_2) = 0.911 \exp(670/T)$  determined and above value of  $k$  based on  $k(\text{CH}_3 + \text{D}_2) = 1.18 \cdot 10^{-12} \exp(-5990/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .
- (e) Shock-tube study of the pyrolysis of  $(\text{CH}_3)_2\text{N}_2$  in the presence of  $\text{H}_2$ . Rate coefficient obtained from a fit of the experimental product-time profiles.
- (f) Pyrolysis of *neo*- $\text{C}_5\text{H}_{12}$  in the presence of  $\text{H}_2$  in a flow system over the temperature range 826–968 K. End

product analysis for  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$ . The cited rate equation for temperature range 372–1370 K includes earlier data.

- (g) Pyrolysis of  $(\text{CH}_3)_2\text{N}_2$  in the presence of  $\text{H}_2$  in a flow system. End product analysis for  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$ . Kinetic treatment of data yields  $k(\text{CH}_3 + \text{H}_2)$  directly without reference to  $k(\text{CH}_3 + \text{CH}_3)$ .
- (h) Shock tube study with time-resolved measurement of  $[\text{CH}_3]$  by absorption at 216.5 nm.  $\text{CH}_3$  produced from decomposition of  $(\text{CH}_3)_4\text{Sn}$ ,  $(\text{CH}_3)_2\text{N}_2$  or  $(\text{CH}_3)_2\text{Hg}$ .
- (i) Shock tube study with time-resolved measurement of  $[\text{CH}_3]$  by absorption at 213.9 nm.  $\text{CH}_3$  produced from decomposition of  $(\text{CH}_3)_2\text{N}_2$  and  $\text{CH}_3\text{I}$ .
- (j) Pulsed laser photolysis of  $(\text{CH}_3)_2\text{CO}$  at 193 nm in the presence of  $\text{H}_2/\text{He}$  mixtures.  $k$  obtained from pseudo-first order decay of  $[\text{CH}_3]$  determined by photoionization mass spectrometry.
- (k) Shock tube study on  $\text{H}_2$  containing small amounts of  $\text{CH}_3\text{I}$  which acts as the methyl radical source.  $[\text{H}]$  was monitored by time-resolved ARAS at 121.6 nm behind reflected shocks. Values of  $k$  were obtained by modeling a detailed mechanism to fit the  $[\text{H}]$  profiles.
- (l) Analysis of data of Refs. 1–8.

**Preferred Values**

$k = 1.8 \cdot 10^{-21} T^{2.88} \exp(-4060/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 370–2000 K.

**Reliability**

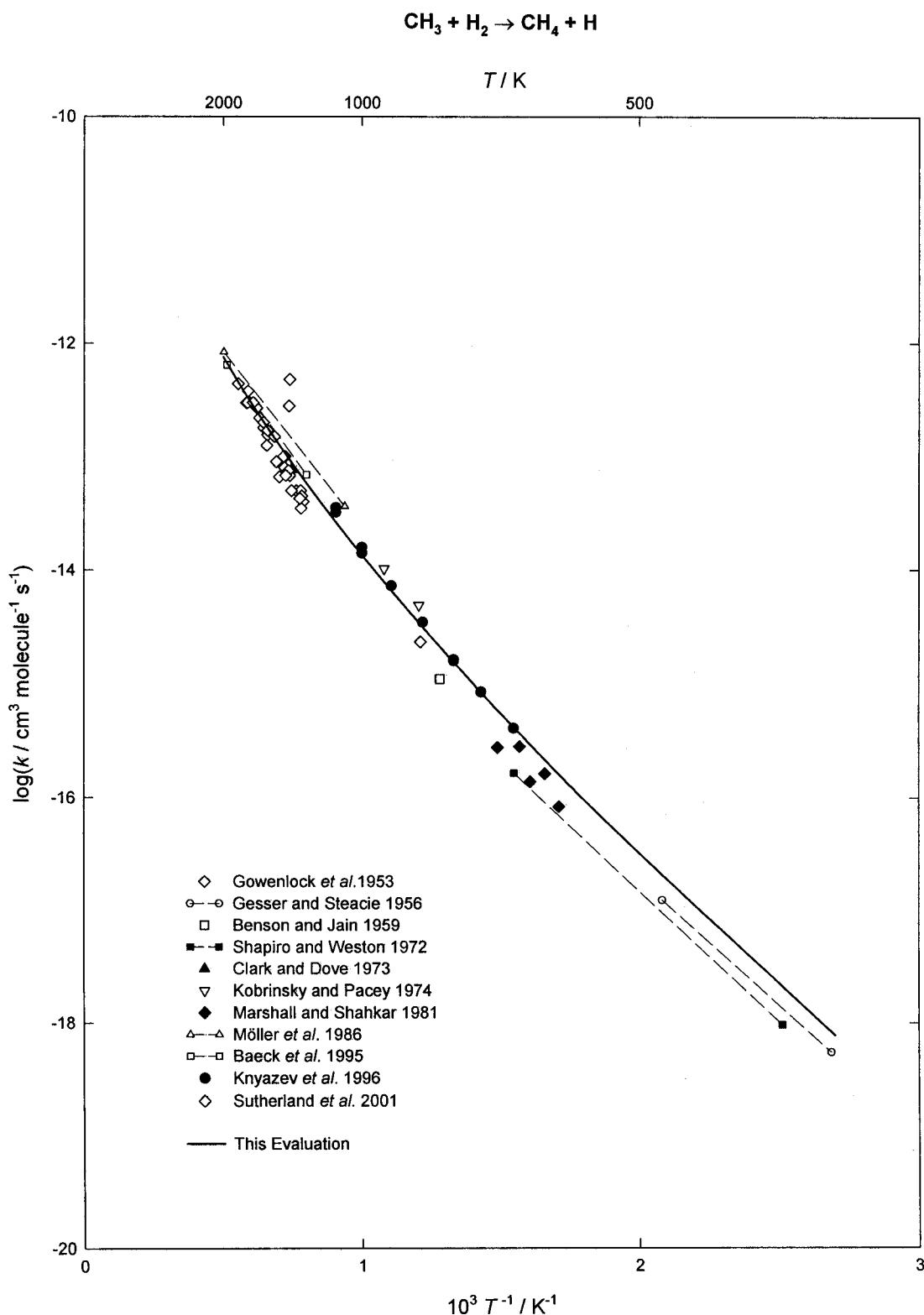
$\Delta \log k = \pm 0.15$  over the range 370–2000 K.

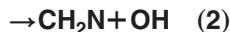
*Comments on Preferred Values*

As can be seen from the Arrhenius diagram the agreement between the various data sets is reasonably good. The derivation of the preferred expression for  $k$  was based largely on the studies of Sutherland *et al.*,<sup>11</sup> Baeck *et al.*,<sup>9</sup> Möller *et al.*,<sup>8</sup> and Knyazev *et al.*<sup>10</sup> and was influenced by the data on the reverse reaction. The expression so obtained, when combined with that on the reverse reaction, is in excellent agreement with the thermodynamic data over the recommended temperature range.

**References**

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#### Thermodynamic Data

$$\begin{aligned}\Delta H^{\circ}_{298}(1) &= -343.36 \text{ kJ mol}^{-1} \\ \Delta S^{\circ}_{298}(1) &= -14.03 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 2.0 \cdot 10^{-1} \exp(+41270/T) \\ (300 \leq T/\text{K} \leq 5000) &\end{aligned}$$

$$\begin{aligned}\Delta H^{\circ}_{298}(2) &= 40.6 \text{ kJ mol}^{-1} \\ \Delta S^{\circ}_{298}(2) &= 3.37 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 3.71 \cdot 10^{-1} T^{0.206} \exp(-4810/T) \\ (300 \leq T/\text{K} \leq 5000) &\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$k = 3.3 \cdot 10^{-14}$	1900	Wolff and Wagner, 1988 <sup>1</sup>	(a)
$k = 2 \cdot 10^{-10} \exp(-14500/T)$	1370–2500	Yang <i>et al.</i> , 1993 <sup>2</sup>	(b)
$k_1 = 1 \cdot 10^{-12} \exp(-7548/T)$	1100–1300	Lifshitz <i>et al.</i> , 1993 <sup>4</sup>	(c)
$k = 6.6 \cdot 10^{-12} \exp(-8500/T)$	1300–1870	Hennig and Wagner, 1994 <sup>6</sup>	(d)
$k_1 = 4.0 \cdot 10^{-12} \exp(-7900/T)$			
$k_2 = 8.6 \cdot 10^{-12} \exp(-12200/T)$			
$k_2 = 1.2 \cdot 10^{-12} \exp(-12140/T)$	1400–2000	Braun-Unkhoff <i>et al.</i> , 1995 <sup>7</sup>	(e)
$k_2 = 1.8 \cdot 10^{-12} \exp(-11240/T)$	1450–1850		(f)

#### Comments

- (a) Shock tube measurements behind incident shock waves. Methyl radicals generated from azomethane pyrolysis in mixtures containing ~150 ppm azomethane with up to 5.5% NO diluted in 270–410 mbar Ar.  $[\text{CH}_3]$  determined by molecular resonance absorption spectroscopy at 216.5 nm and  $[\text{NO}]$  by *in situ* measurement of nonresonant absorption at 214.5 nm.  $\text{CH}_3$  and NO absorption profiles were modeled with  $\sigma_{\text{CH}_3}(\lambda = 216 \text{ nm}) = 1.05 \cdot 10^{-17} \exp(-7.41 \cdot 10^{-4} T/\text{K}) \text{ cm}^2 \text{ molecule}^{-1}$  and  $\sigma_{\text{NO}}(\lambda = 216.5 \text{ nm}) = (1.07 \cdot 10^{-23} T/\text{K} - 1.1 \cdot 10^{-20}) \text{ cm}^2 \text{ molecule}^{-1}$ . Analysis of the recombination reaction  $\text{CH}_3 + \text{NO}(\text{+M}) \rightarrow \text{CH}_3\text{NO}(\text{+M})$  showed no influence under the experimental conditions on  $\text{CH}_3$  consumption.
- (b) Shock tube measurements behind incident shock waves. Methyl radicals generated from azomethane pyrolysis in mixtures containing ~500–2000 ppm azomethane with 2.2%–9.7% NO diluted in 0.13–1.16 bar Ar.  $[\text{CH}_3]$  determined by molecular resonance absorption spectroscopy at 213.9 nm. Absorption profiles were modeled with  $\sigma_{\text{CH}_3}(\lambda = 213.9 \text{ nm}) = 1.08 \cdot 10^{-18} \text{ cm}^{-2} \text{ molecule}^{-1}$  and  $\sigma_{\text{NO}}(\lambda = 213.9 \text{ nm}) = (5.68 \cdot 10^{-23} T/\text{K} - 2.32 \cdot 10^{-21}) \text{ cm}^2 \text{ molecule}^{-1}$ . Correction for the absorption of other products ( $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ , and CO) was made with cross sections taken from Gardiner *et al.*<sup>3</sup> Rate coefficient determined from a fit with a 55-reaction model.
- (c) Single-pulse shock tube measurements behind reflected shock waves at dwell times around 2 ms. Methyl radicals generated from ethane pyrolysis in mixtures containing 1%  $\text{C}_2\text{H}_6$  with 10% NO diluted in 2.7–3.2 bar Ar. Temperature determination by dissociation of 1,1,1-trifluoroethane in  $\text{C}_2\text{H}_6/\text{NO}/\text{Ar}$  mixtures. GC analysis
- (d) Shock tube measurements behind incident shock waves. Methyl radicals generated from azomethane pyrolysis in mixtures containing 16 ppm azomethane with 1% NO diluted in 540–780 mbar Ar.  $[\text{H}]$  determined by atomic resonance absorption spectroscopy and HCN by IR emission at 3.02  $\mu\text{m}$ . Correction for NO absorption applied with  $\sigma_{\text{NO}}(\lambda = 121.6 \text{ nm}) = (8.794 \cdot 10^{-19} + 1.150 \cdot 10^{-21} T/\text{K}) \text{ cm}^2 \text{ molecule}^{-1}$ . Values for  $k_1$ ,  $k_2$ , and  $(k_1 + k_2)$  extracted by fitting the  $[\text{H}]$  profiles with a 31-reaction mechanism. [HCN] profiles could not be used to derive rate coefficients because of calibration problems caused by vibrational relaxation of HCN. Re-evaluation of the OH measurements in the shock tube experiments of Hoffmann *et al.*<sup>5</sup> yielded values for  $k_2$  close to the results of the H-ARAS modeling, but an Arrhenius expression was not given.
- (e) Shock tube measurements behind reflected shock waves. Reaction followed by monitoring H atom formation by ARAS. Methyl radicals generated from methyl iodide pyrolysis in mixtures containing 2–5 ppm  $\text{CH}_3\text{I}$  with 0.2%–0.5% NO diluted in 1.05–5.00 bar Ar.  $k_2$  has been derived with an extrapolated value for  $k_1$  taken from Lifshitz *et al.*<sup>4</sup> OH-consuming reactions, i.e.,  $\text{CH}_3 + \text{OH}$ , are assumed to be not faster than  $1.2 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 1700 K and 2.4 bar Ar.
- (f) Shock tube measurements behind reflected shock waves. Reaction followed by monitoring OH formation by laser absorption spectroscopy. Methyl radicals generated from azomethane pyrolysis in mixtures containing 32–50 ppm azomethane with up to 3% NO diluted in 1.09–4.62 bar Ar. OH-absorption profiles were taken

at the  $Q_{1,5}$ -transition in the  $A^2\Sigma^+ - X^2\Pi(0,0)$  system and corrected for nonresonant absorption of NO with  $\sigma_{NO}(\lambda = 121.6 \text{ nm}) = (1.98 \cdot 10^{-18} + 4.76 \cdot 10^{-22}T/K) \text{ cm}^2 \text{ molecule}^{-1}$ .  $k_2$  has been derived with an extrapolated value for  $k_1$  taken from Lifshitz *et al.*<sup>4</sup> OH-consuming reactions, i.e.,  $\text{CH}_3 + \text{OH}$ , are assumed to be not faster than  $1.2 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 1700 K and 2.4 bar Ar. A significant difference has been found between values of  $k_2$  obtained from H and OH formation, from which it was concluded that Channel (2) could not be the only radical forming channel.

### Preferred Values

$k = 1 \cdot 10^{-12} \exp(-7550/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 1100–1300 K.

#### Reliability

$\Delta \log k = \pm 0.2$  over range 1100–1300 K.

#### Comments on Preferred Values

There are a number of studies<sup>8–17</sup> at low temperatures of the addition channel leading to  $\text{CH}_3\text{NO}$ . These are evaluated on the data sheet which follows the present one. Only the data for  $k_1$  and  $k_2$  are considered on the present sheet.

At  $T > 500$  K experiments have shown that HCN is the major product,<sup>4,6</sup> generated either directly in Channel (1) or following decomposition of  $\text{CH}_2\text{N}$  formed in Channel (2). All studies in this temperature region are indirect, the rate coefficients have been obtained by fitting the observed reactant (Wolff and Wagner,<sup>1</sup> Yang *et al.*<sup>2</sup>) or product (Hoffmann *et al.*<sup>5</sup> Lifshitz *et al.*,<sup>4</sup> Hennig and Wagner<sup>6</sup>) concentration profiles with kinetic models and thus depend on the values taken for the rate coefficients of other reactions, particularly the self reactions of methyl radicals. Hennig and Wagner<sup>6</sup> and Lifshitz *et al.*<sup>4</sup> employed values for  $k(\text{CH}_3 + \text{CH}_3)$  which are in line with those recommended in the present evaluation, whereas Wolff and Wagner<sup>1</sup> and Yang *et al.*<sup>2</sup> did not, and this difference leads to differences in the values of the rate coefficients reported by Wolff and Wagner<sup>1</sup> and Yang *et al.*<sup>2</sup> Over the temperature range of their study of Lifshitz *et al.*<sup>4</sup> state that the influence of Channel (2) is small (<10% of the total reaction). However, in view of the conflicting evidence on the branching ratios (see later) we give a preferred expression for  $k [= (k_1 + k_2)]$  based on the data of Lifshitz *et al.*<sup>4</sup> The temperature coefficient obtained by Hennig and Wagner<sup>6</sup> is in agreement, but the absolute values of  $k$  are systematically higher. The earlier determination of Baldwin and Golden<sup>18</sup> is a lower limit.

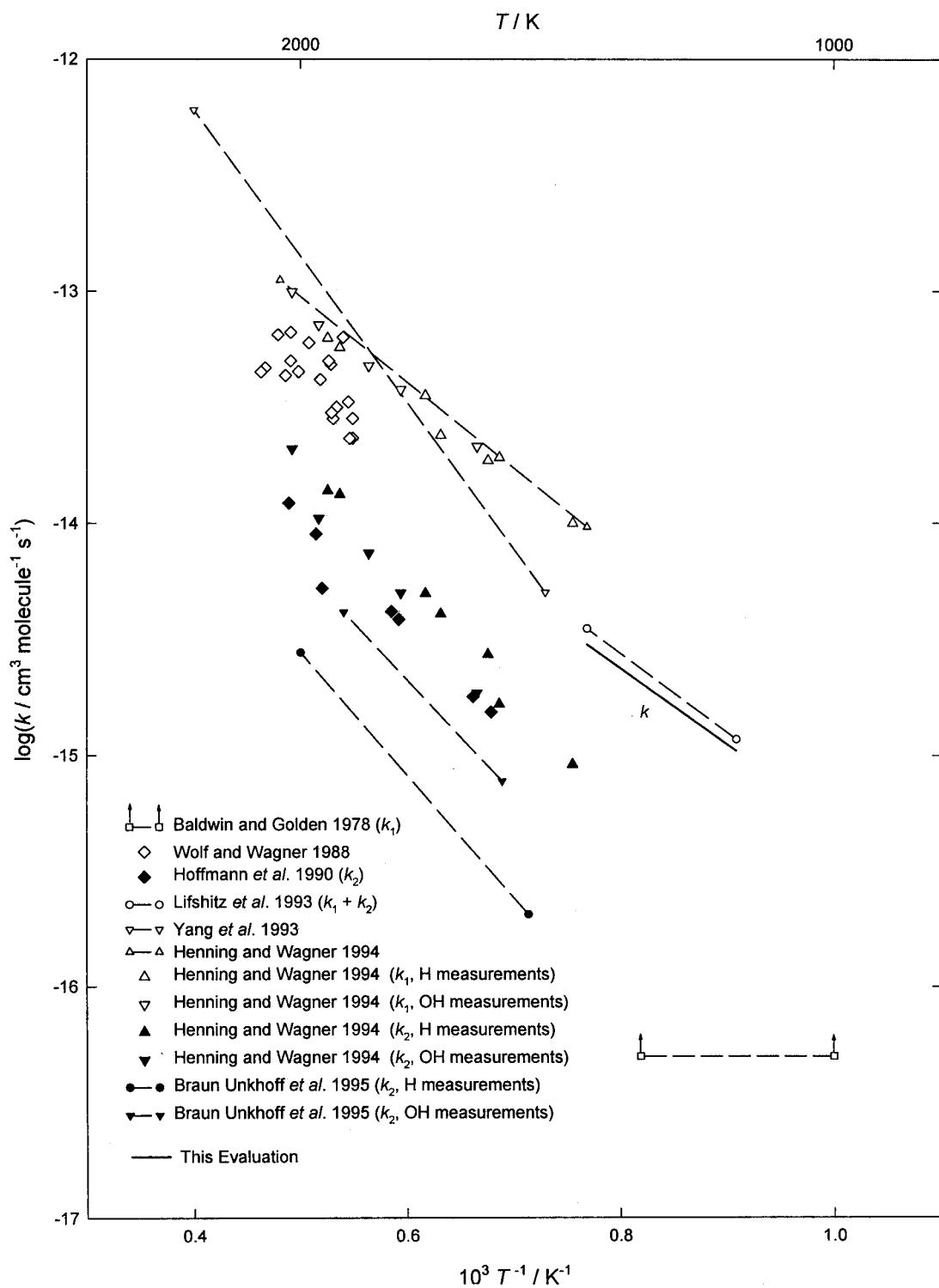
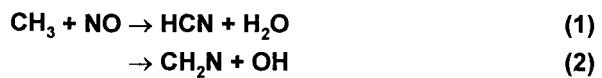
The branching ratio  $k_1/k_2$  at  $T > 1000$  K remains uncertain. Braun-Unkhoff *et al.*<sup>7</sup> determined  $k_2$  by monitoring H and OH production.  $k_2$  determined from H atom production was approximately a factor 4 greater than that from OH production, but showed similar temperature dependence. The authors concluded that the simple 2-channel model was inadequate at these temperatures. Hennig and Wagner<sup>6</sup> deter-

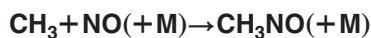
mined  $k_2$  from OH formation and reinterpreted the OH-formation data of Hoffmann *et al.*<sup>5</sup> The results do not show the discrepancy observed by Braun-Unkhoff *et al.*<sup>7</sup> The fraction leading to radical production,  $\alpha = k_2/(k_1 + k_2)$ , may also be estimated from the results of Lifshitz *et al.*<sup>4</sup> and Hennig and Wagner.<sup>6</sup>  $\alpha$  is found to increase from 0.08 to 0.2 over the range 1000–2000 K. On the basis of the current experimental data we cannot recommend values for the branching ratio.

Nguyen *et al.*<sup>19</sup> analyzed the reaction by QRRK techniques. At room temperature the results agree with the experimental data of Davis *et al.*<sup>10</sup> and Kaiser<sup>14</sup> and confirm the complex reaction mechanism with initial adduct formation, competing adduct stabilization and isomerization (H atom migration), and product formation by decomposition of isomerized intermediates. Miller *et al.*<sup>20</sup> modeled the reaction at higher temperatures with a BAC-MP4 surface. The overall rate coefficient calculated by Miller *et al.*<sup>20</sup> agrees well with that of Hennig and Wagner,<sup>6</sup> however, the calculations indicate that Channel (2) is dominant at 1200 K contrary to experimental results. The QRRK calculations of Dean and Bozzelli<sup>21</sup> also indicate that Channel (2) dominates at combustion temperatures. Clearly further work is required to establish the high temperature rate coefficient and branching ratio.

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*Thermodynamic Data*

$$\Delta H_{298}^{\circ}(3) = -166.8 \text{ kJ mol}^{-1}$$

$$\Delta S_{298}^{\circ}(3) = -147.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 3.69 \cdot 10^{-33} T^{1.834} \exp(+20660/T) \text{ cm}^3 \text{ molecule}^{-1}$$

(300 ≤  $T/\text{K}$  ≤ 5000)

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	[M]/molecule cm <sup>-3</sup>	Reference	Comments
<i>Rate Coefficient Measurements</i>				
<i>Intermediate Fall-off Range</i>				
3.04·10 <sup>-12</sup>	295	2.63·10 <sup>18</sup> (He)	Laufer and Bass, 1975 <sup>1</sup>	(a)
3.19·10 <sup>-12</sup>		3.20·10 <sup>18</sup>		
4.04·10 <sup>-12</sup>		5.25·10 <sup>18</sup>		
5.16·10 <sup>-12</sup>		1.09·10 <sup>19</sup>		
8.44·10 <sup>-12</sup>		2.13·10 <sup>19</sup>		
7.90·10 <sup>-12</sup>		2.77·10 <sup>19</sup>		
1.01·10 <sup>-11</sup>		3.75·10 <sup>19</sup>		
3.67·10 <sup>-12</sup>	295	1.65·10 <sup>18</sup> (N <sub>2</sub> )		
3.77·10 <sup>-12</sup>		2.00·10 <sup>18</sup>		
3.75·10 <sup>-12</sup>		2.48·10 <sup>18</sup>		
4.18·10 <sup>-12</sup>		3.26·10 <sup>18</sup>		
5.35·10 <sup>-12</sup>		5.01·10 <sup>18</sup>		
6.61·10 <sup>-12</sup>		1.00·10 <sup>19</sup>		
8.27·10 <sup>-12</sup>		1.84·10 <sup>19</sup>		
3.60·10 <sup>-12</sup>	295	1.66·10 <sup>18</sup> (Ar)		
3.60·10 <sup>-12</sup>		1.94·10 <sup>18</sup>		
4.01·10 <sup>-12</sup>		2.63·10 <sup>18</sup>		
4.86·10 <sup>-12</sup>		2.93·10 <sup>18</sup>		
5.71·10 <sup>-12</sup>		5.21·10 <sup>18</sup>		
1.05·10 <sup>-11</sup>		1.63·10 <sup>19</sup>		
9.8·10 <sup>-14</sup>	298	5.91·10 <sup>16</sup> (He)	Washida, 1980 <sup>2</sup>	(b)
1.4·10 <sup>-13</sup>		7.46·10 <sup>16</sup>		
1.82·10 <sup>-13</sup>		1.25·10 <sup>17</sup>		
2.24·10 <sup>-13</sup>		1.28·10 <sup>17</sup>		
5.04·10 <sup>-13</sup>		1.83·10 <sup>17</sup>		
3.78·10 <sup>-13</sup>		2.03·10 <sup>17</sup>		
1.72·10 <sup>-12</sup>	296	8.8·10 <sup>17</sup> (Ar)	Davies, Green, and Pilling, 1991 <sup>3</sup>	(c)
2.31·10 <sup>-12</sup>		1.76·10 <sup>18</sup>		
2.76·10 <sup>-12</sup>		2.51·10 <sup>18</sup>		
3.18·10 <sup>-12</sup>		3.26·10 <sup>18</sup>		
3.90·10 <sup>-12</sup>		4.89·10 <sup>18</sup>		
4.47·10 <sup>-12</sup>		6.91·10 <sup>18</sup>		
5.08·10 <sup>-12</sup>		8.22·10 <sup>18</sup>		
5.57·10 <sup>-12</sup>		9.88·10 <sup>18</sup>		
5.79·10 <sup>-12</sup>		1.15·10 <sup>19</sup>		
5.9·10 <sup>-12</sup>		1.31·10 <sup>19</sup>		
6.46·10 <sup>-12</sup>		1.48·10 <sup>19</sup>		
6.42·10 <sup>-12</sup>		1.63·10 <sup>19</sup>		
6.62·10 <sup>-12</sup>		1.8·10 <sup>19</sup>		
6.83·10 <sup>-12</sup>		1.97·10 <sup>19</sup>		
0.79·10 <sup>-12</sup>	407	8.39·10 <sup>17</sup> (Ar)		
0.99·10 <sup>-12</sup>		1.24·10 <sup>18</sup>		
1.30·10 <sup>-12</sup>		1.89·10 <sup>18</sup>		
1.46·10 <sup>-12</sup>		2.44·10 <sup>18</sup>		
1.86·10 <sup>-12</sup>		3.53·10 <sup>18</sup>		
2.00·10 <sup>-12</sup>		4.74·10 <sup>18</sup>		
2.28·10 <sup>-12</sup>		5.95·10 <sup>18</sup>		
2.48·10 <sup>-12</sup>		7.11·10 <sup>18</sup>		

$2.78 \cdot 10^{-12}$	8.32 · $10^{18}$		
$2.81 \cdot 10^{-12}$	$9.51 \cdot 10^{18}$		
$2.92 \cdot 10^{-12}$	$1.06 \cdot 10^{19}$		
$3.14 \cdot 10^{-12}$	$1.19 \cdot 10^{19}$		
$3.28 \cdot 10^{-12}$	$1.3 \cdot 10^{19}$		
$3.28 \cdot 10^{-12}$	$1.43 \cdot 10^{19}$		
$0.38 \cdot 10^{-12}$	$4.76 \cdot 10^{17}$ (Ar)		
$0.58 \cdot 10^{-12}$	$9.56 \cdot 10^{17}$		
$0.64 \cdot 10^{-12}$	$1.43 \cdot 10^{18}$		
$0.78 \cdot 10^{-12}$	$1.92 \cdot 10^{18}$		
$0.92 \cdot 10^{-12}$	$2.86 \cdot 10^{18}$		
$1.08 \cdot 10^{-12}$	$3.79 \cdot 10^{18}$		
$1.27 \cdot 10^{-12}$	$4.76 \cdot 10^{18}$		
$1.32 \cdot 10^{-12}$	$5.61 \cdot 10^{18}$		
$1.47 \cdot 10^{-12}$	$6.64 \cdot 10^{18}$		
$1.46 \cdot 10^{-12}$	$7.58 \cdot 10^{18}$		
$1.66 \cdot 10^{-12}$	$8.53 \cdot 10^{18}$		
$1.79 \cdot 10^{-12}$	$9.52 \cdot 10^{18}$		
$1.69 \cdot 10^{-12}$	$1.04 \cdot 10^{19}$		
$1.85 \cdot 10^{-12}$	$1.14 \cdot 10^{19}$		
$2.4 \cdot 10^{-12}$	$3.11 \cdot 10^{17}$ (He)	Vakhtin and Petrov, 1991 <sup>6</sup>	(d)
$1.75 \cdot 10^{-12}$	$9.72 \cdot 10^{17}$		
$2.45 \cdot 10^{-12}$	$2.91 \cdot 10^{18}$		
$1.85 \cdot 10^{-12}$	$4.4 \cdot 10^{18}$		
$3.89 \cdot 10^{-12}$	$5.18 \cdot 10^{18}$		
$3.26 \cdot 10^{-12}$	$6.48 \cdot 10^{18}$		
$3.18 \cdot 10^{-12}$	$8.1 \cdot 10^{18}$		
$3.53 \cdot 10^{-12}$	$9.72 \cdot 10^{18}$		
$4.91 \cdot 10^{-12}$	$1.13 \cdot 10^{19}$		
$4.28 \cdot 10^{-12}$	$1.36 \cdot 10^{19}$		
$4.66 \cdot 10^{-12}$	$1.55 \cdot 10^{19}$		
$4.76 \cdot 10^{-12}$	$1.94 \cdot 10^{19}$		
$7.9 \cdot 10^{-12}$	$2.17 \cdot 10^{19}$		
$8.15 \cdot 10^{-12}$	$2.3 \cdot 10^{19}$		
$5.17 \cdot 10^{-12}$	$2.33 \cdot 10^{19}$		
$1.54 \cdot 10^{-12}$	$8.37 \cdot 10^{17}$ (Ar)	Kaiser, 1993 <sup>7</sup>	(e)
$2.4 \cdot 10^{-12}$	$2.35 \cdot 10^{18}$		
$2.54 \cdot 10^{-12}$	$2.35 \cdot 10^{18}$		
$6.98 \cdot 10^{-12}$	$1.81 \cdot 10^{19}$		
$7.05 \cdot 10^{-12}$	$2.45 \cdot 10^{19}$		
$7.54 \cdot 10^{-12}$	$2.93 \cdot 10^{19}$		
$8.35 \cdot 10^{-12}$	$2.93 \cdot 10^{19}$		
$9.16 \cdot 10^{-12}$	$4.91 \cdot 10^{19}$		
$1.01 \cdot 10^{-11}$	$7.57 \cdot 10^{19}$		
$1.15 \cdot 10^{-11}$	$1.29 \cdot 10^{20}$		
$1.16 \cdot 10^{-11}$	$1.71 \cdot 10^{20}$		
$1.23 \cdot 10^{-11}$	$1.71 \cdot 10^{20}$		
$1.32 \cdot 10^{-11}$	$1.71 \cdot 10^{20}$		
$1.49 \cdot 10^{-11}$	$2.06 \cdot 10^{20}$		
$1.28 \cdot 10^{-11}$	$2.64 \cdot 10^{20}$		
$1.4 \cdot 10^{-11}$	$2.64 \cdot 10^{20}$		

*Reviews and Evaluations*

$k_\infty = 3.2 \cdot 10^{-11}$	295	Laufer and Bass, 1975 <sup>1</sup>	(a)
$k_0[\text{Ar}] = [\text{Ar}] 6.9 \cdot 10^{-32} \exp(1430/T)$	298–509	Davies <i>et al.</i> , 1991 <sup>3</sup>	(c)
$k_\infty = 1.5 \cdot 10^{-11} \exp(-60/T)$			
$k_0[\text{He}] = [\text{He}] 2.3 \cdot 10^{-30}$	298	Vakhtin and Petrov, 1991 <sup>6</sup>	(d)
$k_\infty = 1.7 \cdot 10^{-11}$			
$k_0[\text{Ar}] = [\text{Ar}] 3.5 \cdot 10^{-30}$	298	Kaiser, 1993 <sup>7</sup>	(e)
$k_\infty = 1.68 \cdot 10^{-11}$			
$F_c(\text{Ar}) = 0.46$			

### Comments

- (a) Methyl radicals generated by flash photolysis of azomethane in 67–933 mbar He, N<sub>2</sub> or Ar bath gas. Analysis of stable product species by gas chromatography. In deriving  $k$ , a rate coefficient for the reaction  $2\text{CH}_3(+\text{M}) \rightarrow \text{C}_2\text{H}_6(+\text{M})$  of  $9.5 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 295 K (this evaluation) has been used. Extrapolation to obtain  $k_\infty$  by RRKM calculations.
- (b) Discharge flow experiments, methyl radicals generated by reaction of O atoms with C<sub>2</sub>H<sub>4</sub> in fast-flow reactor. CH<sub>3</sub> monitored with photoionization mass spectrometer. Values measured relative to  $k(\text{O} + \text{CH}_3) = 1.4 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (this evaluation).
- (c) Methyl radicals generated from acetone by flash photolysis at 193 nm. CH<sub>3</sub> monitored by absorption spectroscopy at 216.36 nm. Value for  $k(\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6)/\sigma_{\text{CH}_3}$  taken from Slagle *et al.*<sup>4</sup> and  $\sigma_{\text{CH}_3\text{NO}}/\sigma_{\text{CH}_3} = 0.013, 0.021$ , and  $0.024$  at 296, 407, and 509 K, respectively. Fall-off parameters determined from global fitting procedures based on Troe factorization methods<sup>5</sup> and inverse Laplace transformation.
- (d) Methyl radicals generated by pulsed photolysis of CH<sub>3</sub>I at 308 nm. Formation of CH<sub>3</sub>NO monitored by laser absorption at 632.8 nm. Fall-off parameters determined by fit to Troe formulism.<sup>5</sup>
- (e) Relative rate technique, methyl radicals generated by reaction of Cl with CH<sub>4</sub>. Gas mixtures comprising CH<sub>4</sub>, Cl<sub>2</sub>, NO in Ar were irradiated in a static reactor. After irradiation the contents were analyzed by GC and the concentrations of CH<sub>4</sub> and CH<sub>3</sub>Cl determined. Values for  $k/k(\text{CH}_3 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{Cl})$  placed on absolute basis with  $k(\text{CH}_3 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{Cl}) = 3.95 \cdot 10^{12} \exp(-267/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ <sup>7</sup>, independent of pressure. Fall-off parameters determined by fitting to Troe expression.<sup>15</sup>

### Preferred Values

$k_0 = 2.9 \cdot 10^{-32} \exp(1430/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  for M = Ar over the range 250–550 K.

$k_\infty = 2.05 \cdot 10^{-11} \exp(-60/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 250–550 K.

$F_c = 0.46$  for M = Ar at 298 K.

### Reliability

$\Delta \log k_0 = \pm 0.3$  for M = Ar over the range 250–550 K.

$\Delta \log k_\infty = \pm 0.3$  over the range 250–550 K.

$\Delta F_c = \pm 0.2$  for M = Ar at 298 K.

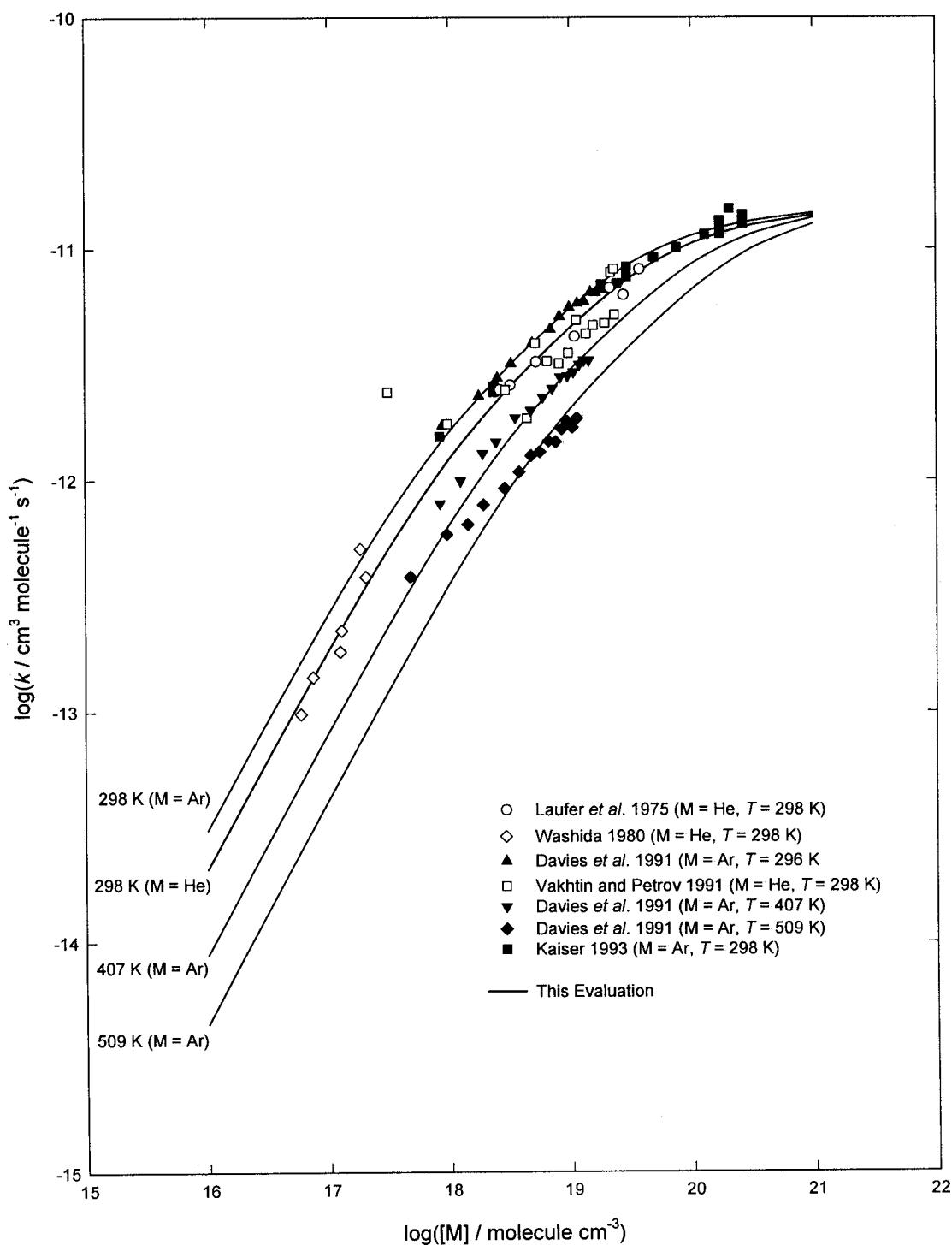
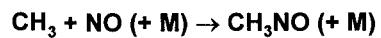
### Comments on Preferred Values

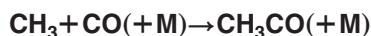
There have been many studies of the adduct formation reaction in the temperature range 295–509 K but for many studies the reported values are dependent on the value taken for methyl radical recombination and in some cases are heavily influenced by other secondary reactions. Davies *et al.*<sup>3</sup> and Kaiser<sup>7</sup> have studied the reaction under conditions where the influence of secondary chemistry and methyl radical combination are unimportant, i.e., [NO] ≫ [CH<sub>3</sub>]. Kaiser<sup>7</sup> has studied the reaction over the widest pressure range at 298 K. His results are in full agreement with those of Davies *et al.*<sup>3</sup> and we therefore base our preferred values for the limiting high and low pressure rate coefficients on the room temperature rate coefficients of Kaiser<sup>7</sup> combined with the temperature dependent rate expressions of Davies *et al.*<sup>3</sup> Values for the broadening factor,  $F_c$ , are available only at room temperature. The results of other studies conducted with Ar or N<sub>2</sub> bath gas (van den Bergh and Callear,<sup>8</sup> Laufer *et al.*,<sup>1</sup> and Pilling *et al.*<sup>9</sup>) are compatible with the preferred values. The results of Laufer *et al.*,<sup>1</sup> Washida,<sup>2</sup> and Vakhtin and Petrov<sup>6</sup> for M = He may be fitted by taking the preferred expression for  $k_0$  with  $k_0 [\text{He}] = k_0 [\text{Ar}] / 1.5$ . The results of Jodkowski *et al.*<sup>10</sup> for M = CH<sub>3</sub>COCH<sub>3</sub> show similar fall-off behavior with  $k_0 [\text{He}] = 3k_0 [\text{Ar}]$ . The preferred values and selected experimental data are shown in the Figure.

Nguyen *et al.*<sup>11</sup> analyzed the reaction by QRRK techniques. At room temperature the results agree with the preferred values and confirm the complex reaction mechanism with initial adduct formation, competing with adduct stabilization and isomerization (H atom migration), and with product formation by decomposition of isomerized intermediates.

### References

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- <sup>3</sup>J. W. Davies, N. J. B. Green, and M. J. Pilling, J. Chem. Soc. Faraday Trans. **87**, 2317 (1991).
- <sup>4</sup>I. R. Slagle, D. Gutman, J. W. Davies, and M. J. Pilling, J. Phys. Chem. **92**, 2455 (1988).
- <sup>5</sup>R. G. Gilbert, K. Luther, and J. Troe, Ber. Bunsenges. Phys. Chem. **87**, 169 (1983).
- <sup>6</sup>A. B. Vakhtin and A. K. Petrov, Chem. Phys. **149**, 427 (1991).
- <sup>7</sup>E. W. Kaiser, J. Phys. Chem. **97**, 11681 (1993).
- <sup>8</sup>H. E. van den Bergh and A. B. Callear, Trans. Faraday Soc. **67**, 2017 (1971).
- <sup>9</sup>M. J. Pilling, J. A. Robertson, and G. J. Rogers, Int. J. Chem. Kinet. **8**, 883 (1976).
- <sup>10</sup>J. T. Jodkowski, E. Ratajczak, A. Sillesen, and P. Pagsberg, Chem. Phys. Lett. **203**, 490 (1993).
- <sup>11</sup>M. T. Nguyen, D. Sengupta, and L. G. Vanquickenborne, J. Phys. Chem. **100**, 10956 (1996).



*Thermodynamic Data*

$$\Delta H_{298}^{\circ} = -45.9 \text{ kJ mol}^{-1}$$

$$\Delta S_{298}^{\circ} = -124.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c = 1.58 \cdot 10^{-29} T^{1.045} \exp(+5780/T) \text{ cm}^3 \text{ molecule}^{-1}$$

(300 ≤ T/K ≤ 5000)

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	[M]/molecule cm <sup>-3</sup>	Reference	Comments
<i>Rate Coefficient Measurements</i>				
<i>Low Pressure Range</i>				
[CO]5.7 · 10 <sup>-36</sup>	303	(3–24) · 10 <sup>18</sup>	Anastasi and Maw, 1982 <sup>1</sup>	(a)
[CO]1.07 · 10 <sup>-35</sup>	343			
<i>Intermediate Fall-off Range</i>				
1.8 · 10 <sup>-18</sup>	298	3.2 · 10 <sup>18</sup> (CO)	Parkes, 1981 <sup>2</sup>	(b)
6.0 · 10 <sup>-18</sup>		2.4 · 10 <sup>19</sup>		
3.6 · 10 <sup>-18</sup>	303	3.0 · 10 <sup>18</sup> (CO)	Anastasi and Maw, 1982 <sup>1</sup>	(a)
5.6 · 10 <sup>-18</sup>		1.6 · 10 <sup>19</sup>		
7.9 · 10 <sup>-18</sup>		2.4 · 10 <sup>19</sup>		
6.1 · 10 <sup>-18</sup>	343	3.0 · 10 <sup>18</sup>		
1.6 · 10 <sup>-17</sup>		1.6 · 10 <sup>19</sup>		
1.7 · 10 <sup>-17</sup>		2.1 · 10 <sup>19</sup>		
<i>High Pressure Range</i>				
>1 · 10 <sup>-17</sup>	298	(3.2–24) · 10 <sup>18</sup> (CO)	Parkes, 1981 <sup>2</sup>	(b)
1.6 · 10 <sup>-17</sup>	303	(3–24) · 10 <sup>18</sup> (CO)	Anastasi and Maw, 1982 <sup>1</sup>	(a)
<i>Reviews and Evaluations</i>				
$k_{\infty} = 7.64 \cdot 10^{-13} \exp(-3073/T)$	266–507		Bencsura <i>et al.</i> , 1992 <sup>3</sup>	(c)
$k_{\infty} = 8.4 \cdot 10^{-13} \exp(-3455/T)$	300–500		CEC, 1994 <sup>4</sup>	(d)
$k_0[\text{He}] = [\text{He}] 3.0 \cdot 10^{-34} \exp(-1910/T)$	400–500			
$k_0[\text{N}_2] = [\text{N}_2] 4.2 \cdot 10^{-36}$	300–350			
$F_c(\text{He}) = 0.5$	400–500			
$F_c(\text{N}_2) = 0.6$	300–350			

**Comments**

- (a) Molecular modulation technique; photolysis of azomethane/CO mixtures. UV absorption detection of CH<sub>3</sub> and CH<sub>3</sub>CO at 216 and 223 nm, respectively.
- (b) Molecular modulation technique; photolysis of azomethane/CO mixtures. UV absorption detection of CH<sub>3</sub> and CH<sub>3</sub>CO at 214 and 223 nm, respectively.  $\sigma(\text{CH}_3\text{CO}) = 1.0 \cdot 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$  at 223 nm was employed.
- (c) Study of the photolysis of CH<sub>3</sub>CO. CH<sub>3</sub>CO generated by photolysis of 2-butanone and detected by mass spectrometry.  $k_{\infty}$  was estimated theoretically.
- (d) The preferred  $k_{\infty}$  and  $k_0$  values were calculated from the recommended CH<sub>3</sub>CO dissociation rate coefficients and the equilibrium constant of Ref. 3.

**Preferred Values**

$k_0 = 1.6 \cdot 10^{-37} T^{1.05} \exp(-1300/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  for M=He over the range 400–500 K.  
 $k_0 = 5.9 \cdot 10^{-36} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  for M=N<sub>2</sub> over the range 300–350 K.

$$k_{\infty} = 3.1 \cdot 10^{-16} T^{1.05} \exp(-2850/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the range 300–500 K.

$$F_c = 0.5 \text{ for } M = \text{He} \text{ over the range } 400–500 \text{ K.}$$

$$F_c = 0.6 \text{ for } M = \text{N}_2 \text{ over the range } 300–350 \text{ K.}$$

**Reliability**

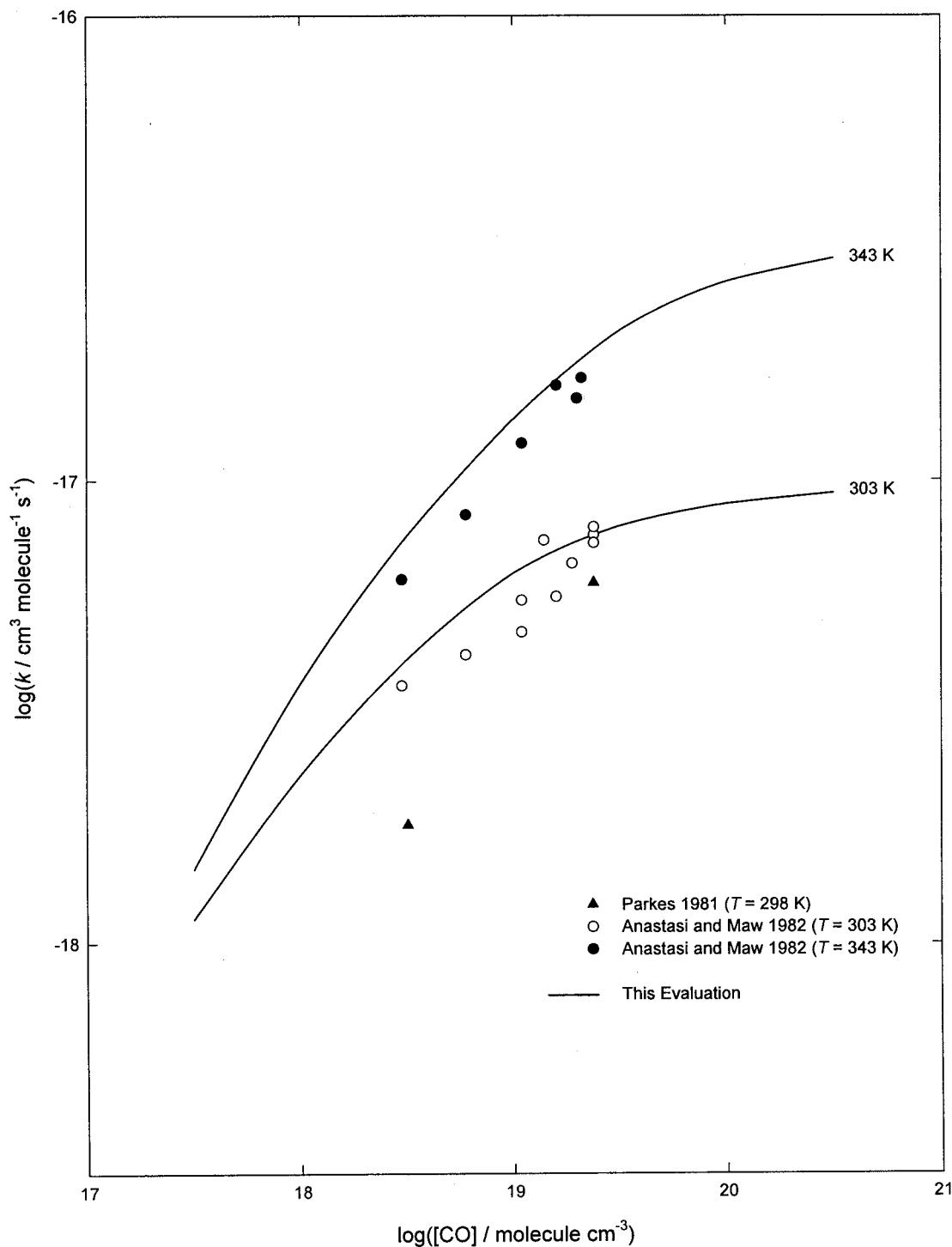
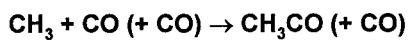
- $\Delta \log k_0 = \pm 0.2$  for M=He over the range 400–500 K.
- $\Delta \log k_0 = \pm 0.5$  for M=N<sub>2</sub> over the range 300–350 K.
- $\Delta \log k_{\infty} = \pm 0.5$  over the range 300–500 K.
- $\Delta \log F_c = \pm 0.1$  for M=He over the range 400–500 K.
- $\Delta \log F_c = \pm 0.1$  for M=N<sub>2</sub> over the range 300–350 K.

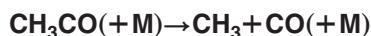
**Comments on Preferred Values**

The preferred rate coefficients  $k_{\infty}$  and  $k_0$  were derived from the preferred dissociation rate coefficients and the equilibrium constant given on this data sheet. In deriving the expression for  $k_0$  the values of  $k_0(M=N_2)$  were assumed to be equal to  $k_0(M=CO)$ . More direct determinations of the kinetics of this reaction are required. The experimental data and fitted fall-off curves<sup>5</sup> are shown in the Figure.

## References

- <sup>1</sup>C. Anastasi and P. R. Maw, J. Chem. Soc. Faraday Trans. 1 **78**, 2423 (1982).  
<sup>2</sup>D. A. Parkes, Chem. Phys. Lett. **77**, 527 (1981).  
<sup>3</sup>A. Bencsura, V. D. Knyazev, I. R. Slagle, D. Gutman, and W. Tsang, Ber. Bunsenges. Phys. Chem. **96**, 1338 (1992).  
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<sup>5</sup>J. Troe, J. Chem. Phys. **83**, 114 (1979).



*Thermodynamic Data*

$$\begin{aligned}\Delta H^\circ_{298} &= 45.9 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298} &= 124.1 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 6.35 \cdot 10^{28} T^{-1.045} \exp(-5780/T) \text{ molecule cm}^{-3} \\ &(300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{s}^{-1}$	$T/\text{K}$	[M]/molecule $\text{cm}^{-3}$	Reference	Comments
<i>Rate Coefficient Measurements</i>				
<i>Intermediate Fall-off Range</i>				
23	353	$6.8 \cdot 10^{18}(\text{Ar})$	Baldwin <i>et al.</i> , 1987 <sup>1</sup>	(a)
52		$2.0 \cdot 10^{19}$		
100		$4.9 \cdot 10^{19}$		
$6.06 \cdot 10^1$	440	$6.0 \cdot 10^{16}(\text{He})$	Bencsura <i>et al.</i> , 1992 <sup>2</sup>	(b)
$1.62 \cdot 10^2$		$1.8 \cdot 10^{17}$		
$1.31 \cdot 10^2$	460	$6.0 \cdot 10^{16}(\text{He})$		
$3.55 \cdot 10^2$		$1.8 \cdot 10^{17}$		
$1.98 \cdot 10^2$	500	$3.0 \cdot 10^{16}(\text{He})$		
$3.88 \cdot 10^2$		$6.0 \cdot 10^{16}$		
<i>Reviews and Evaluations</i>				
$k_\infty = 2.5 \cdot 10^{13} \exp(-8244/T)$	260–507		Bencsura <i>et al.</i> , 1992 <sup>2</sup>	(b)
$k_\infty = 2.8 \cdot 10^{13} \exp(-8630/T)$	300–500		CEC, 1994 <sup>3</sup>	(c)
$k_0[\text{He}] = [\text{He}] 1.0 \cdot 10^{-8} \exp(-7080/T)$	400–500			
$k_0[\text{Ar}] = [\text{Ar}] 7.0 \cdot 10^{-18}$	353			
$F_c(\text{He}) = 0.5$	400–500			

**Comments**

- (a) Photolysis of methyl cyclobutyl ketone at 313 nm (steady-state Hg arc) and 308 nm (pulsed laser photolysis) in Ar. Product analysis by gas chromatography.  $k_\infty$  obtained by modeling results with a 9-step mechanism and RRKM theory using step sizes for deactivation of  $250 \text{ cm}^{-1}$ . Rate coefficients depend on  $k(\text{CH}_3 + \text{CH}_3)$  and also on  $k(\text{CH}_3\text{CO} + \text{CH}_3\text{CO})$  for which values from Ref. 4 were used.
- (b) Laser photolysis of 2-butanone at 248 nm was used to generate  $\text{CH}_3\text{CO}$  radicals. Decay monitored by time-resolved mass spectrometry. The results were interpreted by theoretical analysis using a master equation formalism. The experiments were fitted using a threshold energy of  $65.3 \text{ kJ mol}^{-1}$ .  $k_\infty$  was evaluated theoretically.
- (c) In order to reconcile dissociation and recombination experiments, a value for  $k_\infty$  two times greater than the average value of the results of Refs. 1, 4, and 5 was adopted.  $k_0$  for M=He was based on the experiments of Ref. 2.

**Preferred Values**

$$\begin{aligned}k_0 &= 1.0 \cdot 10^{-8} \exp(-7080/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ for } \text{M} = \text{He} \text{ over the range } 400\text{--}500 \text{ K.} \\ k_0 &= 7.0 \cdot 10^{-18} \text{ s}^{-1} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ for } \text{M} = \text{Ar} \text{ at } 353 \text{ K.}\end{aligned}$$

$k_\infty = 2.0 \cdot 10^{13} \exp(-8630/T) \text{ s}^{-1}$  over the range 300–500 K.

$F_c = 0.5$  for M=He over the range 400–500 K.

*Reliability*

$$\begin{aligned}\Delta \log k_0 &= \pm 0.2 \text{ for } \text{M} = \text{He} \text{ over the range } 400\text{--}500 \text{ K.} \\ \Delta \log k_0 &= \pm 0.4 \text{ for } \text{M} = \text{Ar} \text{ at } 353 \text{ K.} \\ \Delta \log k_\infty &= \pm 0.5 \text{ over the range } 300\text{--}500 \text{ K.} \\ \Delta F_c &= \pm 0.1 \text{ for } \text{M} = \text{He} \text{ over the range } 400\text{--}500 \text{ K.}\end{aligned}$$

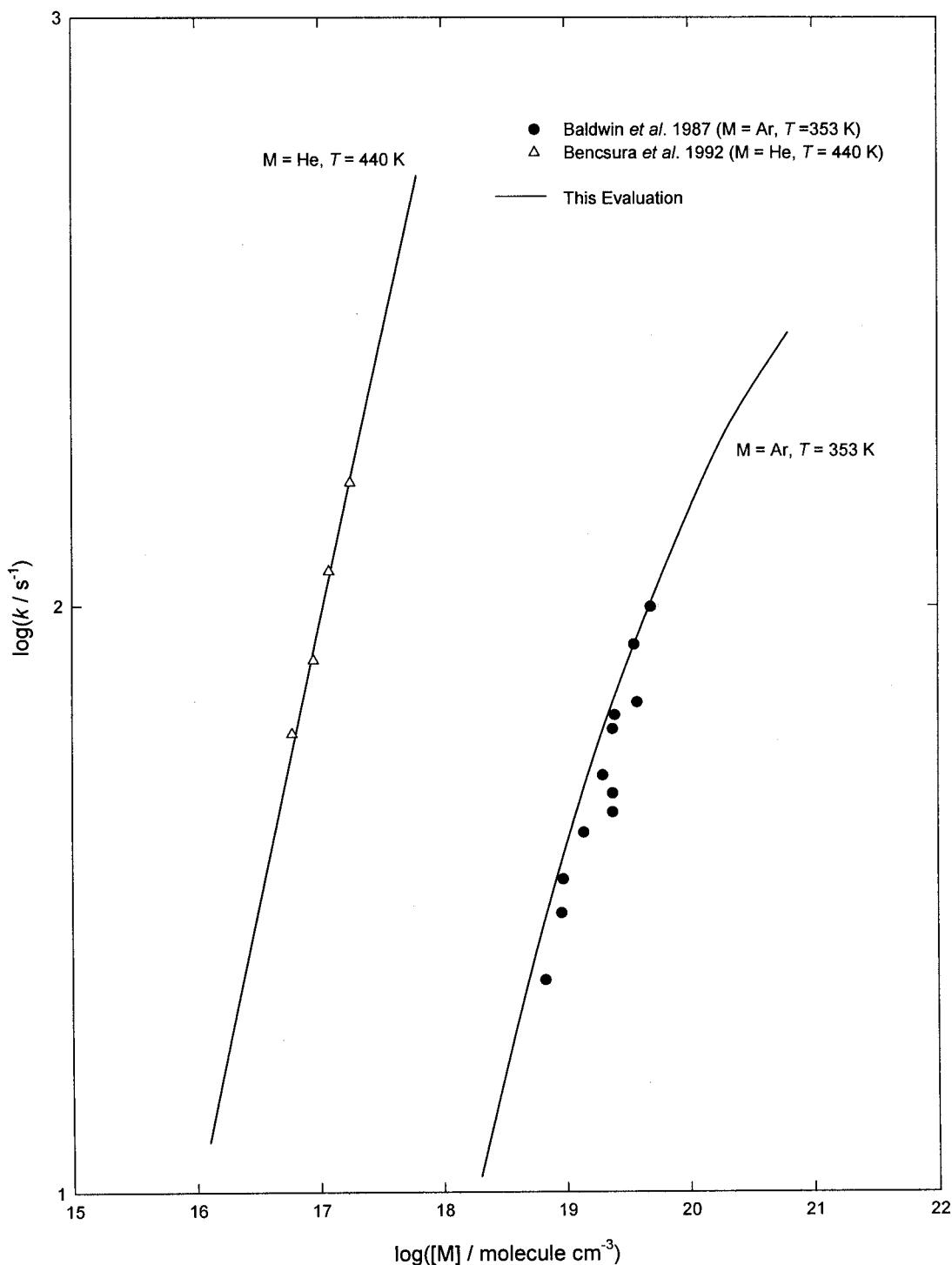
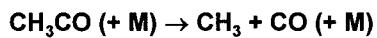
*Comments on Preferred Values*

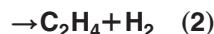
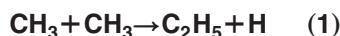
No new experimental measurements have been published since our previous compilation,<sup>3</sup> but in order to reconcile the experimental dissociation and the recombination rate coefficients we have taken for  $k_\infty$ , a value slightly smaller than the value previously recommended, which was based on the results of Refs. 1, 4, and 5. The preferred  $k_0$  values for M=He were derived from the fit to the data of Bencsura *et al.*<sup>2</sup> An analysis in terms of unimolecular rate theory from Ref. 6 (based on a threshold energy of  $E_0 = 65.3 \text{ kJ mol}^{-1}$ )<sup>2</sup> leads to collisional efficiencies for M=He of 0.11 and 0.093 at 420 and 500 K, respectively. These values are consistent with an average energy transferred per collision of  $60 \text{ cm}^{-1}$ .

Experiments by North, Blank, and Lee<sup>7</sup> on the photodissociation of the  $\text{CH}_3\text{COCl}$  at 248 nm lead to a threshold for  $\text{CH}_3\text{CO}$  radical dissociation of  $(71.1 \pm 4.2) \text{ kJ mol}^{-1}$  which is consistent with the  $E_0$  value employed in this evaluation.

## References

- <sup>1</sup>P. Baldwin, C. E. Canosa-Mas, H. M. Frey, and R. Walsh, Int. J. Chem. Kinet. **19**, 997 (1987).  
<sup>2</sup>A. Bencsura, V. D. Knyazev, I. R. Slagle, D. Gutman, and W. Tsang, Ber. Bunsenges. Phys. Chem. **96**, 1338 (1992).  
<sup>3</sup>CEC, Supplement I, 1994 (see references in Introduction).  
<sup>4</sup>C. Anastasi and P. R. Maw, J. Chem. Soc. Faraday Trans. 1 **78**, 2423 (1982).  
<sup>5</sup>K. W. Watkins and W. W. Word, Int. J. Chem. Kinet. **6**, 855 (1975).  
<sup>6</sup>J. Troe, J. Chem. Phys. **66**, 4758 (1977).  
<sup>7</sup>S. North, D. A. Blank, and Y. T. Lee, Chem. Phys. Lett. **224**, 38 (1994).



*Thermodynamic Data*

$$\begin{aligned}\Delta H^\circ_{298}(1) &= 46.07 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(1) &= -26.20 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 1.43 \cdot 10^{-5} T^{1.092} \exp(-4990/T) \\ &(300 \leq T/\text{K} \leq 5000)\end{aligned}$$

$$\begin{aligned}\Delta H^\circ_{298}(2) &= -240.4 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(2) &= -38.15 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 8.17 \cdot 10^{-5} T^{0.657} \exp(+29250/T) \\ &(300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data ( $k = k_1 + k_2$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$k_1 = 4.7 \cdot 10^{-11} \exp(-6840/T)$	1320–2300	Frank and Braun-Unkhoff, 1988 <sup>1</sup>	(a)
$k_1 = (4.7–6.0) \cdot 10^{-11} \exp(-6840/T)$	1400–2200	Hidaka <i>et al.</i> , 1990 <sup>2</sup>	(b)
$k_2 < 2 \cdot 10^{-10} \exp(-16000/T)$			
$k_1 = 5.25 \cdot 10^{-11} \exp(-7384/T)$	1224–1938	Lim and Michael, 1994 <sup>3</sup>	(c)
$k_1 = 4.0 \cdot 10^{-11} \exp(-6480/T)$	1570–1780	Davidson <i>et al.</i> , 1995 <sup>4</sup>	(d)
$k_2 < 1 \cdot 10^{-13}$	1700–2200		
<i>Reviews and Evaluations</i>			
$k_1 = 3 \cdot 10^{-12} \exp(-5248/T)$	300–2500	Tsang and Hampson, 1986 <sup>5</sup>	(e)
$5 \cdot 10^{-11} \exp(-6800/T)$	1300–2500	CEC, 1992; 1994 <sup>6</sup>	(f)

**Comments**

- (a) Shock tube/ARAS study of H with a variety of CH<sub>3</sub> precursors (azomethane, methyl iodide, ethane, all in argon) to cover a wide range of temperatures.
- (b) Shock tube study of the pyrolysis of dilute methane in Ar at 2.3–3.7 bar. Time-resolved IR emission at 3.84 nm and end product analysis by GC were used to follow the reaction. The data were analyzed using a 21-reaction mechanism to obtain values of  $k$ . Inclusion of Channel (2) with previously recommended values of  $k_2$ <sup>7,8</sup> led to too much inhibition and allowed an upper limit to be placed on  $k_2$ .
- (c) Shock tube study using reflected shock waves in CH<sub>3</sub>I/Ar mixtures to produce CH<sub>3</sub>. [H] profiles were monitored by ARAS and fitted by simulation to a 14-reaction mechanism to obtain values of  $k$ . The results are within 15% of those from Ref. 1. At higher temperatures the profiles are influenced by CH<sub>3</sub> dissociation.
- (d) Shock tube study of azomethane/Ar, ethane/methane/Ar, methyl iodide/argon, and ethane/argon mixtures. Time-resolved detection of CH<sub>3</sub> by narrow line laser absorption at 216.615 nm. The methyl decay was dominated by recombination to form ethane, especially at lower temperatures and was well described by the Wardlaw and Wagner expressions.<sup>9</sup> Deviations from the pure recombination profile, for  $T > 1500$  K, were compatible with contributions from Channel (1). The  $T$  dependence of  $k_1$  was fixed by thermodynamics and only  $A$  was adjusted. The resulting expression is within 9% of that from Ref. 1. The CH<sub>3</sub> profiles should be sensitive to Channel (2), but no evidence for this chan-

nel was found. Its contribution was further checked by the addition of methane, which should rapidly regenerate CH<sub>3</sub> via H+CH<sub>4</sub> if Channel (1) predominates. The resulting flat time profiles confirmed the unimportance of Channel (2).

- (e) Based on data for the reverse reaction and an RRKM calculation.
- (f) Based on the study of Frank and Braun-Unkhoff.<sup>1</sup>

**Preferred Values**

$k_1 = 9.0 \cdot 10^{-11} \exp(-8080/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 1200–2500 K.

$k_2 \ll k_1$  over the range 1200–2500 K.

**Reliability**

$\Delta \log k_1 = \pm 0.3$  over the range 1200–2500 K.

**Comments on Preferred Values**

Only the data for Channels (1) and (2) are evaluated on this data sheet; the data for the combination channel, leading to C<sub>2</sub>H<sub>6</sub>, are evaluated separately on the data sheet which follows.

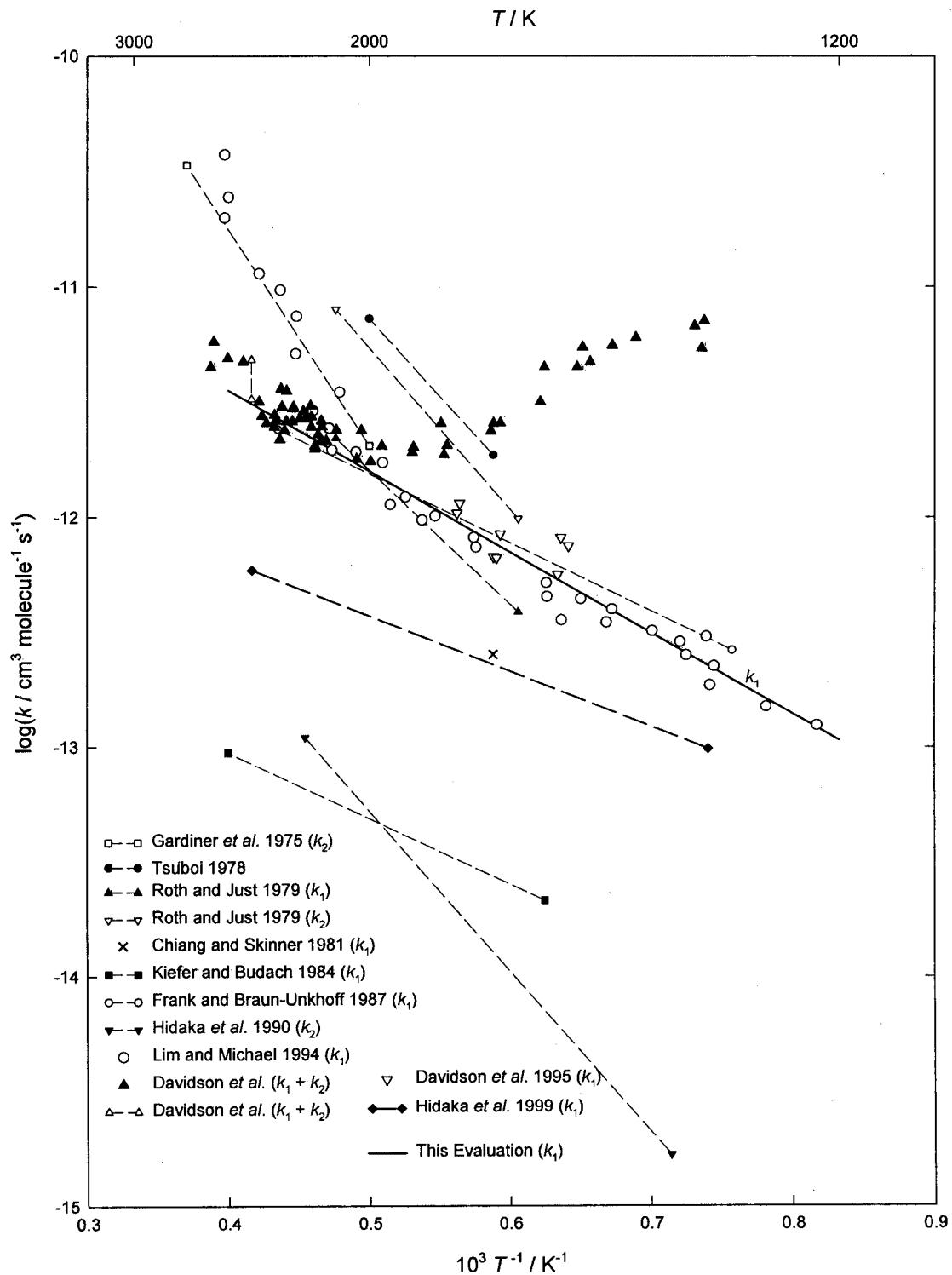
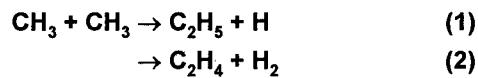
There is excellent agreement between the values of  $k_1$  from Refs. 1, 3, 4, which are the most detailed and direct studies available. Ref. 2 provides confirmatory evidence but, in a later similar study, Hidaka *et al.*<sup>10</sup> fit their results using the expression  $k_1 = 2.5 \cdot 10^{-12} T^{0.1} \exp(-5334/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  which gives significantly lower values of  $k$  than our preferred expression. A number of earlier measurements<sup>8,11,12</sup> gave values of  $k$  close in magnitude to those from more recent work but with a stronger  $T$  depen-

dence, while the measurements of Chiang and Skinner<sup>13</sup> and of Kiefer and Budach<sup>14</sup> are significantly lower. Roth and Just,<sup>8</sup> Tsuboi,<sup>12</sup> and Gardiner *et al.*<sup>11</sup> argued that Channel (2) is significant but the more recent measurements<sup>1–4</sup> provide strong evidence that this channel is not important at temperatures up to 2500 K. There is also a channel leading to  $^1\text{CH}_2 + \text{CH}_4$  but the data on the rate constant for the reverse of this channel combined with the thermodynamic data show that it does not contribute significantly. The preferred expression for  $k_1$  is based on the data of References 1, 3, and 4.

Stewart *et al.*<sup>15</sup> have provided Troe parameters for Channel (1) and the combination channel. However, except at very high pressures, the energized molecules, at energies relevant to Channel (1), are maintained in a Boltzmann distribution by the combination reaction ( $\text{C}_2\text{H}_6$  formation) and its reverse reaction, so that the rate coefficient for Channel (1) is independent of pressure and is linked via the equilibrium constant,  $K_c(1)$ , to the rate coefficient for  $\text{H} + \text{C}_2\text{H}_5 \rightarrow 2\text{CH}_3$ . However it should be noted that the present recommendation gives a rate coefficient at 2000 K that is a factor of 5 larger than that based on the reverse reaction, which may imply that the rate coefficient for the latter increases somewhat with  $T$  as opposed to its assumed independence of  $T$  in our evaluation.

## References

- <sup>1</sup>P. Frank and M. Braun-Unkhoff, 16th Int. Symp. on Shock Tubes and Waves, 1988, p. 379.
- <sup>2</sup>Y. Hidaka, T. Nakamura, H. Tanaka, K. Inami, and H. Kawano, Int. J. Chem. Kinet. **22**, 701 (1990).
- <sup>3</sup>K. P. Lim and J. V. Michael, 25th Symp. (Int.) Combustion, 1994, p. 713.
- <sup>4</sup>D. F. Davidson, M. D. Di Rosa, E. J. Chang, R. K. Hanson, and C. T. Bowman, Int. J. Chem. Kinet. **27**, 1179 (1995).
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- <sup>9</sup>A. F. Wagner and D. M. Wardlaw, J. Phys. Chem. **92**, 2462 (1988).
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- <sup>12</sup>T. Tsuboi, Jpn. J. Appl. Phys. **17**, 709 (1978).
- <sup>13</sup>C. C. Chiang and G. B. Skinner, J. Phys. Chem. **85**, 3126 (1981).
- <sup>14</sup>J. H. Kiefer and K. Budach, Int. J. Chem. Kinet. **16**, 679 (1984).
- <sup>15</sup>P. H. Stewart, C. W. Larson, and D. W. Golden, Combust. Flame **75**, 25 (1989).



*Thermodynamic Data*

$$\Delta H_{298}^{\circ} = -376.7 \text{ kJ mol}^{-1}$$

$$\Delta S_{298}^{\circ} = -158.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c = 1.34 \cdot 10^{-32} T^{1.371} \exp(+45900/T) \text{ cm}^3 \text{ molecule}^{-1}$$

(300  $\leq T/\text{K} \leq 4000$ )

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	[M]/molecule cm <sup>-3</sup>	Reference	Comments
<i>Rate Coefficient Measurements</i>				
<i>Intermediate Fall-off Range</i>				
3.2 $\cdot 10^{-12}$	1350	1.2 $\cdot 10^{18}$ (Ar)	Glänzer, Quack, and Troe, 1976, 1977 <sup>1</sup>	(a)
1.3 $\cdot 10^{-11}$		1.5 $\cdot 10^{19}$		
1.8 $\cdot 10^{-11}$		6.0 $\cdot 10^{19}$		
1.6 $\cdot 10^{-11}$		1.2 $\cdot 10^{20}$		
5.5 $\cdot 10^{-11}$	296	2.5 $\cdot 10^{19}$ (Ar)	Hippler <i>et al.</i> , 1984 <sup>2</sup>	(b)
6.3 $\cdot 10^{-11}$		2.5 $\cdot 10^{20}$		
5.0 $\cdot 10^{-11}$		5.2 $\cdot 10^{21}$		
5.0 $\cdot 10^{-11}$		2.8 $\cdot 10^{19}$ (N <sub>2</sub> )		
4.6 $\cdot 10^{-11}$		2.5 $\cdot 10^{20}$		
2.6 $\cdot 10^{-11}$		2.5 $\cdot 10^{21}$		
1.8 $\cdot 10^{-11}$		5.0 $\cdot 10^{21}$		
5.2 $\cdot 10^{-11}$	296	1.6 $\cdot 10^{17}$ (Ar)	Macpherson, Pilling, and Smith, 1985 <sup>3</sup>	(c)
5.7 $\cdot 10^{-11}$		1.3 $\cdot 10^{18}$		
6.0 $\cdot 10^{-11}$		1.6 $\cdot 10^{19}$		
1.9 $\cdot 10^{-11}$	577	8.4 $\cdot 10^{16}$ (Ar)		
3.5 $\cdot 10^{-11}$		1.1 $\cdot 10^{18}$		
4.1 $\cdot 10^{-11}$		6.6 $\cdot 10^{18}$		
4.4 $\cdot 10^{-11}$	296	3.8 $\cdot 10^{16}$ (Ar)	Slagle <i>et al.</i> , 1988 <sup>4</sup>	(d)
5.2 $\cdot 10^{-11}$		3.4 $\cdot 10^{17}$		
3.4 $\cdot 10^{-12}$	906	4.0 $\cdot 10^{16}$ (Ar)		
1.5 $\cdot 10^{-12}$		7.9 $\cdot 10^{17}$		
2.9 $\cdot 10^{-11}$		6.4 $\cdot 10^{18}$		
6.65 $\cdot 10^{-11}$	200	4.15 $\cdot 10^{17}$ (Ar)	Walter <i>et al.</i> , 1990 <sup>5</sup>	(e)
6.68 $\cdot 10^{-11}$		4.79 $\cdot 10^{18}$		
7.3 $\cdot 10^{-11}$		1.94 $\cdot 10^{19}$		
1.7 $\cdot 10^{-11}$	300	4.7 $\cdot 10^{15}$ (Ar)		
3.3 $\cdot 10^{-11}$		2.4 $\cdot 10^{16}$		
4.1 $\cdot 10^{-11}$		6.95 $\cdot 10^{16}$		
1.1 $\cdot 10^{-11}$	408	6.9 $\cdot 10^{15}$ (Ar)		
2.1 $\cdot 10^{-11}$		3.7 $\cdot 10^{16}$		
2.9 $\cdot 10^{-11}$		7.5 $\cdot 10^{16}$		
6.3 $\cdot 10^{-12}$	1180	6.1 $\cdot 10^{18}$ (Ar)	Du, Hessler, and Ogren, 1996 <sup>6</sup>	(f)
6.3 $\cdot 10^{-12}$	1350	9.1 $\cdot 10^{18}$		
3.2 $\cdot 10^{-12}$	1525	7.8 $\cdot 10^{18}$		
0.97 $\cdot 10^{-12}$	1730	7.3 $\cdot 10^{18}$		
<i>Reviews and Evaluations</i>				
$k_{\infty} = 6.0 \cdot 10^{-11}$	300–2000		CEC, 1992; 1994 <sup>7</sup>	(g)
$k_0[\text{Ar}] = [\text{Ar}] 3.5 \cdot 10^{-7} T^{-7} \exp(-1390/T)$	300–2000			
$F_c(\text{Ar}) = 0.38 \exp(-T/73)$ + 0.62 $\exp(-T/1180)$	300–2000			
$k_{\infty} = 7.71 \cdot 10^{-11} \exp(-T/1298)$	296–1742		Hessler and Ogren, 1996 <sup>8</sup>	(h)
$k_0[\text{Ar}] = [\text{Ar}] 8.06 \cdot 10^{-26} \exp(-T/280)$	296–1742			
$F_c(\text{Ar}) = \exp(-T/333)$	296–1742			

**Comments**

- (a) Shock wave pyrolysis study of azomethane at 1200–1500 K. [CH<sub>3</sub>] determined by absorption at 216 nm. Rate coefficients found for CD<sub>3</sub>+CD<sub>3</sub>(+Ar)→C<sub>2</sub>D<sub>6</sub>(+Ar) were identical to those for methyl recombination.
- (b) Excimer laser flash photolysis of azomethane at 193

nm with detection of CH<sub>3</sub> by absorption 216 nm. Onset of diffusion control seen in high pressure N<sub>2</sub> experiments.

- (c) Excimer laser flash photolysis of azomethane at 193 nm with CH<sub>3</sub> detection at 216 nm. Temperature dependence measured at several temperatures over the range 296 and 577 K.

- (d) Excimer laser flash photolysis of acetone at 193 nm. Analysis by photoionization mass spectrometry at low pressures and by absorption spectroscopy at high pressures. Experiments were also conducted with M=He from 296 K to 810 K. Fall-off curves with M=Ar for several temperatures between 296 and 906 K.
- (e) CH<sub>3</sub> radicals were generated by 193 nm laser photolysis of acetone at 200 K and by the reaction F+CH<sub>4</sub> →HF+CH<sub>3</sub> at 300 and 408 K. At 200 K, CH<sub>3</sub> radicals were monitored by UV absorption at 216.36 nm, while at 300 K and 408 K they were detected by conversion to NO in the reaction CH<sub>3</sub>+NO<sub>2</sub>→CH<sub>3</sub>O+NO. NO concentrations were determined by measuring the NO signal at *m/e*=30 amu. These, and previous measurements from Slagle *et al.*,<sup>4</sup> were interpreted between 200 K and 2000 K using variational RRKM theory.
- (f) Rate coefficients measured in incident shock waves with azomethane/Ar mixtures. [CH<sub>3</sub>] monitored by tuneable-laser flash-absorption technique at 215.94 nm. Experimental data measured between 1177 K and 1742 K and between 1.13 and 2.27 bar have been combined with previous measurements of Glänzer *et al.*,<sup>1</sup> Hippler *et al.*,<sup>2</sup> Slagle *et al.*,<sup>4</sup> Walter *et al.*,<sup>5</sup> and Hwang *et al.*<sup>9</sup> to derive, on the basis of a broadening factor  $F_c = \exp(-T/506)$ , the limiting rate constants,  $k_0(\text{Ar}) = 1.70 \cdot 10^{-5} T^{-7.284} \exp(-2172/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  and  $k_\infty = 1.53 \cdot 10^{-7} T^{-1.203} \exp(-295/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .
- (g) See Comments on Preferred Values.
- (h) Global fits to the pressure and temperature dependences of the rate coefficients from Glänzer *et al.*,<sup>1</sup> Hippler *et al.*,<sup>2</sup> Slagle *et al.*,<sup>4</sup> Walter *et al.*,<sup>5</sup> Du *et al.*,<sup>6</sup> and Hwang *et al.*<sup>9</sup>

### Preferred Values

$k_0 = 3.5 \cdot 10^{-7} T^{-7} \exp(-1390/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  for M=Ar over the range 300–2000 K.

$k_\infty = 6.0 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 300–2000 K.

$F_c = 0.38 \exp(-T/73) + 0.62 \exp(-T/1180)$  for M=Ar over the range 300–2000 K.

### Reliability

$\Delta \log k_0 = \pm 0.3$  for M=Ar over the range 300–2000 K.

$\Delta \log k_\infty = \pm 0.3$  over the range 300–2000 K.

$\Delta F_c = \pm 0.1$  for M=Ar over the range 300–2000 K.

### Comments on Preferred Values

Only the data for the combination reaction channel leading to C<sub>2</sub>H<sub>6</sub> are evaluated here. The data for the bimolecular reaction channels leading to C<sub>2</sub>H<sub>5</sub>+H and C<sub>2</sub>H<sub>4</sub>+H<sub>2</sub> are evaluated on the preceding data sheet.

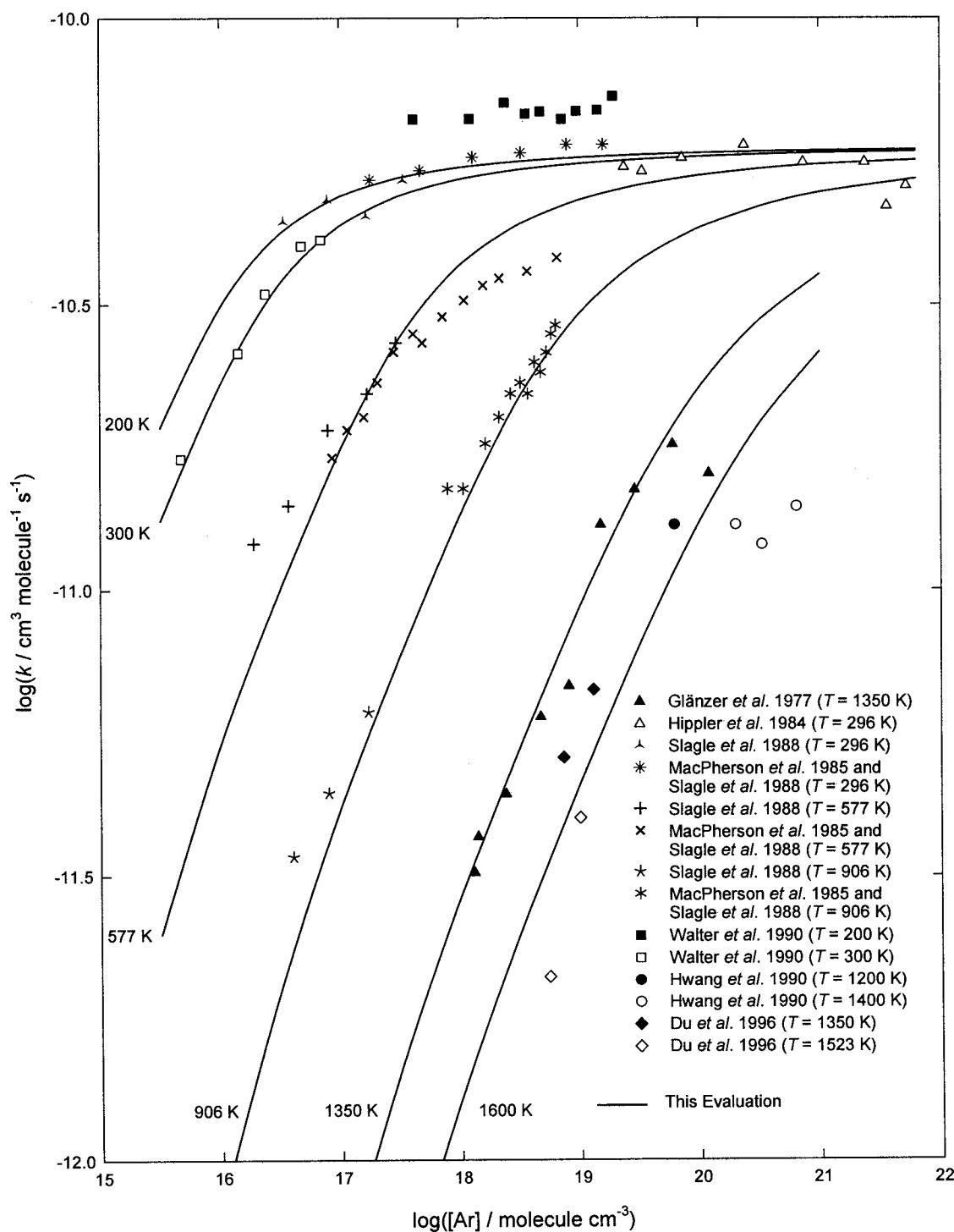
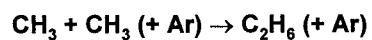
The preferred values are unchanged from our previous evaluation<sup>7</sup> and are based mainly on the data of Glänzer *et al.*,<sup>1</sup> Hippler *et al.*,<sup>2</sup> Macpherson *et al.*,<sup>3</sup> and Slagle *et al.*<sup>4</sup> up to 1350 K and the experiments of Walter *et al.*<sup>5</sup> over the range 200–400 K, which essentially agree with previous measurements.

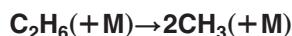
Recent shock wave experiments from Hwang, Rabinowitz, and Gardiner<sup>10</sup> performed between 1300 K and 1700 K and 216–1270 mbar Ar, give rate coefficients in the fall-off range which suggest a slight negative temperature coefficient of  $k_\infty$ . Other experiments<sup>9</sup> carried out between 1200 K and 1400 K also suggest a negative temperature coefficient of the order  $k_\infty \propto T^{-0.69}$ . However, these data appear inconsistent with the results of Glänzer, Quack, and Troe<sup>1</sup> although the same technique was applied. The difference of the rate coefficients (about a factor of 2) is due to the use of different CH<sub>3</sub> absorption coefficients. Because the uncertainty of the high pressure shock wave experiments is probably larger than that of the low pressure shock wave experiments, we prefer the data of Ref. 1 and retain the interpretation of our previous evaluation. Nevertheless, the question of the temperature coefficient of  $k_\infty$  at high temperature remains open.<sup>11–13</sup> The analysis of Du *et al.*<sup>6</sup> and Hessler and Ogren<sup>8</sup> led to negative temperature coefficients for  $k_\infty$  but the analysis of Ref. 8 gave an unrealistic temperature dependence of  $k_0$ . The recommended values are consistent with those of the dissociation reaction and the equilibrium constant given in this evaluation.

For M=N<sub>2</sub>, expressions for  $k_0$  identical with those for M=Ar may be assumed. The figure shows selected fall-off plots and experimental data for M=Ar.

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*Thermodynamic Data*

$$\begin{aligned}\Delta H_{298}^{\circ} &= 376.7 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= 158.9 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 7.5 \cdot 10^{31} T^{-1.371} \exp(-45900/T) \text{ molecule cm}^{-3} \\ &\quad (300 \leq T/\text{K} \leq 4000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{s}^{-1}$	T/K	[M]/molecule cm $^{-3}$	Reference	Comments
<i>Rate Coefficient Measurements</i>				
<i>Intermediate Fall-off Range</i>				
$1.2 \cdot 10^{-7}$	823	$7.9 \cdot 10^{16}(\text{C}_2\text{H}_6)$	Lin and Back, 1966 <sup>1</sup>	(a)
$1.3 \cdot 10^{-7}$		$1.9 \cdot 10^{17}$		
$1.4 \cdot 10^{-7}$		$7.0 \cdot 10^{17}$		
$6.7 \cdot 10^{-6}$	893	$4.4 \cdot 10^{17}$		
$8.4 \cdot 10^{-6}$		$2.3 \cdot 10^{18}$		
$8.9 \cdot 10^{-6}$		$4.9 \cdot 10^{18}$		
$1.7 \cdot 10^{-4}$	999	$9.7 \cdot 10^{15}$		
$5.7 \cdot 10^{-4}$		$1.1 \cdot 10^{17}$		
$1.0 \cdot 10^{-3}$		$8.2 \cdot 10^{17}$		
$3.5 \cdot 10^{-8}$	813	$1.2 \cdot 10^{17}(\text{C}_2\text{H}_6)$	Scacchi, Martin, and Niclause, 1971 <sup>2</sup>	(b)
$5.8 \cdot 10^{-8}$		$6.2 \cdot 10^{17}$		
$7.7 \cdot 10^{-8}$		$2.5 \cdot 10^{18}$		
$2.0 \cdot 10^{-7}$	841	$1.1 \cdot 10^{17}(\text{C}_2\text{H}_6)$	Kanan, Purnell, and Sepehrad, 1983 <sup>3</sup>	(c)
$2.5 \cdot 10^{-7}$		$2.1 \cdot 10^{17}$		
$7.6 \cdot 10^{-7}$	871	$5.4 \cdot 10^{16}$		
$1.1 \cdot 10^{-6}$		$1.6 \cdot 10^{17}$		
$2.0 \cdot 10^{-6}$		$4.2 \cdot 10^{18}$		
$5.7 \cdot 10^{-6}$	913	$5.2 \cdot 10^{16}$		
$1.3 \cdot 10^{-5}$		$2.0 \cdot 10^{17}$		
$3.4 \cdot 10^{-5}$	938	$5.4 \cdot 10^{17}(\text{He})$	Cao and Back, 1984 <sup>5</sup>	(d)
$4.6 \cdot 10^{-5}$		$1.8 \cdot 10^{18}$		
$5.2 \cdot 10^{-5}$		$3.4 \cdot 10^{18}$		
$2.6 \cdot 10^{-4}$	998	$5.1 \cdot 10^{17}$		
$4.2 \cdot 10^{-4}$		$2.0 \cdot 10^{18}$		
$3.6 \cdot 10^{-4}$		$3.2 \cdot 10^{18}$		
$8.0 \cdot 10^{-4}$	1098	$5.0 \cdot 10^{17}$		
$1.1 \cdot 10^{-3}$		$1.1 \cdot 10^{18}$		
$2.4 \cdot 10^{-3}$		$2.8 \cdot 10^{18}$		
$3.72 \cdot 10^{69} T^{-15.95} \exp(-56230/T)$	1348–2108	$(2.4–3.8) \cdot 10^{18}(\text{Ar})$	Davidson <i>et al.</i> , 1993 <sup>6</sup>	(e)
$3.5 \cdot 10^{77} T^{-18.08} \exp(-59700/T)$	1448–2037	$(4.3–6.1) \cdot 10^{18}$		
$3.32 \cdot 10^{81} T^{-14.81} \exp(-56750/T)$	1397–1946	$(1.3–2.0) \cdot 10^{19}$		
$1.56 \cdot 10^{11} \exp(-28250/T)$	1348–2108	$(2.2–3.4) \cdot 10^{18}(\text{Ar})$	Davidson, Hanson, and Bowman, 1995 <sup>9</sup>	(f)
$7.94 \cdot 10^{11} \exp(-30300/T)$	1450–1945	$(3.8–5.1) \cdot 10^{18}$		
$9.89 \cdot 10^{11} \exp(-30290/T)$	1448–2037	$(4.3–6.1) \cdot 10^{18}$		
$1.36 \cdot 10^{13} \exp(-34140/T)$	1397–1946	$(1.5–2.0) \cdot 10^{19}$		
<i>Reviews and Evaluations</i>				
$k_\infty = 1.8 \cdot 10^{21} T^{-1.24} \exp(-45700/T)$	300–2000		CEC, 1992; 1994 <sup>7</sup>	(g)
$k_0[\text{Ar}] = [\text{Ar}] 1.1 \cdot 10^{25} T^{-8.24} \exp(-47090/T)$	300–2000			
$k_0[\text{N}_2] = [\text{N}_2] 1.1 \cdot 10^{25} T^{-8.24} \exp(-47090/T)$	300–2000			
$k_0[\text{C}_2\text{H}_6] = [\text{C}_2\text{H}_6] 4.5 \cdot 10^{-2} \exp(-41930/T)$	800–1000			
$F_c(\text{Ar}) = 0.38 \exp(-T/73) + 0.62 \exp(-T/1180)$	300–2000			
$F_c(\text{C}_2\text{H}_6) = 0.54 \exp(-T/1250)$	800–1000			

**Comments**

- (a) Static reactor study of the dissociation of pure ethane with measurement of the rate of production of methane and butane. Extrapolation to the high pressure limit and comparison with earlier work.
- (b) Pyrolysis of ethane in a static reactor. Analysis of initiation of reaction using manometric and gas chromatographic measurements.

- (c) Ethane pyrolysis in a static reactor with gas chromatographic analysis. Enhanced hydrogen recombination at activated vessel surface. Results in good agreement with those of Trenwith.<sup>4</sup>
- (d) Pyrolysis of  $\text{C}_2\text{H}_6$  in a static reactor. Product analysis by gas chromatography. Collision efficiencies of  $\text{Xe}$  and  $\text{H}_2$  relative to  $\text{C}_2\text{H}_6$  were measured.
- (e) Reflected shock wave study of the  $\text{C}_2\text{H}_6$  thermal de-

composition.  $\text{CH}_3$  radicals detected by absorption at 216.6 nm.  $k$  extracted using a mechanism with 20 reactions. The fits were constrained to coincide with the rate coefficients given by Wagner and Wardlaw<sup>8</sup> at 900 K and 1200 K.

- (f) Re-analysis of the experiments of Ref. 6 applying a re-evaluated absorption coefficient<sup>10</sup> for the  $\text{CH}_3$  radical which was approximately half the value originally employed.
- (g) Preferred values based on the recommended rate coefficients for the reverse reaction,  $\text{CH}_3 + \text{CH}_3(+\text{M}) \rightarrow \text{C}_2\text{H}_6(+\text{M})$  and the equilibrium constant  $K_c = 3.00 \cdot 10^{31} T^{-1.236} \exp(-45700/T)$  molecule cm<sup>-3</sup>. See Comments on Preferred Values.

### Preferred Values

$k_0 = 2.6 \cdot 10^{25} T^{-8.37} \exp(-47290/T)$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for M=Ar over the range 300–2000 K.

$k_0 = 2.6 \cdot 10^{25} T^{-8.37} \exp(-47290/T)$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for M=N<sub>2</sub> over the range 300–2000 K.

$k_0 = 4.5 \cdot 10^{-2} \exp(-41930/T)$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for M=C<sub>2</sub>H<sub>6</sub> over the range 800–1000 K.

$k_\infty = 4.5 \cdot 10^{21} T^{-1.37} \exp(-45900/T)$  s<sup>-1</sup> over the range 300–2000 K.

$F_c = 0.38 \exp(-T/73) + 0.62 \exp(-T/1180)$  for M=Ar and N<sub>2</sub> over the range 300–2000 K.

$F_c = 0.54 \exp(-T/1250)$  for M=C<sub>2</sub>H<sub>6</sub> over the range 800–1000 K.

### Reliability

$\Delta \log k_0 = \pm 0.5$  for M=Ar and N<sub>2</sub> over the range 300–2000 K.

$\Delta \log k_0 = \pm 0.5$  for M=C<sub>2</sub>H<sub>6</sub> over the range 800–1000 K.

$\Delta \log k_\infty = \pm 0.3$  over the range 300–2000 K.

$\Delta F_c = \pm 0.1$  for M=Ar and N<sub>2</sub> over the range 300–2000 K.

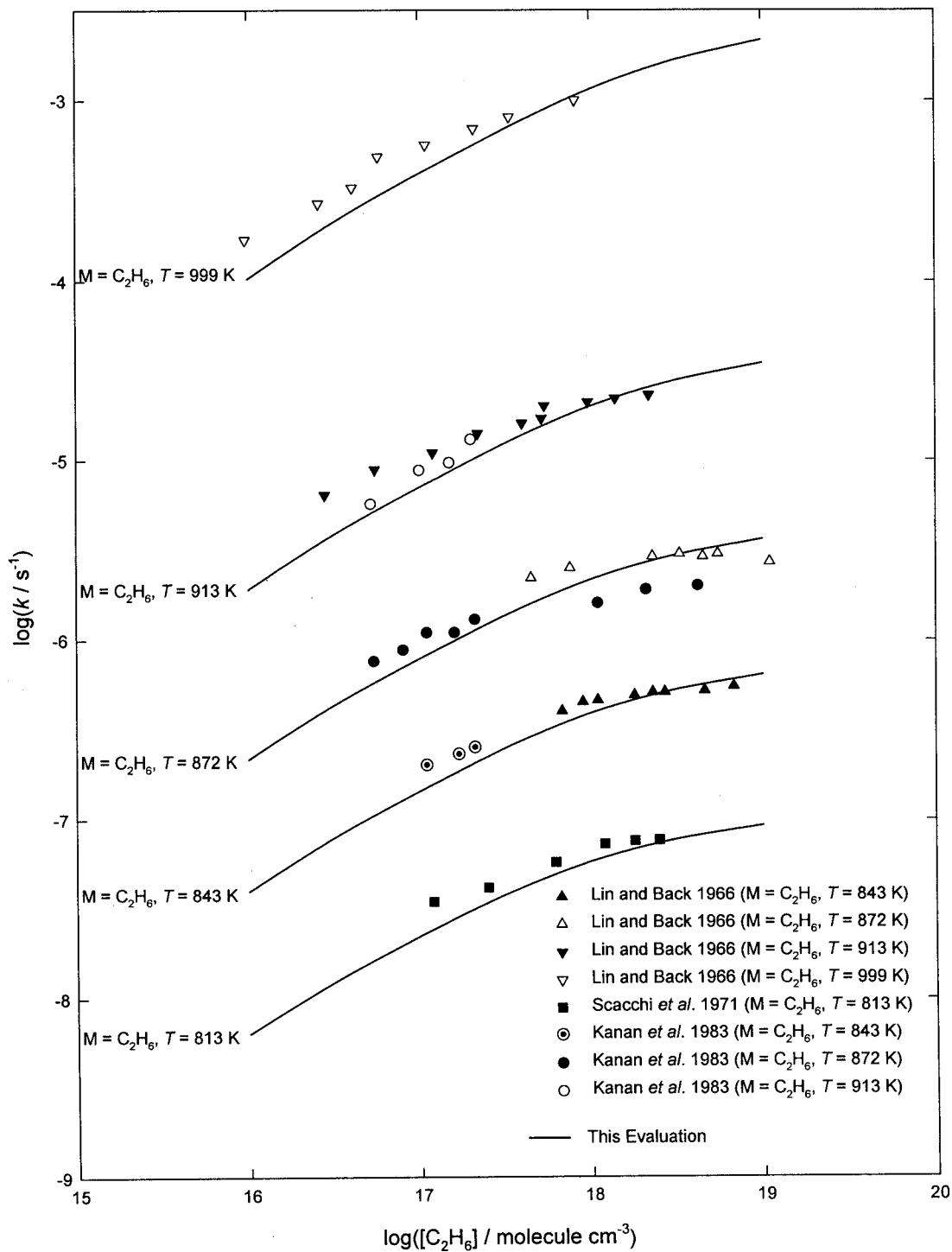
$\Delta F_c = \pm 0.1$  for M=C<sub>2</sub>H<sub>6</sub> over the range 800–1000 K.

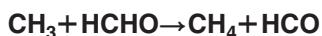
### Comments on Preferred Values

The preferred values for  $k_\infty$  and  $k_0$  (for M=Ar), which are unchanged from our previous evaluations,<sup>7</sup> have been derived from the recommended rate coefficients of the reverse reaction  $2\text{CH}_3(+\text{M}) \rightarrow \text{C}_2\text{H}_6(+\text{M})$  and the expression for the equilibrium constant, both from this evaluation. They are based on the combined evaluation of dissociation and recombination data given in the review of Troe<sup>11</sup> which assumes a nearly temperature independent rate coefficient  $k_\infty$  for the reverse recombination over the range 200–2000 K. Selected fall-off curves and experimental data are shown in the Figure.

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*Thermodynamic Data*

$$\begin{aligned}\Delta H_{298}^{\circ} &= -69.6 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= -2.33 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 1.27 \cdot T^{-0.109} \exp(+8420/T) \\ &(300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$5.33 \cdot 10^{-14}$	1005	Held <i>et al.</i> , 1977 <sup>1</sup>	(a)
$2.1 \cdot 10^{-11} \exp(-5415/T)$	788–935	Manthorne and Pacey, 1978 <sup>2</sup>	(b)
$1.4 \cdot 10^{-12} \exp(-3502/T)$	500–603	Anastasi, 1983 <sup>3</sup>	(c)
$1.7 \cdot 10^{-9} \exp(-11600/T)$	1170–1630	Choudhury, Sanders, and Lin, 1989 <sup>4</sup>	(d)
<i>Reviews and Evaluations</i>			
$1.75 \cdot 10^{-13} \exp(-3080/T)$	300–500	Kerr and Parsonage, 1976 <sup>5</sup>	(e)
$9.2 \cdot 10^{-21} T^{2.81} \exp(-2950/T)$	300–2500	Tsang and Hampson, 1986 <sup>6</sup>	(f)
$1.29 \cdot 10^{-31} T^{6.1} \exp(-990/T)$	300–2000	CEC, 1994 <sup>7</sup>	(g)

**Comments**

- (a) Flow pyrolysis of dimethyl ether to generate  $\text{CH}_3$  and  $\text{HCHO}$ .  $[\text{CH}_3]$  measured by UV absorption and stable products by gas chromatography. Independent values of  $k$  and  $k(\text{CH}_3 + \text{CH}_3)$  reported.
- (b) As (a);  $k$  relative to  $k(\text{CH}_3 + \text{CH}_3) = 4.03 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .
- (c) Molecular modulation; UV absorption detection of  $\text{CH}_3$  at 216 nm in photolysis of acetone. First order rate constants (excess  $\text{HCHO}$ ) corrected for loss by  $\text{CH}_3 + \text{CH}_3\text{COCH}_3$  reaction, based on product analysis by gas chromatography. Choudhury *et al.*<sup>8</sup> have suggested that the values of  $k$  obtained are in error due to neglect of the effects of secondary chemistry and have modeled the system to derive values of  $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} = 6.8 \cdot 10^{-16}$  (500 K),  $9.6 \cdot 10^{-16}$  (532 K),  $1.08 \cdot 10^{-15}$  (547 K),  $1.40 \cdot 10^{-15}$  (603 K).
- (d) Shock tube study of decomposition of trioxane mixtures with kinetic modeling of observed CO formation. The expression:  $1.48 \cdot 10^{-36} T^{7.4} \exp(-483/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was calculated using transition state theory with quantum mechanical tunneling correction, which gave a good description of all reliable data in the temperature range 300–2000 K.
- (e) Based on data of Blake and Kutske<sup>9</sup> and Toby and Kutske<sup>10</sup> obtained from the pyrolysis of di-*t*-butylhydroperoxide and  $\text{CH}_3\text{NNCH}_3$ , respectively.
- (f) Based on data in Refs. 1–3 and the low temperature evaluation of Kerr and Parsonage.<sup>5</sup>
- (g) Least squares fit to data in Refs. 1–4.

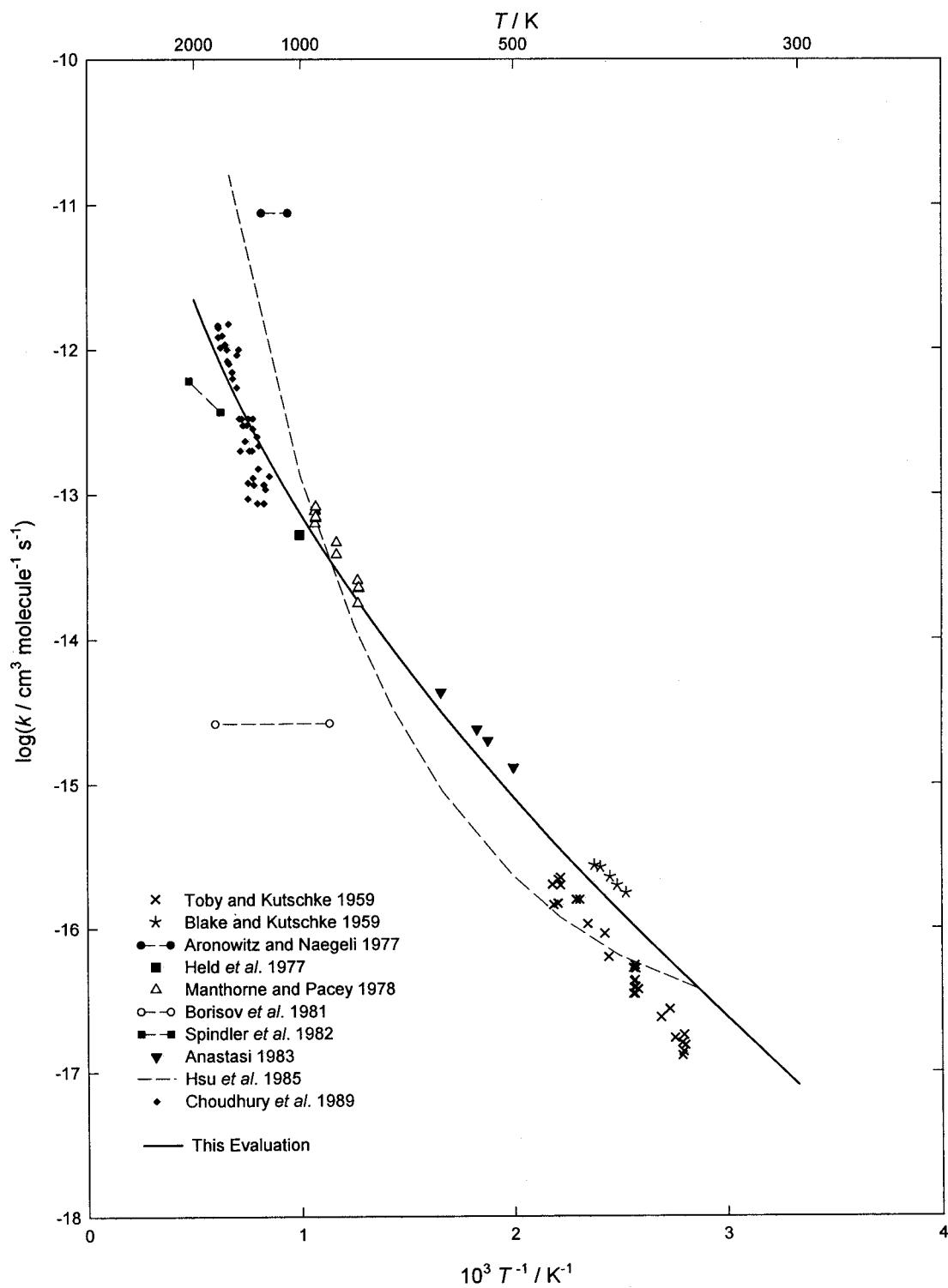
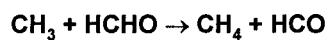
**Preferred Values**

$k = 5.3 \cdot 10^{-23} T^{3.36} \exp(-2170/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$   
over the range 300–2000 K.

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#### Thermodynamic Data

$$\Delta H^{\circ}_{298}(1) = -37.60 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298}(1) = 3.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_e(1) = 0.377 T^{0.085} \exp(+4530/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^{\circ}_{298}(2) = -2.60 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298}(2) = -18.32 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_e(2) = 3.84 \cdot 10^{-3} T^{0.442} \exp(+580/T) \\ (300 \leq T/\text{K} \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$7.3 \cdot 10^{-14} \exp(-4200/T)$	373–523	Phibbs and Darwent, 1950 <sup>1</sup>	(a)
$7.1 \cdot 10^{-14} \exp(-4150/T)$	376–492	Trotman-Dickenson and Steacie, 1951 <sup>2</sup>	(b)
$1.12 \cdot 10^{-13} \exp(-4370/T)$	415–499	Shannon and Harrison, 1963 <sup>3</sup>	(c)
$k_1 = 5.6 \cdot 10^{-13} \exp(-5340/T)$			
$k_2 = 1.38 \cdot 10^{-15} \exp(-2820/T)$			
$1.21 \cdot 10^{-13} \exp(-4230/T)$	395–518	Shaw and Thynne, 1966 <sup>4</sup>	(c)
$k_1 = 6.1 \cdot 10^{-14} \exp(-4100/T)$			
$k_2 = 7.3 \cdot 10^{-14} \exp(-4520/T)$			
$4.6 \cdot 10^{-13} \exp(-4940/T)$	313–523	Gray and Herod, 1968 <sup>5</sup>	(d)
$1.5 \cdot 10^{-11} \exp(-4940/T)$	1600–2100	Spindler and Wagner, 1982 <sup>6</sup>	(e)
$1.3 \cdot 10^{-11} \exp(-6330/T)$	525–603	Anastasi and Hancock, 1990 <sup>7</sup>	(f)
<i>Reviews and Evaluations</i>			
$k_1 = 3.3 \cdot 10^{-13} \exp(-5940/T)$	370–550	Kerr and Parsonage, 1976 <sup>8</sup>	(g)
$k_2 = 1.02 \cdot 10^{-13} \exp(-4880/T)$			
$k_1 = 5.3 \cdot 10^{-23} T^{3.17} \exp(-3609/T)$	300–2000	Tsang, 1987 <sup>9</sup>	(h)
$k_2 = 2.4 \cdot 10^{-23} T^{3.1} \exp(-3490/T)$			

#### Comments

- (a) Relative rate study. Photolysis of  $\text{Hg}(\text{CH}_3)_2$  in presence of  $\text{CH}_3\text{OH}$ .  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  yields determined by separation and volume measurement. Values of  $k/k_{\text{ref}}^{1/2}$ , where  $k_{\text{ref}} = k(\text{CH}_3 + \text{CH}_3)$ , have been used with values of  $k(\text{CH}_3 + \text{CH}_3)$  from this evaluation to obtain the expression cited in the table.
- (b) Relative rate study. Photolysis of  $\text{CH}_3\text{COCH}_3/\text{CH}_3\text{OH}$  mixtures. Products determined by mass spectrometry. The measured values of  $k/k_{\text{ref}}^{1/2}$ , where  $k_{\text{ref}} = k(\text{CH}_3 + \text{CH}_3)$ , have been used with values of  $k(\text{CH}_3 + \text{CH}_3)$  taken from the present evaluation to obtain the expression cited in the table.
- (c) Technique as in (b) with mass spectrometric analysis of products. Rate constants for individual channels derived from studies using deuterated methanols. Original data have been corrected, where possible, using more recent values of the reference rate constant,  $k(\text{CH}_3 + \text{CH}_3)$ , but there is insufficient information on the pressures used for full corrections.
- (d) Technique as in (c). The approximate expression  $k_1 = 5.3 \cdot 10^{-14} \exp(-4780/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was derived from studies using deuterated species.
- (e) Reflected shock waves passed through  $\text{CH}_3\text{OH}/\text{Ar}$  mixtures.  $[\text{CH}_3]$  and  $[\text{OH}]$  monitored by resonance ab-

sorption at 216 and 308 nm, respectively.  $k$  obtained by modeling the assumed mechanism and fitting the  $[\text{CH}_3]$  and  $[\text{OH}]$  profiles.

(f) Molecular modulation technique used in which  $\text{CH}_3\text{OH}$  was photolyzed at 254 nm and  $[\text{CH}_3]$  was monitored by absorption at 216 nm. Product yields were determined by gas chromatography.

(g) Based on the data from Refs. 1–5.

(h) Based on the evaluation of Kerr and Parsonage<sup>8</sup> together with a BEBO calculation.

#### Preferred Values

$k = 5.0 \cdot 10^{-23} T^{3.45} \exp(-4020/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 300–2000 K.

$k_1/k = 0.33$  over the range 300–525 K.

$k_2/k = 0.67$  over the range 300–525 K.

#### Reliability

$\Delta \log k = \pm 0.2$  at 300 K, rising to  $\pm 1.0$  at 2000 K.

$\Delta(k_1/k_2) = \Delta(k_2/k) = \pm 0.2$  over the range 300–525 K.

#### Comments on Preferred Values

There is reasonable agreement on the value for the overall rate constant among all of the studies<sup>1–5,7</sup> at temperatures

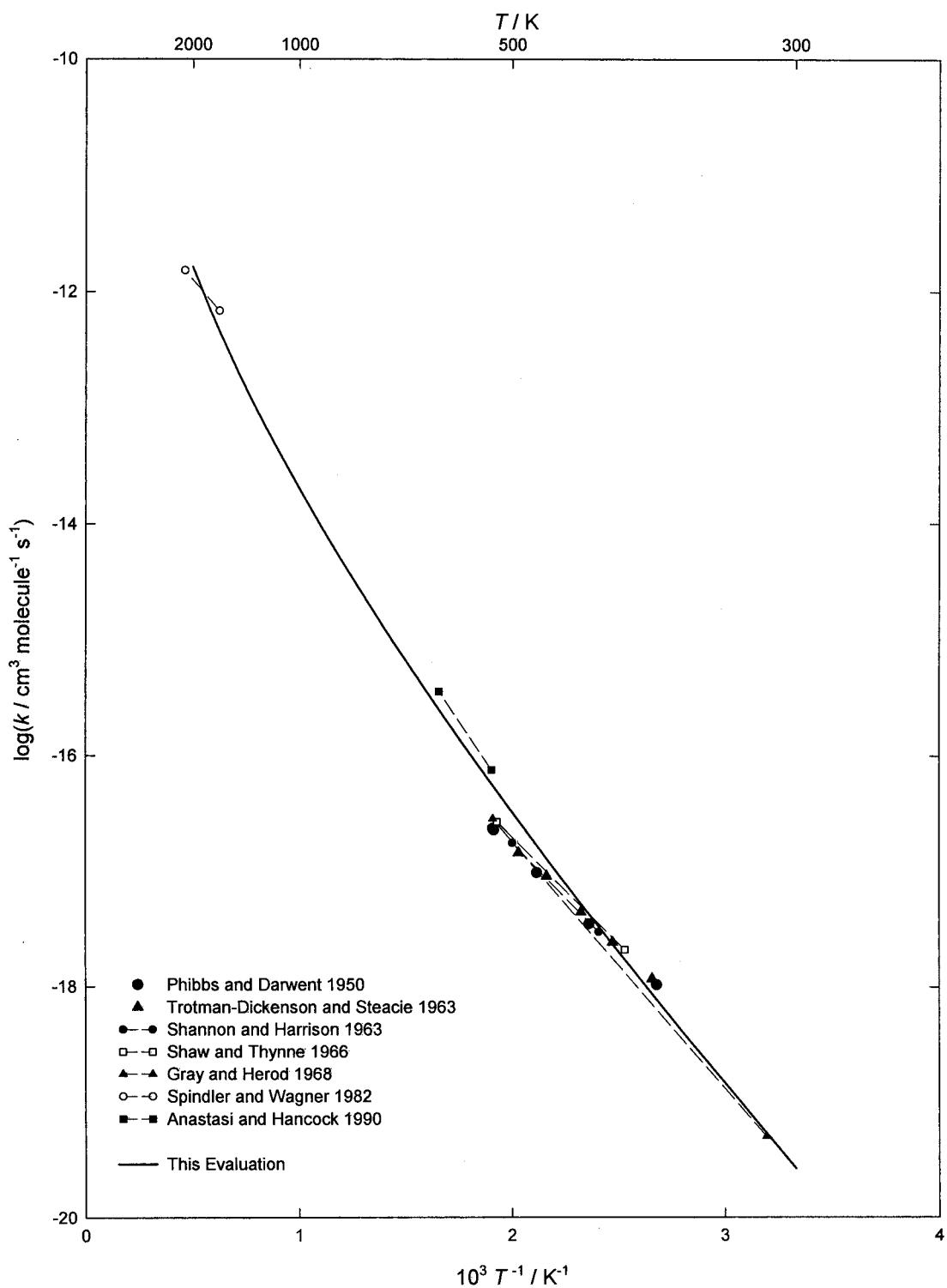
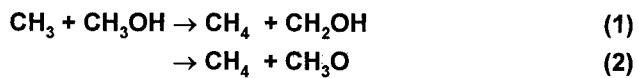
between 300 K and 600 K even though the Arrhenius expressions derived in the individual studies differ significantly. The preferred Arrhenius expression is compatible with the results from all of the low temperature studies and, in this temperature region gives values of  $k$  very similar to the expression derived by Kerr and Parsonage.<sup>8</sup>

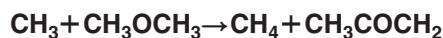
In the only study at combustion temperatures,<sup>6</sup> the rate constant determination was indirect and substantial error limits must be assigned. For the values of  $k$  from this high temperature study to be compatible with the low temperature studies requires curvature of the Arrhenius plot, which is to be expected since two reaction channels with different activation energies and temperature dependent pre-exponential factors are contributing to the overall reaction. Tsang<sup>9</sup> has used a BEBO calculation to characterize this curvature in his evaluation. In the present case the curvature has been incorporated empirically to fit the existing data but recognizing the sparsity of reliable data above 600 K large error limits are assigned at high temperatures.

The only experimental data on the individual reaction channels comes from relative rate studies in the temperature range 313–525 K making use of CH<sub>3</sub>OD and CD<sub>3</sub>OH. The results suggest that in this temperature range  $k_1/k_2 \approx 2$  but there is too much variability in the data to extrapolate to higher temperatures.

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*Thermodynamic Data*

$$\begin{aligned}\Delta H_{298}^{\circ} &= -37.3 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= 6.66 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 6.85 T^{-0.195} \exp(+4500/T) \\ (300 \leqslant T/\text{K} \leqslant 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$3.4 \cdot 10^{-13} \exp(-4680/T)$	381–471	Trotman-Dickenson and Steacie, 1951 <sup>1</sup>	(a)
$1.02 \cdot 10^{-12} \exp(-5100/T)$	473–573	Loucks, 1967 <sup>2</sup>	(b)
$7.3 \cdot 10^{-13} \exp(-5032/T)$	408–523	Gray and Herod, 1968; <sup>3</sup> Arthur, Gray, and Herod, 1969 <sup>4</sup>	(a)
$1.30 \cdot 10^{-11} \exp(-6586/T)$	783–935	Pacey, 1975 <sup>5</sup>	(c)
$2.21 \cdot 10^{-14}$	1005	Held <i>et al.</i> , 1977 <sup>6</sup>	(d)
$3.5 \cdot 10^{-13} \exp(-4781/T)$	373–473	Batt <i>et al.</i> , 1982 <sup>7</sup>	(e)
$1.3 \cdot 10^{-11} \exp(-6290/T)$	1305–1566	Hidaka, Sato, and Yamane, 2000 <sup>8</sup>	(f)
<i>Reviews and Evaluations</i>			
$6.9 \cdot 10^{-13} \exp(-5032/T)$	300–500	Kerr and Parsonage, 1976 <sup>9</sup>	(g)

**Comments**

- (a) Relative rate study. Photolysis of  $\text{CH}_3\text{COCH}_3/\text{CH}_3\text{OCH}_3$  mixtures. Product yields determined by mass spectrometry; values of  $k/k^{1/2}(\text{CH}_3 + \text{CH}_3)$  were derived. Values cited here are based on  $k(\text{CH}_3 + \text{CH}_3)$  from this evaluation.
- (b) Relative rate study. Hg photosensitized decomposition of  $\text{CH}_3\text{OCH}_3$  with product yields determined by classical analysis.  $k/k^{1/2}(\text{CH}_3 + \text{CH}_3)$  obtained from yields of  $\text{C}_2\text{H}_6$  and  $\text{CH}_4$ . Expression cited is derived from values of  $k(\text{CH}_3 + \text{CH}_3)$  from this evaluation. Values of  $k(\text{CH}_3\text{OCH}_2 + \text{M})/k(\text{CH}_3 + \text{CH}_3\text{OCH}_2)$  were also determined but are not used in this evaluation.
- (c) Relative rate study. Pyrolysis of  $\text{CH}_3\text{OCH}_3$  in flow system. Products analyzed by gas chromatography. Values of  $k/k^{1/2}(\text{CH}_3 + \text{CH}_3)$  were derived from product yields using a Rice-Herzfeld mechanism for the chain reaction. Expression for  $k$  cited is based on values of  $k(\text{CH}_3 + \text{CH}_3)$  from this evaluation.
- (d) Technique as in (c) but steady state concentration of  $\text{CH}_3$  also measured by light absorption in the 216 nm region.  $k$  derived by fitting product concentrations to a substantial reaction mechanism. The value tabulated has not been corrected to more recent values of the rate constants used in the simulation.
- (e) Relative rate study. Photolysis of  $(\text{CH}_3)_2\text{N}_2/\text{CH}_3\text{OCH}_3$  mixtures. Products analyzed by gas chromatography. Insufficient details are given to correct the rate constant values for changes in the reference rate constant  $k(\text{CH}_3 + \text{CH}_3)$  but such corrections should be small.
- (f) Shock tube study of pyrolysis of  $\text{CH}_3\text{OCH}_3/\text{Ar}$  mixtures. Three different shock tubes were used, one for

time resolved and single pulse studies with provision for GC analysis of products, the other two for time-resolved optical studies on reactants and products. Comparison of results from 2.0% and 4.0% mixtures showed that the rate of change of  $[\text{CH}_3\text{OCH}_3]$  and the  $[\text{CH}_4]$  were sensitive to  $k$ . Values of  $k$  were obtained by fitting the profiles of these quantities using a detailed mechanism.

- (g) Based on the data of Marcus *et al.*,<sup>10</sup> Trotman-Dickenson and Steacie,<sup>1</sup> Gray and Herod,<sup>3</sup> and Arthur, Gray, and Herod.<sup>4</sup>

**Preferred Values**

$$k = 1.0 \cdot 10^{-20} T^{2.68} \exp(-4190/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the range 300–1600 K.

**Reliability**

$$\Delta \log k = \pm 0.2 \text{ at } 300 \text{ K, rising to } \pm 0.4 \text{ at } 1600 \text{ K.}$$

**Comments on Preferred Values**

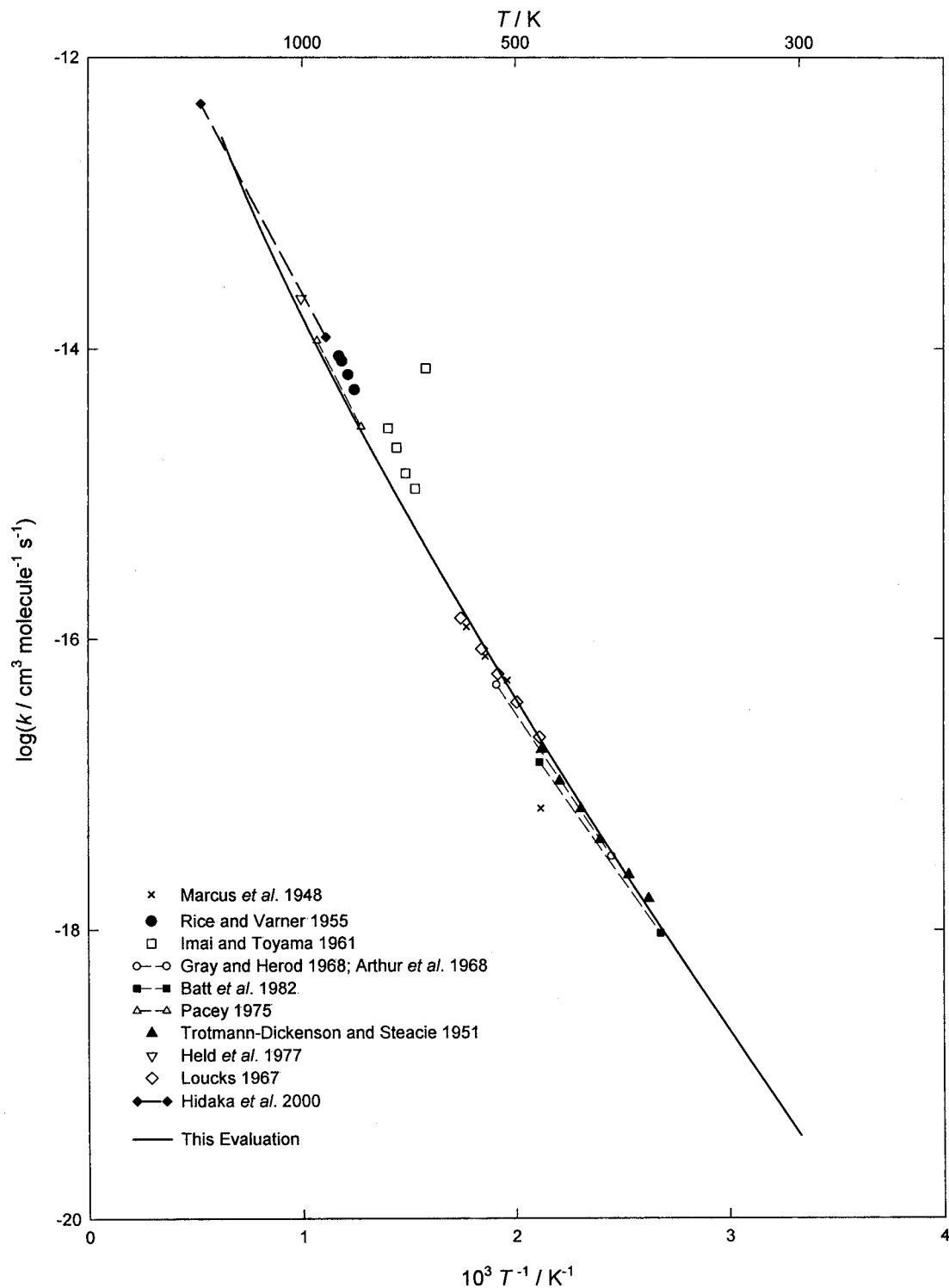
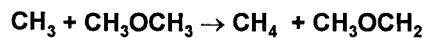
Most of the data on this reaction come from relative rate studies. At temperatures below 600 K they are, in general, in good agreement. These studies have been reviewed by Kerr and Parsonage<sup>9</sup> whose analysis we accept. Some of the older studies,<sup>10,11</sup> or studies where there is lack of information leading to uncertainties in the value of the reference rate constant, have not been used in arriving at the preferred expression but, nevertheless, they are in reasonable agreement with it.

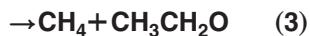
At higher temperatures the preferred expression is based on the shock tube study of Hidaka *et al.*<sup>8</sup> and the pyrolysis studies of Held *et al.*<sup>6</sup> and of Pacey<sup>5</sup> all of which are in good

agreement. Pacey's analysis of his product yields was based on a relatively simple mechanism, but Held *et al.*<sup>6</sup> used a more substantial mechanism and computer modeling to fit the product yields, as did Hidaka *et al.*<sup>8</sup> Results from the older studies of Rice and Varnerin<sup>12</sup> and of Imai and Toyama,<sup>13</sup> when reanalyzed, as far as is possible, using more recent values of the reference rate constants, also give results which are compatible with the preferred expression.

## References

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#### Thermodynamic Data

$$\Delta H^{\circ}_{298}(1) = -37.9 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298}(1) = -7.61 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 5.1 T^{-0.42} \exp(+4540/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^{\circ}_{298}(2) = -22.4 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298}(2) = -13.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 8.2 \cdot 10^{-4} T^{0.81} \exp(+2950/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^{\circ}_{298}(3) = -1.6 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298}(3) = -14.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 4.1 \cdot 10^{-2} T^{-0.15} \exp(+420/T) \\ (300 \leq T/\text{K} \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2 + k_3$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$1.5 \cdot 10^{-12} \exp(-4930/T)$	462–614	Trotman-Dickenson and Steacie, 1951 <sup>1</sup>	(a)
$9.9 \cdot 10^{-13} \exp(-4880/T)$	403–523	Gray and Herod, 1968 <sup>2</sup>	(b)
$k_1 = 7.8 \cdot 10^{-13} \exp(-4880/T)$			
$k_3 = 1.5 \cdot 10^{-13} \exp(-4730/T)$			
<i>Reviews and Evaluations</i>			
$8.5 \cdot 10^{-13} \exp(-4880/T)$	400–625	Kerr and Parsonage, 1976 <sup>3</sup>	(c)
$k_1 = 6.6 \cdot 10^{-13} \exp(-4880/T)$			
$k_3 = 1.3 \cdot 10^{-13} \exp(-4730/T)$			
$k_1 = 1.21 \cdot 10^{-21} T^{2.99} \exp(-4000/T)$	300–2500	Marinov, 1999 <sup>4</sup>	(d)
$k_2 = 3.63 \cdot 10^{-22} T^{3.18} \exp(-4842/T)$			
$k_3 = 2.41 \cdot 10^{-22} T^{2.99} \exp(-3850/T)$			

#### Comments

- (a) Relative rate study. Photolysis of  $\text{CH}_3\text{COCH}_3/\text{C}_2\text{H}_5\text{OH}$  mixtures with products determined by mass spectrometry. Values of  $k/k_{\text{ref}}^{1/2}$  which were obtained, where  $k_{\text{ref}} = k(\text{CH}_3 + \text{CH}_3)$ , have been combined with values of  $k(\text{CH}_3 + \text{CH}_3)$  taken from the present evaluation to obtain the expression in the table.
- (b) Technique as in (a). Rate constants for individual channels were derived from studies on deuterated ethanol. The original data have been corrected, where possible, using more recent values of the reference rate constant,  $k(\text{CH}_3 + \text{CH}_3)$ , but there is insufficient information on the pressures used for a full correction.
- (c) The results of Gray and Herod<sup>2</sup> are accepted. The difference between the values recommended by Kerr and Parsonage<sup>3</sup> and the cited expression of Gray and Herod is due to different values of  $k(\text{CH}_3 + \text{CH}_3)$  being used.
- (d) Estimated expressions. A  $T^{3.3}$  dependence was applied to the data of Gray and Herod<sup>2</sup> to obtain an expression for  $k$  for extrapolation to higher temperatures and the branching ratios were also based on the data of Gray and Herod.<sup>2</sup>

#### Preferred Values

$k = 9.9 \cdot 10^{-13} \exp(-4880/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 400–700 K.

$k_1 = 7.8 \cdot 10^{-13} \exp(-4880/T) \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$  over the temperature range 400–700 K.

$k_2 = 6 \cdot 10^{-14} \exp(-4880/T) \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$  over the temperature range 400–700 K.

$k_3 = 1.5 \cdot 10^{-13} \exp(-4730/T) \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$  over the temperature range 400–700 K.

#### Reliability

$\Delta \log k = \Delta \log k_1 = \Delta \log k_3 = \pm 0.2$  at 400 K, rising to  $\pm 0.3$  at 700 K.

$\Delta \log k_2 = \pm 0.3$  at 400 K, rising to  $\pm 0.5$  at 700 K.

#### Comments on Preferred Values

There is good agreement between the studies of Trotman-Dickenson and Steacie<sup>1</sup> and of Gray and Herod.<sup>2</sup> The expressions derived from the latter study<sup>2</sup> are taken as the preferred values, in agreement with the evaluation of Kerr and Parsonage<sup>3</sup> who point out that, unlike Trotman-Dickenson and Steacie,<sup>1</sup> Gray and Herod<sup>2</sup> took account of effects of

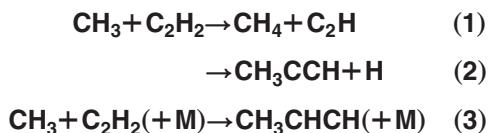
isotopic exchange in their study. There is also a value of  $k$  at 423 K determined by Bansal and Freeman<sup>5</sup> from radiolysis of ethanol in the presence of propene. The chemistry in such a system is complex, the value of  $k$  derived is approximately a factor of 5 lower than the value from the other studies,<sup>1,2</sup> and is not used in this evaluation.

The only measurements of the branching ratios are those of Gray and Herod.<sup>2</sup> Their expressions for  $k_1$  and  $k_3$  are adopted as preferred values. In their study, values of  $k_2$  could only be derived from the difference between  $k$  and  $k_1 + k_3$  which, because the difference is small compared with the error limits on  $k$ ,  $k_1$ , and  $k_3$ , gave, therefore, only approximate values of  $k_2$ . However they state that at 423 K,  $k_1:k_2:k_3 \approx 0.75:0.05:0.15$  and the expression for  $k_2$  is an estimate based on these branching ratios. The expressions derived by Marinov<sup>4</sup> agree reasonably well with our preferred expressions over the recommended temperature range but, although Marinov<sup>4</sup> has shown that his expressions are

compatible with data from a  $\text{C}_2\text{H}_5\text{OH}$  pyrolysis study of Borisov *et al.*<sup>6</sup> at 950 K, the temperature dependence used is very uncertain and very substantial error limits should be considered in using the Marinov<sup>4</sup> expressions at high temperatures.

## References

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### Thermodynamic Data

$$\Delta H_{298}^{\circ}(1) = 116.6 \text{ kJ mol}^{-1}$$

$$\Delta S_{298}^{\circ}(1) = 4.48 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 9.52 T^{-0.309} \exp(-13990/T) \quad (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H_{298}^{\circ}(2) = 28.3 \text{ kJ mol}^{-1}$$

$$\Delta S_{298}^{\circ}(2) = -31.97 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 3.51 \cdot 10^{-5} T^{-0.90} \exp(-3010/T) \quad (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H_{298}^{\circ}(3) = -111.9 \text{ kJ mol}^{-1}$$

$$\Delta S_{298}^{\circ}(3) = -123.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 2.40 \cdot 10^{-29} T^{0.927} \exp(+13830/T) \text{ cm}^3 \text{ molecule}^{-1} \quad (300 \leq T/\text{K} \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

### Rate Coefficient Data ( $k = k_1 + k_2 + k_3$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$k_3 = 1.3 \cdot 10^{-13} \exp(-2760/T)$	417–514	Mandelcorn and Steacie, 1954 <sup>1</sup>	(a)
$k_3 = 4.2 \cdot 10^{-13} \exp(-3900/T)$	371–479	Garcia-Dominguez and Trotman-Dickenson, 1962 <sup>2</sup>	(b)
$k_3 = 1.0 \cdot 10^{-12} \exp(-3900/T)$	379–487	Holt and Kerr, 1977 <sup>3</sup>	(c)
$k_2 = 1.0 \cdot 10^{-11} \exp(-8554/T)$	1400–2200	Hidaka <i>et al.</i> , 1990 <sup>5</sup>	(d)
$k_3 = 2.5 \cdot 10^{-13} \exp(-3490/T)$	371–479	Diau and Lin, 1995 <sup>4</sup>	(e)
<i>Reviews and Evaluations</i>			
$k_3 = 1 \cdot 10^{-12} \exp(-3900/T)$	300–600	CEC, 1992; 1994 <sup>6</sup>	(f)

### Comments

- (a) Steady-state photolysis of  $(\text{CH}_3)_2\text{CO}$  in the presence of  $\text{C}_2\text{H}_2$  at total pressures of 40–75 mbar. End product analysis for  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ , and  $\text{CO}$ .  $k_1$  derived from a kinetic analysis based on a mass balance, and calculated relative to  $k(\text{CH}_3 + \text{CH}_3) = 3.6 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , independent of temperature.

- (b) Steady-state photolysis of  $\text{CH}_3\text{CHO}$  in the presence of  $\text{C}_2\text{H}_2$  at total pressures of 40–120 mbar. End-product analysis of adduct products and radical dimer.  $k_1$  derived from rate of formation of adduct and calculated relative to  $k(\text{CH}_3 + \text{CH}_3) = 3.6 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , independent of temperature.
- (c) Steady-state photolysis of  $(\text{CH}_3\text{CO})_2$  in the presence of  $\text{C}_2\text{H}_2$  and  $i\text{-C}_4\text{H}_{10}$  at a total pressure of 930 mbar.

End-product analysis for CH<sub>4</sub> and CO.  $k_1$  derived from a kinetic analysis based on a mass balance and calculated relative to the value  $k(\text{CH}_3 + i\text{-C}_4\text{H}_{10}) = 1.38 \cdot 10^{-13} \exp(-4030/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

- (d) Single pulse shock-tube pyrolysis of 2%–5% CH<sub>4</sub> in Ar (2.3–3.7 bar) with GC analysis of products, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, and C<sub>4</sub>H<sub>2</sub>.  $k_2$  derived from computer modeling of the CH<sub>3</sub>C≡CH production.
- (e) Recalculation of data of Ref. 2 based on kinetic modeling with sensitivity analyses. Arrhenius equation cited in the Table calculated here from revised values of  $k_3$  given in Ref. 4.
- (f) Based on data of Holt and Kerr.<sup>3</sup>

### Preferred Values

$$k_3 = 1.0 \cdot 10^{-12} \exp(-3900/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad \text{over the range } 300\text{--}600 \text{ K at a pressure of 1 bar.}$$

See Comments on Preferred Values for information on the other channels.

### Reliability

$$\Delta \log k_3 = \pm 0.5 \text{ over the range } 300\text{--}600 \text{ K.}$$

### Comments on Preferred Values

Diau and Lin<sup>4</sup> have reanalyzed the experimental data of Refs. 1–3 based on kinetic modeling with sensitivity analyses. The kinetically modeled results indicate that the values of  $k_3$  derived by Mandelcorn and Steacie<sup>1</sup> have been overestimated whereas those of Garcia-Dominguez and Trotman-Dickenson<sup>2</sup> have been underestimated. The reanalysed<sup>4</sup> values of  $k_3$  from the experimental data of Garcia-Dominguez and Trotman-Dickenson<sup>2</sup> yield the Arrhenius expression listed above. The reanalyses of Diau and Lin<sup>4</sup> also reveals that there could be significant uncertainty in the data of Holt and Kerr,<sup>3</sup> owing to the nature of the kinetic analysis and the greater sensitivity of the values of  $k_3$  to the rate of the photolytic formation of the CH<sub>3</sub> radicals than to the rate of reaction (3).

A theoretical study of the CH<sub>3</sub>+C<sub>2</sub>H<sub>2</sub> reaction has been carried out by Diau, Lin, and Melius,<sup>7</sup> involving multichannel RRKM calculations based on the molecular and transition-state parameters predicted by the BAC-MP4 method. The results of this study show that the values of  $k_3$  are markedly pressure dependent within the pressure regions of the experiments of Refs. 1–3. Thus the values of  $k_3$  of Holt and Kerr<sup>3</sup> (930 mbar) lie considerably closer to the high-pressure limits than those of Garcia-Dominguez and Trotman-Dickenson<sup>2</sup> (40–120 mbar).

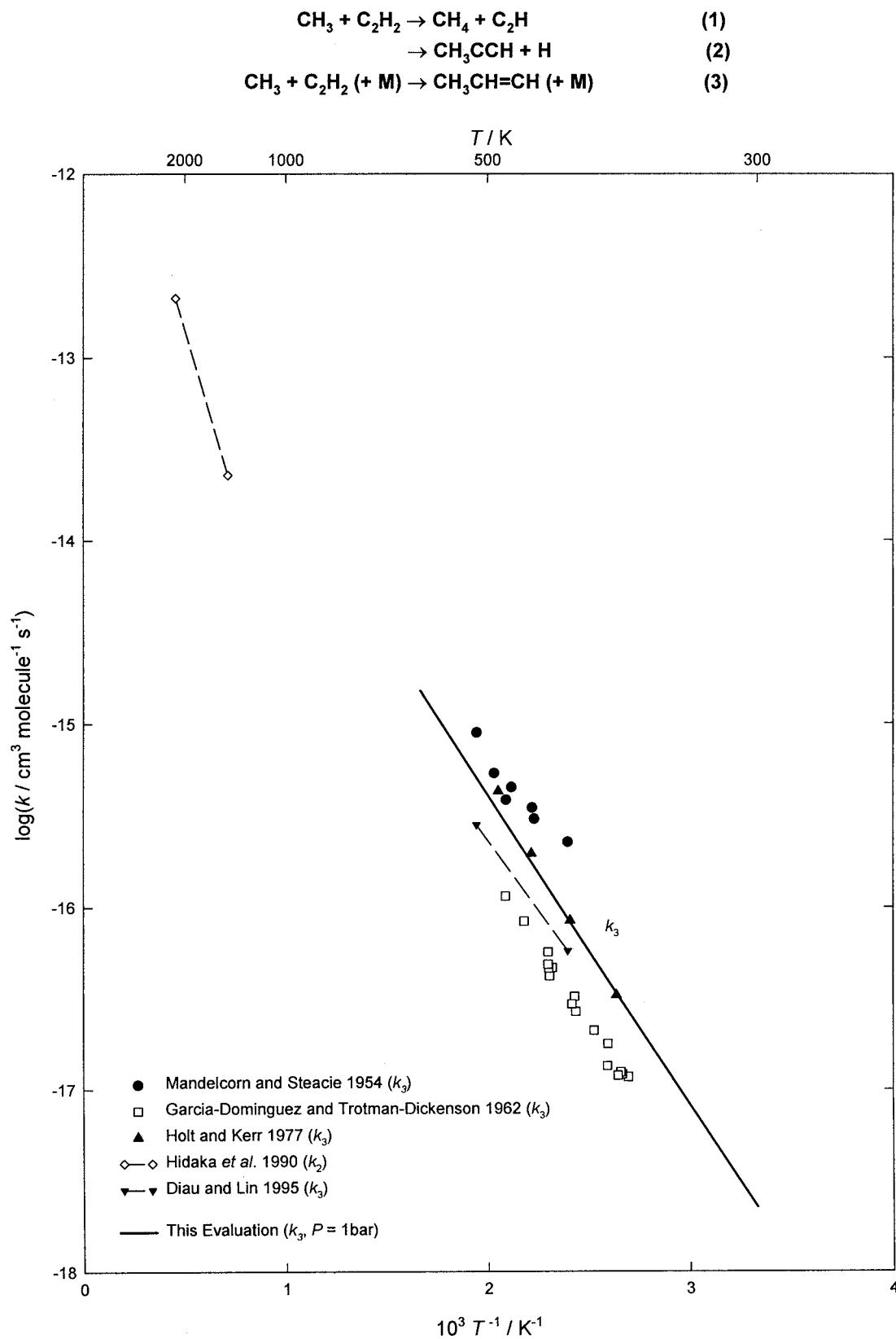
On the basis of the pressure effect upon  $k_3$  we continue to recommend the data of Holt and Kerr<sup>3</sup> but with large error limits to allow for the uncertainties in the interpretation of the measurements. Use of the preferred rate equation at temperatures above 600 K could involve uncertainty limits of  $\Delta \log k_3 = \pm 1.0$ .

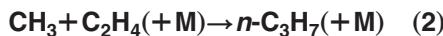
There are still no published data on the rate coefficient  $k_1$  but in view of the endothermicity of Channel (1), it is expected to be a considerably slower channel than (3). We estimate a value of  $k_1 < 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 600 K, based on  $\Delta H^\circ(1) = 117 \text{ kJ mol}^{-1}$  and an assumed value of  $A_1 < 1 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

We are unable to make a recommendation for  $k_2$ . The results of Hidaka *et al.*<sup>5</sup> are indirect and are incompatible with the thermodynamics and an estimate of  $k_{-2}^\infty \approx 1.0 \cdot 10^{-11} \exp(-1300/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , based on data<sup>8</sup> for the analogous reaction H+CHCH→products.

### References

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- <sup>4</sup>E. W. Diau and M. C. Lin, Int. J. Chem. Kinet. **27**, 855 (1995).
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- <sup>6</sup>CEC, 1992; Supplement I, 1994 (see references in Introduction).
- <sup>7</sup>E. W. Diau, M. C. Lin, and C. F. Melius, J. Chem. Phys. **101**, 3923 (1994).
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*Thermodynamic Data*

$$\begin{aligned}\Delta H_{298}^{\circ}(1) &= 26.0 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ}(1) &= 6.88 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 2.01 T^{-0.005} \exp(-3070/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

$$\begin{aligned}\Delta H_{298}^{\circ}(2) &= -98.4 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ}(2) &= -123.7 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 2.00 \cdot 10^{-31} T^{1.703} \exp(+12300/T) \text{ cm}^3 \text{ molecule}^{-1} \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data ( $k = k_1 + k_2$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$k_1 = 1.7 \cdot 10^{-15}$	1038	Chen, Back, and Back, 1976 <sup>1</sup>	(a)
$k_2 = 3.5 \cdot 10^{-13} \exp(-3700/T)$	305–503	Holt and Kerr, 1977 <sup>2</sup>	(b)
$k_1 = 8.3 \cdot 10^{-12} \exp(-6540/T)$	1950–2770	Tabayashi and Bauer, 1979 <sup>3</sup>	(c)
$k_1 = 1.2 \cdot 10^{-11} \exp(-9030/T)$	673–733	Ahonkhai and Back, 1988 <sup>4</sup>	(d)
$k_1 = 1.0 \cdot 10^{-12} \exp(-8030/T)$	673–766	Ahonkhai, Lin, and Back, 1989 <sup>5</sup>	(e)
$k_1 = 1.3 \cdot 10^{-12} \exp(-8630/T)$	673–766		(e)
$k_1 = 4.5 \cdot 10^{-13} \exp(-6980/T)$	650–770	Zhang and Back, 1990 <sup>6</sup>	(f)
<i>Reviews and Evaluations</i>			
$k_1 = 6.9 \cdot 10^{-12} \exp(-5600/T)$	400–3000	CEC, 1992; 1994 <sup>7</sup>	(g)
$k_2 = 3.5 \cdot 10^{-13} \exp(-3700/T)$	300–600		(h)

**Comments**

- (a) Pyrolysis of  $\text{CH}_4$  in static reaction vessel with end-product analysis by GC. Value of  $k_1$  derived from measured ratio  $k_3 K_2 / k_1$  (obtained from yields of propene and acetylene) where  $k_3$  refers to the reaction  $n\text{-C}_3\text{H}_7 \rightarrow \text{C}_3\text{H}_6 + \text{H}$  (3) and  $K_2$  to the equilibrium  $\text{CH}_3 + \text{C}_2\text{H}_4 \rightleftharpoons n\text{-C}_3\text{H}_7$  (2).
- (b) Steady-state photolysis of  $(\text{CH}_3\text{CO})_2$  in the presence of  $\text{C}_2\text{H}_4$  and  $i\text{-C}_4\text{H}_{10}$  with end-product analysis for  $\text{CH}_4$  and CO.  $k_2$  derived from a kinetic analysis based on a mass balance and calculated relative to  $k(\text{CH}_3 + i\text{-C}_4\text{H}_{10}) = 1.38 \cdot 10^{-13} \exp(-4030/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Data incorporated into an updated evaluation of previous data considered by Kerr and Parsonage,<sup>9</sup> to yield the above equation.
- (c) Shock-tube study of the early stages of the pyrolysis of  $\text{CH}_4$ . Rate expression derived from a computer fit of observed density gradients, based on a mechanism of twelve elementary reactions.
- (d) Pyrolysis of  $\text{C}_2\text{H}_4$  in a static reaction vessel with end-product analysis by GC.  $k(\text{CH}_3 + \text{C}_2\text{H}_6)/k_1 = 1.0 \exp(+9030/T)$  derived from a study of the effect of small quantities of  $\text{C}_2\text{H}_6$  on the rates of formation of the  $\text{CH}_4$  product. Above value of  $k_1$  derived from  $k(\text{CH}_3 + \text{C}_2\text{H}_6) = 1.16 \cdot 10^{-11} \exp(-7270/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 673–733 K (this evaluation).
- (e) Similar study to that described in comment (d) but with  $\text{C}_3\text{H}_8$  or  $i\text{-C}_4\text{H}_8$  instead of  $\text{C}_2\text{H}_6$  as the reference compound. Values of  $k(\text{CH}_3 + \text{C}_3\text{H}_8)/k_1 = 0.32$

$\times \exp(+1610/T)$  and  $k(\text{CH}_3 + i\text{-C}_4\text{H}_{10})/k_1 = 0.11 \times \exp(+2315/T)$  were obtained from the rates of formation of  $\text{CH}_4$ . Cited values of  $k_1$  based on  $k(\text{CH}_3 + \text{C}_3\text{H}_8) = 3.3 \cdot 10^{-13} \exp(-4830/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k(\text{CH}_3 + i\text{-C}_4\text{H}_{10}) = 1.4 \times 10^{-13} \times \exp(-4030/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Ref. 8).

- (f) Similar study to that described in comment (d) but with  $\text{H}_2$  instead of  $\text{C}_2\text{H}_6$  as the reference compound. A value of  $k(\text{CH}_3 + \text{H}_2)/k_1 = 20 \exp(+4811/T)$  was derived from the rates of formation of  $\text{CH}_4$ . The cited value of  $k_1$  is based on  $k(\text{CH}_3 + \text{H}_2) = 1.8 \cdot 10^{-21} T^{2.83} \exp(-4060/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 650–770 K (this evaluation).
- (g) Evaluation of Kerr and Parsonage,<sup>8</sup> based on the date of Trotman-Dickenson and Steacie<sup>14</sup> and Tabayashi and Bauer.<sup>3</sup>
- (h) Evaluation of Holt and Kerr<sup>2</sup> which updates Kerr and Parsonage<sup>8</sup> based on data of Brinton,<sup>10</sup> Hogg and Kebarle,<sup>11</sup> Endrenyi and LeRoy,<sup>12</sup> and Cveticanovic and Irwin.<sup>13</sup>

**Preferred Values**

$k_1 = 1.0 \cdot 10^{-16} T^{1.56} \exp(-8370/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 650–2800 K.

$k_2 = 3.5 \cdot 10^{-13} \exp(-3700/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 300–600 K.

**Reliability**

$\Delta \log k_1 = \pm 0.5$  over the range 650–2800 K.

$\Delta \log k_2 = \pm 0.3$  over the range 300–600 K.

#### Comments on Preferred Values

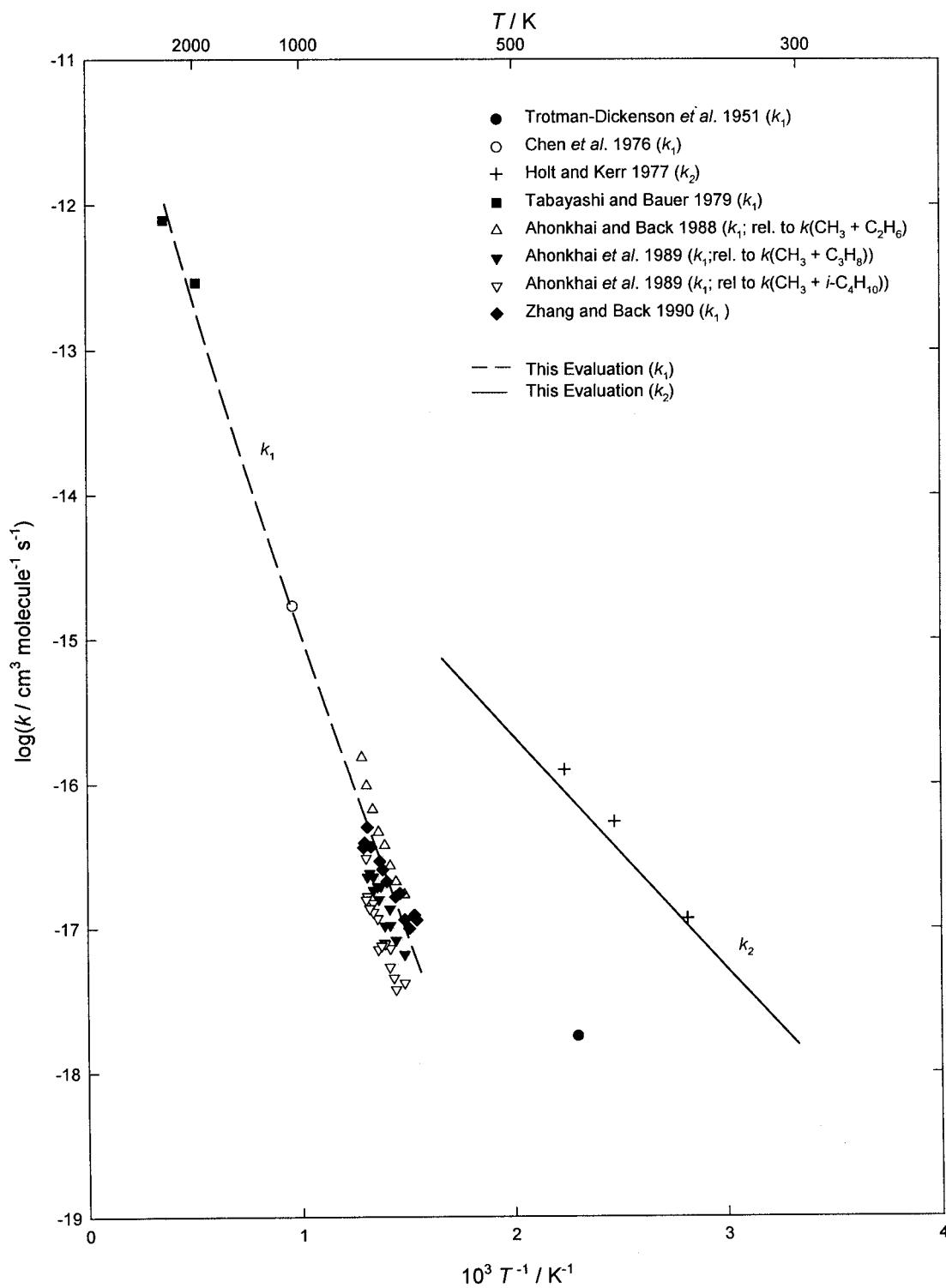
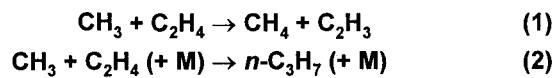
The preferred value of  $k_1$  has been altered from our previous evaluation<sup>7</sup> to take account of the relative rate studies of Ahonkhai and Back,<sup>4</sup> Ahonkhai *et al.*,<sup>5</sup> and Zhang and Back,<sup>6</sup> which indicate that the earlier value of  $k_1$  by Trotman-Dickenson and Steacie<sup>14</sup> is seriously overestimated. As seen from the Figure the values of  $k_1$  derived by the Back group<sup>4–6</sup> are not in good agreement and this probably arises from the uncertainties in the rate coefficients of some of the reference reactions. The present recommendation of  $k_1$  is based on the relative rate studies<sup>4,6</sup> involving the  $\text{CH}_3 + \text{H}_2$  and  $\text{CH}_3 + \text{C}_2\text{H}_6$  reactions for which the rate coefficients are reasonably well defined. These values of  $k_1$ , in conjunction with the higher temperature studies of Tabayashi and Bauer<sup>3</sup> and Chen, Back, and Back,<sup>1</sup> indicate some slight curvature in the Arrhenius plot of  $k_1$ .

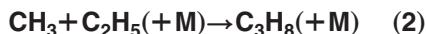
The recommended value of  $k_2$  is unchanged from our previous evaluation,<sup>7</sup> and is based on the study of Kerr and

Holt<sup>2</sup> which includes an update of the evaluation of Kerr and Parsonage<sup>9</sup> based on several earlier studies.<sup>10–13</sup>

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- <sup>2</sup>P. M. Holt and J. A. Kerr, Int. J. Chem. Kinet. **9**, 185 (1977).
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- <sup>4</sup>S. I. Ahonkhai and M. H. Back, Can. J. Chem. **66**, 578 (1988).
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- <sup>11</sup>A. M. Hogg and P. Kebarle, J. Am. Chem. Soc. **86**, 4558 (1964).
- <sup>12</sup>L. Endrenyi and D. J. LeRoy, J. Phys. Chem. **71**, 1334 (1967).
- <sup>13</sup>R. J. Cvetanovic and R. S. Irwin, J. Chem. Phys. **46**, 1694 (1967).
- <sup>14</sup>A. F. Trotman-Dickenson and E. W. R. Steacie, J. Chem. Phys. **19**, 169 (1951).





#### Thermodynamic Data

$$\begin{aligned}\Delta H_{298}^{\circ}(1) &= -289.7 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ}(1) &= -35.8 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 1.13 \cdot 10^{-2} T^{-0.067} \exp(+35040/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

$$\begin{aligned}\Delta H_{298}^{\circ}(2) &= -372.0 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ}(2) &= -170.9 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 1.53 \cdot 10^{-34} T^{1.869} \exp(+45390/T) \text{ cm}^3 \text{ molecule}^{-1} \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	[M]/molecule cm $^{-3}$	Reference	Comments
<i>Rate Coefficient Measurements</i>				
<i>High Pressure Range</i>				
$4.73 \cdot 10^{-11}$	308	$(4.7-21.9) \cdot 10^{18} (\text{N}_2)$	Anastasi and Arthur, 1987 <sup>1</sup>	(a)
$9.3 \cdot 10^{-11}$	300	$1.2 \cdot 10^{17} (\text{Ar})$	Garland and Bayes, 1990 <sup>2</sup>	(b)
$6.6 \cdot 10^{-11}$	298	$2.4 \cdot 10^{18} (\text{H}_2)$	Sillesen, Ratajczak, and Pagsberg 1993 <sup>3</sup>	(c)
<i>Reviews and Evaluations</i>				
$k_2^{\infty} = 4.7 \cdot 10^{-11} (T/300)^{-0.5}$	300–2500		Tsang and Hampson, 1986 <sup>4</sup>	(d)
$k_2^{\infty} = 3 \cdot 2 \cdot 10^{-10} T^{-0.32}$	300–2500		Tsang, 1989 <sup>5</sup>	(e)
$k_2^{\infty} = 5.6 \cdot 10^{-11}$	300–2000		CEC, 1994 <sup>6</sup>	(f)

#### Comments

- (a) Molecular modulation spectroscopy with  $\text{CH}_3$  and  $\text{C}_2\text{H}_5$  produced from the photolyses of the corresponding azo compounds at 350 nm.  $[\text{CH}_3]$  and  $[\text{C}_2\text{H}_5]$  were monitored by UV absorption. Values of  $k$  were obtained from a computer simulation of the concentration profiles.
- (b) Cophotolysis of acetone (1.3–46 mbar) and 3-pentanone (6.6 mbar).  $[\text{CH}_3]$  and  $[\text{C}_2\text{H}_5]$  decays monitored by photoionization mass spectrometry; radicals were ionized using lines at 121.6 and 147 nm. Concentration profiles of the two radicals were simulated by computer modeling to obtain values of  $k$ . The rate coefficients were assumed to be at the high pressure limit.
- (c) Pulse radiolysis of  $\text{H}_2/\text{C}_2\text{H}_4$  mixtures.  $[\text{CH}_3]$  monitored by IR absorption at the  $Q(3,3)$  line of the  $\nu_2 = 0 \rightarrow 1$  vibrational transition at  $602.12 \text{ cm}^{-1}$ . Values of  $k$  were derived using an 11-reaction mechanism. A value of  $k_1/(k_1+k_2)=0.5$  was estimated by gas-chromatographic analysis.
- (d) Derived from the rate coefficients of  $\text{CH}_3$  and  $\text{C}_2\text{H}_5$  self-combination and the geometric mean rule for the radical-radical cross combination ratio.
- (e) Derived from the results of Parkes and Quinn<sup>7</sup> for the  $\text{C}_2\text{H}_5$  self-recombination over the range 300–800 K and the geometric mean rule of cross-combination ratios.
- (f) Based on a weighted average of the experimental results of Anastasi and Arthur<sup>1</sup> and Garland and Bayes,<sup>2</sup>

and the values derived by Tsang and Hampson<sup>4</sup> and Tsang.<sup>5</sup> The recommended value is in agreement with the value from SACM calculations.<sup>8</sup>

#### Preferred Values

$k_1 = 1.5 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 300–2000 K.

$k_2^{\infty} = 6.1 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 300–2000 K.

#### Reliability

$\Delta \log k_1 = \pm 0.4$  at 300 K, rising to  $\pm 0.7$  at 2000 K.

$\Delta \log k_2^{\infty} = \pm 0.3$  over the range 300–2000 K.

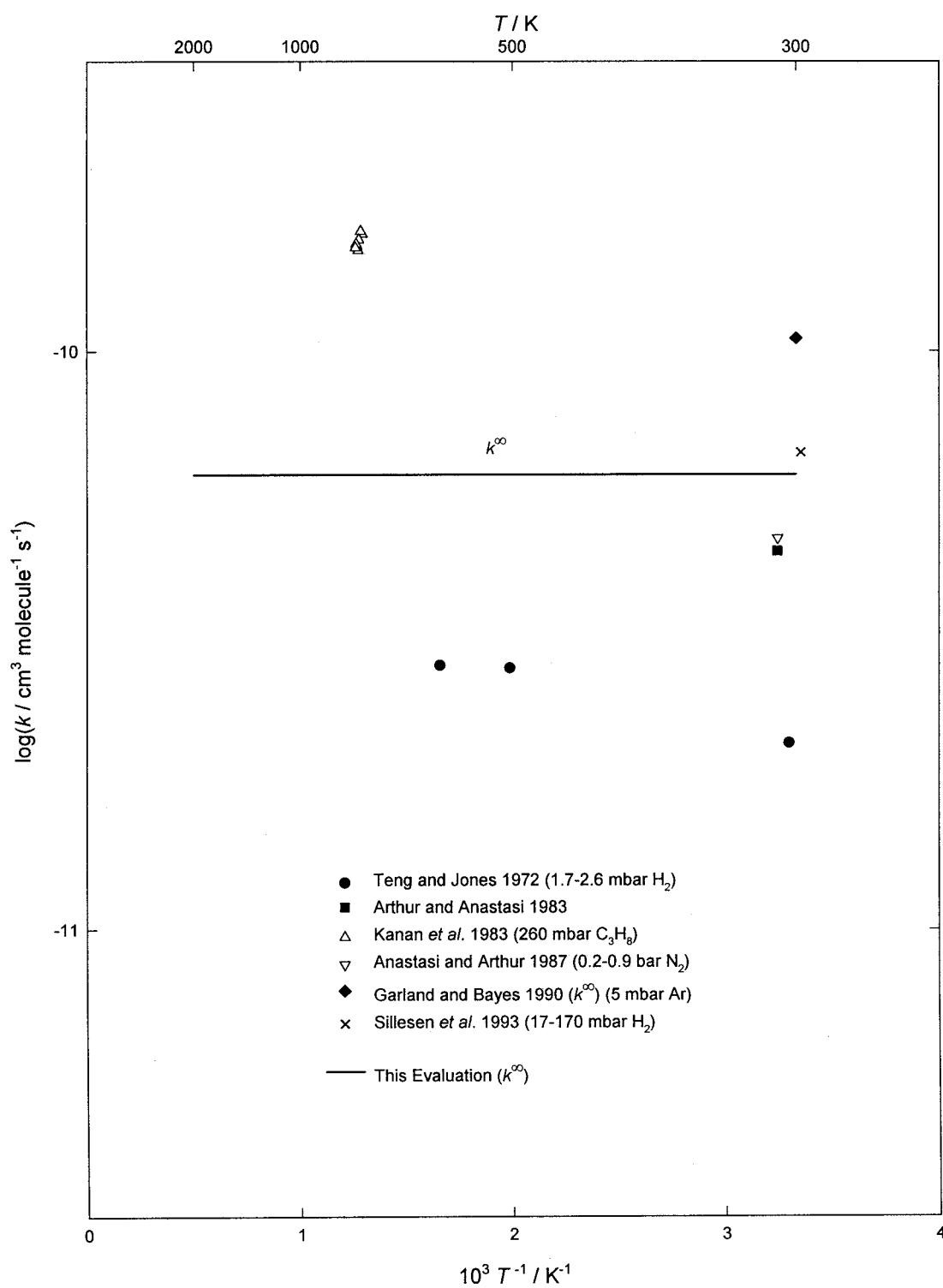
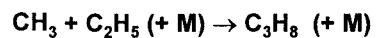
#### Comments on Preferred Values

The recommended value of  $k_2^{\infty}$  is an average of the data of Anastasi and Arthur,<sup>1</sup> Garland and Bayes,<sup>2</sup> and Sillesen et al.,<sup>3</sup> together with the values found by Tsang and Hampson<sup>4</sup> and by Tsang<sup>5</sup> by applying the geometric mean rule for radical-radical cross combination reactions. There are a number of high temperature studies,<sup>9–12</sup> all of them rather indirect, which are not used in deriving the preferred values, and a number at lower temperatures<sup>13–16</sup> in reasonable agreement with the preferred values. The recommended values are in agreement with SACM calculations<sup>8</sup> which give  $k_2^{\infty} = 5.6 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . A temperature independent value of  $k_2^{\infty}$  is assumed until more definitive experimental information is available. At 300 K the branching ratio  $k_1/k_2=0.04$ , which is in keeping with other disproportionation/combination ratios, has been

recommended.<sup>4,17</sup> This ratio,  $k_1/k_2$ , is not expected to be appreciably temperature dependent and forms the basis of our preferred value for  $k_2$ .

## References

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*Thermodynamic Data*

$$\Delta H_{298}^{\circ} = 372.0 \text{ kJ mol}^{-1}$$

$$\Delta S_{298}^{\circ} = 170.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c = 6.5 \cdot 10^{33} T^{-1.869} \exp(-45390/T) \text{ molecule cm}^{-3}$$

(300 ≤ T/K ≤ 5000)

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data ( $k = k_1 + k_2$ )**

$k/\text{s}^{-1}$	T/K	[M]/molecule cm $^{-3}$	Reference	Comments
<i>Rate Coefficient Measurements</i>				
<i>Intermediate Fall-off Range</i>				
$1.3 \cdot 10^{16} \exp(-41800/T)$	1050–1250	$1 \cdot 10^{19}$ (Ar)	Lifshitz and Frenklach, 1975 <sup>1</sup>	(a)
12.5	1250	$(2.6 \text{--} 6.0) \cdot 10^{18}$ (Ar)	Bradley, 1979 <sup>2</sup>	(b)
$6.7 \cdot 10^{16} \exp(-45390/T)$	1200–1450	$1.5 \cdot 10^{19}$ (Ar)	Chiang and Skinner, 1981 <sup>3</sup>	(c)
$4.5 \cdot 10^{16} \exp(-42623/T)$	873–1053	$2.0 \cdot 10^{18}$ (N <sub>2</sub> )	Juste, Scacchi, and Niclause, 1981 <sup>4</sup>	(d)
$3.6 \cdot 10^{14} \exp(-37600/T)$	1300–1700	$9.0 \cdot 10^{18}$ (Ar, N <sub>2</sub> )	Simmie, Gardiner, and Eubank, 1982 <sup>5</sup>	(e)
$5.1 \cdot 10^{16} \exp(-41969/T)$	773–793	$2.5 \cdot 10^{18}$ (C <sub>3</sub> H <sub>8</sub> )	Kanan, Purnell, and Smith, 1983 <sup>6</sup>	(f)
$7.74 \cdot 10^{11} \exp(-28030/T)$	1400–1800	$(0.9 \text{--} 3.6) \cdot 10^{18}$ (Kr)	Al-Alami and Kiefer, 1983 <sup>7</sup>	(g)
$4.5 \cdot 10^{-7} \exp(-28030/T)$ [Kr]	1800–2300	$(0.5 \text{--} 1.0) \cdot 10^{18}$ (Kr)		
$1.1 \cdot 10^{16} \exp(-42270/T)$	1100–1450	$1 \cdot 10^{19}$ (Ar)	Hidaka, Oki, and Kawano, 1989 <sup>8</sup>	(h)
$1.86 \cdot 10^{17} \exp(-43800/T)$	743–803	$2.5 \cdot 10^{17}$ (C <sub>3</sub> H <sub>8</sub> )	Belmeliani, Perrin, and Martin, 1994 <sup>9</sup>	(i)
<i>Reviews and Evaluations</i>				
$k_{\infty} = 5.0 \cdot 10^{15} \exp(-42100/T)$	800–2000		Warnatz, 1984 <sup>10</sup>	(j)
$k_{\infty} = 1.1 \cdot 10^{17} \exp(-42470/T)$	700–2000		CEC, 1994 <sup>11</sup>	(k)
$k_0[\text{Ar}] = [\text{Ar}] 1.3 \cdot 10^{-5} \exp(-32700/T)$	700–2000			
$F_c(\text{Ar}) = 0.24 \exp(-T/1946)$ + 0.76 exp( $-T/38$ )	700–2000			

**Comments**

- (a) Shock wave study of mixtures comprising 0.4%–1.6% C<sub>3</sub>H<sub>8</sub> in Ar. Reactant and product concentrations were measured by gas chromatography. The reaction mechanism is discussed; overall 29 reactions are considered. The results can be reproduced with a condensed mechanism comprising 11 reactions.
- (b) Pyrolysis of C<sub>3</sub>H<sub>8</sub> in Ar studied in a single-pulse shock tube. Analysis of products by gas chromatography.
- (c) Pyrolysis of C<sub>3</sub>H<sub>8</sub>-Ar mixtures behind reflected shock waves. H atoms monitoring by ARAS.
- (d) Thermal decomposition of C<sub>3</sub>H<sub>8</sub> in a continuous jet-stirred reactor. Reaction products measured by gas chromatography.
- (e) Shock wave study of mixtures comprising 5% C<sub>3</sub>H<sub>8</sub> in Ar and N<sub>2</sub>. Analysis by IR laser absorption kinetic spectroscopy.
- (f) Pyrolysis of C<sub>3</sub>H<sub>8</sub> in a static reactor. Products analyzed by GC.
- (g) Pyrolysis of C<sub>3</sub>H<sub>8</sub> studied in incident shock waves with laser-Schlieren analysis. Observed density gradients interpreted using a mechanism with 30 reactions.
- (h) Thermal decomposition of C<sub>3</sub>H<sub>8</sub> studied in reflected

shock waves monitoring absorption-time profiles at 3.39 μm to which C<sub>3</sub>H<sub>8</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, and CH<sub>4</sub> contribute.

- (i) Pyrolysis of C<sub>3</sub>H<sub>8</sub> in a static Pyrex reactor at constant volume. Reaction products analyzed by gas chromatography.
- (j) Survey of literature data up to 1981; recommendation based on data of Lifshitz and Frenklach,<sup>1</sup> Bradley,<sup>2</sup> Chiang and Skinner,<sup>3</sup> and Pratt and Rogers.<sup>12</sup>
- (k) See Comments on Preferred Values.

**Preferred Values**

$k_0 = 1.3 \cdot 10^{-5} \exp(-32700/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for M = Ar over the range 700–2000 K.

$k_{\infty} = 4.0 \cdot 10^{23} T^{-1.87} \exp(-45394/T) \text{ s}^{-1}$  over the range 700–2000 K.

$F_c = 0.24 \exp(-T/1946) + 0.76 \exp(-T/38)$  for M = Ar over the range 700–2000 K.

**Reliability**

$\Delta \log k_0 = \pm 0.5$  for M = Ar over the range 700–2000 K.

$\Delta \log k_{\infty} = \pm 0.3$  over the range 700–2000 K.

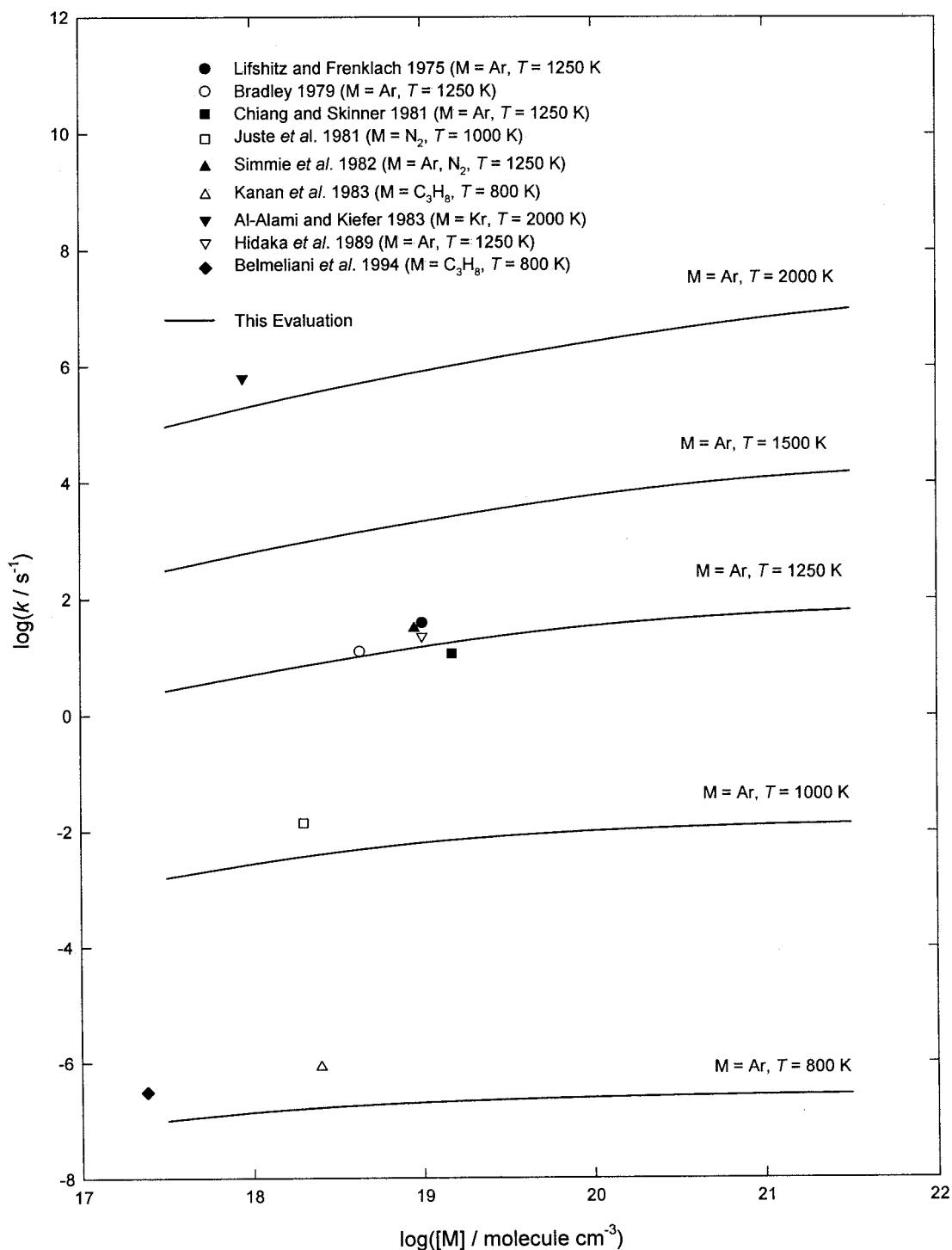
$\Delta F_c = \pm 0.2$  for M = Ar over the range 700–2000 K.

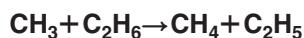
*Comments on Preferred Values*

The preferred low pressure rate coefficient is unchanged from our previous evaluation.<sup>11</sup> The preferred values are mainly based on theoretical modeling<sup>13–15</sup> which is required to reconcile the widely scattered experimental data. These calculations predict for the high pressure rate coefficient of the reverse recombination reaction a value of  $5.6 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 300–2000 K. The value at 300 K is in good agreement with the recommended  $k_\infty$  value of  $6.1 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  which is based on direct experiments. The preferred dissociation rate coefficient,  $k_\infty$ , is obtained using the recommended  $k_\infty$  for the recombination reaction and the equilibrium constant given in this evaluation. The recommended  $k_0$  was estimated using a collision efficiency of about 0.2 between 700 and 2000 K. The theoretical fall-off curves and selected experimental data are shown in the Figure.

**References**

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*Thermodynamic Data*

$$\begin{aligned}\Delta H_{298}^{\circ} &= -16.5 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= 10.2 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 15.1 T^{-0.254} \exp(+2040/T) \\ &\quad (300 \leq T/\text{K} \leq 4000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$3.3 \cdot 10^{-13} \exp(-5250/T)$	389–567	Trotman-Dickenson, Birchard, and Steacie, 1951 <sup>1</sup>	(a)
$7.1 \cdot 10^{-13} \exp(-5710/T)$	435–614	Wijnen, 1955 <sup>2</sup>	(b)
$1.32 \cdot 10^{-12} \exp(-5810/T)$	519–797	McNesby and Gordon, 1955 <sup>3</sup>	(c)
$5.9 \cdot 10^{-13}$	1350	Clark <i>et al.</i> , 1971 <sup>4</sup>	(d)
$8.3 \cdot 10^{-10} \exp(-10800/T)$	920–1040	Pacey and Purnell, 1972 <sup>5</sup>	(e)
$7.4 \cdot 10^{-11} \exp(-8770/T)$	980–1130	Yampoloskii and Rybin, 1974 <sup>6</sup>	(f)
$5.4 \cdot 10^{-11} \exp(-9060/T)$	1055–1325	Bradley and West, 1976 <sup>7</sup>	(g)
$7.6 \cdot 10^{-15}$	880	Chen, Back, and Back, 1976 <sup>8</sup>	(h)
$1.0 \cdot 10^{-14}$	995		
$2.2 \cdot 10^{-14}$	1038		
$2.5 \cdot 10^{-14}$	1068		
$1.1 \cdot 10^{-13}$	1206	Lee and Yeh, 1979 <sup>9</sup>	(i)
$6.8 \cdot 10^{-15}$	902	Pacey and Wimalasena, 1984 <sup>10</sup>	(j)
$3.3 \cdot 10^{-11} \exp(-6800/T)$	1100–1400	Möller <i>et al.</i> , 1987 <sup>11</sup>	(k)
<i>Reviews and Evaluations</i>			
$2.45 \cdot 10^{-31} T^6 \exp(-3043/T)$	300–1500	CEC, 1992; 1994 <sup>12</sup>	(l)

**Comments**

- (a) Photolysis of  $(\text{CD}_3)\text{CO}/\text{C}_2\text{H}_6$  mixtures with MS analysis of  $\text{CD}_3\text{H}$  and  $\text{C}_2\text{D}_6$ , relative to  $k(\text{CD}_3 + \text{CD}_3) = 4.15 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , independent of temperature.
- (b) Photolysis of  $(\text{CD}_3)_2\text{CO}/\text{C}_2\text{H}_6$  mixtures with MS analysis of  $\text{CD}_3\text{H}$  and  $\text{CD}_4$ , relative to  $k(\text{CD}_3 + \text{CD}_3\text{COCD}_3) = 8.0 \cdot 10^{-13} \exp(-5760/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .
- (c) Same system as for comment (b).
- (d) Shock-tube pyrolysis of  $(\text{CH}_3\text{N})_2$  or  $(\text{CH}_3)_2\text{Hg}$  in Ne with MS analysis of products.  $k$  derived from computer simulation of product yields.
- (e) Pyrolysis of  $\text{C}_2\text{H}_6$  in a flow system with end-product analysis by GC.  $k$  determined from a kinetic analysis and recalculated relative to  $k(2\text{CH}_3 \rightarrow \text{C}_2\text{H}_6) = 2.3 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .
- (f) Pyrolysis of  $\text{C}_2\text{H}_6/\text{D}_2$  mixtures with end-products analysis by GC.  $k$  obtained relative to  $k(\text{CH}_3 + \text{D}_2)$  and based on  $k(\text{CH}_3 + \text{D}_2) = 2.3 \cdot 10^{-11} \exp(-8120/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .
- (g) Shock-tube pyrolysis of  $(\text{CH}_3)_2\text{C}=\text{CH}_2$  in Ar with end-product analysis by GC.  $k$  derived from computer simulation of product yields.
- (h) Pyrolysis of  $\text{CH}_4/\text{C}_2\text{H}_6$  mixtures in a static reaction system with end-product analysis by GC.  $k$  derived from a kinetic analysis based on rate of consumption of  $\text{C}_2\text{H}_6$ .

- (i) Shock-tube pyrolysis of  $\text{C}_2\text{H}_6$  in Ar with end-product analysis by GC.  $k$  determined from computer simulation of product yields.
- (j) Flow pyrolysis of  $\text{C}_2\text{H}_6$  with end-product analysis by GC.  $k$  determined from a kinetic analysis and relative to  $k(2\text{CH}_3 \rightarrow \text{C}_2\text{H}_6) = 4.15 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .
- (k) Shock-tube pyrolysis of  $(\text{CH}_3\text{N})_2$  or  $(\text{CH}_3)_2\text{Hg}$  in mixtures of  $\text{C}_2\text{H}_6/\text{Ar}$  with time-resolved measurement of  $[\text{CH}_3]$  by UV absorption at 216.5 nm.  $k$  derived from computer simulation of  $[\text{CH}_3]$  profiles.
- (l) Based on Refs. 1–11.

**Preferred Values**

$$k = [9.3 \cdot 10^{-14} \exp(-4740/T) + 1.4 \cdot 10^{-9} \exp(-11200/T)] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the range } 350 \text{--} 1500 \text{ K.}$$

**Reliability**

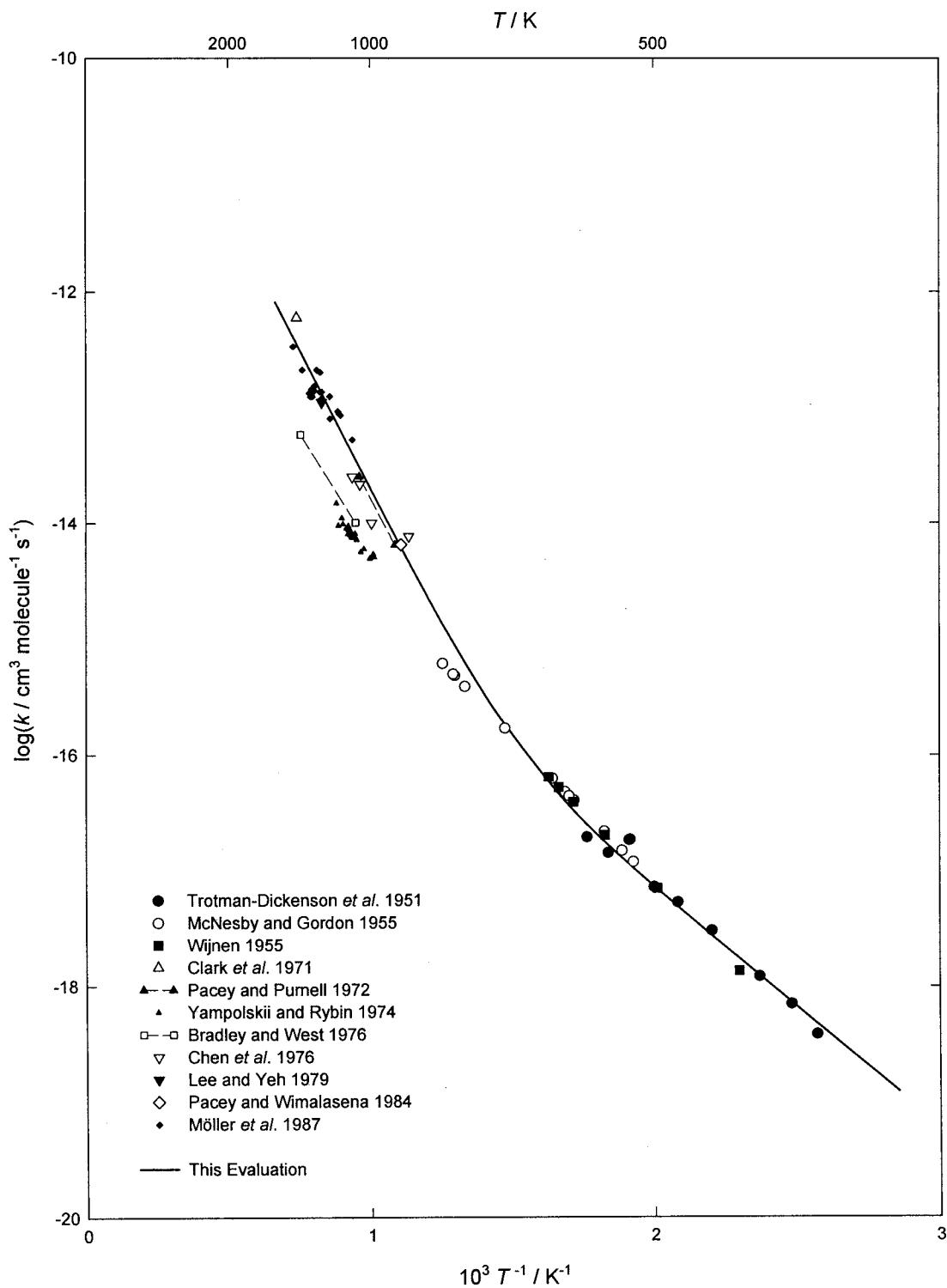
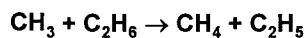
$$\Delta \log k = \pm 0.1 \text{ at } 350 \text{ K, rising to } \pm 0.2 \text{ at } 1500 \text{ K.}$$

**Comments on Preferred Values**

Although the available data base for this reaction is unchanged from our previous evaluation<sup>12</sup> we have altered our recommendation which now gives more weight to the data of Möller *et al.*<sup>11</sup> which are derived from direct measurements of the  $\text{CH}_3$  concentrations in their shock-tube study. The data indicate substantial curvature of the Arrhenius plot which is best fitted as the sum of two simple Arrhenius expressions.

## References

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*Thermodynamic Data*

$$\begin{aligned}\Delta H^\circ_{298}(1) &= -65.1 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(1) &= -4.40 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 74.1 T^{-0.730} \exp(+7630/T) \\ (300 \leqslant T/\text{K} \leqslant 5000)\end{aligned}$$

$$\begin{aligned}\Delta H^\circ_{298}(2) &= -44.6 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(2) &= -3.93 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 2.08 T^{-0.205} \exp(+5360/T) \\ (300 \leqslant T/\text{K} \leqslant 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data ( $k = k_1 + k_2$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$6.8 \cdot 10^{-14} T^{0.5} \exp(-3890/T)$	391–564	Dodd, 1955 <sup>1</sup>	(a)
$2.16 \cdot 10^{-12} \exp(-3953/T)$	395–447	Birrel and Trotman-Dickenson, 1960 <sup>2</sup>	(b)
$1.02 \cdot 10^{-13} \exp(-2770/T)$	298–400	Kerr and Calvert, 1965 <sup>3</sup>	(c)
$k_1 = 1.77 \cdot 10^{-14}$	796	Laidler and Liu, 1967 <sup>4</sup>	(d)
$k_2 = 1.52 \cdot 10^{-17}$			
$4.34 \cdot 10^{-12} \exp(-4492/T)$	342–448	Buchanan and McRae, 1968 <sup>5</sup>	(e)
$1.17 \cdot 10^{-12} \exp(-3032/T)$	713–813	Baldwin <i>et al.</i> , 1970 <sup>6</sup>	(f)
$1.72 \cdot 10^{-31} T^{5.9} \exp(-860/T)$	1051–1225	Colket, Naegeli, and Glassman, 1975 <sup>7</sup>	(g)
<i>Reviews and Evaluations</i>			
$6.2 \cdot 10^{-12} \exp(-3020/T)$	300–525	Kerr and Parsonage, 1976 <sup>8</sup>	(h)
$3.3 \cdot 10^{-30} T^{5.64} \exp(-1240/T)$	300–1250	CEC, 1992; 1994 <sup>9</sup>	(i)

**Comments**

- (a) Relative rate study; photolysis of  $\text{CH}_3\text{CHO}$  using radiation at 313 nm and over the range 290–330 nm. Products separated by low temperature distillation.  $k$  determined relative to  $k(\text{CH}_3 + \text{CH}_3)$ . Expression cited is based on  $k(\text{CH}_3 + \text{CH}_3)$  from this evaluation.
- (b) Relative rate study using thermal decomposition of *di-t*-butyl peroxide to generate  $\text{CH}_3$  radicals. Products separated by low temperature distillation and analyzed by volume measurements and GC. Cited expression is based on  $k(\text{CH}_3 + \text{CH}_3)$  from this evaluation.
- (c) Relative rate study; photolysis of  $(\text{CH}_3)_2\text{N}_2$  at 366 nm in the presence of  $\text{CH}_3\text{CHO}$ . Products analyzed by GC. Cited expression is based on  $k(\text{CH}_3 + \text{CH}_3)$  from this evaluation.
- (d) Relative rate study using pyrolysis of  $\text{CH}_3\text{CHO}$ . Products analyzed by GC. Cited data are based on  $k(\text{CH}_3 + \text{CH}_3)$  from this evaluation.
- (e) Relative rate study using photolysis of  $\text{CH}_3\text{CHO}$  at 313 nm. Products ( $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ) analyzed by GC. Cited expression based on  $k(\text{CH}_3 + \text{CH}_3)$  from this evaluation.
- (f) Relative rate study using slow oxidation of  $\text{CH}_3\text{CHO}/\text{O}_2$  mixtures. Products analyzed by GC ( $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{CH}_3\text{OH}$ ,  $\text{H}_2$ ,  $\text{C}_2\text{H}_6$ ) and wet analysis ( $\text{H}_2\text{O}_2$ ,  $\text{HCHO}$ ). Cited expression based on  $k(\text{CH}_3 + \text{CH}_3)$  from this evaluation.
- (g) Relative rate study using pyrolysis of  $\text{CH}_3\text{CHO}$  in a flow system at a pressure of 1 bar  $\text{N}_2$ . Expression for  $k$  based on  $k(\text{CH}_3 + \text{CH}_3) = 4.0 \cdot 10^{-10} T^{-0.4} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  which is in good agreement with

$k(\text{CH}_3 + \text{CH}_3)$  from this evaluation over the range of conditions used. Authors take into account low temperature data reviewed by Kerr and Parsonage<sup>8</sup> in deriving expression for  $k$ .

- (h) Based mainly on low temperature relative rate studies in Refs. 1, 2, 3, 5.
- (i) Based on the expression from the low temperature data derived by Kerr and Parsonage<sup>8</sup> and the data of Liu and Laidler<sup>10</sup> and Colket *et al.*<sup>7</sup>

**Preferred Values**

$$k = 5.8 \cdot 10^{-32} T^{6.21} \exp(-820/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the range 298–1250 K.

**Reliability**

$$\Delta \log k = \pm 0.1 \text{ at } 298 \text{ K, rising to } \pm 0.3 \text{ at } 1250 \text{ K.}$$

**Comments on Preferred Values**

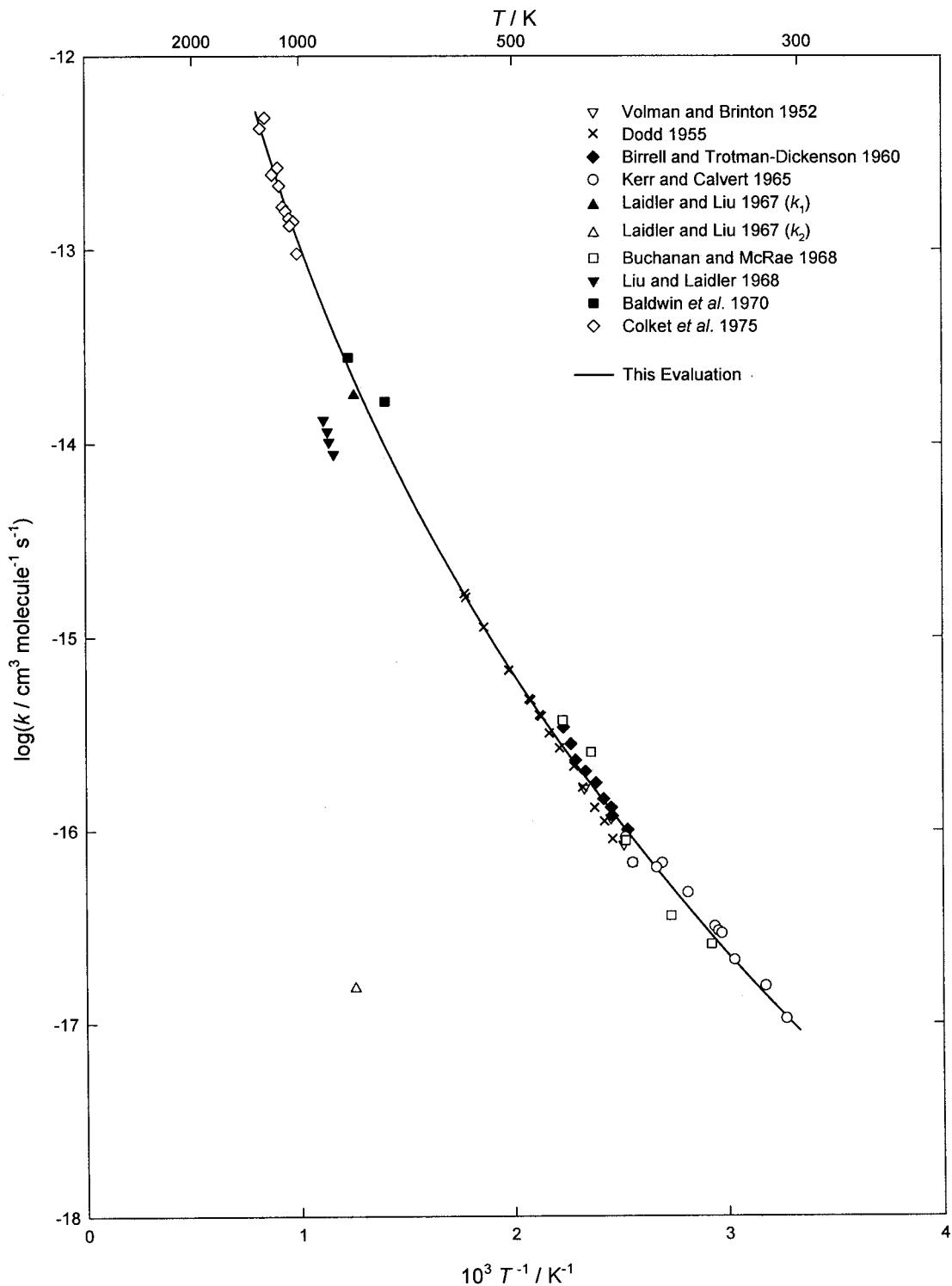
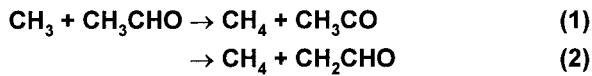
All of the values of the rate constant of this reaction have been obtained in relative rate studies using methyl radical recombination as the reference reaction. The results of Colket *et al.*,<sup>7</sup> at  $T > 1000$  K, show a significantly higher activation energy than the low temperature studies, indicative of the non-Arrhenius behavior of the overall rate constant, which may, in part, be due to contributions from both reaction channels becoming important at temperatures above 1000 K. The preferred expression for  $k$  is a three parameter least squares fit to the low temperature data of Dodd,<sup>1</sup> Birrel

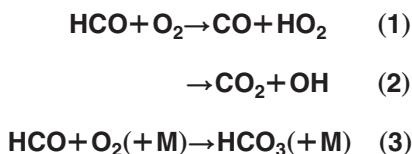
and Trotman-Dickenson,<sup>2</sup> Kerr and Calvert,<sup>3</sup> and Buchanan and McRae,<sup>5</sup> together with the results of Laidler and Liu,<sup>4</sup> Baldwin *et al.*,<sup>6</sup> and Colket *et al.*<sup>7</sup> at higher temperatures. The earlier data of Volman and Brinton<sup>11</sup> are in good agreement with the preferred expression for  $k$  but the study of Liu and Laidler,<sup>10</sup> at intermediate temperatures, appears to give anomalously low values of  $k$ .

There are no reliable data on the branching ratios. The thermodynamics of the possible reaction channels suggest that Channel (1) should be favored over the temperature range covered by the preferred values. If it is assumed that  $k_2 = \frac{1}{2}k(\text{CH}_3 + \text{C}_2\text{H}_6)$  then Channel (2) contributes approximately 0.7% and 5.3% to the overall rate constant at 500 K and 1000 K, respectively.

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*Thermodynamic Data*

$$\begin{aligned}\Delta H^\circ_{298}(1) &= -140.0 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(1) &= -2.83 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 1.90 T^{-0.139} \exp(+16790/T) \\ &(300 \leq T/\text{K} \leq 5000)\end{aligned}$$

$$\begin{aligned}\Delta H^\circ_{298}(2) &= -399.5 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(2) &= -32.01 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 2.86 \cdot 10^{-3} T^{0.315} \exp(+48110/T) \\ &(300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data ( $k = k_1 + k_2 + k_3$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$5.7 \cdot 10^{-12}$	297	Washida, Martinez, and Bayes, 1974 <sup>1</sup>	(a)
$1.3 \cdot 10^{-11}$	$\sim 2000$	Tsuboi, 1976 <sup>2</sup>	(b)
$5.6 \cdot 10^{-12}$	298	Shibuya <i>et al.</i> , 1977 <sup>3</sup>	(c)
$5.5 \cdot 10^{-11} T^{-0.4}$	298–503	Veyret and Lesclaux, 1981 <sup>4</sup>	(d)
$5.8 \cdot 10^{-12}$	$\sim 1000$	Cherian <i>et al.</i> , 1981 <sup>5</sup>	(e)
$5.2 \cdot 10^{-12}$	296	Temps and Wagner, 1984 <sup>6</sup>	(f)
$4.7 \cdot 10^{-12}$	295	Langford and Moore, 1984 <sup>7</sup>	(g)
$4.3 \cdot 10^{-12}$	298	Dóbé, Wagner, and Ziemer, 1995 <sup>8</sup>	(h)
$2.2 \cdot 10^{-12} \exp(170/T)$	200–298	Nesbitt, Gleason, and Stief, 1999 <sup>9</sup>	(i)
$5.0 \cdot 10^{-12}$	294	Hanoune <i>et al.</i> , 2001 <sup>10</sup>	(j)
<i>Reviews and Evaluations</i>			
$5.0 \cdot 10^{-12}$	300–2500	CEC, 1992; 1994 <sup>11</sup>	(k)
$3.5 \cdot 10^{-12} \exp(140/T)$	200–300	NASA, 1997 <sup>12</sup>	(l)
$5.5 \cdot 10^{-12}$	200–400	IUPAC, 1997 <sup>13</sup>	(m)

**Comments**

- (a) Discharge flow system used to study the O+C<sub>2</sub>H<sub>4</sub> reaction. [CHO] monitored by photoionization mass spectrometry. Variation of steady state value of [CHO] gives  $k/k(\text{CHO}+\text{O}) = 2.7 \cdot 10^{-2}$ . Cited value of  $k$  is based on  $k(\text{O}+\text{C}_2\text{H}_4) = 2.1 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  measured in the same study.
- (b) Induction periods and concentration profiles of species in flames modeled using a substantial reaction mechanism.
- (c) Flash photolysis of CH<sub>3</sub>CHO/O<sub>2</sub>/He mixtures. [CHO] monitored in absorption at 613.8 nm. No pressure dependence of  $k$  was observed over the range 13–700 mbar.
- (d) Flash photolysis of HCHO or CH<sub>3</sub>CHO/O<sub>2</sub>/N<sub>2</sub> mixtures. [CHO] monitored by laser absorption at 614.5 nm. No variation of  $k$  with pressure found over the range 60–660 mbar.
- (e) Burning velocities of premixed CH<sub>4</sub>/air flames measured and simulated by computer modeling of reaction mechanism.
- (f) Discharge flow study; [CHO], [HO<sub>2</sub>], and [HO] monitored by laser magnetic resonance at total pressures of 1.3–4.1 mbar. Channel (1) was found to be predominant ( $k_2/k < 4 \cdot 10^{-3}$ ;  $k_3/k < 0.07$ ).
- (g) Pulsed laser photolysis of HCHO or (CHO)<sub>2</sub> at total pressures up to 1.3 bar N<sub>2</sub>. [CHO] monitored by resonance absorption. No variation of  $k$  with pressure observed. Higher value of  $k$  found for corresponding reaction of DCO suggesting that the reaction occurs by formation of the HCOO<sub>2</sub> adduct rather than by direct abstraction.
- (h) Discharge flow study; CHO produced by the F + HCHO reaction. [HCO] and [HO<sub>2</sub>] monitored by LMR. Values of  $k$  obtained by modeling [HO<sub>2</sub>] profiles. The only products were CO+HO<sub>2</sub>. Total pressure, 1.7 mbar (He bath gas).
- (i) Discharge flow study in which CHO radicals were produced by the Cl+CH<sub>2</sub>CO reaction in the presence of a large excess of O<sub>2</sub>. [CHO] was monitored by photoionization mass spectrometry. A detailed mechanism was modeled to check for influences of secondary chemistry. The cited expression covers the range 200–298 K but  $k$  was also measured at 398 K giving a value of  $4.46 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  suggesting that  $k$  may rise with increasing temperature at  $T > 298$  K.
- (j) Pulsed laser photolysis at 355 nm of Cl<sub>2</sub>/HCHO/O<sub>2</sub>/N<sub>2</sub> mixtures used to produce CHO radicals by the Cl+HCHO reaction at total pressures in the range 6.3–61.2 mbar. [CO] was monitored by time-resolved diode laser absorption spectroscopy at 2165.601 cm<sup>-1</sup> or 2169.1979 cm<sup>-1</sup>.

- (k) Based on the consensus value at 298 K (NASA and IUPAC recommendations) and the studies of Veyret and Lesclaux<sup>4</sup> and Cherian *et al.*<sup>5</sup>
- (l) Based on the studies of Washida *et al.*,<sup>1</sup> Shibuya *et al.*,<sup>3</sup> Veyret and Lesclaux,<sup>4</sup> and Langford and Moore.<sup>7</sup>
- (m) Based on the studies of Washida *et al.*,<sup>1</sup> Shibuya *et al.*,<sup>3</sup> Veyret and Lesclaux,<sup>4</sup> Timonen *et al.*,<sup>14</sup> and Stief *et al.*<sup>15</sup>

### Preferred Values

$k = 4.5 \cdot 10^{-14} T^{0.68} \exp(236/T)$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> over the range 200–2500 K.

See Comments on Preferred Values for information on the branching ratios.

### Reliability

$\Delta \log k = \pm 0.15$  at 200 K, rising to  $\pm 0.5$  at 2500 K.

### Comments on Preferred Values

The low temperature data have been reviewed by the NASA and IUPAC Panels.<sup>12,13</sup> There are a number of studies at 298 K in reasonable agreement,<sup>1,3,4,6–10,15</sup> giving a mean value of  $k$  of  $5.2 \cdot 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at that temperature. These studies are preferred to a number of others using intracavity laser absorption<sup>16–18</sup> which give rather lower values of  $k$ . However it should be noted that the most recent study using discharge flow and mass-spectroscopic detection of CHO also gave a low value and that the values of  $k$  at 298 K scatter rather more than might be expected. The temperature dependence of  $k$  in this temperature region (<700 K) appears to be very slight with small positive<sup>14</sup> or small negative<sup>4,9,15</sup> values of  $E/R$  having been obtained.

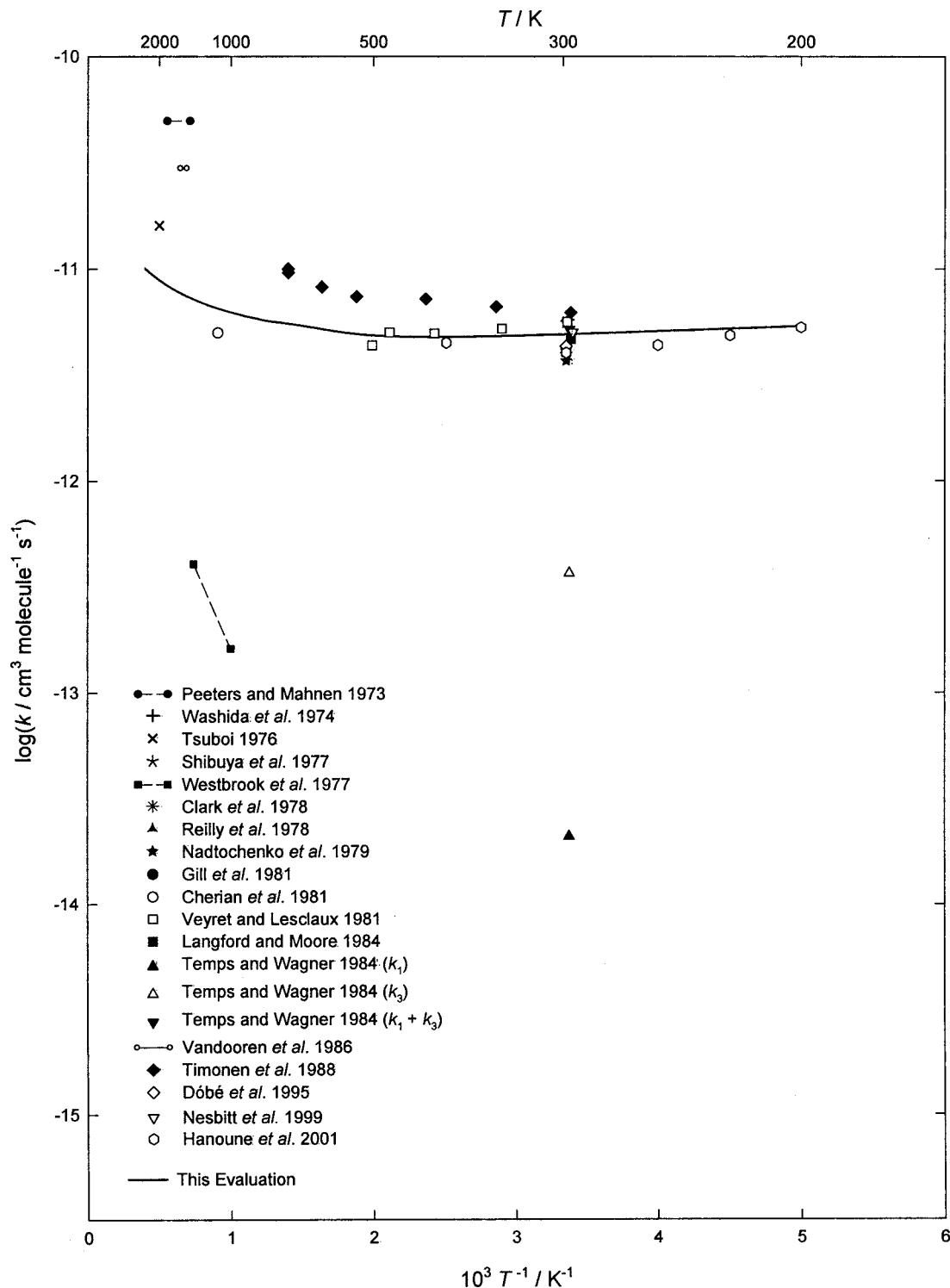
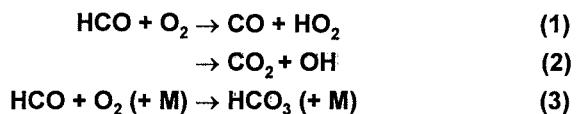
The data at high temperatures (>1000 K) are widely scattered with no reliable indication of the temperature dependence of  $k$  at such temperatures. However in a theoretical study Hsu *et al.*<sup>19</sup> have derived an expression for  $k$  which is in good agreement with the low temperature data and is compatible with results of Cherian *et al.*,<sup>5</sup> and Tsuboi<sup>2</sup> at high temperatures. The temperature dependence of  $k$  given by this theoretical expression<sup>19</sup> is combined with the value of  $k$  at 298 K to give the preferred expression for  $k$ . The data of Peeters and Mahnen<sup>20</sup> and Vandooren *et al.*<sup>21</sup> are higher and those of Westbrook *et al.*<sup>22</sup> much lower than predicted by this preferred expression.

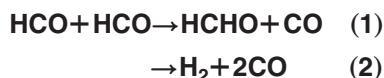
Theoretical modeling of the reaction mechanism by Hsu *et al.*<sup>19</sup> suggests that the reaction proceeds by addition followed by very rapid decomposition of the adduct exclusively

to form HO<sub>2</sub> + CO. The isotope effect observed by Langford and Moore<sup>7</sup> supports the idea of adduct formation and the lack of any observed pressures dependence up to  $\sim 1.3$  bar<sup>4,7</sup> is in accord with rapid decomposition of the adduct. At higher temperatures direct abstraction may become competitive but will lead once again to HO<sub>2</sub> + CO. Thus Channel (1) is expected to be predominant under all conditions relevant to combustion. There have been experimental studies suggesting significant participation of Channels (2) and (3)<sup>17,23</sup> but the upper limits set to the yields of Channel (2) of  $4 \cdot 10^{-3}$  and of Channel (3) of <0.07 at 298 K in the studies of Temps and Wagner<sup>6</sup> and Horowitz *et al.*<sup>24</sup> are in agreement with the predictions of the theoretical study of Hsu *et al.*<sup>19</sup>

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*Thermodynamic Data*

$$\begin{aligned}\Delta H^{\circ}_{298}(1) &= -305.3 \text{ kJ mol}^{-1} \\ \Delta S^{\circ}_{298}(1) &= -32.35 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 1.76 \cdot 10^{-2} T^{-0.027} \exp(+36830/T) \\ (300 \leq T/\text{K} \leq 5000) \end{aligned}$$

$$\begin{aligned}\Delta H^{\circ}_{298}(2) &= -307.3 \text{ kJ mol}^{-1} \\ \Delta S^{\circ}_{298}(2) &= 77.01 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 5.84 \cdot 10^{25} T^{-0.822} \exp(+36710/T) \text{ molecule cm}^{-3} \\ (300 \leq T/\text{K} \leq 5000) \end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data ( $k = k_1 + k_2$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$(3-10) \cdot 10^{-11}$	298	Reilly <i>et al.</i> , 1978 <sup>1</sup>	(a)
$3.0 \cdot 10^{-11}$	298	Nadtochenko, Sarkisov, and Vedenev, 1979 <sup>2</sup>	(b)
$2.3 \cdot 10^{-11}$	298	Hochanadel, Sworsky, and Ogren, 1980 <sup>3</sup>	(c)
$3.4 \cdot 10^{-11}$	298–475	Veyret, Lesclaux, and Roussel, 1984 <sup>4</sup>	(d)
$4.5 \cdot 10^{-11}$	296	Temps and Wagner, 1985 <sup>5</sup>	(e)
$5 \cdot 10^{-11}$	298	Stoeckel <i>et al.</i> , 1985 <sup>6</sup>	(f)
$7.5 \cdot 10^{-11}$	295	Baggott <i>et al.</i> , 1986 <sup>7</sup>	(g)
$6.3 \cdot 10^{-11}$	298	Zhu, Kellis, and Ding, 1996 <sup>8</sup>	(h)
$6.0 \cdot 10^{-11}$	298	Chen and Zhu, 2001 <sup>9</sup>	(i)
<i>Reviews and Evaluations</i>			
$3.0 \cdot 10^{-11}$	300–2500	Tsang and Hampson, 1986 <sup>10</sup>	(j)
$5.0 \cdot 10^{-11}$	300	CEC, 1992; 1994 <sup>11</sup>	(k)

**Comments**

- (a) Near-UV pulsed photolysis of pure HCHO at a pressure of 13 mbar. [HCO] was monitored by intracavity dye laser absorption at 613.8 nm or 614.5 nm. The value of  $k$  was derived from the modeling of a detailed kinetic scheme. Large error limits were assigned due to the nonuniform distribution of HCO in the reaction cell.
- (b) Pulsed laser photolysis of  $\text{CH}_3\text{CHO}/\text{Ar}$  mixtures at total pressures in the range 13–260 mbar. [HCO] was monitored by intracavity laser absorption spectroscopy.
- (c) Flash photolysis study on  $\text{H}_2\text{O}/\text{CO}$  mixtures at total pressures in the range 1–3 bar. [HCO] and  $[\text{CH}_3]$  were monitored by UV absorption. Values of  $k$  were derived from modeling a detailed reaction mechanism.
- (d) Flash photolysis study on HCHO at total pressures of 13–26 mbar. [HCO] was monitored by resonance absorption at 614.5 nm. The value of  $k$  was independent of temperature over the range studied. The initial concentration of radicals was determined by measuring the yields of molecular hydrogen using mass spectrometry in the presence and absence of hydrogen atom scavengers.
- (e) Discharge flow study. [HCO],  $[\text{HO}_2]$ , and  $[\text{OH}]$  were monitored by laser magnetic resonance.
- (f) Pulsed laser photolysis at 266 nm of acetaldehyde at pressures in the range 0.13–13 mbar. [HCO] was monitored by time resolved intracavity absorption determina-
- (g) Pulsed laser photolysis at 308 nm of glyoxal or HCHO at pressures in the range 13–40 mbar. [CHO] was monitored by time-resolved laser absorption at 614.6 nm. Author concludes that the discrepancies with other results are due to differences in the measured absorption cross sections of HCO.
- (h) Photodissociation study using pulsed laser photolysis of  $(\text{CHO})_2/\text{N}_2$  mixtures at 248, 308, and 351 nm. [HCO] was monitored by cavity ring down spectroscopy. Absorption cross sections determined in the same study were used to obtain absolute concentrations of HCO.
- (i) Photodissociation study on  $\text{C}_2\text{H}_5\text{CHO}$  using technique similar to that in (h). [HCO] profile modeled using detailed reaction mechanism.
- (j) Based largely on the data of Reilly *et al.*,<sup>1</sup> Nadtochenko *et al.*,<sup>2</sup> Hochanadel *et al.*,<sup>2</sup> and Mullenko.<sup>12</sup> A branching ratio of  $k_1/k_2 \sim 5.8$  is also recommended based on the study of Horowitz and Calvert.<sup>13</sup>
- (k) Based on the data from Refs. 1, 2, 3, 4, 5, 7.

**Preferred Values**

$$k = 5.0 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the range } 230-1000 \text{ K.}$$

*Reliability*

$\Delta \log k = \pm 0.2$  at 230 K, rising to  $\pm 0.3$  at 1000 K.

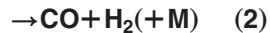
*Comments on Preferred Values*

The overall rate constant for this reaction has been measured by a variety of techniques at, or close to, 298 K. The values obtained vary by approximately a factor of 4. Much of this variation is due to the uncertainty in the optical absorption cross section at the wavelength used to monitor  $[HCO]$ , usually at  $\lambda \sim 615.5$  nm. The preferred value of  $k$  is taken in the middle of the range with substantial error limits. The only determination of the temperature dependence of the rate constant<sup>4</sup> found it to be independent of temperature over the range 298–475 K. This finding is probably reliable but requires confirmation. Provisionally a temperature independent value is recommended.

The only information on the branching ratios come from a number of photolysis studies<sup>13–17</sup> at ambient temperatures and at pressures extending up to  $\sim 150$  mbar, in which overall product yields were measured. It seems generally agreed that the combination reaction forming  $(CHO)_2$  is unimportant under these conditions and that the Channel (1) is the major reaction pathway. However, Horowitz and Calvert<sup>13</sup> obtain a value of  $k_1/k_2 \sim 5.8$  whereas Förgeteg *et al.*<sup>17</sup> suggest a value of  $\sim 2$ . At this stage we make no recommendation for the branching ratio.

**References**

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*Thermodynamic Data*

$$\Delta H^\circ_{298}(1) = 369.6 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = 120.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 3.9 \cdot 10^{26} T^{-0.325} \exp(-44590/T) \text{ molecule cm}^{-3} \quad (300 \leq T/K \leq 5000)$$

$$\Delta H^\circ_{298}(2) = -1.96 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = 109.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 4.41 \cdot 10^{27} T^{-0.829} \exp(+162/T) \text{ molecule cm}^{-3} \quad (300 \leq T/K \leq 4000)$$

See Section 3 for source of the Thermodynamic Data

**Rate Coefficient Data ( $k = k_1 + k_2$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$5.25 \cdot 10^{-9} \exp(-37700/T)$ (M=Ar)	2200–2650	Saito <i>et al.</i> , 1985 <sup>1</sup>	(a)
$k_1 = 2.7 \cdot 10^{12} T^{-5.54} \exp(-48660/T)$ (M=Ar)	1700–3200	Irdam <i>et al.</i> , 1992 <sup>2</sup>	(b)
$k_1 = 9.20 \cdot 10^{-9} \exp(-37750/T)$ (M=Ar)	1400–2000	Hidaka <i>et al.</i> , 1993 <sup>3</sup>	(c)
$k_1 = 1.02 \cdot 10^{-8} \exp(-38706/T)$ (M=Kr)	2004–2367	Kumaran, Carroll, and Michael, 1998 <sup>4</sup>	(d)
$k_2 = 4.66 \cdot 10^{-9} \exp(-32110/T)$ (M=Kr)			
<i>Reviews and Evaluations</i>			
$k_1 = 2.7 \cdot 10^{-12} T^{-5.54} \exp(-48660/T)$ (M=Ar)	2000–3000	CEC, 1992; 1994 <sup>5</sup>	(e)
$k_1/k = 0.29$	2000–3000		

### Comments

- (a) Thermal decomposition of HCHO behind reflected shock waves. HCHO decay and CO production monitored by IR emission; H atoms by atom resonance absorption. M=Ar. Channel (2) appeared to be a minor channel.
- (b) Shock tube study. Thermal dissociation of 1,3,5 trioxane used to generate HCHO. Results analyzed by RRKM treatment based on *ab initio* potential surface. The simulations show that Channel (2) is 2–3 times more important than Channel (1) between 2000 and 3000 K.
- (c) Shock tube pyrolysis of HCHO/Ar mixtures. Pressure 1.4–2.5 bar. [HCHO] monitored by time resolved IR laser absorption and IR emission. Computer simulation of results over range of [HCHO] (0.01%–4.0%) used to derive  $k_1$ . Channel (2) not needed to explain data.
- (d) Shock tube pyrolysis of HCHO/Kr mixtures at pressures of 0.2–0.4 bar. [H] was monitored by time resolved ARAS. Conditions were chosen such that the effects of secondary chemistry were negligible and the [H] profiles could be interpreted in terms of Channels (1) and (2).
- (e) Accepts the expression of Irdam *et al.*<sup>2</sup> for  $k_1$ ; branching ratio from Irdam *et al.*,<sup>2</sup> and Rimpel and Just (unpublished).

### Preferred Values

$k_1 = 8.09 \cdot 10^{-9} \exp(-38050/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for M=Ar over the range 1700–3000 K.

$k_2 = 4.7 \cdot 10^{-9} \exp(-32110/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for M=Ar over the range 1700–3000 K.

See Note added in proof.

### Reliability

$\Delta \log k_1 = \pm 0.3$  over the range 1700–3000 K.

$\Delta \log k_2 = \pm 0.4$  over the range 1700–3000 K.

### Comments on Preferred Values

The reaction is second order under all conditions relevant to combustion and the expression given for  $k_1$  is probably within a few percent<sup>4</sup> of  $k_1^0$ . The shock tube results of Saito *et al.*,<sup>1</sup> Hidaka *et al.*<sup>3</sup> (low temperature range), Irdam *et al.*,<sup>2</sup> and Kumaran *et al.*<sup>4</sup> are in good agreement in the range where they overlap, and the preferred expression for  $k_1$  is based on these studies.<sup>1–4</sup> Over the temperature range of our recommendations it agrees closely with the expression derived by Irdam *et al.*<sup>2</sup> The results of Eiteneer *et al.*<sup>6</sup> appear to be slightly high. Much of the earlier experimentation also seems to have produced anomalously high rates for HCHO decomposition. These studies<sup>9–12</sup> and a number of others<sup>13–18</sup> are not used in this evaluation.

There is limited information concerning the rate coefficient  $k_2$  as most studies have been carried out under conditions where the results were insensitive to Channel (2). The

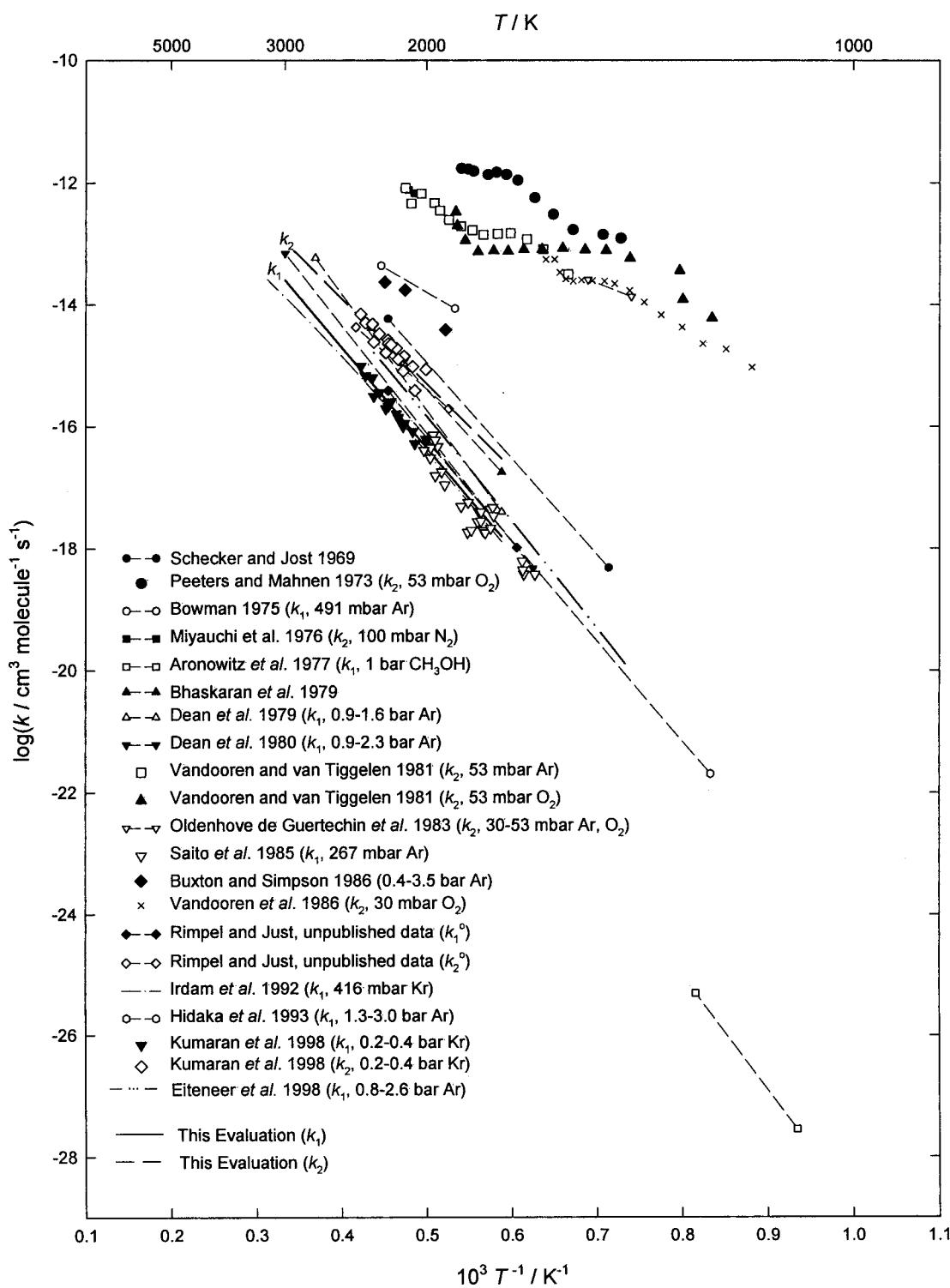
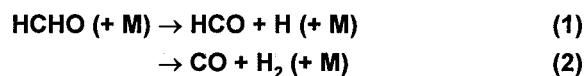
data of Saito *et al.*,<sup>1</sup> Hidaka *et al.*,<sup>3</sup> and the earlier data of Dean *et al.*,<sup>7</sup> and Buxton and Simpson<sup>8</sup> suggested that Channel (2) is unimportant near 2000 K. On the other hand the theoretical analysis of Irdam *et al.*<sup>2</sup> suggests that Channel (2) predominates and the experimental data of Kumaran *et al.*,<sup>4</sup> and of Rimpel and Just (quoted in Ref. 5) give branching ratios,  $k_1/k$ , of 0.075 and 0.16, respectively, at 2000 K. Provisionally the expression derived by Kumaran *et al.*<sup>4</sup> is accepted for  $k_2$  with which the unpublished results of Rimpel and Just are in fair agreement. The preferred expressions predict that Channel (2) is dominant but there is a significant increase in  $k_1/k$  over the temperature range recommended.

Note added in proof.

Since this data sheet was compiled, Friedriches *et al.* [Int. J. Chem. Kinet. **36**, 157 (2004)] have studied the decomposition kinetics of HCHO behind shock waves, by monitoring [HCHO] and [HCO], the former by VUV absorption and the latter by FM spectroscopy. The branching ratio is found to be strongly pressure dependent. Channel (2) is the main channel at low pressures switching to Channel (1) as the pressure is raised over the range 1–50 bar. At an average pressure of 1.2 bar  $k_1$  is given by  $k_1 = 8.3 \cdot 10^{-9} \exp(-3705/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 1675–2080 K. This is in good agreement with our recommended expression.

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*Thermodynamic Data*

$$\begin{aligned}\Delta H^0_{298}(1) &= 35.0 \text{ kJ mol}^{-1} \\ \Delta S^0_{298}(1) &= -14.5 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 1.39 \cdot 10^2 T^{0.316} \exp(-3980/T) \\ (200 \leq T/\text{K} \leq 6000)\end{aligned}$$

$$\begin{aligned}\Delta H^0_{298}(2) &= 127.2 \text{ kJ mol}^{-1} \\ \Delta S^0_{298}(2) &= 89.4 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 9.7 \cdot 10^{24} T^{-0.449} \exp(-15180/T) \text{ molecule cm}^{-3} \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{s}^{-1}$	T/K	[M]/molecule $\text{cm}^{-3}$	Reference	Comments
<i>Rate Coefficient Measurements</i>				
<i>Intermediate Fall-off Range</i>				
$3 \cdot 10^9 \exp(-14600/T)$	1545–2180	$(5.7\text{--}17) \cdot 10^{19}(\text{Ar})$	Bowman, 1975 <sup>1</sup>	(a)
$1.3 \cdot 10^{10} \exp(-14600/T)$	1500–1900	$6.0 \cdot 10^{18}(\text{Ar})$	Tsuboi <i>et al.</i> , 1981 <sup>2</sup>	(b)
$5.6 \cdot 10^{10} \exp(-14600/T)$		$3.0 \cdot 10^{19}$		
$1.0 \cdot 10^{11} \exp(-14600/T)$		$6.0 \cdot 10^{19}$		
$4.4 \cdot 10^{15} \exp(-15097/T)$	1372–1842	$(1.1\text{--}1.3) \cdot 10^{19}(\text{Ar})$	Hidaka <i>et al.</i> , 1989 <sup>3</sup>	(c)
$5.0 \cdot 10^{14} \exp(-12642/T)$	323	$(2.0\text{--}5.7) \cdot 10^{18}(\text{M})$	Bradley <i>et al.</i> , 1991 <sup>4</sup>	(d)
$1.0 \cdot 10^{14} \exp(-12629/T)$	1800–2740	$(7.8\text{--}31) \cdot 10^{17}(\text{He, Ar})$	Cribb, Dove, and Yamazaki, 1992 <sup>5</sup>	(e)
<i>Reviews and Evaluations</i>				
$k_0 = 1.0 \cdot 10^{14} \exp(-12630/T)$	1000–2200		Warnatz, 1984 <sup>7</sup>	(f)
$k_\infty = 1.6 \cdot 10^{14} \exp(-12630/T)$	300–2000			
$k_\infty = 7 \cdot 10^{14} \exp(-14915/T)$	1000		Greenhill, O'Grady, and Gilbert, 1986 <sup>10</sup>	(g)
$k_0[\text{Ar}] = [\text{Ar}] 2 \cdot 10^{-8} \exp(-12990/T)$	600–2000			
$k_0[\text{N}_2] = [\text{N}_2] 75 T^{-2.5} \exp(-17205/T)$	900–2500		Tsang, 1987 <sup>11</sup>	(h)
$k_0[\text{N}_2] = [\text{N}_2] 1 \cdot 10^{10} T^{-5.39} \exp(-18217/T)$	300–2500		Held and Dryer, 1998 <sup>12</sup>	(i)
$k_\infty = 2.8 \cdot 10^{14} T^{-0.73} \exp(-16515/T)$	300–2500			
$F_c(\text{N}_2) = (1 - 0.96) \exp(-T/67.6) + 0.96 \times \exp(-T/1855) + \exp(-7543/T)$	300–2500			

**Comments**

- (a) Oxidation of  $\text{CH}_3\text{OH}$  behind reflected shock waves.  $[\text{OH}]$ ,  $[\text{O}]$ , and  $[\text{H}_2\text{O}]$  measured by spectroscopic techniques. OH determined by absorption at 308 nm, O atoms detected by chemiluminescence generated in the reaction  $\text{O} + \text{CO}$ ,  $\text{H}_2\text{O}$  monitored by IR emission at 6.3  $\mu\text{m}$ . Observed concentration profiles interpreted with a mechanism comprising 19 reactions.
- (b) Thermal decomposition of  $\text{CH}_3\text{OH}$  behind incident and reflected shock waves. The reactions were followed by the UV absorption and the IR emission of  $\text{CH}_3\text{OH}$  at 190–200 nm and 2.4–5.2  $\mu\text{m}$ , respectively. Rate coefficients were derived by modeling the results with a mechanism comprising 26 reactions, assuming an activation energy of 121.3  $\text{kJ mol}^{-1}$ .
- (c) Pyrolysis of  $\text{CH}_3\text{OH}$  studied behind reflected shock waves.  $\text{CH}_3\text{OH}$  was monitored by IR laser absorption spectroscopy at 3.39  $\mu\text{m}$ . The reaction products were analyzed by gas chromatography and results analyzed with a mechanism comprising 26 reactions.
- (d) Measurement of burning velocities of flat, premixed, laminar, methanol-air adiabatic flames.  $[\text{CH}_3\text{OH}]$ ,  $[\text{O}_2]$ ,  $[\text{H}_2]$ ,  $[\text{CO}_2]$ , and  $[\text{CO}]$  were measured by gas chromatography together with profiles of gas temperature and flame velocity which were compared with the predictions of a kinetic mechanism.
- (e) Thermal decomposition of  $\text{CH}_3\text{OH}$  in shock waves was studied by laser Schlieren densitometry and dynamic mass spectrometry. The concentrations of  $\text{CH}_3\text{OH}$ ,  $\text{CH}_2\text{O}$ ,  $\text{CO}$ ,  $\text{C}_2\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{CH}_3$ , and  $\text{H}_2\text{O}$  were monitored. The results were interpreted with a mechanism comprising 92 reactions, based on the model for methanol combustion of Westbrook and Dryer.<sup>6</sup>
- (f) Evaluation of literature data. Low pressure rate coefficient based on the studies of Bowman,<sup>1</sup> Brabbs and Brokow,<sup>8</sup> Westbrook and Dryer,<sup>6</sup> and Tsuboi and Hashimoto.<sup>2</sup> High pressure rate coefficient based on the study of Batt and Robinson.<sup>9</sup>
- (g) RRKM calculations, with a Gorin model for the activated complexes of the reactions,  $\text{CH}_3\text{OH}(\text{+M}) \rightarrow \text{CH}_2\text{OH} + \text{H}(\text{+M})$  and  $\text{CH}_2\text{OH}(\text{+M}) \rightarrow \text{CH}_2\text{O} + \text{H}(\text{+M})$ . Fall-off effects taken into account in a master equation treatment.
- (h) Derived from RRKM modeling, assuming a high pressure A factor of  $2 \cdot 10^{13}$  at 500 K and an activation energy for the reverse process of 13  $\text{kJ mol}^{-1}$ .
- (i) Detailed modeling of  $\text{CH}_3\text{OH}$  oxidation. A mechanism

with 89 reactions was used to interpret literature data from studies carried out in static<sup>13–17</sup> and flow reactors,<sup>18–20</sup> shock tubes,<sup>2,5,6,21</sup> and premixed laminar flames.<sup>4,22,23</sup> Recommended rate data obtained from a fit of the RRKM results of Tsang<sup>11</sup> with a Troe fall-off formulations using  $-\langle \Delta E \rangle_{\text{down}} = 500 \text{ cm}^{-1}$ .

### Preferred Values

$k_2^{\circ} = 1 \cdot 10^{10} T^{-5.39} \exp(-18217/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for M=N<sub>2</sub> over the range 300–2500 K.

$k_2^{\infty} = 2.8 \cdot 10^{14} T^{-0.73} \exp(-16515/T) \text{ s}^{-1}$  over the range 300–2500 K.

$F_{2,c} = 0.04 \exp(-T/67.6) + 0.96 \exp(-T/1855) + \exp(-7543/T)$  for M=N<sub>2</sub> over the range 300–2500 K.

### Reliability

$\Delta \log k_0 = \pm 0.5$  for M=N<sub>2</sub> over the range 300–2500 K.

$\Delta \log k_{\infty} = \pm 0.5$  over the range 300–2500 K.

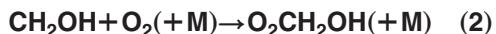
$\Delta F_c = \pm 0.5$  for M=N<sub>2</sub> over the range 300–2500 K.

### Comments on Preferred Values

Although a significant number of studies have been published recently, no detailed study of the pressure dependence has been undertaken. Nevertheless, the published studies and the evaluation of Ref. 10 indicate that fall-off effects play an important role. There are large discrepancies between the evaluations of Warnatz,<sup>7</sup> Greenhill, O'Grady, and Gilbert,<sup>10</sup> Tsang,<sup>11</sup> and Held and Dryer.<sup>12</sup> Additional information on this reaction is required. In the absence of definitive experimental data on the pressure dependence, we recommend the evaluation of  $k_2$  of Ref. 12. No recommendation for  $k_1$  is made.

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*Thermodynamic Data*

$$\begin{aligned}\Delta H_{298}^{\circ}(1) &= -77.2 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ}(1) &= 0.55 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 3.56 T^{-0.273} \exp(+9340/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$2.3 \cdot 10^{-10}$	1000–2000	Vandooren and Van Tiggelen, 1980 <sup>1</sup>	(a)
$1.7 \cdot 10^{-11}$	1300–1750	Tsuboi and Hashimoto, 1981 <sup>2</sup>	(b)
$9.5 \cdot 10^{-12}$	298	Grotheer <i>et al.</i> , 1985 <sup>3</sup>	(c)
$10.2 \cdot 10^{-12}$	296	Dóbé <i>et al.</i> , 1985 <sup>4</sup>	(d)
$8.6 \cdot 10^{-12}$	298	Payne <i>et al.</i> , 1988 <sup>5</sup>	(e)
$2.5 \cdot 10^{-9} T^{-1} + 4.0 \cdot 10^{-10} \exp(-2525/T)$	298–682	Grotheer <i>et al.</i> , 1988 <sup>6</sup>	(f)
$8.6 \cdot 10^{-12}$	300	Nesbitt <i>et al.</i> , 1988 <sup>7</sup>	(g)
$7.5 \cdot 10^{-12}$	250		
$4.9 \cdot 10^{-12}$	239		
$3.3 \cdot 10^{-12}$	230		
$2.5 \cdot 10^{-12}$	215		
$8.8 \cdot 10^{-12}$	298	Pagsberg <i>et al.</i> , 1989 <sup>8</sup>	(h)
$11.7 \cdot 10^{-12}$	296	Miyoshi <i>et al.</i> , 1990 <sup>9</sup>	(i)
$10.0 \cdot 10^{-12}$	294	Hanoune <i>et al.</i> , 2001 <sup>10</sup>	(j)
<i>Reviews and Evaluations</i>			
$2.6 \cdot 10^{-9} T^{-1} + 1.2 \cdot 10^{-10} \exp(-1800/T)$	300–1200	CEC, 1992; 1994 <sup>11</sup>	(k)
$9.1 \cdot 10^{-12}$	250–300	NASA, 1997 <sup>12</sup>	(l)
$9.6 \cdot 10^{-12}$	298	IUPAC, 1999 <sup>13</sup>	(m)

**Comments**

- (a) Mass spectrometric investigation of three low pressure (53 mbar) methanol flames ( $\phi=0.89, 0.36, 0.21$ ).  $\text{CH}_2\text{OH}/\text{CH}_3\text{O}$  were detected but it was not possible to discriminate between them, and their calibration is uncertain.
- (b) Shock tube study at densities between  $6 \cdot 10^{18}$  and  $1.2 \cdot 10^{20}$  molecules  $\text{cm}^{-3}$ , Ar. Highly diluted methanol-oxygen mixtures ( $\phi=0\text{--}2.0$ ). Concentration profiles for  $\text{CH}_3\text{OH}$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , CO, and  $\text{CH}_2\text{O}$  measured by IR emission.  $k$  was obtained by computer modeling of the system.
- (c) Discharge flow reactor with  $\text{CH}_3\text{OH}+\text{Cl}$  as the  $\text{HCHOH}$  source. The title reaction was isolated.  $k$  was obtained from  $\text{CH}_2\text{OH}$  profiles, measured by a mass spectrometer. From absolute  $\text{HCHO}$  measurements it was concluded that this is the major product.
- (d) Method as in (c) but  $\text{CH}_2\text{OH}$  monitored by LMR. From  $\text{HO}_2$  build-up rates, it was concluded that the major channel gives  $\text{HO}_2(+\text{HCHO})$ . No pressure dependence observed for  $k$  in the range 0.7–6.5 mbar. This led to the suggestion that the reaction proceeds via an excited state of a bound intermediate.

- (e) Method as in (c). Mass spectrometric  $\text{CH}_2\text{OH}$  detection.
- (f) Method as in (c). Significant non-Arrhenius behavior of  $k$  in the temperature range used. Authors suggest that the reaction mechanism is composed of a path proceeding via an adduct, and an abstraction path which dominates at high temperatures. This picture is supported by the absence of a  $\text{CH}_2\text{OH}/\text{CH}_2\text{OD}$  isotope effect at ambient temperature.
- (g) Method as in (e). Extension to temperatures below ambient. Large intercepts in the  $k$  versus  $[\text{O}_2]$  plots may indicate a wall problem, particularly at lower temperatures.
- (h) Static reactor; 1 bar, Ar.  $\text{CH}_2\text{OH}$  source was  $\text{CH}_3\text{OH} + \text{F}$  with F atoms produced from pulse radiolysis of  $\text{SF}_6$ .  $\text{CH}_2\text{OH}$  detection by UV absorption.
- (i) Pulsed laser photolysis at 193 nm of a flowing  $\text{He}/\text{O}_2/\text{CH}_3\text{COCH}_2\text{OH}$  gas mixture.  $[\text{CH}_2\text{OH}]$  monitored by photoionization mass spectrometry.
- (j) Pulsed laser photolysis at 355 nm of  $\text{Cl}_2/\text{CH}_3\text{COH}/\text{O}_2/\text{N}_2$  mixtures used to produce  $\text{CH}_2\text{COH}$  radicals by the  $\text{Cl}+\text{CH}_3\text{COH}$  reaction at total pressures in the range 5.83–15.2 mbar.  $[\text{HCHO}]$

was monitored by time-resolved diode laser absorption spectroscopy at 1707.9234 cm<sup>-1</sup> or 1707.8158 cm<sup>-1</sup>.

- (k) See Comments on Preferred Values.
- (l) Based on the data of Refs. 3–7.
- (m) Based on the data of Refs. 3–9.

### Preferred Values

$$k = [4.8 \cdot 10^{-8} T^{-1.5} + 1.2 \cdot 10^{-10} \exp(-1880/T)] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the range 298–1200 K.

### Reliability

$\Delta \log k = \pm 0.1$  at 298 K, increasing to  $\pm 0.3$  at 1200 K.

### Comments on Preferred Values

There is excellent agreement among a number of more recent measurements<sup>3–10</sup> of the rate constant at room temperature and the expression for the preferred value has been adjusted to fit the mean of them. Two earlier studies,<sup>14,15</sup> in which the reaction progress was followed by monitoring HO<sub>2</sub> production rather than OH removal, gave low values for *k* and are not used in this evaluation.

At high temperatures the results from the flame study of Vandooren and Van Tiggelen<sup>1</sup> and from the shock tube study of Tsuboi and Hashimoto<sup>2</sup> differ significantly. The results from the work of Grotheer *et al.*<sup>6</sup> over the temperature range 298–682 K extrapolate better to the results of the flame study and the preferred expression at higher temperatures is based on the work of Grotheer *et al.*<sup>6</sup> and Vandooren and Van Tiggelen.<sup>1</sup> The expression for the preferred values derived in CEC, 1994<sup>11</sup> has been modified slightly to give a better fit at low temperatures.

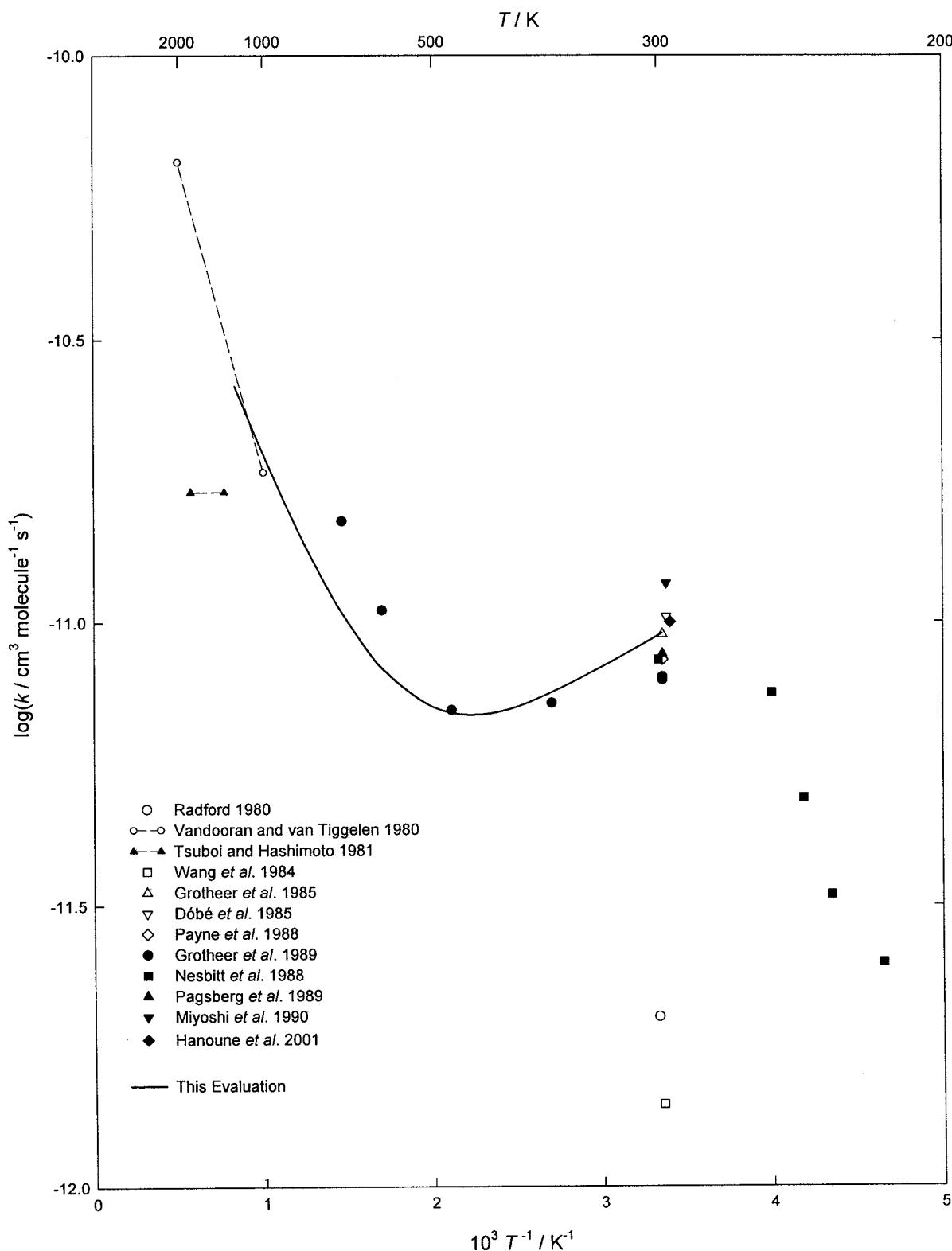
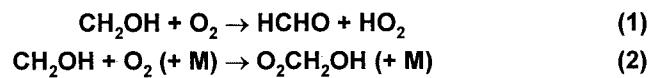
The temperature dependence of the rate constant is unusual. As the temperature is increased from 215 K the rate constant increases until, at approximately 300 K, it declines slowly with further temperature increase to a minimum at  $\sim 450$  K and then increases more rapidly as combustion temperatures are approached. It has been suggested<sup>6,7</sup> that this

behavior is consistent with formation of an adduct HOCH<sub>2</sub>OO which can dissociate back to reactants or isomerize to OCH<sub>2</sub>OOH which, in turn can dissociate to form the products HO<sub>2</sub> and HCHO. Grotheer *et al.*<sup>3</sup> showed that at 298 K the H<sub>2</sub>CO produced accounted for 95%  $\pm$  5% of the CH<sub>2</sub>OH reacted. Thus, as the temperature is raised from room temperature, dissociation competes more favorably with isomerization leading to a decline in *k* characterized by the first term in the preferred expression for *k*. At temperatures  $> 450$  K another channel, which may be direct abstraction and is characterized by the second term in the preferred expression for *k*, becomes predominant. Analogous behavior is observed for the CH<sub>3</sub>CHOH + O<sub>2</sub> reaction. The decline in *k* below room temperature is ascribed to the isomerization process having a significant activation energy.<sup>7</sup>

The expression for the preferred values of *k* is limited to temperatures above 300 K until the very low temperature results are confirmed.

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**CH<sub>2</sub>OH+CH<sub>2</sub>OH→Products****Rate Coefficient Data**

<i>k</i> /cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	<i>T</i> /K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
1.5·10 <sup>-11</sup>	298	Meier <i>et al.</i> , 1985 <sup>1</sup>	(a)
8.6·10 <sup>-11</sup>	298	Pagsberg <i>et al.</i> , 1988 <sup>2</sup>	(b)
<i>Reviews and Evaluations</i>			
1.5·10 <sup>-11</sup>	300–2500	Tsang, 1987 <sup>3</sup>	(c)

**Comments**

- (a) Discharge flow study of the OH+CH<sub>3</sub>OH reaction in a He carrier gas at total pressures of a few mbar. [OH] and [CH<sub>2</sub>OH] profiles were monitored by LIF and mass spectrometry, respectively. *k* was obtained from the [CH<sub>2</sub>OH] profiles measured as a function of the initial [CH<sub>2</sub>OH].
- (b) Pulse radiolysis study of Ar/SF<sub>6</sub>/HCl/CH<sub>3</sub>OH mixtures at a pressure of 1 bar. [CH<sub>2</sub>OH] monitored by absorption spectroscopy at 285.3 nm.
- (c) The value of Meier *et al.*<sup>1</sup> is accepted for *k*. The branching ratio *k*(CH<sub>3</sub>OH+HCHO)/*k*(CH<sub>2</sub>OH.CH<sub>2</sub>OH)=0.5 is also recommended based on the thermochemistry and a comparison with alkyl radical combination/disproportionation ratios.

**Preferred Values**

*k*=1.5·10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K.

**Reliability**

Δ log *k*=±0.5 at 298 K.

*Comments on Preferred Values*

The only two available studies<sup>1,2</sup> have both been carried out at 298 K but at very different pressures and give values of *k* which differ by a factor of 6. The value of *k* obtained by Meier *et al.*<sup>1</sup> is provisionally accepted but substantial error limits are assigned.

The reaction products have not been identified experimentally but the likely reaction channels are those giving the dimer CH<sub>2</sub>OH.CH<sub>2</sub>OH and the disproportionation products CH<sub>3</sub>OH+HCHO, which have exothermicities of 356.6 kJ mol<sup>-1</sup> and 274.5 kJ mol<sup>-1</sup>, respectively. Tsang's estimates<sup>3</sup> suggest equal probability for the two channels.

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*Thermodynamic Data*

$$\begin{aligned}\Delta H_{298}^{\circ} &= 92.2 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= 104.0 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 1.27 \cdot 10^{27} T^{-0.843} \exp(-11250/T) \text{ molecule cm}^3 \\ (300 \leqslant T/\text{K} \leqslant 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$k_0[\text{N}_2] = [\text{N}_2] 4.3 \cdot 10^{-9} \exp(-10115/T)$	610–740	Oguchi <i>et al.</i> , 2000 <sup>1</sup>	(a)
$k_0[\text{N}_2] = [\text{N}_2] 31 T^{-3.0} \exp(-12230/T)$	610–740	Hippler, Striebel, and Viscolcz, 2001 <sup>2</sup>	(b)
$k_{\infty} = 6.8 \cdot 10^{13} \exp(-13170/T)$	678–808		
$F_c(\text{N}_2) = 0.97 - T/1950$	610–740		
<i>Reviews and Evaluations</i>			
$3.16 \cdot 10^2 T^{-2.7} \exp(-15400/T)$	300–2000	Tsang and Hampson, 1986 <sup>3</sup>	(c)
$k_0[\text{He}] = [\text{He}] 9.0 \cdot 10^{-11} \exp(-6790/T)$	300–1700	CEC, 1994 <sup>4</sup>	(d)

**Comments**

- (a) Pulsed laser photolysis at 193 nm of flowing  $\text{CH}_3\text{OH}/\text{He}/(\text{or N}_2)$  mixtures.  $[\text{CH}_3\text{O}]$  was monitored by time resolved LIF using excitation at 293 nm. Total pressures in the range 130–590 mbar were used. Values of  $k_0$  were derived for  $\text{M}=\text{He}$  and for  $\text{M}=\text{N}_2$  by fitting the  $[\text{CH}_3\text{O}]$  profiles by an RRKM treatment including allowance for tunneling effects. The expression for  $k_0$  obtained for  $\text{M}=\text{N}_2$  is cited in the Table, that for  $\text{M}=\text{He}$  is,  $k_0 = 2.8 \cdot 10^{-9} \exp(-10140/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .
- (b) Photolysis at 193 nm of methyl benzoate/He mixtures at total pressures in the range 1–90 bar.  $[\text{CH}_3\text{O}]$  was monitored by time-resolved nonresonant fluorescence excited at 292.8 nm and detected at  $360 \pm 25 \text{ nm}$  under conditions in which the  $[\text{CH}_3\text{O}]$  undergoes first order decay. Values of  $k_0 = 0.3 T^{-2.4} \exp(-12320/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $F_c(\text{He}) = 0.715 - T/4340$  were obtained. The experimental results were found to agree well with those of Oguchi *et al.*<sup>1</sup> The results of Oguchi *et al.*<sup>1</sup> for  $\text{M}=\text{N}_2$  were therefore reanalyzed to obtain the expressions for  $k_0$  and  $F_c(\text{N}_2)$  which are cited in the Table. The expression for  $k_{\infty}$  cited is derived from the results of Hippler *et al.*<sup>2</sup>
- (c) Based on an RRKM calculation using a value of  $k$  obtained by Batt<sup>5</sup> from thermochemical considerations and an assumed  $A$  factor. Collision efficiencies and strong collision values given in tabular form.
- (d) Based on the data of Choudhury *et al.*<sup>6</sup>

**Preferred Values**

$$\begin{aligned}k_0 &= 31 T^{-3.0} \exp(-12230/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ for } \text{M} = \text{N}_2 \text{ over the range 500–1000 K.} \\ k_{\infty} &= 6.8 \cdot 10^{13} \exp(-13170/T) \text{ s}^{-1} \text{ over the range 500–1000 K.}\end{aligned}$$

$$F_c = 0.97 - (T/1950) \text{ for } \text{M} = \text{N}_2 \text{ over the range 500–1000 K.}$$

**Reliability**

$$\Delta \log k_0 = \pm 0.3 \text{ for } \text{M} = \text{N}_2 \text{ over the range 500–1000 K.}$$

$$\Delta \log k_{\infty} = \pm 0.5 \text{ over the range 500–1000 K.}$$

$$\Delta F_c = \pm 0.1 \text{ for } \text{M} = \text{N}_2 \text{ over the range 500–1000 K.}$$

**Comments on Preferred Values**

The experimental results of Hippler *et al.*<sup>2</sup> and of Oguchi *et al.*<sup>1</sup> are in good agreement and the expressions for the limiting low pressure rate constant which they derive agree to within a factor of  $\sim 2$ . Because of the more extensive data set, and the thorough analysis used, the expressions derived by Hippler *et al.*<sup>2</sup> from their own experimental data and that of Oguchi *et al.*<sup>1</sup> are preferred. There are also studies from Zaslonsko *et al.*,<sup>7</sup> Wantuck *et al.*,<sup>8</sup> and Choudhury *et al.*<sup>6</sup> The results of Zaslonsko *et al.*<sup>7</sup> appear to be too low by nearly an order of magnitude and those of Wantuck *et al.*<sup>8</sup> by a factor of  $\sim 3$ –4. The study of Choudhury *et al.*<sup>6</sup> gave rather high values of  $k$  and it was suggested that this might be due to contributions from tunneling.<sup>6,9</sup> However, Hippler *et al.*<sup>2</sup> find no significant tunneling effect and the high results of Choudhury *et al.*<sup>6</sup> may be related to the complexity of the system used by them.

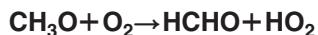
Theoretical calculations suggest that the alternative, isomerization channel,  $\text{CH}_3\text{O} + \text{M} \rightarrow \text{CH}_2\text{OH} + \text{M}$ , makes only a very small contribution.<sup>1</sup>

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#### Thermodynamic Data

$$\begin{aligned}\Delta H_{298}^{\circ} &= -112.2 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= 13.3 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 3.5 \cdot 10^2 T^{-0.629} \exp(+13290/T) \\ &\quad (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$1.05 \cdot 10^{-13} \exp(-1310/T)$	413–628	Gutman, Sanders, and Butler, 1982 <sup>1</sup>	(a)
$5.5 \cdot 10^{-14} \exp(-1000/T)$	298–450	Lorenz <i>et al.</i> , 1985 <sup>2</sup>	(b)
$1.1 \cdot 10^{-13} \exp(-1300/T)$	700–900	Zaslonsko <i>et al.</i> , 1988 <sup>3</sup>	(c)
$7.28 \cdot 10^{-43} T^{9.5} \exp(2768/T)$	298–973	Wantuck <i>et al.</i> , 1987 <sup>4</sup>	(d)
<i>Reviews and Evaluations</i>			
$3.6 \cdot 10^{-14} \exp(-880/T)$	300–1000	CEC, 1992; 1994 <sup>5</sup>	(e)
$7.2 \cdot 10^{-14} \exp(-1080/T)$	290–610	IUPAC, 1997 <sup>6</sup>	(f)

#### Comments

- (a) Laser photolysis of  $\text{CH}_3\text{ONO}$  at 266 nm;  $[\text{CH}_3\text{O}]$  monitored by LIF.
- (b) Laser photolysis of  $\text{CH}_3\text{ONO}$  at 248 nm;  $[\text{CH}_3\text{O}]$  decay in excess  $\text{O}_2$  monitored by LIF.  $k$  is independent of pressures in the range 100–200 mbar.
- (c) Shock tube decomposition of  $\text{CH}_3\text{ONO}$ ;  $[\text{CH}_3\text{O}]$  monitored by chemiluminescence from  $\text{HCHO}^*$  formed by  $\text{CH}_3\text{O}$  decomposition.
- (d) Laser photolysis of  $\text{CH}_3\text{ONO}$  or  $\text{CH}_3\text{OH}$  at 193 nm;  $[\text{CH}_3\text{O}]$  monitored by LIF. Non-Arrhenius behavior of  $k$  observed over whole temperature range. Bi-exponential expression derived to fit their own data and those from Refs. 1 and 2:  $k = [1.5 \cdot 10^{-10} \times \exp(-6028/T) + 3.6 \cdot 10^{-14} \exp(-880/T)] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .
- (e) Low E/R component of bi-exponential expression of Wantuck *et al.*<sup>4</sup> recommended.
- (f) Based on data from Refs. 1 and 2, together with those from the lower temperature range from Ref. 4.

#### Reliability

$\Delta \log k = \pm 0.1$  at 298 K, rising to  $\pm 0.3$  at 1000 K.

#### Comments on Preferred Values

The preferred values are based on the direct measurements of  $k$  obtained by Gutman *et al.*,<sup>1</sup> Lorenz *et al.*,<sup>2</sup> Zaslonsko *et al.*,<sup>3</sup> and Wantuck *et al.*<sup>4</sup> In the overlapping temperature ranges the experimental data agree well except for the data of Zaslonsko *et al.*<sup>3</sup> and Wantuck *et al.*<sup>4</sup> at  $T > 600$  K, the latter results exhibiting strong non-Arrhenius behavior which was attributed to the additional channel,  $\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{HCHO} + \text{H} + \text{O}_2$ , which is essentially the thermal decomposition,  $\text{CH}_3\text{O} + \text{M} \rightarrow \text{HCHO} + \text{HO}_2$ , with  $\text{M} = \text{O}_2$ , becoming significant at higher temperatures. The recommended expression is the low temperature component of the bi-exponential expression obtained by Wantuck *et al.*<sup>4</sup> and is unchanged from our previous evaluation.<sup>5</sup> It applies only to the channel forming  $\text{HCHO}$  and  $\text{HO}_2$  as products. There are a number of earlier studies<sup>7–12</sup> at temperatures below 400 K, which are not used in this evaluation, but are in general agreement with the recommendations. The most recent theoretical study of the reaction mechanism<sup>13</sup> suggests that the reaction proceeds by direct H atom transfer rather than by addition to form  $\text{CH}_3\text{OOO}$  followed by its decomposition to  $\text{HCHO} + \text{HO}_2$ .

Studies in the range 1000–2000 K and at higher tempera-

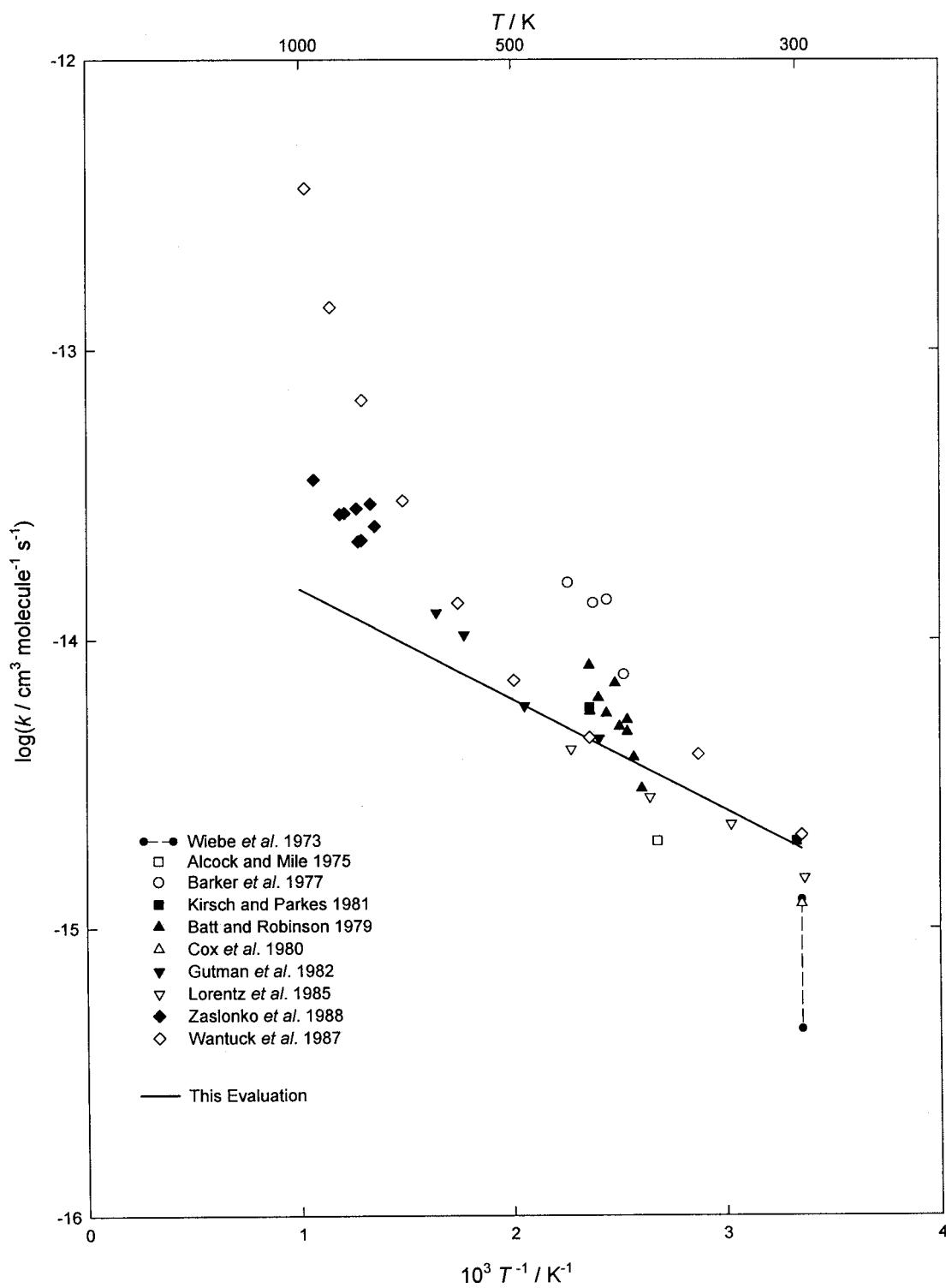
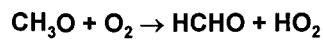
#### Preferred Values

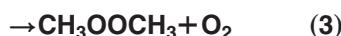
$k = 3.6 \cdot 10^{-14} \exp(-880/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 298–1000 K.

tures of both the rate constants and the products are badly needed.

## References

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#### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = -5.8 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = 124.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 9.2 \cdot 10^{27} T^{-0.781} \exp(+570/T) \text{ molecule cm}^{-3} \\ (300 \leqslant T/\text{K} \leqslant 5000)$$

$$\Delta H^\circ_{298}(2) = -350.3 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = 124.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 9.8 \cdot 10^{30} T^{-1.849} \exp(+41740/T) \text{ molecule cm}^{-3} \\ (300 \leqslant T/\text{K} \leqslant 5000)$$

$$\Delta H^\circ_{298}(3) = -165.9 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = -22.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 7.3 \cdot 10^{-5} T^{0.990} \exp(+20330/T) \\ (300 \leqslant T/\text{K} \leqslant 5000)$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2 + k_3$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$3.6 \cdot 10^{-13}$	298	Simon, Schneider, and Moortgat, 1990 <sup>1</sup>	(a)
$1.3 \cdot 10^{-13} \exp(365/T)$	248–573	Lighfoot, Veyret, and Lesclaux, 1990 <sup>2</sup>	(b)
$1.3 \cdot 10^{-13} \exp(297/T)$ at 14 mbar	268–350	Jenkin and Cox, 1991 <sup>3</sup>	(c)
$8.9 \cdot 10^{-14} \exp(424/T)$ at 1 bar			(d)
$1.0 \cdot 10^{-13} \exp(416/T)$	248–650	Lightfoot <i>et al.</i> , 1991 <sup>4</sup>	(e)
<i>Branching Ratio Measurements</i>			
$k_1/k_2 = 7.5 \exp(-760/T)$	376–430	Ballod <i>et al.</i> , 1989 <sup>5</sup>	(a)
$k_1/(k_2+k_3) = 45 \exp(-1470/T)$	388–573	Lightfoot, Veyret, and Lesclaux, 1990 <sup>2</sup>	(f)
$k_1/(k_2+k_3) = 19 \exp(-1131/T)$	223–333	Horie, Crowley, and Moortgat, 1990 <sup>6</sup>	(c)
$k_1/k_2 = 0.67$	298	Tyndall, Wallington, and Ball, 1998 <sup>7</sup>	(g)
<i>Reviews and Evaluations</i>			
$9.2 \cdot 10^{-14} \exp(390/T)$	250–600	Wallington, Dagaut, and Kurylo, 1992 <sup>8</sup>	(i)
$k_1/(k_2+k_3) = 37.3 \exp(-1350/T)$			
$9.1 \cdot 10^{-14} \exp(416/T)$	248–650	Lightfoot <i>et al.</i> , 1992 <sup>9</sup>	(j)
$k_1/(k_2+k_3) = 25 \exp(-1165/T)$	228–573		
$9.1 \cdot 10^{-14} \exp(420/T)$	298–700	CEC, 1994 <sup>10</sup>	(k)
$k_1/k_2 = 25 \exp(-1170/T)$	298–700		
$k_3 = 0$	298–700		
$2.5 \cdot 10^{-13} \exp(190/T)$	200–300	NASA, 1997 <sup>11</sup>	(l)
$1.1 \cdot 10^{-13} \exp(365/T)$	200–400	IUPAC, 1999 <sup>12</sup>	(m)
$k_2 = 5.9 \cdot 10^{-13} \exp(-509/T)$	220–330		
$9.5 \cdot 10^{-14} \exp(390/T)$	—	Tyndall <i>et al.</i> , 2001 <sup>13</sup>	(n)
$k_1/k_2 = 26.2 \exp(-1130/T)$			

#### Comments

- (a) Studies on this reaction undertaken prior to 1989 (Refs. 14–30) are not listed explicitly but have been discussed previously in the NASA<sup>11</sup> and IUPAC<sup>12</sup> evaluations and in the reviews of peroxy radical chemistry.<sup>8,9</sup>
- (b) Molecular modulation study of the broad-band photolysis (280–370 nm) of Cl<sub>2</sub>/CH<sub>4</sub>/O<sub>2</sub> mixtures. The UV absorption spectrum of CH<sub>3</sub>O<sub>2</sub> was recorded between 220 and 270 nm and calibrated by determining the rate of loss of Cl<sub>2</sub>. Numerical analysis of individual wave forms between 230 and 260 nm was undertaken with an assumed mechanism, and the branching ratios taken from the study of Niki *et al.*<sup>23</sup>

- (c) Flash photolysis of Cl<sub>2</sub>/CH<sub>4</sub>/O<sub>2</sub>/N<sub>2</sub> mixtures with UV absorption detection between 210 and 260 nm. Composite transient absorption profiles due to CH<sub>3</sub>O<sub>2</sub> and HO<sub>2</sub> analyzed using UV absorption cross sections taken from McAdam *et al.*<sup>27</sup> Absorption cross sections used (units of 10<sup>-18</sup> cm<sup>2</sup> molecule<sup>-1</sup>) are CH<sub>3</sub>O<sub>2</sub>, σ<sub>210</sub>=2.5, σ<sub>240</sub>=4.8, σ<sub>260</sub>=3.6; HO<sub>2</sub>, σ<sub>210</sub>=5.3, σ<sub>240</sub>=1.8; σ<sub>260</sub>=0.3. At higher temperatures pairs of composite wave forms were analyzed simultaneously.
- (d) Molecular modulation study of the 254 nm photolysis of CH<sub>3</sub>I/O<sub>2</sub>/N<sub>2</sub> mixture with UV absorption detection. UV absorption spectrum of CH<sub>3</sub>O<sub>2</sub> recorded between 210 nm and 320 nm but presence of a second absorber, tentatively assigned to CH<sub>3</sub>OOI, observed at longer

- wavelengths. MM wave forms recorded between 210 nm and 240 nm were consistent with those obtained from  $\text{Cl}_2/\text{CH}_4/\text{O}_2$  system. Difficulties were apparent in using photolysis rate of  $\text{CH}_3\text{I}$  to calibrate absorption spectrum of  $\text{CH}_3\text{O}_2$ . Only the ratio  $k/\sigma$  was given but rate parameters have been derived using the UV absorption spectrum and temperature branching ratios recommended by Lightfoot *et al.*<sup>9</sup>
- (e) Flash photolysis of  $\text{O}_2/\text{CH}_4/\text{CH}_3\text{OH}$  mixtures between 600 and 719 K with UV absorption detection. The earlier data of Lightfoot *et al.*<sup>2</sup> were reanalyzed using temperature dependent absorption cross sections<sup>32</sup> and combined with the results of this study.
- (f) Thermal decomposition of static mixtures of *di-t*-butylperoxide and  $\text{O}_2$  used to study branching ratios over the temperature range 376–430 K. Chromatographic analysis used for acetone and methanol.  $\text{HCHO}$  converted into a complex with chromotropic acid and detected spectrophotometrically. Iodometric analysis used for  $\text{CH}_3\text{OOH}$ . Arrhenius fit to experimental data undertaken with their preferred value of the branching ratio, ( $k_1/k_2=0.6$ ) at 298 K.
- (g) Continuous photolysis of  $\text{Cl}_2/\text{CH}_4/\text{O}_2$  mixtures with molecular beam sampling. Molecular beam deposited onto a cold finger at 50 K before cooling to 5 K. FTIR spectroscopy used to identify products and quantify yields.
- (h) Steady-state photolysis of mixtures of  $(\text{CH})_3\text{N}_2$  or  $\text{Cl}_2/\text{CH}_4$  in  $\text{O}_2/\text{N}_2$  at total pressures of 910 mbar, with monitoring of reactants and products by FTIR spectroscopy. No evidence was found for the formation of  $\text{CH}_3\text{OOCH}_3$ .
- (i) Wallington *et al.*<sup>8</sup> have used their recommended spectrum for  $\text{CH}_3\text{O}_2$  ( $\sigma_{240}=4.42 \cdot 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ ) to deduce rate parameters from the observed  $k/\sigma$  values. They derived  $k_{\text{obs}}=4.6 \cdot 10^{-13} \text{ cm}^2 \text{ molecules}^{-1} \text{ s}^{-1}$  (omitting the Sander and Watson<sup>24</sup> kinetic data obtained at 270 nm). A single unweighted Arrhenius fit of the kinetic data obtained Sander and Watson,<sup>24</sup> Kurylo and Wallington,<sup>26</sup> Jenkin and Cox,<sup>3</sup> Lightfoot *et al.*,<sup>2</sup> and the unpublished work of Anastasi *et al.*<sup>29</sup> gave  $k_{\text{obs}}=2.5 \cdot 10^{-13} \exp(180/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Wallington *et al.*<sup>8</sup> noted the good agreement between the different studies of the branching ratios at room temperature and recommended  $k_1/k=0.35$ ,  $k_2/k=0.58$ , and  $k_3/k=0.07$  which is based on an average of the studies of Parkes,<sup>16</sup> Weaver *et al.*,<sup>14</sup> Kan *et al.*,<sup>19</sup> Niki *et al.*,<sup>23</sup> and Horie *et al.*<sup>6</sup> A linear regression analysis of all of the data except the 388 K data point of Lightfoot *et al.*<sup>2</sup> was undertaken in which either  $\alpha (=k_1/k)$  or  $\log_e \beta [\beta=k_1/(k_2+k_3)]$  was plotted against the inverse of the absolute temperature from which  $\alpha=1.24-(280/T)$  and  $\beta=37.3 \exp(-1350/T)$  were obtained.
- (j) Lightfoot *et al.*<sup>9</sup> have recommended a UV absorption spectrum for  $\text{CH}_3\text{O}_2$  based on an average of the measurements of Jenkin *et al.*,<sup>28</sup> Moortgat *et al.*,<sup>30</sup> Simon *et al.*,<sup>1</sup> Jenkin and Cox,<sup>3</sup> Dagaut and Kurylo,<sup>31</sup> and Lightfoot and Jemi-Alade.<sup>32</sup> The spectrum was normalized to a value of  $4.58 \cdot 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$  at 240 nm based on the above studies but excluding the relative spectra reported by Jenkin and Cox,<sup>3</sup> and Lightfoot and Jemi-Alade.<sup>32</sup> The spectrum was used to scale the  $k/\sigma$  values reported in the different kinetics studies to give  $k_{\text{obs}}=4.9 \cdot 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The branching ratio data were analyzed simultaneously to give the temperature dependent expression  $\beta=25 \exp(-1165/T)$  which was used to derive  $k_{298}$  as  $3.7 \cdot 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The temperature dependent branching ratio was used to convert the observed rate constant into the elementary rate constant. The studies of Sander and Watson,<sup>24</sup> Kurylo and Wallington,<sup>26</sup> Lightfoot *et al.*,<sup>2</sup> and Jenkin and Cox<sup>3</sup> (at 1 bar) all gave  $E/R$  values which lay between –365 K and –481 K. The study of Jenkin and Cox<sup>3</sup> at lower pressures (145 mbar) gave a slightly lower value of –297 K for  $E/R$  which was significant at the  $1\sigma$  level. Lightfoot *et al.*<sup>9</sup> took the  $E/R$  value derived by Lightfoot *et al.*<sup>4</sup> and combined this with the value  $k_{298}=3.7 \cdot 10^{-13} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$  to give their recommended expression.
- (k) See Comments on Preferred Value.
- (l)  $k_{298}$  was based on the data of Cox and Tyndall,<sup>20</sup> Sander and Watson,<sup>24</sup> McAdam *et al.*,<sup>27</sup> Kurylo and Wallington,<sup>26</sup> Jenkin *et al.*,<sup>28</sup> Lightfoot *et al.*,<sup>2</sup> and Simon *et al.*<sup>1</sup>  $E/R$  was derived from the data of Sander and Watson,<sup>24</sup> Kurylo and Wallington,<sup>26</sup> Lightfoot *et al.*,<sup>2</sup> and Jenkin and Cox.<sup>3</sup>
- (m)  $k_{298}/\sigma_{\text{HO}_2}(250 \text{ nm})$  based on data in the references listed in Comment (i) and  $\sigma(250 \text{ nm})$  taken from Simon *et al.*<sup>1</sup>  $E/R$  based on data of Lightfoot *et al.*<sup>2</sup>
- (n) Tyndall *et al.*<sup>13</sup> have used the data of McAdam *et al.*,<sup>27</sup> Moortgat *et al.*,<sup>30</sup> Simon *et al.*,<sup>1</sup> Lightfoot and Jemi-Alade,<sup>32</sup> Jenkin and Cox,<sup>3</sup> and Maricq and Wallington,<sup>33</sup> to establish the shape of the  $\text{CH}_3\text{O}_2$  absorption spectrum which was then normalized to a value of  $4.24 \cdot 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$  at 240 nm based on the studies of Dagaut and Kurylo,<sup>31</sup> Lightfoot and Jemi-Alade,<sup>32</sup> Maricq and Wallington,<sup>33</sup> Wallington *et al.*,<sup>34</sup> and Roehl *et al.*<sup>35</sup> The spectrum was used to scale the  $k/\sigma$  values reported in the different kinetics studies. Analysis of the rescaled data on the branching ratios gave a value of  $k_1/(k_2+k_3)=0.37$  at 298 K based on the data of Parkes,<sup>16</sup> Weaver *et al.*,<sup>14</sup> Kan *et al.*,<sup>19</sup> Niki *et al.*,<sup>23</sup> Horie *et al.*,<sup>6</sup> and Tyndall *et al.*<sup>7</sup> This was combined with data for the temperature dependence from the studies of Horie *et al.*,<sup>6</sup> and Lightfoot *et al.*,<sup>2</sup> and Alcock and Mile<sup>15</sup> to give  $k_1/k_2=26.2 \exp(-1130/T)$ . The temperature dependent branching ratio was used to convert the observed rate constant into the elementary rate constant and a value of  $k_{298}=3.5 \cdot 10^{-13} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$  was derived which was combined with a temperature dependence

based on the studies of Sander and Watson,<sup>24</sup> Kurylo and Wallington,<sup>26</sup> and Lightfoot *et al.*,<sup>2</sup> to obtain their recommended expression for  $k$ .

### Preferred Values

$k = 9.5 \cdot 10^{-14} \exp(390/T)$  over the range 250–700 K.  
 $k_1/k_2 = 26.2 \exp(-1130/T)$ ;  $k_3/k = 0$  over the range 250–700 K.

### Reliability

$\Delta \log k = \pm 0.1$  at 250 K, rising to  $\pm 0.3$  at 700 K.  
 $\Delta(k_1/k_2) = \pm 0.1$  at 250 K, rising to  $\pm 0.3$  at 700 K.

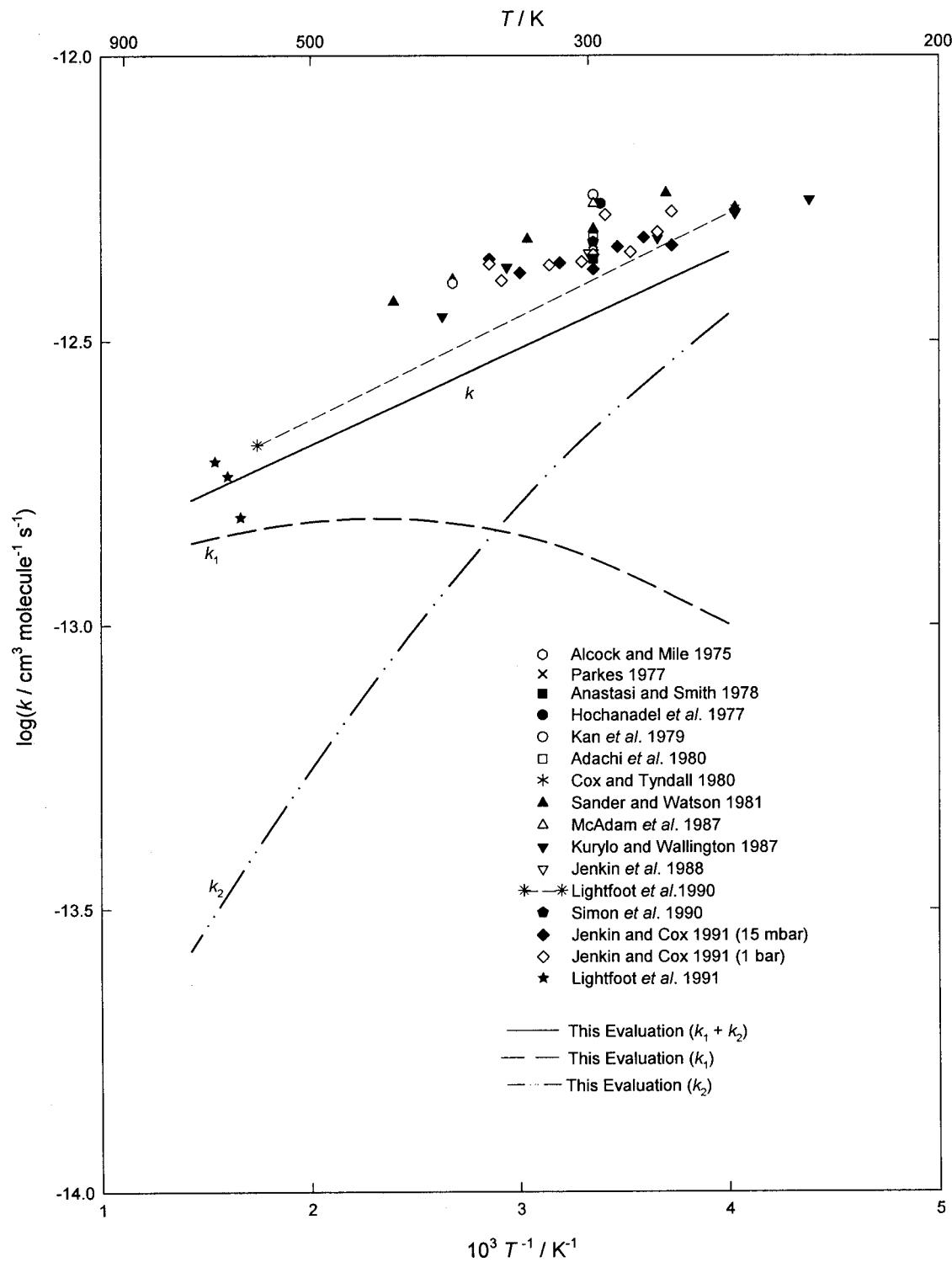
### Comments on Preferred Values

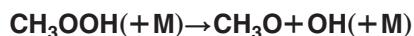
Experimental determinations of the rate constants for the  $\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2$  reaction are usually carried out by monitoring the decrease in concentration of  $\text{CH}_3\text{O}_2$ , leading to the rate law  $d[\text{CH}_3\text{O}_2]/dt = -2k_{\text{obs}}[\text{CH}_3\text{O}_2]$ . The rate constant,  $k_{\text{obs}}$ , defined by this equation is only identical with  $k (= k_1 + k_2 + k_3)$  when the experiments are carried out in the absence of  $\text{O}_2$ . For experiments performed in the presence of  $\text{O}_2$ ,  $k_{\text{obs}}$  is related to  $k$  by  $k_{\text{obs}} = k(1 + \alpha)$  where  $\alpha$  is the branching ratio for Channel (1), i.e.,  $\alpha = k_1/k$ . This arises because the  $\text{CH}_3\text{O}$  formed via Channel (1) reacts rapidly with  $\text{O}_2$  to form  $\text{HO}_2$ . The reaction of  $\text{HO}_2$  with  $\text{CH}_3\text{O}_2$  is about 20 times faster at room temperature than the self-reaction of  $\text{CH}_3\text{O}_2$  so that a second  $\text{CH}_3\text{O}_2$  is rapidly lost on the time scale of the  $\text{CH}_3\text{O}_2$  decay. Under such experimental conditions it is therefore necessary to have values of  $\alpha$  to derive values of  $k$ .

Most studies have monitored  $\text{CH}_3\text{O}_2$  by UV absorption and the derivation of accurate values of  $k$  is also critically dependent on the quality of the data on the UV absorption cross sections. Wallington *et al.*,<sup>8</sup> Lightfoot *et al.*,<sup>9</sup> and Tyndall *et al.*<sup>13</sup> have independently undertaken a critical appraisal of the available literature on the UV absorption spectrum of  $\text{CH}_3\text{O}_2$  and the kinetic and mechanistic data on the self-reaction of  $\text{CH}_3\text{O}_2$ . Differences in rate parameters between studies reflect, in part, the different values used for the absorption cross sections. The reviews recommend cross sections at 240 nm of  $4.42 \cdot 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$  (Wallington *et al.*<sup>8</sup>),  $4.58 \cdot 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$  (Lightfoot *et al.*<sup>9</sup>), and  $4.24 \cdot 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$  (Tyndall *et al.*<sup>13</sup>). The recommended rate expressions in the three reviews also give similar values over the temperature range of the experimental data. The expressions derived in the most recent of these reviews, that of Tyndall *et al.*,<sup>13</sup> for the overall rate constant and for the branching ratios are taken as our preferred values. It is generally accepted that Channel (3) does not occur to any significant degree.

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*Thermodynamic Data*

$$\Delta H^\circ_{298} = 194.6 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298} = 141.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c = 1.57 \cdot 10^{29} T^{-0.894} \exp(-23600/T) \text{ molecule cm}^{-3}$$

(300 ≤  $T/\text{K}$  ≤ 5000)

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$6.3 \cdot 10^{14} \exp(-21300/T)$	600–719	Lightfoot <i>et al.</i> , 1990 <sup>1</sup>	(a)
<i>Reviews and Evaluations</i>			
$k_\infty = 4.1 \cdot 10^{15} \exp(-21600/T)$	450–1000	CEC, 1992; 1994 <sup>2</sup>	(b)

**Comments**

- (a) UV flash photolysis of  $\text{CH}_4/\text{CH}_3\text{OH}/\text{O}_2$  mixtures;  $[\text{CH}_3\text{O}_2]$  monitored by optical absorption in the range 200–300 nm.  $\text{CH}_3\text{OOH}$  is formed as an intermediate which rapidly decomposes at the temperatures of the experiments to give products which reform  $\text{CH}_3\text{O}_2$ , thus affecting the decay kinetics of  $\text{CH}_3\text{O}_2$ , from which values of  $k$  can be derived.
- (b) Based on data for  $\text{C}_7$  hydroperoxides<sup>3</sup> and thermodynamic data.

**Preferred Values**

$k = 6 \cdot 10^{14} \exp(-21300/T) \text{ s}^{-1}$  over the range 500–800 K at a pressure of 1 bar.

**Reliability**

$\Delta \log k = \pm 0.2$  at 500 K, rising to  $\pm 0.5$  at 800 K.

**Comments on Preferred Values**

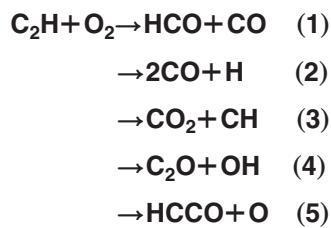
The expression obtained by Lightfoot *et al.*<sup>1</sup> is accepted. All earlier measurements of the decomposition kinetics of  $\text{CH}_3\text{OOH}$  have given unreliable results due to heterogeneous decomposition on the vessel walls.

**References**

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<sup>2</sup>CEC, 1992; Supplement I, 1994 (see references in Introduction).

<sup>3</sup>K. A. Sahetchian, A. Heiss, R. Rigny, and R. I. Ben Aim, *Int. J. Chem. Kinet.* **14**, 1325 (1982).

*Thermodynamic Data*

$$\Delta H^\circ_{298}(1) = -633.5 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = 3.44 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 5.4 \cdot 10^2 T^{-0.881} \exp(+75950/T) \quad (300 \leqslant T/\text{K} \leqslant 5000)$$

$$\Delta H^\circ_{298}(3) = -363.2 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = -21.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 8.6 \cdot 10^{-2} T^{-0.059} \exp(+43750/T) \quad (300 \leqslant T/\text{K} \leqslant 5000)$$

$$\Delta H^\circ_{298}(5) = -141.6 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(5) = -12.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(5) = 6.4 \cdot 10^{-2} T^{0.199} \exp(+17080/T) \quad (200 \leqslant T/\text{K} \leqslant 6000)$$

$$\Delta H^\circ_{298}(2) = -569.2 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = 91.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 3.69 \cdot 10^{27} T^{-1.233} \exp(+68190/T) \text{ molecule cm}^{-3} \quad (300 \leqslant T/\text{K} \leqslant 5000)$$

$$\Delta H^\circ_{298}(4) = -146.0 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(4) = -1.73 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(4) = 0.809 T^{0.021} \exp(+17510/T) \quad (300 \leqslant T/\text{K} \leqslant 5000)$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data ( $k = k_1 + k_2 + k_3 + k_4 + k_5$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$2.9 \cdot 10^{-11}$	298	Lander <i>et al.</i> , 1990 <sup>1</sup>	(a)
$1.5 \cdot 10^{-11} \exp(230/T)$	193–350	Opansky <i>et al.</i> , 1993 <sup>2</sup>	(b)
$1.9 \cdot 10^{-11} \exp(160/T)$	295–450	Van Look and Peeters, 1995 <sup>3</sup>	(c)
$7.8 \cdot 10^{-11} T^{-0.16}$	295–700	Thiesmann and Taatjes, 1997 <sup>4</sup>	(d)
See Comments	15–295	Chastaing <i>et al.</i> , 1998 <sup>5</sup>	(e)
$3.8 \cdot 10^{-11}$	103	Vakhtin <i>et al.</i> , 2001 <sup>6</sup>	(f)
<i>Reviews and Evaluations</i>			
$3 \cdot 0 \cdot 10^{-11}$	300	CEC, 1992; 1994 <sup>7</sup>	(g)

**Comments**

- (a) Pulsed laser photolysis of  $\text{CF}_3\text{C}_2\text{H}$  at 193 nm. Transient infrared absorption of  $\text{C}_2\text{H}$  monitored.
- (b) Pulsed laser photolysis of  $\text{C}_2\text{H}_2$  at 193 nm in excess of  $\text{O}_2$  in flowing system.  $[\text{C}_2\text{H}]$  monitored by infrared laser absorption. He carrier gas used with total pressures in the range 13–133 mbar.  $k$  was found to be independent of pressure in this range.
- (c) Pulsed laser photolysis of  $\text{C}_2\text{H}_2$  at 193 nm in excess of  $\text{O}_2$  in flowing system. Chemiluminescence of  $\text{CH}(\text{A}^2\Delta)$ , produced in small yields from the reaction with  $\text{O}_2$ , was monitored at 430 nm. Total pressure varied over the range 1.3–13.3 mbar.
- (d) Technique as in (c) but total pressure varied over the range 26–400 mbar (He carrier gas). No dependence of  $k$  on pressure found.
- (e) Low temperatures were achieved using the CRESU technique in which  $\text{C}_2\text{H}_2/\text{O}_2$  mixtures in an inert carrier gas (He, Ar, or  $\text{N}_2$ ) were expanded through a Laval nozzle.  $\text{C}_2\text{H}$  radicals were generated by pulsed laser photolysis at 193 nm of the  $\text{C}_2\text{H}_2$  and the reaction

progress was monitored by observation of the chemiluminescence from the  $\text{C}_2\text{H} + \text{O}_2$  reaction. Values of  $k$  were obtained at 295 K, 149 K, 112 K, 63 K, 54 K, 39 K, 27 K, 25 K, and 15 K, but no functional relationship between  $k$  and  $T$  was derived.

(f) Experiment as in Comment (e) but a pulsed expansion through the Laval nozzle was used to check that the pulsed and continuous expansion techniques give identical results. The results were in good agreement with those from the previous study.

(g) Value based on the data of Stephens *et al.*<sup>8</sup> and Renlund *et al.*<sup>9</sup>

**Preferred Values**

$$k = 2.7 \cdot 10^{-10} T^{-0.35} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the range } 200\text{--}1500 \text{ K.}$$

**Reliability**

$$\Delta \log k = \pm 0.2 \text{ at } 200 \text{ K, rising to } \pm 0.3 \text{ at } 1500 \text{ K.}$$

*Comments on Preferred Values*

The preferred values are obtained from a fit to the data of Lander *et al.*,<sup>1</sup> Opansky *et al.*,<sup>2</sup> Van Look and Peeters,<sup>3</sup> Thiesmann and Taatjes,<sup>4</sup> Chastaing *et al.*,<sup>5</sup> and Vakhtin *et al.*<sup>6</sup> which are in excellent agreement over the range 15–700 K. The values obtained by Stephens *et al.*<sup>8</sup> and Renlund *et al.*<sup>9</sup> are also in reasonable agreement with the preferred expression for  $k$  but those of Laufer and Lechleider,<sup>10</sup> and Lange and Wagner,<sup>11</sup> also in this temperature range, appear to be too low. There is also a recent study of Lee and Leone<sup>12</sup> which work from the same group<sup>6</sup> suggests is not consistent with the body of results from the studies cited in the Table. Vakhtin *et al.*<sup>6</sup> have pointed out that the data show some slight evidence of a pressure effect but this requires further study.

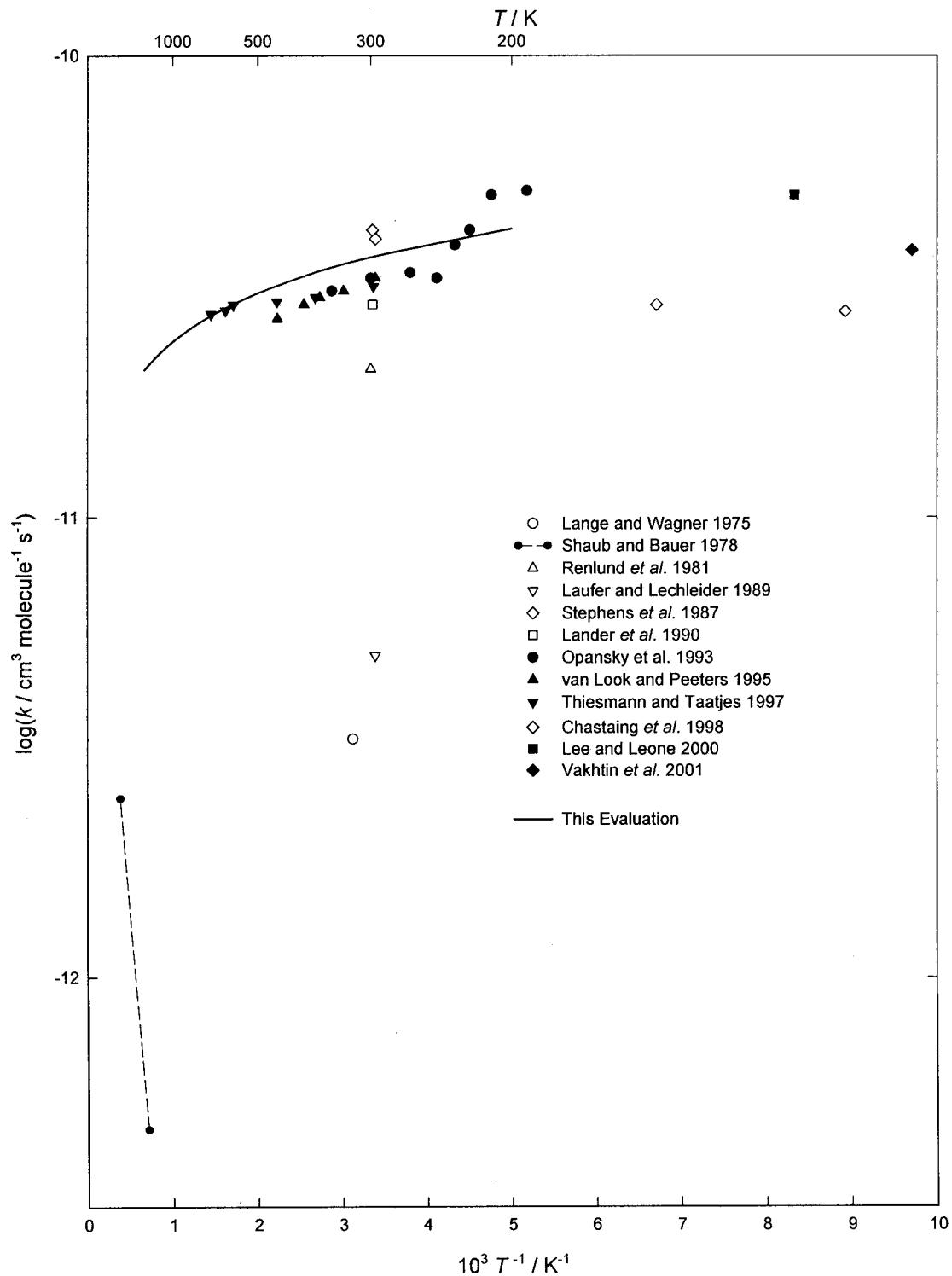
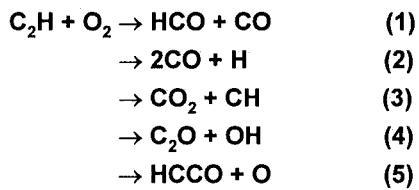
Unfortunately there are few data available at high temperatures. The shock tube study of Shaub and Bauer<sup>13</sup> gives values of  $k$  which cannot be reconciled with the low temperature results.

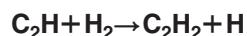
The temperature coefficient of the rate constant, and its lack of any clear pressure dependence,<sup>2–4</sup> suggest formation of a peroxy species, HCCOO, which is too short lived to be collisionally stabilized at the pressures used in these studies (up to 400 mbar) and probably much higher. The products of decomposition of the HCCOO are uncertain. HCCO,<sup>11</sup> CO,<sup>9,10,14,15</sup> CO<sub>2</sub>,<sup>9,14,15</sup> and CH<sup>9,15</sup> have been detected with CO formation probably being a major channel [Channel (1) and/or (2)]. A recent study<sup>16</sup> at low pressures using time resolved FTIR emission spectroscopy to observe product formation found a branching ratio for nascent CO:CO<sub>2</sub> production of 9:1. However more studies are required before any recommendations can be made.

Van Look *et al.*<sup>3</sup> showed that there is a very minor channel producing CH( $A\ ^2\Delta$ ) + CO and leading to chemiluminescence from the CH( $A\ ^2\Delta \rightarrow X\ ^2\Pi$ ) transition. Subsequent work by Devriendt *et al.*<sup>17</sup> suggested a value of  $1.1 \cdot 10^{-3}$  for the CH( $A\ ^2\Delta$ ) yield.

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- <sup>13</sup>W. M. Shaub and S. H. Bauer, *Combust. Flame* **32**, 35 (1978).
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- <sup>17</sup>K. Devriendt, H. Van Look, B. Ceusters, and J. Peeters, *Chem. Phys. Lett.* **270**, 580 (1997).



*Thermodynamic Data*

$$\begin{aligned}\Delta H^\circ_{298} &= -119.9 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298} &= -28.4 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 2.1 \cdot 10^{-4} T^{0.677} \exp(+14810/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the origin and quality of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$7.4 \cdot 10^{-13}$	298	Laufer and Bass, 1979 <sup>1</sup>	(a)
$9.3 \cdot 10^{-12}$	625–3400	Tanzawa and Gardiner, 1980 <sup>2</sup>	(b)
$1.3 \cdot 10^{-11}$	1800–2500	Koike and Morinaga, 1981; <sup>3</sup> Gardiner <i>et al.</i> , 1985 <sup>4</sup>	(c)
$1.2 \cdot 10^{-11}$	2300–3200	Kiefer <i>et al.</i> , 1983 <sup>5</sup>	(d)
$4.8 \cdot 10^{-13}$	298	Stephens <i>et al.</i> , 1987 <sup>6</sup>	(e)
$4.4 \cdot 10^{-13}$	298	Lander <i>et al.</i> , 1990 <sup>7</sup>	(f)
$1.8 \cdot 10^{-11} \exp(-1090/T)$	298–438	Koshi <i>et al.</i> , 1992 <sup>8</sup>	(g)
$7.1 \cdot 10^{-13}$	293	Koshi, Nishida, and Matsui, 1992 <sup>9</sup>	(h)
$5.1 \cdot 10^{-13}$			
$9 \cdot 44 \cdot 10^{-14} T^{0.9} \exp(-1003/T)$	295–854	Farhat, Morter, and Glass, 1993 <sup>10</sup>	(e)
$1 \cdot 2 \cdot 10^{-11} \exp(-988/T)$	178–359	Opansky and Leone, 1996 <sup>11</sup>	(i)
$5 \cdot 3 \cdot 10^{-12} \exp(-598/T)$	295–440	Peeters, Van Look, and Ceursters, 1996 <sup>12</sup>	(j)
$1.23 \cdot 10^{-9} \exp(-3400/T)$	2890–3180	Kruse and Roth, 1997 <sup>13</sup>	(k)
<i>Reviews and Evaluations</i>			
$1.8 \cdot 10^{-11} \exp(-1090/T)$	300–2500	CEC, 1992; 1994 <sup>14</sup>	(l)

**Comments**

- (a) Relative rate study using VUV flash photolysis of  $\text{C}_2\text{H}_2$  with and without added  $\text{H}_2$ ;  $[\text{C}_4\text{H}_2]$  monitored by gas chromatographic sampling and VUV absorption at 144.6 nm. Total pressures, 27 or 930 mbar He.  $k(\text{C}_2\text{H} + \text{H}_2)/k(\text{C}_2\text{H} + \text{C}_2\text{H}_2) = 4.9 \cdot 10^{-3}$  obtained. Value of  $k$  cited is based on  $k(\text{C}_2\text{H} + \text{C}_2\text{H}_2)$  from this evaluation.
- (b) Modeling study of  $\text{C}_2\text{H}_2$  pyrolysis in shock tubes, flow reactors, and bulb dissociation experiments. Wrong data transcription in the table in the paper; corrected in Ref. 4.
- (c) Shock heating of  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_2/\text{H}_2$ , or  $\text{C}_2\text{H}_4$  in 0.5 bar Ar. Absorption measurements at 216 nm and 230 nm. Numerical modeling of substantial reaction mechanism.  $k$  adjusted to fit the absorption profile of  $\text{C}_4\text{H}_2$ . Wrong thermochemical data for  $\text{C}_2\text{H}$ ; correction in Ref. 4.
- (d) Pyrolysis of  $\text{C}_2\text{H}_4/\text{Kr}$  mixtures behind incident shock waves; laser-Schlieren measurements. Total pressure 270–980 mbar. Numerical modeling of substantial reaction mechanism based on that in Ref. 2.
- (e) Flash photolysis of  $\text{CF}_3\text{C}_2\text{H}$  at 193 nm. Ground state  $\text{C}_2\text{H}$  monitored by IR absorption at  $3594.4 \text{ cm}^{-1}$ . Total pressure 27 mbar He.  $\text{SF}_6$  added to ensure rapid vibrational relaxation of  $\text{C}_2\text{H}$ .
- (f) Technique as in (e). Effects of pressure change over the range 11–90 mbar He studied. No effect on  $k$  found.

- (g) Relative rate measurement. Pulsed ArF laser photolysis of  $\text{C}_2\text{H}_2/\text{H}_2$  mixtures to generate  $\text{C}_2\text{H}$  and  $\text{H}$ . Formation of  $\text{C}_4\text{H}_2$  by the reaction  $\text{C}_2\text{H} + \text{C}_2\text{H}_2 \rightarrow \text{C}_4\text{H}_2 + \text{H}$  monitored by time-resolved mass spectrometry. Yield of  $\text{C}_4\text{H}_2$  as a function of  $[\text{H}_2]$  gives  $k/k_{\text{ref}}$  where  $k_{\text{ref}}$  refers to the reaction of  $\text{C}_2\text{H}$  with  $\text{C}_2\text{H}_2$  to give  $\text{C}_4\text{H}_2$ . Value of  $k_{\text{ref}} = 1.5 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  used, obtained from a shock tube study in the same laboratory.<sup>2</sup>
- (h) Pulsed ArF laser photolysis of  $\text{C}_2\text{H}_2/\text{H}_2$  mixtures. Reaction monitored by LIF detection of  $\text{H}$  and by time-resolved mass spectrometric detection of  $\text{C}_4\text{H}_2$  in separate experiments. The former gives  $k = (7.1 \pm 1.1) \cdot 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .
- (i) Pulsed laser photolysis of  $\text{C}_2\text{H}_2$  at 193 nm in the presence of an excess of  $\text{H}_2$  in a flowing system.  $[\text{C}_2\text{H}]$  monitored by infrared laser absorption at  $3594.4 \text{ cm}^{-1}$ . Using their own and data from earlier studies the authors derive the expression,  $k = 9.2 \cdot 10^{-18} T^{2.17} \exp(-478/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .
- (j) Pulsed laser photolysis of  $\text{C}_2\text{H}_2$  at 193 nm in the presence of excess  $\text{H}_2/\text{O}_2$  mixtures. Chemiluminescence of  $\text{CH}(A^2\Delta)$  produced in reaction with  $\text{O}_2$  was monitored.  $[\text{H}_2]$  varied in constant  $[\text{O}_2]$ .
- (k) Shock tube study on the pyrolysis of  $\text{C}_2\text{H}_2/\text{Ar}$  and  $\text{C}_2\text{H}_2/\text{H}_2/\text{Ar}$  mixtures at pressures of about 2 bar.  $[\text{C}_2]$ ,  $[\text{C}]$ , and  $[\text{C}_3 \text{ radicals}]$  were monitored by ring dye-laser absorption, ARAS, and emission spectroscopy, respectively. Values of  $k$  were derived by fitting the concentration profiles using a detailed mechanism.

(I) Accepted the expression derived by Koshi *et al.*<sup>9</sup>

### Preferred Values

$k = 3.5 \cdot 10^{-18} T^{2.32} \exp(-444/T)$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>  
over the range 180–3000 K.

### Reliability

$\Delta \log k = \pm 0.15$  at 300 K, rising to  $\pm 0.2$  at 180 K and  $\pm 0.5$  at 3000 K.

### Comments on Preferred Values

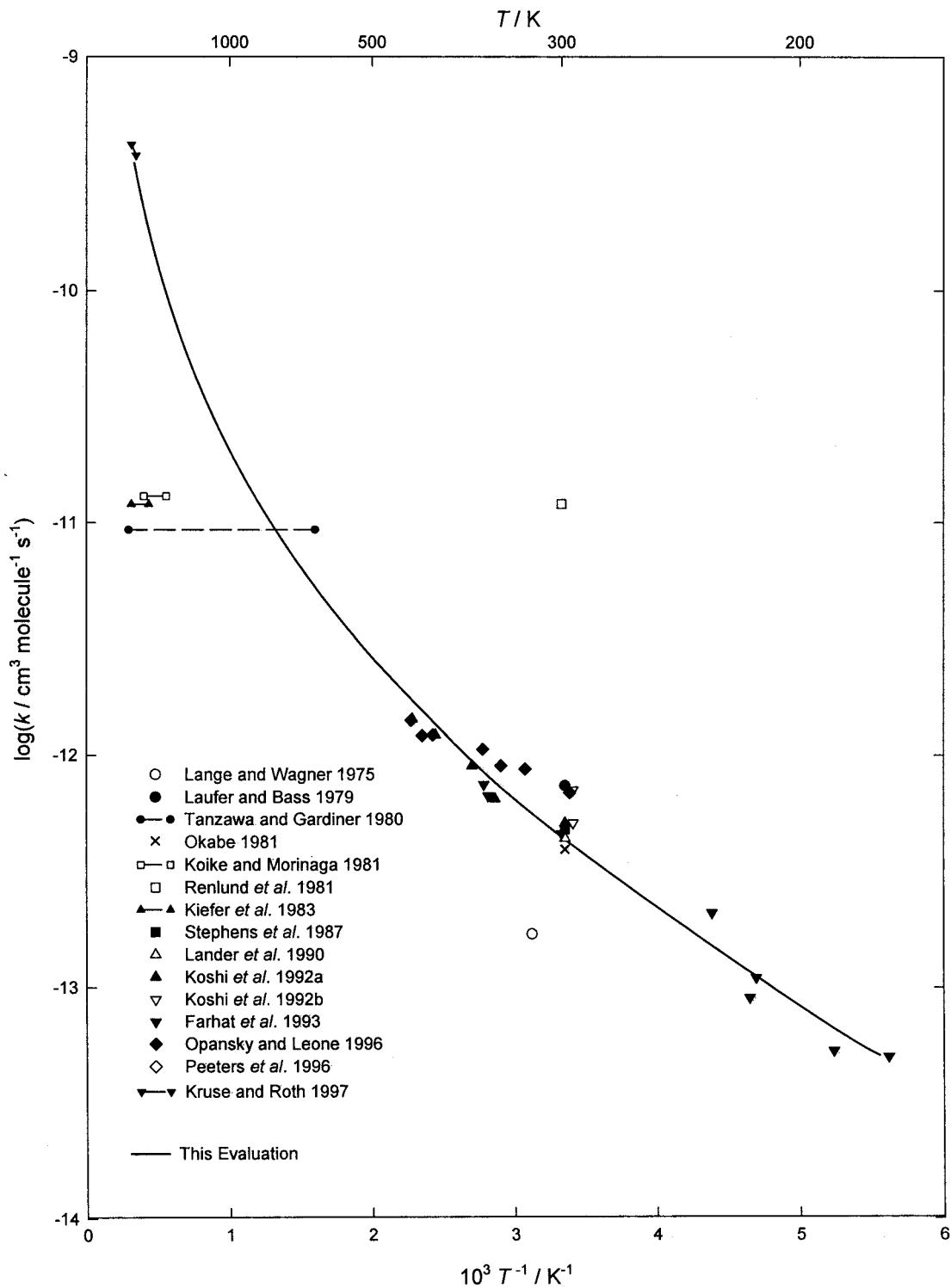
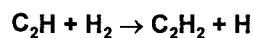
Since our previous evaluation<sup>14</sup> there have been three low temperature studies<sup>10–12</sup> of the temperature dependence of  $k$ , together covering the range 178–854 K, and a shock tube study<sup>13</sup> covering the range 2890–3180 K. The temperature dependence found in one of the low temperature studies<sup>12</sup> is considerably smaller ( $E/R = 598$  K) than found in the other two<sup>10,11</sup> ( $E/R \approx 1000$  K) but the absolute values of  $k$  are in good agreement and in accord with most of the earlier data<sup>1,6–9</sup> except that of Lange and Wagner,<sup>15</sup> Renlund *et al.*,<sup>16</sup> and Okabe<sup>17</sup> which are not used in arriving at our preferred values.

The values of  $k$  from the high temperature studies ( $T > 1000$  K)<sup>2–5,13</sup> differ by more than an order of magnitude at comparable temperatures. The study of Kruse and Roth,<sup>13</sup> in which several species were monitored and the system was modeled using more recent kinetic data, appears to be the most reliable, but until more high temperature studies are available we base our preferred expression on data at temperatures below 1000 K. For our preferred expression we

have modified slightly the expression derived by Opansky and Leone<sup>11</sup> [see Comment (i)] so that it extrapolates reasonably well to the high temperature data of Kruse and Roth.<sup>13</sup> The expression for  $k$  so derived represents the data for the cited studies in the range 178–854 K to within  $\sim 10\%$  and we recommend its use at higher temperatures with increased error limits.

### References

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- <sup>12</sup> J. Peeters, H. Van Look, and B. Ceusters, J. Phys. Chem. **100**, 15124 (1996).
- <sup>13</sup> T. Kruse and P. Roth, J. Phys. Chem. A **101**, 2138 (1997).
- <sup>14</sup> CEC, 1992; Supplement I, 1994 (see references in Introduction).
- <sup>15</sup> W. Lange and H. Gg. Wagner, Ber. Bunsenges. Phys. Chem. **79**, 165 (1975).
- <sup>16</sup> A. M. Renlund, F. Shokoohi, H. Reisler, and C. Wittig, Chem. Phys. Lett. **84**, 293 (1981).
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**C<sub>2</sub>H+H<sub>2</sub>O→Products****Rate Coefficient Data**

<i>k/cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup></i>	<i>T/K</i>	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$1.9 \cdot 10^{-11} \exp(-200/T)$	295–451	Van Look and Peeters, 1995 <sup>1</sup>	(a)

**Comments**

- (a) Pulsed laser photolysis of C<sub>2</sub>H<sub>2</sub>/O<sub>2</sub> mixtures. Chemiluminescence of CH(A<sup>2</sup>Δ) at 430 nm produced by reaction of C<sub>2</sub>H with O<sub>2</sub> monitored as a function of time and of [C<sub>2</sub>H<sub>2</sub>]/[O<sub>2</sub>].

**Preferred Values**

No recommendation. See Comments on Preferred Values.

*Comments on Preferred Values*

There is only one experimental study of this reaction. The values obtained for *k*, which are surprisingly high, and the small value of *E/R*, are both suggestive of an addition mechanism rather than abstraction. Ding *et al.*<sup>2</sup> have investi-

gated this possibility using various levels of theory to model the reaction. They come to the conclusion that direct abstraction to give C<sub>2</sub>H<sub>2</sub>+OH is kinetically much more competitive than other dissociation or association–elimination mechanisms but the values of the rate constant are predicted to be much smaller than the values found experimentally. The experimental technique used has proved reliable in studying other reactions of C<sub>2</sub>H but, until this anomalous result is investigated further, we make no recommendation.

**References**

<sup>1</sup>H. Van Look and J. Peeters, *J. Phys. Chem.* **99**, 16284 (1995).

<sup>2</sup>Y. Ding, X. Zhang, Z. Li, X. Huang, and C. Sun, *J. Phys. Chem. A* **105**, 8206 (2001).

**C<sub>2</sub>H+NO→Products****Rate Coefficient Data**

<i>k/cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup></i>	<i>T/K</i>	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$3.5 \cdot 10^{-11}$	298	Stephens <i>et al.</i> , 1987 <sup>1</sup>	(a)
$3.6 \cdot 10^{-11}$	298	Lander <i>et al.</i> , 1990 <sup>2</sup>	(b)
$1.0 \cdot 10^{-10} \exp(-287/T)$	295–414	Peeters, Van Look, and Ceusters, 1996 <sup>3</sup>	(c)

**Comments**

- (a) Pulsed laser photolysis of C<sub>2</sub>H<sub>2</sub> at 193 nm. [C<sub>2</sub>H] monitored by IR absorption at 3594.4 cm<sup>-1</sup>. Total pressure 27 mbar He. SF<sub>6</sub> added to ensure rapid vibrational relaxation of C<sub>2</sub>H.
- (b) Pulsed laser photolysis of CF<sub>3</sub>CCH at 193 nm in presence of 25 mbar He and 0.26 mbar of SF<sub>6</sub> to quench the excited state of C<sub>2</sub>H produced. [C<sub>2</sub>H] monitored by diode laser absorption at 2089.07 cm<sup>-1</sup> in the presence of excess NO.
- (c) Pulsed laser photolysis of C<sub>2</sub>H<sub>2</sub> or C<sub>2</sub>HCF<sub>3</sub> in presence of excess NO/O<sub>2</sub> mixtures. Chemiluminescence of CH(A<sup>2</sup>Δ) produced in the reaction of C<sub>2</sub>H with O<sub>2</sub> was monitored as a function of time and of [C<sub>2</sub>H<sub>2</sub>]/[O<sub>2</sub>]. *k* was found to be independent of pressure over the range 2.7–13.3 mbar.

**Preferred Values**

*k*= $1.0 \cdot 10^{-10} \exp(-287/T)$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> over the temperature range 295–450 K.

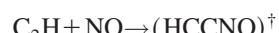
*Reliability*

$\Delta \log k = \pm 0.2$  over the range 295–450 K.

*Comments on Preferred Values*

The preferred expression for *k* is that determined by Peeters *et al.*<sup>3</sup> which is the only study over a temperature range. It is in excellent agreement with the only other available data at 298 K.<sup>1,2</sup>

Possible exothermic product channels are:

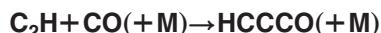


Peeters *et al.*<sup>3</sup> find no pressure dependence of the rate constant over the range 2.7–13.3 mbar and the values at these pressures agree with the value obtained by Stephens *et al.*<sup>1</sup> at 27 mbar. Since the reaction also has a high rate constant it seems that the mechanism is one of addition followed by very rapid rearrangement and/or decomposition and, on that basis, Sengupta *et al.*<sup>4</sup> have carried out *ab initio* calculations which lead them to propose that the main channels are Channels (1), (2), and (3) with Channel (1) being the most favorable. Su *et al.*<sup>5</sup> have studied the reaction at low pressures using time-resolved FTIR emission spectroscopy to observe product formation. HCN, HNC, and HCO were observed

confirming the occurrence of Channels (1), (2), (3) but no branching ratios were derived.

## References

- <sup>1</sup>J. W. Stephens, J. L. Hall, H. Solka, W. B. Yan, R. F. Curl, and G. P. Glass, *J. Phys. Chem.* **91**, 5740 (1987).
- <sup>2</sup>D. R. Lander, K. G. Unfried, G. P. Glass, and R. F. Curl, *J. Phys. Chem.* **94**, 7759 (1990).
- <sup>3</sup>J. Peeters, H. Van Look, and B. Ceusters, *J. Phys. Chem.* **100**, 15124 (1996).
- <sup>4</sup>D. Sengupta, J. Peeters, and M. T. Nguyen, *Chem. Phys. Lett.* **283**, 91 (1998).
- <sup>5</sup>H. Su, J. Yang, Y. Ding, W. Feng, and F. Kong, *Chem. Phys. Lett.* **326**, 73 (2000).



### Thermodynamic Data

$$\Delta H_{298}^{\circ} = -83.6 \text{ kJ mol}^{-1}$$

$$\Delta S_{298}^{\circ} = -144.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c = 1.11 \cdot 10^{-31} T^{1.418} \exp(+10440/T) \text{ cm}^3 \text{ molecule}^{-1}$$

(300 ≤ T/K ≤ 5000)

See Section 3 for the source of the Thermodynamic Data.

### Rate Coefficient Data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	[M]/molecule $\text{cm}^{-3}$	Reference	Comments
<i>Rate Coefficient Measurements</i>				
$[\text{He}] 2.4 \cdot 10^{-30}$	298	$(0.3-2.3) \cdot 10^{18}$	Lander <i>et al.</i> , 1990 <sup>1</sup>	(a)
<i>Reviews and Evaluations</i>				
$k_{\infty} = 2.5 \cdot 10^{-13} \exp(-2420/T)$	300–2500		Tsang and Hampson, 1986 <sup>2</sup>	(b)

### Comments

- (a) Pulsed laser photolysis at 193 nm of  $\text{CF}_3\text{C}_2\text{H}/\text{SF}_6/\text{He}$  mixtures. The  $\text{SF}_6$ , present in small amounts, efficiently relaxes excited  $\text{C}_2\text{H}$ .  $[\text{C}_2\text{H}]$  monitored by time resolved infrared diode laser absorption spectroscopy. The increase of the measured second order rate constant with He pressure deviates from linearity over the pressure range 13–90 mbar.
- (b) Estimated by analogy with the  $\text{C}_2\text{H}_5 + \text{CO}$  reaction.

### Preferred Values

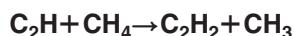
No recommendation.

### Comments on Preferred Values

The only study of the rate constant of this reaction is that of Lander *et al.*<sup>1</sup> From the effect of pressure on the measured second order rate constant it was concluded that the reaction occurred by addition. However, the pressure dependence was not linear over the range studied and, until further data become available, no recommendations are made.

## References

- <sup>1</sup>D. R. Lander, K. G. Unfried, G. P. Glass, and R. F. Curl, *J. Phys. Chem.* **94**, 7759 (1990).
- <sup>2</sup>W. Tsang and R. F. Hampson, *J. Phys. Chem. Ref. Data* **15**, 1087 (1986).

*Thermodynamic Data*

$$\begin{aligned}\Delta H^\circ_{298} &= -116.6 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298} &= -4.48 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 0.105 T^{0.309} \exp(+13990/T) \\ &\quad (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$3.0 \cdot 10^{-12}$	298	Lander <i>et al.</i> , 1990 <sup>1</sup>	(a)
$1.2 \cdot 10^{-11} \exp(-491/T)$	154–359	Opansky and Leone, 1996 <sup>2</sup>	(b)
$1.39 \cdot 10^{-18} T^{2.34} \exp(380/T)$	295–779	Ceursters <i>et al.</i> , 2000 <sup>3</sup>	(c)
<i>Reviews and Evaluations</i>			
$3.0 \cdot 10^{-12}$	298	CEC, 1992; 1994 <sup>4</sup>	(d)

**Comments**

- (a) Pulsed laser photolysis of  $\text{CF}_3\text{CCH}$  at 193 nm in the presence of approximately 25 mbar He and 0.26 mbar  $\text{SF}_6$  to quench the excited state of  $\text{C}_2\text{H}$  produced.  $[\text{C}_2\text{H}]$  monitored by tunable diode laser absorption at  $2089.07 \text{ cm}^{-1}$  in the presence of an excess of  $\text{CH}_4$ .  $k$  was shown to be independent of pressure over the range 11–90 mbar He.
- (b) Pulsed laser photolysis of  $\text{C}_2\text{H}_2$  at 193 nm in the presence of a large excess of  $\text{CH}_4$  in a flowing system.  $[\text{C}_2\text{H}]$  monitored by color center laser absorption at 3593.68 nm. He buffer gas pressure varied over the range 20–100 mbar. No effect of pressure was observed. The rate constant for the reaction of  $\text{C}_2\text{H}$  with  $\text{CD}_4$  was also measured giving  $k(\text{C}_2\text{H} + \text{CD}_4) = 8.7 \cdot 10^{-12} \exp(-650/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .
- (c) Pulsed laser photolysis at 193 nm of  $\text{C}_2\text{H}_2/\text{O}_2/\text{CH}_4/\text{He}$  mixtures.  $[\text{C}_2\text{H}]$  was monitored by time-resolved measurements of the intensity of the chemiluminescence produced from the  $\text{C}_2\text{H} + \text{O}_2$  reaction.  $\text{O}_2$  was present in large excess and in constant amounts, the  $[\text{CH}_4]$  also in large excess was varied. An *ab initio* calculation suggested that the reaction occurs by direct H abstraction.
- (d) Accepts the value of Lander *et al.*<sup>1</sup>

**Preferred Values**

$k = 3.6 \cdot 10^{-14} T^{0.94} \exp(-328/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$   
over the range 150–780 K.

*Reliability*

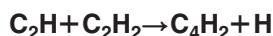
$\Delta \log k = \pm 0.2$  over the range 150–780 K.

*Comments on Preferred Values*

The recommended expression for  $k$  is a least squares fit to the data of Lander *et al.*,<sup>1</sup> Opansky and Leone,<sup>2</sup> and Ceursters *et al.*<sup>3</sup> The techniques used by Opansky and Leone<sup>2</sup> and by Ceursters *et al.*<sup>3</sup> have proved reliable in other studies<sup>5–7</sup> of  $\text{C}_2\text{H}$  reactions and the study of Lander *et al.* at 298 K, which was taken as the preferred value in our previous evaluation,<sup>4</sup> is in good agreement. Okabe<sup>8</sup> obtained a value of  $4.8 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K using an indirect relative rate technique and Renlund *et al.*<sup>9</sup> also obtained a rather high value using a pulsed photolysis system and monitoring CH chemiluminescence. This latter technique is known to have complications.<sup>10</sup> Laufer<sup>11</sup> obtained a value of  $k = 1.2 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , monitoring  $\text{C}_2\text{H}_2$  production in pulsed photolysis of  $\text{CF}_3\text{C}_2\text{H}/\text{CH}_4$  mixtures. The reason for this low value is not clear. The data from the studies of Okabe,<sup>8</sup> Renlund *et al.*,<sup>9</sup> and Laufer<sup>10</sup> were not used in the present evaluation.

**References**

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- <sup>2</sup>B. J. Opansky and S. R. Leone, *J. Phys. Chem.* **100**, 4888 (1996).
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- <sup>5</sup>B. J. Opansky and S. R. Leone, *J. Phys. Chem.* **100**, 19004 (1996).
- <sup>6</sup>H. Van Look and J. Peeters, *J. Phys. Chem.* **99**, 16284 (1995).
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- <sup>9</sup>A. M. Renlund, F. Shokoohi, H. Reisler, and C. Wittig, *Chem. Phys. Lett.* **84**, 293 (1981).
- <sup>10</sup>F. Shokoohi, T. A. Watson, H. Reisler, F. Kong, A. M. Renlund, and C. Wittig, *J. Phys. Chem.* **90**, 5695 (1986).
- <sup>11</sup>A. H. Laufer, *J. Phys. Chem.* **85**, 3828 (1981).

*Thermodynamic Data*

$$\begin{aligned}\Delta H_{298}^{\circ} &= -109.0 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= -49.5 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 3.3 \cdot 10^{-6} T^{1.035} \exp(+13320/T) \\ &\quad (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$(5\text{--}6) \cdot 10^{-11}$	2300–2700	Frank and Just, 1980 <sup>1</sup>	(a)
$1.5 \cdot 10^{-10}$	298	Stephens <i>et al.</i> , 1987 <sup>2</sup>	(b)
$1.3 \cdot 10^{-10}$	298	Shin and Michael, 1991 <sup>3</sup>	(c)
$2.5 \cdot 10^{-10}$	1236–1475		
$1.6 \cdot 10^{-10}$	293	Koshi, Nishida, and Matsui, 1992 <sup>4</sup>	(d)
$1.4 \cdot 10^{-10}$			
$(1.4\text{--}1.9) \cdot 10^{-10}$	298–2177	Koshi <i>et al.</i> , 1993 <sup>5</sup>	(e)
$1.1 \cdot 10^{-10} \exp(28/T)$	170–350	Pedersen, Opansky, and Leone, 1993 <sup>6</sup>	(f)
$1.6 \cdot 10^{-10}$	295–854	Farhat, Morter, and Glass, 1993 <sup>7</sup>	(b)
$1.3 \cdot 10^{-10}$	295–450	Van Look and Peeters, 1995 <sup>8</sup>	(g)
$8.6 \cdot 10^{-16} T^{1.8} \exp(474/T)$	143–359	Opansky and Leone, 1996 <sup>9</sup>	(h)
$(2.27\text{--}1.06) \cdot 10^{-10}$	15–295	Chastaing <i>et al.</i> , 1998 <sup>10</sup>	(i)
$1.3 \cdot 10^{-10}$	448–777	Ceursters <i>et al.</i> , 2000 <sup>11</sup>	(j)
$1.3 \cdot 10^{-10}$	103	Vakhtin <i>et al.</i> , 2001 <sup>12</sup>	(k)
<i>Reviews and Evaluations</i>			
$1.5 \cdot 10^{-10}$	300–2700	CEC, 1992; 1994 <sup>13</sup>	(l)

**Comments**

- (a) Thermal decomposition of  $\text{C}_2\text{H}_2$  and  $\text{C}_4\text{H}_2$  behind reflected shock waves. [H] monitored by atomic resonance absorption spectroscopy at 121.5 nm. Total pressures 1.5–4 bar Ar.
- (b) Pulsed laser photolysis of  $\text{C}_2\text{H}_2$  at 193 nm;  $[\text{C}_2\text{H}]$  monitored by IR absorption at  $3594.4 \text{ cm}^{-1}$ . Total pressure 27 mbar He;  $\text{SF}_6$  added to ensure rapid vibrational relaxation of  $\text{C}_2\text{H}$ .
- (c) Pulsed laser photolysis at 193 nm of  $\text{C}_2\text{H}_2/\text{He}$  mixtures. [H] monitored by atomic resonance absorption. High temperature experiments carried out by pulsed photolysis of shock heated  $\text{C}_2\text{H}_2/\text{He}$  mixtures. Scatter on results is such that they can be interpreted in terms of a temperature independent  $k$  or can be represented by the expression  $k = 3.02 \cdot 10^{-10} \exp(-235/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .
- (d) Pulsed ArF laser photolysis of  $\text{C}_2\text{H}_2$ . Reaction monitored by LIF detection of H or by time-resolved mass spectrometric detection of  $\text{C}_4\text{H}_2$  in separate experiments. The former gives  $k = (1.6 \pm 0.1) \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and the latter,  $k = (1.4 \pm 0.1) \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .
- (e) Measurement in the range 298–438 K were carried out by pulsed laser photolysis with time-resolved mass spectrometric detection of  $\text{C}_4\text{H}_2$  [see Comment (d)]. For experiments at higher temperatures shock heating

of  $\text{C}_2\text{H}_2/\text{Ar}$  mixtures was employed with pulsed ArF laser photolysis of the heated mixture behind the reflected shock wave. [H] was monitored by ARAS.

- (f) Pulsed laser photolysis of  $\text{C}_2\text{H}_2$  at 193 nm in He buffer gas at total pressures in the range 13–130 mbar.  $[\text{C}_2\text{H}]$  monitored by color laser absorption at  $3594.39 \text{ cm}^{-1}$ .  $k$  was found to be independent of pressure.
- (g) Pulsed laser photolysis of  $\text{C}_2\text{H}_2/\text{O}_2/\text{He}$  mixtures. Chemiluminescence at 430 nm of  $\text{CH}(A^2\Delta)$ , produced by reaction of  $\text{C}_2\text{H}$  with  $\text{O}_2$ , monitored as a function of time and of  $[\text{C}_2\text{H}_2]/[\text{O}_2]$ .
- (h) Technique as in (f). Data set and temperature range expanded. Combined results from this study and previous work<sup>6</sup> gives quoted expression for  $k$ .
- (i) Low temperatures were achieved using the CRESU technique in which  $\text{C}_2\text{H}_2/\text{O}_2$  mixtures in an inert carrier gas (He, Ar, or  $\text{N}_2$ ) were expanded through a Laval nozzle.  $\text{C}_2\text{H}$  radicals were generated by pulsed laser photolysis at 193 nm of the  $\text{C}_2\text{H}_2$  and the reaction progress was monitored by observation of the chemiluminescence from the  $\text{C}_2\text{H} + \text{O}_2$  reaction. Values of  $k$  were obtained at 295 K, 149 K, 112 K, 63 K, 54 K, 39 K, 25 K, and 15 K. The rate constant increases from  $1.06 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 295 K to  $2.27 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 15 K but no functional relationship between  $k$  and  $T$  was derived.
- (j) Technique as in (g). Theoretical study also undertaken.

- (k) Experiment as in Comment (i) but a pulsed expansion through the Laval nozzle was used. Preliminary results were reported in Refs. 14 and 15.  
 (l) Based on data from Refs. 1–5.

### Preferred Values

$k = 1.3 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 200–2700 K.

### Reliability

$\Delta \log k = \pm 0.1$  over the range 200–1000 K, rising to  $\pm 0.5$  at 2700 K.

### Comments on Preferred Values

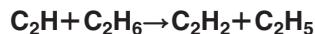
Apart from the early studies of Lange and Wagner<sup>16</sup> and of Laufer and Bass,<sup>17</sup> which are not used in this evaluation, all of the studies are in good agreement. The values obtained at 298 K fall in the range  $(1.3\text{--}1.6) \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  apart from that of Chastaing *et al.*<sup>10</sup> which is a little lower at  $1.06 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . At lower temperatures there are indications of a small increase in the rate constant with decreasing temperature<sup>6,9,10</sup> perhaps indicating a very small negative temperature coefficient for  $k$  but there is no evidence that this trend persists above 300 K. A number of studies indicate no significant change in  $k$  over the range 298–854 K but at high temperatures the data are more scattered<sup>1,3,5</sup> varying by about a factor of 4 at 2000 K

and this is reflected in the higher error limits assigned at such temperatures.

The reaction is believed to proceed by the addition of C<sub>2</sub>H to C<sub>2</sub>H<sub>2</sub> to give C<sub>4</sub>H<sub>3</sub> which rapidly decomposes to CHCCH+H.<sup>3,11</sup>

### References

- <sup>1</sup>P. Frank and Th. Just, Combust. Flame **38**, 231 (1980).
- <sup>2</sup>J. W. Stephens, J. L. Hall, H. Solka, W.-B. Yan, R. F. Curl, and G. P. Glass, J. Phys. Chem. **91**, 5740 (1987).
- <sup>3</sup>K. S. Shin and J. V. Michael, J. Phys. Chem. **95**, 5864 (1991).
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- <sup>5</sup>M. Koshi, K. Fukuda, K. Kamiya, and H. Matsui, J. Phys. Chem. **96**, 9839 (1992).
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- <sup>7</sup>S. K. Farhat, C. L. Morter, and G. P. Glass, J. Phys. Chem. **97**, 12789 (1993).
- <sup>8</sup>H. Van Look and J. Peeters, J. Phys. Chem. **99**, 16284 (1995).
- <sup>9</sup>B. J. Opansky and S. R. Leone, J. Phys. Chem. **100**, 4888 (1996).
- <sup>10</sup>D. Chastaing, P. L. James, I. R. Sims, and I. W. M. Smith, Faraday Discuss. Chem. Soc. **109**, 165 (1998).
- <sup>11</sup>B. Ceusters, H. M. T. Nguyen, J. Peeters, and M. T. Nguyen, Chem. Phys. **262**, 243 (2000).
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- <sup>17</sup>A. H. Laufer and A. M. Bass, J. Phys. Chem. **83**, 310 (1979).



### Thermodynamic Data

$$\begin{aligned}\Delta H_{298}^o &= -133 \text{ kJ mol}^{-1} \\ \Delta S_{298}^o &= 5.8 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 1.1 T^{0.098} \exp(+16000/T) \\ (300 \leq T/\text{K} \leq 4000)\end{aligned}$$

See Section 3 for quality and origin of Thermodynamic Data.

### Rate Coefficient Data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$3.5 \cdot 10^{-11} \exp(2.9/T)$	153–357	Opansky and Leone, 1996 <sup>1</sup>	(a)
$1.19 \cdot 10^{-12} T^{0.54} \exp(180/T)$	295–779	Ceursters <i>et al.</i> , 2001 <sup>2</sup>	(b)
<i>Reviews and Evaluations</i>			
No recommendation		CEC, 1992; 1994 <sup>3</sup>	(c)

### Comments

- (a) Pulsed laser photolysis of C<sub>2</sub>H<sub>2</sub> at 193 nm in the presence of excess C<sub>2</sub>H<sub>6</sub>. [C<sub>2</sub>H] monitored by infrared laser absorption at 3594.4 cm<sup>-1</sup>. The pressure variation of  $k$  reported by Lander *et al.*<sup>1</sup> could not be detected in this study.  
 (b) Pulsed laser photolysis at 193 nm of

C<sub>2</sub>H<sub>2</sub>/O<sub>2</sub>/C<sub>2</sub>H<sub>6</sub>/He mixtures. [C<sub>2</sub>H] was monitored by time-resolved measurements of the intensity of the chemiluminescence produced from the C<sub>2</sub>H+O<sub>2</sub> reaction. O<sub>2</sub> was present in large excess and in constant amounts; the [C<sub>2</sub>H<sub>6</sub>] also in large excess was varied. An *ab initio* calculation suggested that the reaction occurs by direct H abstraction.  
 (c) Available data not considered sufficiently reliable.

### Preferred Values

$k = 6.75 \cdot 10^{-12} T^{0.28} \exp(62/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 150–780 K.

### Reliability

$\Delta \log k = \pm 0.2$  over the range 150–780 K.

### Comments on Preferred Values

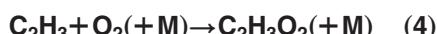
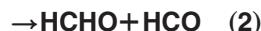
The values of  $k$  measured at 298 K are scattered.<sup>1,2,4–6</sup> In the two most recent studies, those of Opansky and Leone<sup>1</sup> and Ceusters *et al.*,<sup>2</sup> the rate constant was measured over a temperature range using techniques that have proved to be reliable in other studies. We have therefore based our preferred expression for  $k$  on the results from these two studies despite the fact that, in the temperature range where the studies overlap, they give values of  $k$  differing by  $\sim 25\%$ . To obtain our preferred expression we have normalized the results of Ceusters *et al.*<sup>2</sup> and Opansky and Leone<sup>1</sup> to a mean of their values of  $k$  at 298 K and obtained the temperature

dependence of  $k$  by a least squares fit of the normalized rate constants. The studies of Lander *et al.*<sup>4</sup> and of Okabe<sup>6</sup> give values of  $k$  at 298 K in good agreement with the preferred expression.

Landers *et al.*<sup>4</sup> reported a small pressure effect in their rate constant measurements but Opansky and Leone<sup>1</sup> could find no such effect and, in accord with this, the *ab initio* calculations of Ceusters *et al.*<sup>2</sup> indicate that the reaction mechanism is one of direct hydrogen abstraction.

### References

- <sup>1</sup> B. J. Opansky and S. R. Leone, *J. Phys. Chem.* **100**, 19904 (1996).
- <sup>2</sup> B. Ceusters, H. M. T. Nguyen, J. Peeters, and L. Vereecken, *Phys. Chem. Chem. Phys.* **3**, 3070 (2001).
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### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = -57.9 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = -9.08 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 0.114 T^{0.194} \exp(+6950/T) \\ (300 \leqslant T/\text{K} \leqslant 5000)$$

$$\Delta H^\circ_{298}(3) = 89.3 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = 83.5 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 8.26 \cdot 10^4 T^{-0.241} \exp(-10700/T) \\ (300 \leqslant T/\text{K} \leqslant 5000)$$

$$\Delta H^\circ_{298}(2) = -366.2 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = 4.00 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 2.31 \cdot 10^2 T^{-0.744} \exp(+43720/T) \\ (300 \leqslant T/\text{K} \leqslant 5000)$$

$$\Delta H^\circ_{298}(4) = -283.1 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(4) = -300.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(4) = 3.69 \cdot 10^{-39} T^{1.230} \exp(+34290/T) \text{ cm}^3 \text{ molecule}^{-1} \\ (300 \leqslant T/\text{K} \leqslant 5000)$$

See Section 3 for the source of the Thermodynamic Data.

### Rate Coefficient Data ( $k = k_1 + k_2 + k_3 + k_4$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$k_2 = 6.6 \cdot 10^{-12} \exp(125/T)$	291–602	Slagle <i>et al.</i> , 1984 <sup>1</sup>	(a)
$k_2 = 1.0 \cdot 10^{-11}$	296	Park, Heaven, and Gutman, 1984 <sup>2</sup>	(b)
$k_2 = 1.0 \cdot 10^{-11}$	298	Krueger and Weitz, 1988 <sup>3</sup>	(c)
$6.7 \cdot 10^{-12}$	298	Fahr and Laufer, 1988 <sup>4</sup>	(d)
$6.92 \cdot 10^{-12} \exp(120/T)$	299–1005	Knyazev and Slagle, 1995 <sup>5</sup>	(e)
<i>Reviews and Evaluations</i>			
$k_2 = 9.2 \cdot 10^{-12}$	300–2000	CEC, 1992; 1994 <sup>6</sup>	(f)

## Comments

- (a) Pulsed laser photolysis at 193 nm of  $\text{C}_2\text{H}_3\text{Br}/\text{O}_2$  mixtures at pressures in the range 1–4.7 mbar.  $[\text{C}_2\text{H}_3]$ ,  $[\text{CHO}]$ , and  $[\text{HCHO}]$  monitored by photoionization mass spectrometry. Products of Channel (1) not observed, hence  $k_1 \ll k_2$ . The same conclusion was reached by Baldwin and Walker<sup>7</sup> from the results of their study at 753 K.
- (b) Technique as in (a). Pressures in the range 0.5–5 mbar.
- (c) Pulsed laser photolysis at 248 nm of  $\text{C}_2\text{H}_3\text{I}/\text{HCl}/\text{O}_2$  mixtures at pressures of ~9 mbar.  $[\text{C}_2\text{H}_4]$  monitored by infrared laser diode spectroscopy.  $k$  derived from the effect of  $[\text{O}_2]$  on rate of formation of  $\text{C}_2\text{H}_4$ .
- (d) Flash photolysis of  $\text{Sn}(\text{C}_2\text{H}_3)_4$  or  $\text{Hg}(\text{C}_2\text{H}_3)_2$  in the presence of excess  $\text{O}_2$ .  $[\text{C}_2\text{H}_3]$  monitored by optical absorption at 164.71 nm and 168.33 nm.
- (e) Pulsed laser photolysis at 193 nm of  $\text{CH}_3\text{C}(\text{O})\text{C}_2\text{H}_3/\text{O}_2$  mixtures in He bath gas at concentrations in the range  $(3–18) \cdot 10^{16}$  molecules  $\text{cm}^{-3}$ .
- (f) Based on the data of Slagle *et al.*<sup>1</sup> and of Krueger and Weitz.<sup>3</sup>

## Preferred Values

$k_2 = 6.4 \cdot 10^{-12} \exp(120/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 290–900 K.

### Reliability

$\Delta \log k_2 = \pm 0.1$  at 290 K, rising to  $\pm 0.3$  at 900 K.

### Comments on Preferred Values

The preferred values for  $k_2$  are obtained from the mean of the 298 K measurements of the cited studies and the temperature dependence of Knyazev and Slagle.<sup>5</sup> The measured rate coefficient shows no pressure dependence.

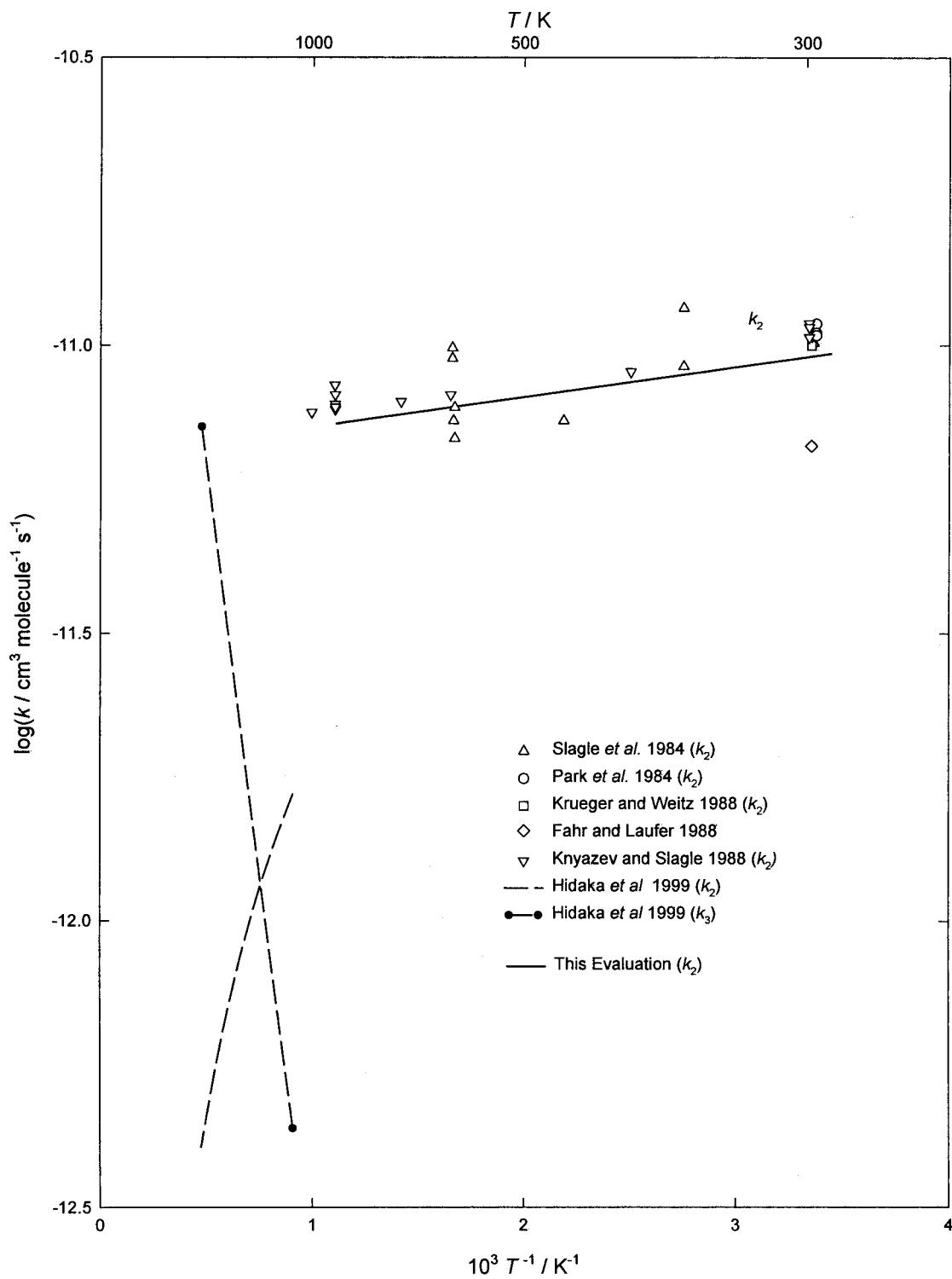
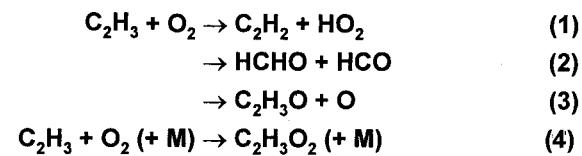
There is only very limited information on the branching ratios. Wang *et al.*<sup>8</sup> have investigated the reaction products at room temperatures and low pressures by time-resolved FTIR emission spectroscopy and find that Channel (2) predominates. At higher temperatures, Marinov and Malte<sup>9</sup> have modeled the product yields from ethylene oxidation at 1053–1253 K in a well-stirred reactor. They suggest use of  $k$

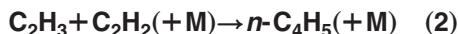
$= 6.6 \cdot 10^{-12} \exp(125/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  with branching ratios  $k_1:k_2:k_3$  of 0.086:1.0:1.4 at 1053 K, and 0.117:1.0:2.05 at 1253 K. Hidaka *et al.*<sup>10</sup> have derived expressions for  $k_2$ , and  $k_3$  from a shock tube study of  $\text{C}_2\text{H}_4$  oxidation over the range 1100–2100 K. These studies<sup>9,10</sup> are compatible with the preferred expression for  $k_2$  and predict that Channel (2) will predominate at low temperatures but that Channel (3) will become predominant above  $\sim 1000$  K. At even higher temperatures, flame modeling<sup>11</sup> suggests that Channel (1) also becomes significant.

This general picture is supported by theoretical studies. Bozzelli and Dean,<sup>12</sup> using RRK theory, and Mebel *et al.*<sup>13</sup> using *ab initio* methods and RRKM calculations, obtain similar results with the computed low temperature rate constant for  $k_2$  in quantitative agreement with experiment and the overall rate constant showing little pressure dependence. However, the calculations<sup>13</sup> also show that stabilization of the initial adduct to form  $\text{C}_2\text{H}_3\text{OO}$  is dominant at atmospheric pressure and 298 K with Channel (2) only becoming predominant at  $T > 500$  K. At  $T > 900$  K Channel (3) is the major channel and at still higher temperatures ( $T > 2000$  K) Channel (1) becomes competitive. No recommendations for the branching ratios can be given with any confidence but the calculations of Mebel *et al.*<sup>13</sup> probably offer the best current guide.

## References

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- <sup>12</sup>J. W. Bozzelli and A. N. Dean, *J. Phys. Chem.* **97**, 4427 (1993).
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#### Thermodynamic Data

$$\begin{aligned}\Delta H_{298}^{\circ}(1) &= -24.5 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ}(1) &= -41.3 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 6.72 \cdot 10^{-6} T^{1.027} \exp(+3380/T) \\ (300 \leq T/\text{K} \leq 5000) \end{aligned}$$

$$\begin{aligned}\Delta H_{298}^{\circ}(2) &= -182.8 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ}(2) &= -146.2 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 1.03 \cdot 10^{-31} T^{1.417} \exp(+22320/T) \text{ cm}^3 \text{ molecule}^{-1} \\ (300 \leq T/\text{K} \leq 5000) \end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$k_2 = 2.1 \cdot 10^{-16}$	300	Callear and Smith, 1986 <sup>1</sup>	(a)
$k_2 = 3.1 \cdot 10^{-15}$	400		
$k_1 = 3.2 \cdot 10^{-12} \exp(-3025/T)$	630–980	Knyazev, Stoliarov, and Slagle, 1996 <sup>2</sup>	(b)

#### Comments

- (a) Relative rate study using mercury photosensitized photolysis of  $\text{H}_2$  in the presence of small amounts of  $\text{C}_2\text{H}_2$  at total pressures in the range 60–1000 mbar. Primary products (ethene, 1,3-butadiene, benzene, 1,3,5-hexatriene) were measured by gas chromatography and other minor products were also detected. Product formation was interpreted in terms of Channel (2). A steady state treatment gave  $k_2/k(\text{C}_2\text{H}_3 + \text{H}_2) = 30$  at 300 K and 24 at 400 K. The values of  $k_2$  cited in the Table are derived using  $k(\text{C}_2\text{H}_3 + \text{H}_2) = 7.1 \cdot 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 300 K and  $1.3 \cdot 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 400 K.<sup>3</sup>
- (b) Pulsed laser photolysis at 248 nm of  $\text{C}_2\text{H}_3\text{Br}/\text{C}_2\text{H}_2/\text{He}$  mixtures at total pressures in the range 2.6–14.8 mbar. Reactants and products were monitored by photoionization mass spectrometry. The reaction  $\text{C}_2\text{H}_3 + \text{C}_2\text{D}_2$  was also studied. There was no evidence for the occurrence of channel (2) under the conditions used.

#### Preferred Values

$k = 2.3 \cdot 10^{-12} \exp(-2764/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 300–1000 K.

#### Reliability

$\Delta \log k = \pm 0.6$  at 300 K, decreasing to  $\pm 0.2$  at 1000 K.

#### Comments on Preferred Values

The values of  $k_2$  obtained from the relative rate study of Callear and Smith,<sup>1</sup> when more recent values of the reference rate constant are used,<sup>3</sup> are in excellent agreement with the values predicted by extrapolation of the expression for  $k_1$

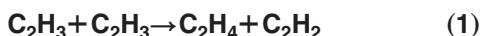
obtained by Knyazev *et al.*<sup>2</sup> at much higher temperatures. Knyazev *et al.*<sup>2</sup> have suggested that this can be understood if, under the conditions used by Callear and Smith<sup>1</sup>  $k_2 \gg k_1$ , while at the higher temperatures and lower pressures of their own measurements,  $k_1 \gg k_2$  so that in both cases the overall  $k$  effectively is being measured and that this overall  $k$  is relatively pressure independent. They cite in support of this argument the RRKM analysis of the reaction by Wang and Frenklach<sup>4</sup> which suggests that, although both  $k_1$  and  $k_2$  are pressure dependent, the total rate constant  $k$  ( $=k_1+k_2$ ) is relatively independent of pressure in the range 1–550 mbar up to temperatures of 2000 K. Knyazev *et al.*<sup>2</sup> have therefore combined their own results with those of Callear and Smith<sup>1</sup> to derive the expression for  $k$  which we accept as our recommendation, but substantial error limits are suggested until confirmatory studies are carried out.

In the absence of experimental data no recommendations are made for the branching ratios but the theoretical treatment of Wang and Frenklach<sup>4</sup> offers a guide.

As well as the cited studies Duran *et al.*<sup>5</sup> have derived a value of  $k_1$  from a study of  $\text{C}_2\text{H}_2$  pyrolysis and Fahr and Stein<sup>6</sup> have obtained values of  $k_1/k(\text{C}_2\text{H}_3 + \text{C}_2\text{H}_3 \rightarrow \text{C}_4\text{H}_4 + 2\text{H})$  but the reference rate constant is too poorly defined to give a reliable value of  $k_1$ .

#### References

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*Thermodynamic Data*

$$\Delta H^\circ_{298}(1) = -318.8 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = -97.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 1.14 \cdot 10^{-3} T^{0.13} \exp(+38400/T) \\ (300 \leq T/\text{K} \leq 3000)$$

$$\Delta H^\circ_{298}(2) = -489.4 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = -189.6 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 2.82 \cdot 10^{-35} T^{1.86} \exp(+59500/T) \text{ cm}^3 \text{ molecule}^{-1} \\ (300 \leq T/\text{K} \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data ( $k = k_1 + k_2$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$1.0 \cdot 10^{-10}$	298	Fahr and Laufer, 1990 <sup>1</sup>	(a)
$1.4 \cdot 10^{-10}$	298	Fahr <i>et al.</i> , 1991 <sup>2</sup>	(b)
$1.4 \cdot 10^{-10}$	298	Thorn, Payne, and Stief, 1996 <sup>3</sup>	(c)
<i>Reviews and Evaluations</i>			
$1.8 \cdot 10^{-11}$		Tsang and Hampson, 1986 <sup>4</sup>	(d)

**Comments**

- (a) Vacuum UV flash photolysis of divinylmercury/He mixtures at a total pressure of 530 mbar was used to generate vinyl radicals which were monitored by UV absorption at 164.7 nm using photographic plate detection. Products ( $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ , 1,3 butadiene) were analyzed by gas chromatography.
- (b) Pulsed laser photolysis at 248 nm of divinylmercury/He mixtures at a total pressure of 132 mbar. The reaction progress was followed by monitoring 1,3 butadiene using UV absorption at a number of wavelengths in the range 210–216.4 nm.
- (c) Discharge flow technique used with He carrier gas at 1.3 mbar total pressure.  $\text{C}_2\text{H}_3$  radicals produced by  $\text{F} + \text{C}_2\text{H}_4$  reaction. Mass spectrometry was used to monitor  $[\text{C}_2\text{H}_3]$  and detect products. No butadiene,  $\text{C}_4\text{H}_5$ , or  $\text{C}_3\text{H}_3$  were detected.
- (d) Estimate based on analogy with ethyl radical recombination.

**Preferred Values**

$$k = 1.4 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

See Comments on Preferred Values for information on the branching ratios.

*Reliability*

$$\Delta \log k = \pm 0.2 \text{ at } 298 \text{ K.}$$

*Comments on Preferred Values*

The only experimental data on  $k$  are at 298 K. The preferred value is based on the measurements of Fahr *et al.*<sup>1,2</sup>

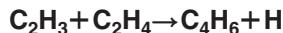
and Thorn *et al.*<sup>3</sup> which employ different techniques but give values of  $k$  in very good agreement. These three studies cover a pressure range of 1.3–530 mbar giving pressure independent values of  $k$  over this range. There is also another flash photolysis study of MacFadden and Currie<sup>5</sup> which was carried out at lower pressures (0.18–0.26 mbar) and gives a much lower value of  $k$  ( $5.3 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ). This could indicate some pressure dependence of  $k$  at very low pressures but is more likely to be due to experimental difficulties.

Colket *et al.*<sup>6</sup> have used a value of  $k = 3.3 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  to fit their results from acetylene pyrolysis at approximately 1000 K but there are no direct experimental determinations at high temperatures. Since the value of  $k$  at 298 K is close to the hard sphere collision value,  $k$  is not expected to increase greatly with temperature increase.

There is conflicting evidence on the values of the branching ratio even among the direct studies<sup>1–3</sup> which are in agreement on the value of  $k$ . Thorn *et al.*<sup>3</sup> find no 1,3-butadiene to be produced in their low pressure (1.3 mbar) study whereas Fahr *et al.*,<sup>1,2</sup> using higher pressures (132 and 530 mbar) find it to be the major product. MacFadden and Currie<sup>5</sup> also find  $\text{C}_2\text{H}_2$  and  $\text{C}_2\text{H}_4$  to be the main products at low pressures (0.18–0.26 mbar). Thorn *et al.*<sup>3</sup> have suggested a mechanism giving a pressure independent  $k$  but a pressure dependent branching ratio to explain these findings at pressures above  $\sim 1$  mbar. A number of less direct studies based on product analysis from thermal,<sup>7,8</sup> pulsed photolysis,<sup>9</sup> and a variety of steady-state photolysis systems,<sup>10–13</sup> give values of the branching ratio in the range 1–50. Until more definitive studies are carried out no recommendations are made for the branching ratios.

## References

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- <sup>9</sup> A. Fahr, W. Braun, and A. J. Laufer, J. Phys. Chem. **97**, 1502 (1993).
- <sup>10</sup> N. A. Weir, J. Chem. Soc. 6870 (1965).
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### Thermodynamic Data

$$\begin{aligned}\Delta H_{298}^{\circ} &= -24.2 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= -8.90 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 2.56 T^{-0.209} \exp(+3010/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

### Rate Coefficient Data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$2.3 \cdot 10^{-13}$	1100	Fahr and Stein, 1988 <sup>1</sup>	(a)
<i>Reviews and Evaluations</i>			
$8.3 \cdot 10^{-13} \exp(-3676/T)$	300–2500	Tsang and Hampson, 1986 <sup>2</sup>	(b)

### Comments

- (a) Relative rate study using a very low pressure pyrolysis reactor (Knudsen cell) in which vinyl radicals were produced by the decomposition of divinyl mercury or phenylvinylsulfone in the presence of an excess of  $\text{C}_2\text{H}_4$ . Reactants and products were detected by a quadrupole mass spectrometer. Yields of  $\text{C}_4\text{H}_6$  and  $\text{C}_4\text{H}_4$ , lead to values of  $k/k[\text{C}_2\text{H}_3 + \text{C}_2\text{H}_3 \rightarrow \text{C}_4\text{H}_4 + \text{H}_2(\text{or } 2\text{H})]$ . The value of  $k$  is based on an estimated value of  $k(\text{C}_2\text{H}_3 + \text{C}_2\text{H}_3)$  of  $3.3 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .
- (b) Expression based on the analysis by Benson and Haugen<sup>3</sup> of the results from a shock tube study of ethylene pyrolysis by Skinner and Sokolski.<sup>4</sup>

### Preferred Values

$$k = 1.3 \cdot 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 1100 \text{ K.}$$

### Reliability

$$\Delta \log k = \pm 1 \text{ at } 1100 \text{ K.}$$

### Comments on Preferred Values

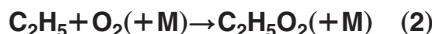
The only experimental data for this reaction comes from a relative rate study of Fahr and Stein<sup>1</sup> in which a value of  $k/k(\text{C}_2\text{H}_3 + \text{C}_2\text{H}_3 \rightarrow \text{C}_4\text{H}_4 + 2\text{H})$  was determined. The value

of the reference rate constant is not well established and to obtain values of  $k$ , Fahr and Stein<sup>1</sup> had to use an estimated value. However, in the same study, an analogous rate constant ratio was determined for the reaction of vinyl radicals with ethene. We have combined the two ratios to obtain  $k/k(\text{C}_2\text{H}_3 + \text{C}_2\text{H}_2) = 0.7$  and, using the expression for  $k(\text{C}_2\text{H}_3 + \text{C}_2\text{H}_3)$  (this evaluation), which is rather better established we obtain the value of  $k$  which is taken as our preferred value.

There is no experimental information on the mechanism of the reaction. It is assumed to occur by addition followed by decomposition of the adduct. Fahr and Stein's<sup>1</sup> study was carried out at very low pressures favoring adduct decomposition and the data obtained may not apply under other conditions. In view of the uncertainties in the quality of the data and the mechanism substantial uncertainties are assigned.

### References

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*Thermodynamic Data*

$$\begin{aligned}\Delta H_{298}^{\circ}(1) &= -54.8 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ}(2) &= -3.99 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 0.96 T^{-0.070} \exp(+6580/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

$$\begin{aligned}\Delta H_{298}^{\circ}(2) &= -148.3 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ}(2) &= -138.5 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 6.70 \cdot 10^{-32} T^{1.640} \exp(+18200/T) \text{ cm}^3 \text{ molecule}^{-1} \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data ( $k = k_1 + k_2$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$1.02 \cdot 10^{-13}$	904	Slagle, Feng, and Gutman, 1984 <sup>1</sup>	(a)
$0.79 \cdot 10^{-13}$	1002	McAdam and Walker, 1987 <sup>2</sup>	(b)
$k_1 = 5.0 \cdot 10^{-14}$	733		
$k_1 = 4.6 \cdot 10^{-14}$	753		
$1.11 \cdot 10^{-13}$	750	Wagner <i>et al.</i> , 1990 <sup>3</sup>	(c)
$1.17 \cdot 10^{-13}$	850		
<i>Reviews and Evaluations</i>			
$k_1 = 1.4 \cdot 10^{-12} \exp(-1950/T)$	300–2500	Tsang and Hampson, 1986 <sup>4</sup>	(d)
$k_1 = 1.7 \cdot 10^{-14} \exp(1100/T)$	600–1200	CEC, 1992; 1994 <sup>5</sup>	(e)

**Comments**

- (a) Pulsed laser photolysis study on slowly flowing  $\text{CFCl}_3/\text{C}_2\text{H}_6/\text{O}_2/\text{He}/\text{N}_2$  mixtures.  $\text{C}_2\text{H}_5$  radicals are produced by the reaction of  $\text{C}_2\text{H}_6$  with Cl atoms from the multiphoton dissociation of  $\text{CFCl}_3$ .  $[\text{C}_2\text{H}_5]$  and  $[\text{C}_2\text{H}_4]$  were monitored by time resolved photoionization mass spectrometry and values of  $k$  were obtained from the pseudo first order decay of  $[\text{C}_2\text{H}_5]$  in excess  $\text{O}_2$ . Experiments were carried out over the range 294–1002 K but below  $\sim 700$  K the overall rate constant is pressure dependent and only the data obtained at temperatures above 700 K are cited in the Table. Values of the yield of  $\text{C}_2\text{H}_4$  were found to increase with temperature reaching a value of 0.77 at 688 K, the maximum temperature at which it was measured.
- (b) The thermal reaction of  $\text{C}_2\text{H}_5\text{CHO}/\text{O}_2/\text{N}_2$  mixtures was studied in a static system. Yields of  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_6$  were determined by gas chromatography during the early stages of the reaction and from the ratios of these yields the expression  $k_1/k(\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5\text{CHO}) = 6.76 \cdot 10^{-2} \exp(4414/T)$  was derived. Values of  $k_1$  were derived using  $k(\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5\text{CHO}) = 2.7 \cdot 10^{-13} \exp(-3656/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  as evaluated by McAdam and Walker<sup>2</sup> from the literature data. The reaction was studied over the range 593–753 K but only the data in the pressure independent region ( $T > 700$  K) are cited.
- (c) Technique as in (a) but the  $\text{C}_2\text{H}_5$  was produced by pulsed UV laser photolysis of  $\text{C}_2\text{H}_5\text{Br}$  for the measurements of  $k$  and by pulsed UV photolysis of  $\text{CCl}_4/\text{C}_2\text{H}_6$  mixtures for the measurements of  $[\text{C}_2\text{H}_4]/[\text{C}_2\text{H}_6]$ .

Measurements of  $k$  covered the range 296–850 K but only those in the pressure independent region ( $T > 700$  K) are cited. Values of the yield of  $\text{C}_2\text{H}_4$  were found to increase with temperature reaching a value of 0.99 at 723 K, the maximum temperature at which it was measured.

- (d) Based on the study of Baldwin *et al.*<sup>8</sup>
- (e) Based on the data of Slagle *et al.*<sup>1</sup> and of McAdam and Walker.<sup>2</sup>

**Preferred Values**

$k_1 = 1.0 \cdot 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 700–1500 K, independent of pressure.

Expressions for modeling in the pressure dependent region at lower temperatures are given in Comments on Preferred Values.

**Reliability**

$\Delta \log k_1 = \pm 0.2$  at 700 K, rising to  $\pm 0.4$  at 1500 K.

**Comments on Preferred Values**

There is now a substantial quantity of data on this reaction<sup>1–3,6–17</sup> which shows that, at temperatures below  $\sim 700$  K,  $k$  increases with pressure and has a small negative temperature dependence whereas at higher temperatures  $k$  appears to be relatively independent of temperature and pressure. To explain these findings Wagner *et al.*<sup>3</sup> have developed a model in which the reaction proceeds initially by addition to form the activated species  $\text{C}_2\text{H}_5\text{O}_2^*$  which may be collisionally quenched to form  $\text{C}_2\text{H}_5\text{O}_2$  [Channel (2)], or

it may decompose, either back to reactants, or to form  $\text{C}_2\text{H}_4 + \text{HO}_2$  [Channel (1)]. Miller *et al.*<sup>18,19</sup> have extended the model, identifying three regimes of temperature and pressure in which the rate constant of the reaction exhibits distinctly different behavior. At low temperatures ( $T < \sim 575$  K) the rate constant is temperature and pressure dependent in the manner expected from adduct formation, i.e. as pressure is increased and temperature decreased, increased concentration of the adduct is favored over formation of  $\text{HO}_2 + \text{C}_2\text{H}_4$ . Thus, at 300 K and atmospheric pressure, Channel (2) predominates with Channel (1) contributing less than 1%. The low temperature measurements<sup>7–17</sup> fit the model well and have been evaluated in reviews of the NASA<sup>20</sup> and IUPAC<sup>21</sup> Panels which should be consulted for details.

In the high temperature regime ( $T > 750$  K) the rate constant becomes independent of pressure and shows only a small dependence on temperature. The adduct is no longer present in appreciable amounts and the reaction is effectively behaving as an elementary reaction yielding  $\text{HO}_2 + \text{C}_2\text{H}_4$  [Channel (1)]. The temperature regime  $575 \text{ K} < T < 750 \text{ K}$  is a transition region between the two extremes.

The rate constant data and measurements of product yields are compatible with this model. Thus the production of  $\text{HO}_2$  in the reaction at temperatures of 294–698 K has been measured by Clifford *et al.*<sup>22</sup> using time-resolved infrared frequency modulated spectroscopy and has been successfully fitted by them and Miller *et al.*<sup>19</sup> Miller *et al.*<sup>19</sup> also calculate a small yield of  $\text{C}_2\text{H}_4\text{O} + \text{OH}$  from a minor channel in excellent agreement with the yield measured by Baldwin *et al.*<sup>8</sup> over the range 673–813 K.

The present evaluation is confined to the high temperature data ( $> 700$  K) which relate to Channel (1). The preferred value of  $k_1$  is based on the data of Slagle *et al.*<sup>1</sup> and Wagner *et al.*<sup>3</sup> The less direct relative rate study of McAdam and Walker<sup>2</sup> gives values of  $k$  within a factor of  $\sim 2$ . There are also two shock tube studies on  $\text{C}_2\text{H}_6/\text{O}_2/\text{Ar}$  mixtures.<sup>23,24</sup> In one of them<sup>23</sup> a value of “about  $1.7 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ” at 1726 K was required to model the system, which is also compatible with the preferred expression. In the other,<sup>24</sup> the expression  $k = 9.1 \cdot 10^{-13} \exp(-1953/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was required for the range 950– $\sim 1400$  K which gives slightly higher values than our preferred expression at the higher end of the temperature range. From their theoretical model Miller *et al.*<sup>19</sup> have derived the expression  $k = 2.34 \cdot 10^{-17} T^{1.09} \exp(993/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at high temperatures, which is in excellent agreement with our preferred value. Channel (1) could also proceed by direct abstraction but the available experimental data suggest that this mechanism is not significant below 1000 K. Further measurements of  $k$  at temperatures above 1000 K are clearly desirable. Miller and Klippenstein<sup>19</sup> have also derived a set of expressions for all of the steps in the mechanism by fitting their theoretical model to the available data. These provide the means of modeling the system in the pressure dependent region at temperatures below 700 K. They suggest the use of the follow-

ing set of elementary reactions and their associated phenomenological rate constants:



$$k_a^\infty = 3.36 \cdot 10^{-14} T^{0.980} \exp(32/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

$$k_a^0 = 2.34 \cdot 10^{-18} T^{-4.29} \exp(-111/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}.$$

$$F_{a,c} = 0.897 \exp(-T/601).$$



$$k_b^\infty = 6.85 \cdot 10^{-12} T^{6.53} \exp(420/T) \text{ s}^{-1}.$$

$$k_b^0 = 2.34 \cdot 10^{-17} T^{1.09} \exp(994/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

$$F_{b,c} = 0.45.$$



$$k_c^\infty = 7.14 \cdot 10^4 T^{2.32} \exp(-14089/T) \text{ s}^{-1}.$$

$$k_c^0 = 1.38 \cdot 10^{-2} T^{-0.651} \exp(-11520/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

$$F_{c,c} = \exp(-T/106).$$

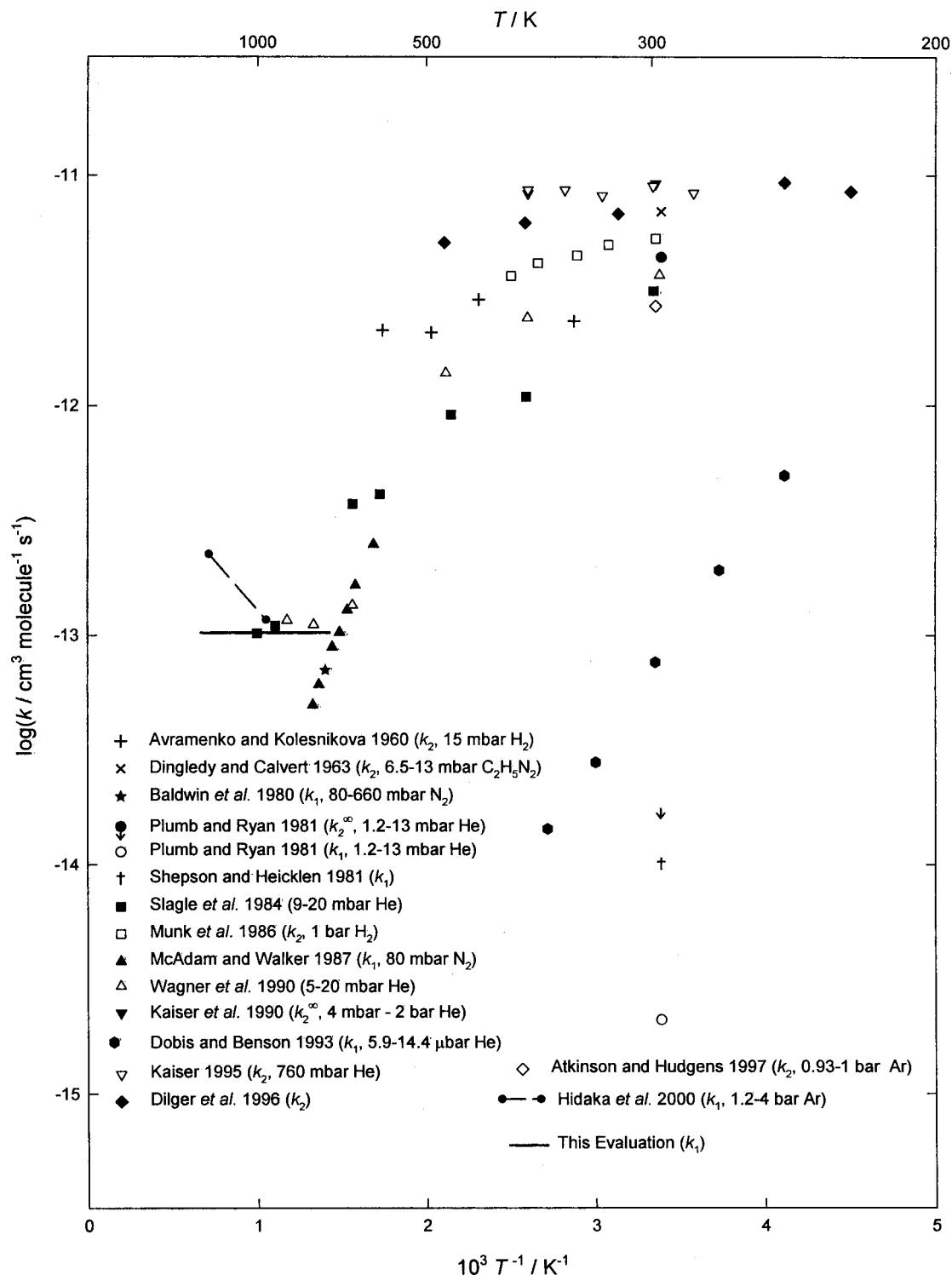
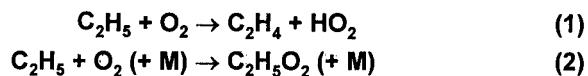
The expressions for reaction (c) are not as accurate as those for the other reactions because they do not allow for depletion of the  $[\text{C}_2\text{H}_5\text{O}_2]$  as a function of pressure by the reverse of reaction (a). The original paper<sup>19</sup> should be consulted for details.

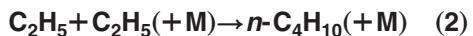
The mechanism, rate constant, and branching ratios of the  $\text{C}_2\text{H}_5 + \text{O}_2$  reaction are now reasonably well characterized up to at least 1000 K but they present a problem for the interpretation of the data on the reverse,  $\text{C}_2\text{H}_4 + \text{HO}_2$ , reaction. The lack of any marked temperature dependence of  $k(\text{C}_2\text{H}_5 + \text{O}_2)$  and the theoretically calculated potential energy surfaces suggest that there is no energy barrier along the reaction coordinate leading to  $\text{C}_2\text{H}_4 + \text{HO}_2$  that is significantly higher than the potential energy of the reactants. This is difficult to reconcile with the data on the  $\text{HO}_2 + \text{C}_2\text{H}_4$  reaction. Baldwin *et al.*<sup>25</sup> find that this proceeds to form  $\text{C}_2\text{H}_4\text{O} + \text{OH}$  with a substantial activation energy (74.7 kJ mol<sup>-1</sup>) for the initial addition step, implying a barrier in the reaction coordinate some 20 kJ mol<sup>-1</sup> above the potential energy of  $\text{C}_2\text{H}_5 + \text{O}_2$ . This problem and the relationship between the measured rate constants for  $\text{HO}_2 + \text{CH}_4$  and  $\text{C}_2\text{H}_5 + \text{O}_2$  remain to be resolved.

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#### Thermodynamic Data

$$\begin{aligned}\Delta H_{298}^{\circ}(1) &= -273.2 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ}(1) &= -46.1 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 1.34 \cdot 10^{-3} T^{0.111} \exp(+33010/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

$$\begin{aligned}\Delta H_{298}^{\circ}(2) &= -367.6 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ}(2) &= -184.5 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 2.69 \cdot 10^{-36} T^{2.314} \exp(+44800/T) \text{ cm}^3 \text{ molecule}^{-1} \\ (300 \leq T/\text{K} \leq 4000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$1.5 \cdot 10^{-11}$	296	Parkes and Quinn, 1976 <sup>1</sup>	(a)
$2.4 \cdot 10^{-11}$	296	Adachi, Basco, and James, 1979 <sup>2</sup>	(b)
$9.3 \cdot 10^{-12}$	803	Corbel, Marquaire, and Come, 1981 <sup>3</sup>	(c)
$2.0 \cdot 10^{-11}$	296	Demissy and Lesclaux, 1982 <sup>4</sup>	(d)
$2.2 \cdot 10^{-11}$	903	Pacey and Wimalasena, 1984 <sup>5</sup>	(e)
$1.9 \cdot 10^{-11}$	296	Munk <i>et al.</i> , 1986 <sup>6</sup>	(f)
$1.63 \cdot 10^{-11}$	300–373	Arthur, 1986 <sup>7</sup>	(a)
$1.69 \cdot 10^{-11}$	308	Anastasi and Arthur, 1987 <sup>8</sup>	(g)
$k_1 = 2.0 \cdot 10^{-12}$	203–343	Dobis and Benson, 1991 <sup>9</sup>	(h)
$1.99 \cdot 10^{-11}$	295	Atkinson and Hudgens, 1997 <sup>10</sup>	(i)
<i>Reviews and Evaluations</i>			
$k_2 = 1.8 \cdot 10^{-11}$	300–2500	Tsang and Hampson, 1986 <sup>11</sup>	(j)
$k_1 = 2.3 \cdot 10^{-12}$	300–2500	CEC, 1992: 1994 <sup>12</sup>	(k)
$k_\infty = 1.9 \cdot 10^{-11}$	300–1200		
$k_1 = 2.3 \cdot 10^{-12}$	300–1200		

#### Comments

- (a) Molecular modulation spectroscopic study.  $\text{C}_2\text{H}_5$  radicals were produced from photolysis of  $(\text{C}_2\text{H}_5\text{N})_2$  in the presence of  $\text{N}_2$  and  $[\text{C}_2\text{H}_5]$  was monitored by UV absorption spectroscopy. Values of  $k$  were obtained by simulation of concentration profiles.
- (b) Flash photolysis of mixtures of  $(\text{C}_2\text{H}_5\text{N})_2$  and  $n\text{-C}_5\text{H}_{12}$ .  $[\text{C}_2\text{H}_5]$  monitored by UV absorption spectroscopy.
- (c) Pyrolysis of  $\text{C}_2\text{H}_6$  in a continuous-flow stirred-tank reactor with end-product analysis by gas chromatography. Values of  $k$  were determined by fitting the rates of formation of  $\text{C}_2\text{H}_4$  as a function of residence time in the reactor, based on a mechanism of 6 elementary reactions.
- (d) Flash photolysis of  $\text{NH}_3/\text{C}_2\text{H}_4$  mixtures in which  $\text{NH}_2$  radicals were produced by photolysis of the  $\text{NH}_3$  and  $\text{C}_2\text{H}_5$  radicals were produced by the  $\text{H} + \text{C}_2\text{H}_4$  reaction.  $[\text{NH}_2]$  was monitored by absorption at 597.73 nm. Values of  $k(\text{NH}_2 + \text{C}_2\text{H}_5)$  and  $k(\text{C}_2\text{H}_5\text{C}_2\text{H}_5)$  were derived from fitting the  $[\text{NH}_2]$  profiles.
- (e) Pyrolysis of  $\text{C}_2\text{H}_6$  in a flow system with end-product analysis by gas chromatography. Values of  $k$  were determined from a fit of the rates of formation of  $\text{C}_2\text{H}_4$  as a function of residence time in the reactor, based on a mechanism of 12 elementary reactions. Preliminary results: Pacey and Wimalasena.<sup>25</sup>

- (f) Pulse radiolysis study with  $[\text{C}_2\text{H}_5]$  monitored by UV absorption.  $\text{C}_2\text{H}_5$  radicals were produced by the  $\text{C}_2\text{H}_4$  reaction. Values of  $k$  were derived from a computer simulation of the  $[\text{C}_2\text{H}_5]$  temporal profiles.
- (g) Experimental procedure as in (a). Preliminary results reported in Arthur and Anastasi.<sup>26</sup>
- (h) Very low pressure pyrolysis (VLPR) study on  $\text{Cl}_2/\text{C}_2\text{H}_6$  mixtures. Concentrations of  $\text{Cl}_2$ ,  $\text{Cl}$ ,  $\text{HCl}$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_5$ ,  $\text{C}_2\text{H}_4$ , and  $\text{C}_2\text{H}_2$  were monitored by mass spectrometry. Values of  $k$  were derived by a steady-state treatment of a mechanism of 6 reactions. No  $n$ -butane was found in the products indicating that at the pressure used ( $4 \cdot 10^{-3}$  mbar) Channel (1) was at least a factor of 400 below its high pressure limit.
- (i) Pulsed laser photolysis at 308 nm of  $\text{Cl}_2/\text{C}_2\text{H}_6$  mixtures.  $[\text{C}_2\text{H}_5]$  was monitored by cavity ring-down spectroscopy at 220 nm. Absorption cross sections for  $\text{C}_2\text{H}_5$  at 220 nm were determined by comparison with absorption by  $\text{C}_2\text{H}_5\text{O}_2$  radicals at the same wavelength.
- (j) Based on the literature data prior to 1981.
- (k) Based on the data from Refs. 1–8, cited in the Table.

#### Preferred Values

$k_1 = 2.3 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 295–1200 K.

$k_\infty = 1.9 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 295–1200 K.

### Reliability

$\Delta \log k_1 = \pm 0.3$  over the range 295–1200 K.  
 $\Delta \log k_\infty = \pm 0.3$  over the range 295–1200 K.

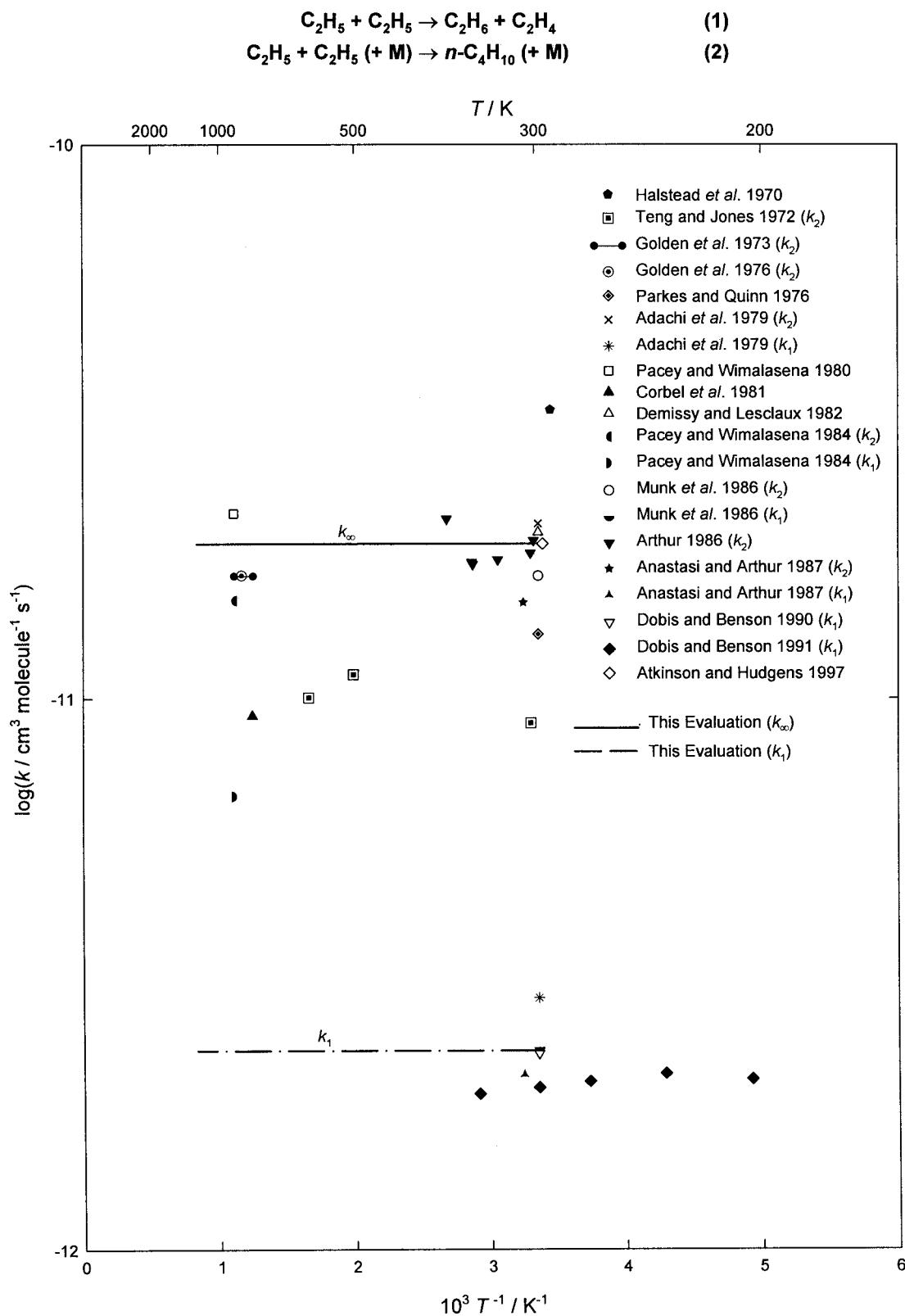
### Comments on Preferred Values

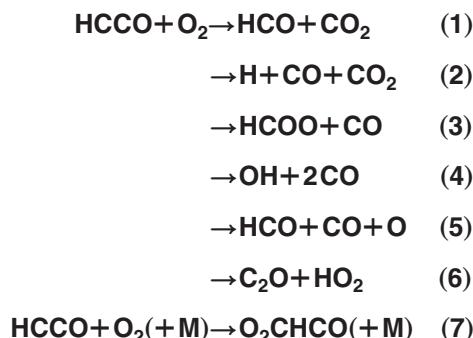
The preferred rate constant is the mean of the results of Parkes and Quinn,<sup>1</sup> Adachi *et al.*,<sup>2</sup> Demissy and Lesclaux,<sup>4</sup> Pacey and Wimalasena,<sup>5</sup> Munk *et al.*,<sup>6</sup> Arthur,<sup>7</sup> Arthur and Anastasi,<sup>8</sup> and Atkinson and Hudgens<sup>10</sup> which are all in substantial agreement. The measurements of  $k$  cover a wide pressure range from a few mbar up to pressures approaching 1 bar and show no evidence of any variation of  $k$  over that range, suggesting that  $k$  is at its high pressure limit. There have been several determinations of the disproportionation/combination ratio in excellent agreement.<sup>13–18</sup> A value of  $k_1/k_2 = 0.14$  is widely accepted at low temperatures<sup>19</sup> and appears to be applicable also at high temperatures.<sup>20</sup> This value has been combined with our preferred value for  $k_\infty$  to obtain the preferred value for  $k_1$ . The value so obtained for  $k_1$  is in excellent agreement with the value measured by Dobis and Benson.<sup>9</sup> There are a number of older studies<sup>21–24</sup> which are also in reasonable agreement with the preferred expressions.

There are no studies of the reaction at temperatures above 1000 K, hence the restricted range over which the preferred values are recommended.

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*Thermodynamic Data*

$$\Delta H_{298}^{\circ}(1) = -525.7 \text{ kJ mol}^{-1}$$

$$\Delta S_{298}^{\circ}(1) = -12.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 1.13 T^{-0.284} \exp(+63250/T) \quad (300 \leq T/K \leq 5000)$$

$$\Delta H_{298}^{\circ}(4) = -359.3 \text{ kJ mol}^{-1}$$

$$\Delta S_{298}^{\circ}(4) = 128.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(4) = 1.64 \cdot 10^{31} T^{-1.799} \exp(+42720/T) \text{ molecule cm}^{-3} \quad (300 \leq T/K \leq 5000)$$

$$\Delta H_{298}^{\circ}(6) = -223.4 \text{ kJ mol}^{-1}$$

$$\Delta S_{298}^{\circ}(6) = 11.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(6) = 1.13 T^{0.165} \exp(-17360/T) \quad (300 \leq T/K \leq 5000)$$

$$\Delta H_{298}^{\circ}(2) = -461.4 \text{ kJ mol}^{-1}$$

$$\Delta S_{298}^{\circ}(2) = 75.5 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 7.74 \cdot 10^{24} T^{-0.636} \exp(+55490/T) \text{ molecule cm}^{-3} \quad (300 \leq T/K \leq 5000)$$

$$\Delta H_{298}^{\circ}(5) = 6.42 \text{ kJ mol}^{-1}$$

$$\Delta S_{298}^{\circ}(5) = 132.5 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(5) = 7.82 \cdot 10^{29} T^{-1.318} \exp(-1010/T) \text{ molecule cm}^{-3} \quad (300 \leq T/K \leq 5000)$$

$$\Delta H_{298}^{\circ}(7) = -258.6 \text{ kJ mol}^{-1}$$

$$\Delta S_{298}^{\circ}(7) = -295.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(7) = 2.60 \cdot 10^{-39} T^{1.403} \exp(+31330/T) \text{ cm}^3 \text{ molecule}^{-1} \quad (300 \leq T/K \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data ( $k = k_1 + k_2 + k_3 + k_4 + k_5 + k_6 + k_7$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$2.9 \cdot 10^{-12}$ (M=N <sub>2</sub> , 2.6 mbar)	296	Jones and Bayes, 1973 <sup>1</sup>	(a)
$2.7 \cdot 10^{-12} \exp(-430/T)$ (M=He, 2.6 mbar)	290–535	Peeters, Schaekers, and Vinckier, 1986 <sup>2</sup>	(b)
$1.4 \cdot 10^{-12}$ (M=He, 2.6 mbar)	298	Van de Ven and Peeters, 1990 <sup>3</sup>	(c)
$6.5 \cdot 10^{-13}$ (M=He, 40 mbar)	298	Murray <i>et al.</i> , 1992 <sup>4</sup>	(d)
$2.2 \cdot 10^{-13}$ (M=He, 1.4 mbar)	298	Temps, Wagner, and Wolf, 1992 <sup>5</sup>	(e)
<i>Reviews and Evaluations</i>			
$2 \cdot 7 \cdot 10^{-12} \exp(-430/T)$ (M=He, 2.6 mbar)	300–550	CEC, 1992; 1994 <sup>6</sup>	(f)

**Comments**

- (a) Discharge flow study; O atoms generated by N+NO reaction. HCCO produced as an intermediate from the C<sub>2</sub>H<sub>2</sub>+O reaction. [HCCO] and [O] measured by photoionization mass spectrometry. [HCCO] measured in the presence and absence of O<sub>2</sub> and  $k/k(\text{HCCO} + \text{O}) = (0.018 \pm 0.003)$  at 296 K obtained from Stern-Volmer plot. The value of  $k$  tabulated is obtained from this ratio and the value of  $k(\text{HCCO} + \text{O})$  from the present evaluation.
- (b) Reported by Peeters *et al.*<sup>2</sup> No experimental details given but experimental technique probably similar to

later reported work [see Comment (c)] and  $k$  derived from Stern-Volmer plots. No temperature range quoted but in other work<sup>7</sup> this group use the expression in the range 300–550 K.

- (c) Fast flow discharge study; H atoms generated by a discharge in He/H<sub>2</sub> mixture are reacted with C<sub>3</sub>O<sub>2</sub> to generate HCCO. [HCCO] monitored by molecular beam mass spectrometry in the presence of varying concentrations of O<sub>2</sub>.  $k$  obtained from fitting the [HCCO] profile using a substantial reaction scheme.
- (d) Pulsed laser photolysis of ketene at 193 nm in a He

carrier gas was used to generate HCCO radicals. [HCCO] decay in the presence of a large excess of O<sub>2</sub> was monitored by diode laser infrared spectroscopy.

- (e) Discharge flow system. HCCO generated by the reaction of H atoms with C<sub>2</sub>H<sub>2</sub>. [HCCO] monitored by far infrared laser magnetic resonance in a large excess of O<sub>2</sub>. Some corrections for the effects of secondary chemistry made to the measured values of  $k$ .
- (f) Accepts the expression reported by Peeters *et al.*<sup>2</sup>

### Preferred Values

$k = 2.7 \cdot 10^{-12} \exp(-430/T)$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> over the range 290–550 K (M=He,  $P \leq 40$  mbar).

### Reliability

$\Delta \log k = \pm 0.7$  over the range 290–550 K.

### Comments on Preferred Values

There are now a number of experimental values of  $k$  available at ambient temperatures but they vary by an order of magnitude. The two most recent studies,<sup>4,5</sup> using pseudo first order conditions and direct detection of HCCO, are potentially reliable but still give values which differ by more than a factor of 3. The pressures used in the two studies were very different but it is unlikely that this can explain the discrepancy.

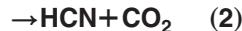
There is also a recent study by Hidaka *et al.*<sup>8</sup> who measured ketene and CO<sub>2</sub> concentration profiles behind reflected shock waves in ketene/O<sub>2</sub> and ketene/N<sub>2</sub>O mixtures over the temperature range 1050–2050 K. However, to fit the ketene and CO<sub>2</sub> profiles, they find it necessary to use values of  $k$  much smaller than those measured by others at room temperatures.

The previously recommended expression, reported by Peeters *et al.*,<sup>2</sup> which is in reasonable agreement with the more recent data at 298 K, is adopted and assigned error limits sufficiently wide to encompass all of the low temperature measurements. Until effects of pressure on the rate constant are studied care should be taken in using the preferred values at high pressures.

There is no information available on the relative importance of the possible reaction channels.

### References

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- <sup>6</sup>CEC, 1992; Supplement I, 1994 (see references in Introduction).
- <sup>7</sup>C. Vinckier, M. Schaeckers, and J. Peeters, J. Phys. Chem. **89**, 508 (1985).
- <sup>8</sup>Y. Hidaka, K. Kimura, K. Hattori, and T. Okuno, Combust. Flame **106**, 155 (1996).



### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = -203.1 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = -33.30 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 2.83 \cdot 10^{-3} T^{0.284} \exp(+24570/T) \\ (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^\circ_{298}(2) = -523.9 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = -40.44 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 1.67 \cdot 10^{-3} T^{0.174} \exp(+63200/T) \\ (300 \leq T/\text{K} \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

### Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$3.9 \cdot 10^{-11}$	298	Unfried <i>et al.</i> , 1991 <sup>1</sup>	(a)
$2.2 \cdot 10^{-11}$	296	Temps <i>et al.</i> , 1992 <sup>2</sup>	(b)
$3.1 \cdot 10^{-11}$	290	Boullart <i>et al.</i> , 1994 <sup>3</sup>	(c)
$4.9 \cdot 10^{-11}$	400		
$5.8 \cdot 10^{-11}$	530		
$6.1 \cdot 10^{-11}$	670		
<i>Branching Ratio Measurements</i>			
$k_2/k = 0.23 \pm 0.09$	700	Boullart <i>et al.</i> , 1994 <sup>3</sup>	(c)
$k_1/k = 0.64 \pm 0.12$	298	Eickhoff and Temps, 1999 <sup>4</sup>	(d)
$k_2/k = 0.28 \pm 0.10$			
$k_1/k = 0.88 \pm 0.04$	296	Rim and Hershberger, 2000 <sup>5</sup>	(e)
$k_2/k = 0.14 \pm 0.04$			

### Comments

- (a) Flow reactor study with HCCO production by ArF (193 nm) laser photolysis of ketene in ketene/NO/He mixtures with HCCO detection by infrared absorption near  $2038\text{ cm}^{-1}$ . Pseudo-first-order analysis of the HCCO decay in an excess of NO to determine the rate at a total pressure of 33 mbar. The temperature was not specified, but most probably is room temperature.
- (b) Discharge flow reactor study in  $\text{C}_2\text{H}_2/\text{O}_2/\text{NO}/\text{He}$  mixtures with HCCO detection by far-infrared laser magnetic resonance. Pseudo-first-order analysis of the HCCO decay in an excess of NO to determine the rate at a total pressure of 1.3 mbar.
- (c) Discharge flow reactor study in  $\text{C}_2\text{H}_2/\text{O}_2/\text{NO}/\text{He}$  mixtures at a total pressure of 2.7 mbar. Multiple species detection using molecular beam mass spectrometry. The overall rate coefficient was derived relative to the rate of  $\text{HCCO} + \text{O} \rightarrow \text{products}$  by a complex fitting procedure. The branching ratio into CO and  $\text{CO}_2$  product channels was determined from measured CO and  $\text{CO}_2$  yields.
- (d) Static cell study using 312 nm photolysis of  $\text{NO}_2/\text{C}_2\text{H}_2/\text{NO}/\text{Ar}$  mixtures at a total pressure of 570 mbar. Products were detected using FTIR spectroscopy. Product branching ratios were determined by detailed kinetic modeling.
- (e) Reaction cell study using excimer laser photolysis (193 nm) of  $\text{CH}_2\text{CO}/\text{NO}/\text{SF}_6/\text{CF}_4/\text{Xe}$  mixtures at total pressures of approximately 8 mbar. CO and  $\text{CO}_2$  detection by infrared laser absorption.

### Preferred Values

$k = 1.0 \cdot 10^{-10} \exp(-350/T)$   $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 300–2000 K.

$k_1/k = 0.8$  over the range 300–2000 K.

$k_2/k = 0.2$  over the range 300–2000 K.

### Reliability

$\Delta \log k = \pm 0.2$  at 300 K, rising to  $\pm 0.4$  at 2000 K.

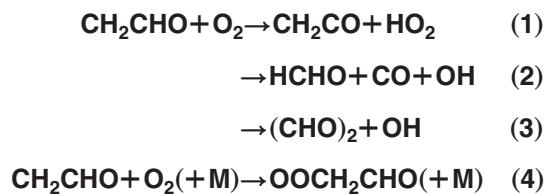
$\Delta(k_1/k) = \Delta(k_2/k) = \pm 0.1$  over the range 300–2000 K.

### Comments on Preferred Value

There is a reasonable consensus among the three room-temperature studies<sup>1–3</sup> on the overall reaction rate. Boullart *et al.*<sup>3</sup> report a modest positive temperature dependence of the overall rate constant,  $k = 1.0 \cdot 10^{-10} \exp(-350/T)$   $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the temperature range 290–670 K, and this is the expression adopted here. The theoretical study of Nguyen *et al.*<sup>6</sup> identified several energetically accessible product channels in addition to (1) and (2), including that leading to  $\text{HNCO} + \text{CO}$ , but these other channels are expected to be unimportant at combustion temperatures. Eickhoff and Temps<sup>4</sup> and Rim and Hershberger<sup>5</sup> report room temperature values of  $k_1/k$  and  $k_2/k$ , and Boullart *et al.*<sup>3</sup> report  $k_2/k$  at 700 K. These experimental values indicate that Channel (1) is the dominant pathway in this temperature range. The theoretical study of Vereecken *et al.*<sup>7</sup> gives a temperature-dependent expression,  $k_2/k = 0.0652 + 0.220 \exp(-T/918)$  for  $T = 300$ –2500 K, in agreement with experimental data. In contrast, the theoretical study of Miller *et al.*<sup>8</sup> reports a temperature-dependent expression,  $k_2/k = 0.985 \exp(-T/1748)$ , that gives  $k_2/k = 0.83$  at 298 K, decreasing to 0.31 at 2000 K. The recommended branching ratios are based on the three experimental studies.<sup>3–5</sup>

### References

- <sup>1</sup>K. G. Unfried, G. P. Glass, and R. F. Curl, Chem. Phys. Lett. **177**, 33 (1991).
- <sup>2</sup>F. Temps, H. Gg. Wagner, and M. Wolf, Z. Phys. Chem. **176**, 27 (1992).
- <sup>3</sup>W. Boullart, M. T. Nguyen, and J. Peeters, J. Phys. Chem. **98**, 8036 (1994).
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- <sup>5</sup>K. T. Rim and J. F. Hershberger, J. Phys. Chem. A **104**, 293 (2000).
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- <sup>7</sup>L. Vereecken, R. Sumathy, S. A. Carl, and J. Peeters, Chem. Phys. Lett. **344**, 400 (2001).
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*Thermodynamic Data*

$$\begin{aligned} \Delta H^\circ_{298}(1) &= -43.4 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(1) &= -2.07 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 0.634 T^{0.058} \exp(+5180/T) \\ &(300 \leq T/\text{K} \leq 5000) \end{aligned}$$

$$\begin{aligned} \Delta H^\circ_{298}(2) &= -188.1 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(2) &= 127.0 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 9.34 \cdot 10^{30} T^{-1.736} \exp(+22040/T) \text{ molecule cm}^{-3} \\ &(300 \leq T/\text{K} \leq 4000) \end{aligned}$$

$$\begin{aligned} \Delta H^\circ_{298}(3) &= -181.0 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(3) &= -17.04 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(3) &= 5.31 \cdot 10^{-3} T^{0.492} \exp(+21880/T) \\ &(300 \leq T/\text{K} \leq 5000) \end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data ( $k = k_1 + k_2 + k_3 + k_4$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$k_4^\infty = 2.6 \cdot 10^{-13}$	300	Lorenz <i>et al.</i> , 1984 <sup>1</sup>	(a)
$k_1^o[\text{He}] = [\text{He}] 2 \cdot 10^{-30}$			
$F_c = 0.6$			
$k_4 = 2.7 \cdot 10^{-14} \exp(668/T)$ (130 mbar He)	300–500		
$4.46 \cdot 10^{-13}$ (132 mbar N <sub>2</sub> )	295	Gutman and Nelson, 1983 <sup>2</sup>	(b)
$2.50 \cdot 10^{-13}$ (118 mbar SF <sub>6</sub> )	295		
$k_4^\infty = 1.9 \cdot 10^{-13}$	298	Zhu and Johnston, 1995 <sup>3</sup>	(c)
$k_4^o[\text{N}_2] = [\text{N}_2] 1.6 \cdot 10^{-30}$			
$F_c = 0.5$			
<i>Branching Ratios</i>			
$k_2/k = 0.2$	298	Lorenz <i>et al.</i> , 1984 <sup>1</sup>	(a)
<i>Reviews and Evaluations</i>			
$k_\infty = 2 \cdot 6 \cdot 10^{-13}$	250–500	CEC, 1992; 1994 <sup>4</sup>	(d)
$k_2 = 3.0 \cdot 10^{-14}$	300		

**Comments**

- (a) Pulsed laser photolysis of CH<sub>3</sub>OCHCH<sub>2</sub> at 193 nm. LIF detection of CH<sub>2</sub>CHO at 337 nm. Reaction is pressure dependent between 10 and 280 mbar He. Derivation of  $k_\infty$  and  $k_0$  was based on an assumed value of  $F_c = 0.6$ . The OH yield, measured by LIF, was 0.2.
- (b) Laser photolysis of CH<sub>3</sub>OCHCH<sub>2</sub> at 193 nm. LIF detection of CH<sub>2</sub>CHO. Reaction is pressure dependent between 2.0 and 132 mbar. Data given are for highest pressures of N<sub>2</sub> and SF<sub>6</sub> used.
- (c) Pulsed laser photolysis of CH<sub>3</sub>OCHCH<sub>2</sub>/N<sub>2</sub> mixtures at 193 nm over a total pressure range of 3.3–526 mbar. [CH<sub>2</sub>CHO] was monitored by time resolved cavity ring down spectroscopy at 347.7 nm. The products glyoxal (CHO)<sub>2</sub>, and HCHO were detected by cavity ring down spectroscopy. The glyoxal appeared not to be a primary product and was produced with a yield of 0.15 but that of HCHO could not be determined.
- (d) See Comments on Preferred Values.

**Preferred Values**

$$\begin{aligned} k_4^\infty &= 1.9 \cdot 10^{-13} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.} \\ k_4^o &= 1.6 \cdot 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \text{ for M=N}_2 \text{ at } 298 \text{ K.} \\ F_{c,4} &= 0.5 \text{ for M=N}_2 \text{ at } 298 \text{ K.} \\ k_2/k &= 0.2 \text{ at } 298 \text{ K.} \end{aligned}$$

*Reliability*

$$\begin{aligned} \Delta \log k_4^\infty &= \Delta \log k_4^o = \pm 0.3 \text{ at } 298 \text{ K.} \\ \Delta F_{c,4} &= \pm 0.1 \text{ for M=N}_2 \text{ at } 298 \text{ K.} \\ \Delta(k_2/k) &= \pm 0.2 \text{ at } 298 \text{ K.} \end{aligned}$$

*Comments on Preferred Values*

The results from all of the cited studies are compatible, but the most recent of them, that of Zhu and Johnston,<sup>3</sup> provides more precise data over a wider pressure range than the earlier studies, and the results from this most recent work are accepted as our preferred values. All of the studies are consistent with the addition reaction, Channel (4), as the main re-

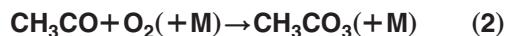
action path with no firm evidence for alternative processes. Glyoxal<sup>1</sup> (with a yield of 0.15), HCHO,<sup>3</sup> and OH<sup>1</sup> (with a yield of 0.2) are produced. The time scale of the glyoxal production shows that it is not a primary product. The recommended value of  $k_2$  is based on the study of Lorenz *et al.*<sup>1</sup> and may only apply at low pressures.

The temperature dependence of  $k$  has only been studied at one pressure (130 mbar), which is in the fall-off region, but

the results suggest only a small dependence on temperature up to 500 K.

## References

- <sup>1</sup>K. Lorenz, D. Rhäsa, R. Zellner, and B. Fritz, Ber. Bunsenges. Phys. Chem. **89**, 341 (1985).
- <sup>2</sup>D. Gutman and H. H. Nelson, J. Phys. Chem. **87**, 3902 (1983).
- <sup>3</sup>L. Zhu and G. Johnston, J. Phys. Chem. **99**, 15114 (1995).
- <sup>4</sup>CEC, 1992; Supplement I, 1994 (see references in Introduction).



### Thermodynamic Data

$$\begin{aligned}\Delta H^\circ_{295}(2) &= -165.0 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298}(2) &= -152.9 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(2) &= 4.37 \cdot 10^{-36} T^{2.814} \exp(+20570/T) \text{ cm}^3 \text{ molecule}^{-1} \\ (300 \leqslant T/\text{K} \leqslant 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

### Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$2.0 \cdot 10^{-12}$	298	McDade <i>et al.</i> , 1982 <sup>1</sup>	(a)
$3.0 \cdot 10^{-12}$	296	Kaiser and Wallington, 1995 <sup>2</sup>	(b)
$3.2 \cdot 10^{-12}$	298	Tyndall <i>et al.</i> , 1997 <sup>3</sup>	(c)
$3.3 \cdot 10^{-12}$	228		
<i>Reviews and Evaluations</i>			
$2 \cdot 10^{-12}$ ( $P = 1-5$ mbar)	298	CEC, 1992; 1994 <sup>4</sup>	(d)
$3.2 \cdot 10^{-12}$	220-300	IUPAC, 1999 <sup>5</sup>	(e)

### Comments

- (a) Flow system with CH<sub>3</sub>CO formed by pulsed photolysis of CH<sub>3</sub>COCH<sub>3</sub> or CH<sub>3</sub>COCH<sub>2</sub>COCH<sub>3</sub>. [CH<sub>3</sub>CO] monitored by photoionization mass spectrometry. 1.3–5 mbar pressure.
- (b)  $k$  measured relative to  $k(\text{CH}_3\text{CO} + \text{Cl}_2)$ , ( $k/k_{\text{ref}} = 7.9 \pm 0.5$  at 930 mbar pressure). Cited value obtained using  $k_{\text{ref}} = 2.4 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .<sup>5</sup>
- (c) Three types of photolysis experiments were carried out in an environmental chamber interfaced to an FTIR spectrometer for time resolved product analysis. The experiments involved: (i) Photolysis of Cl<sub>2</sub>/CH<sub>3</sub>CHO/O<sub>2</sub>/N<sub>2</sub> mixtures and monitoring of the [CH<sub>3</sub>CHO] and [CH<sub>3</sub>COCl] which gave values of  $k/k(\text{CH}_3\text{CO} + \text{Cl}_2)$ , as in (b), but covering the pressure range 0.13–1460 mbar at 298 K. (ii) Relative rate studies on the reactions of Cl atoms with CH<sub>3</sub>CHO and <sup>13</sup>CH<sub>3</sub>CHO as a function of pressure. (iii) Product yield studies on the Cl initiated oxidation of CH<sub>3</sub>CHO as a

function of pressure.  $k$  increased with pressure up to ~400 mbar and remained approximately constant above that.

- (d) Accepts the value of McDade *et al.*<sup>1</sup>
- (e) Based on the data of Kaiser and Wallington<sup>2</sup> and of Tyndall *et al.*<sup>3</sup>

### Preferred Values

$k = 3.2 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 220–500 K at a pressure of 1 bar.

### Reliability

$\Delta \log k = \pm 0.2$  at 220 K, rising to  $\pm 0.3$  at 500 K.

### Comments on Preferred Values

The data for this reaction have been reviewed by the IUPAC Panel and their findings<sup>5</sup> are accepted as the basis for our preferred values. The results of Tyndall *et al.*<sup>3</sup> confirm

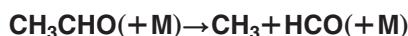
that the temperature coefficient of  $k_2$  is small at low temperatures and thus provide a basis for extending our recommendations up to 500 K with increasing error limits.

The rate constant,  $k_2$ , has been shown to be pressure dependent. At 298 K,  $k_2$  is close to its high pressure limit at pressures greater than  $\sim 140$  mbar but decreases rapidly at lower pressures. The reaction mechanism appears to involve initial formation of an internally excited adduct,  $\text{CH}_3\text{C}(\text{O})\text{O}_2$ , which may be collisionally stabilized or undergo decomposition. There is good indirect evidence from the study of Tyndall *et al.*<sup>3</sup> and from low pressure flow tube studies on the  $\text{OH} + \text{CH}_3\text{CHO}$  reaction,<sup>6,7</sup> that one of the products of the adduct decomposition is OH radicals. Tyndall *et al.*<sup>3</sup> have suggested that the other product accompanying OH formation is  $\text{CH}_2\text{C}(\text{O})\text{O}$  [Channel (1)]. However this remains to be confirmed and there are insufficient data to indicate branching ratios as a function of temperature and pressure.

At higher temperatures there are studies of the reaction by Hoare and Whytock<sup>8</sup> and Nieman and Feklisov<sup>9</sup> but their interpretation is unclear because of the uncertainties in the reaction mechanism, its dependence on temperature, and pressure and in the reference rate constants used.

## References

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- <sup>2</sup>E. W. Kaiser and T. J. Wallington, *J. Phys. Chem.* **99**, 8669 (1995).
- <sup>3</sup>G. S. Tyndall, J. J. Orlando, T. J. Wallington, and M. D. Hurley, *Int. J. Chem. Kinet.* **29**, 655 (1997).
- <sup>4</sup>CEC, 1992; Supplement I, 1994 (see references in Introduction).
- <sup>5</sup>IUPAC, Supplement VII, 1999.
- <sup>6</sup>G. S. Tyndall, T. A. Staffelbach, J. J. Orlando, and J. G. Calvert, *Int. J. Chem. Kinet.* **27**, 1009 (1995).
- <sup>7</sup>J. V. Michael, D. G. Keil, and R. B. Klemm, *J. Chem. Phys.* **83**, 1631 (1985).
- <sup>8</sup>D. E. Hoare and D. A. Whytock, *Can. J. Chem.* **45**, 865 (1967).
- <sup>9</sup>M. B. Neiman and G. I. Feklisov, *Russ. J. Phys. Chem.* **35**, 521 (1961).



### Thermodynamic Data

$$\begin{aligned}\Delta H_{298}^{\circ} &= 355.7 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= 154.3 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 2.68 \cdot 10^{31} T^{-1.404} \exp(-43070/T) \text{ molecule cm}^{-3} \\ (200 \leq T/\text{K} \leq 6000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

### Rate Coefficient Data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$2.0 \cdot 10^{15} \exp(-39800/T)$	753–813	Liu and Laidler, 1968 <sup>1</sup>	(a)
$7.1 \cdot 10^{15} \exp(-41100/T)$	1000–1200	Colket <i>et al.</i> , 1975 <sup>2</sup>	(b)
$k_{\infty} = 2.1 \cdot 10^{16} \exp(-41135/T)$	1350–1650	Ernst, Spindler, and Wagner, 1976 <sup>3</sup>	(c)
<i>Reviews and Evaluations</i>			
$k(1 \text{ bar}) = 7.1 \cdot 10^{15} \exp(-41100/T)$	750–1200	CEC, 1992; 1994 <sup>4</sup>	(d)

### Comments

- (a) Static pyrolysis of  $\text{CH}_3\text{CHO}$ ;  $k$  determined from time dependence of  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_6$  production at low conversion.
- (b) Turbulent flow reactor at 1 bar pressure of  $\text{N}_2$ ;  $k$  determined as in (a).
- (c) Pyrolysis of  $\text{CH}_3\text{CHO}$  studied behind reflected shock waves in  $\text{CH}_3\text{CHO}/\text{Ar}$  mixtures at pressures in the range 0.2–73 bar.  $[\text{CH}_3\text{CHO}]$  was monitored by absorption spectroscopy at 290 nm. The pressure dependence of  $k$  was analyzed by construction of fall-off curves and extrapolation to obtain expressions for  $k_0$  and  $k_{\infty}$ .  $k_0 = 1.3 \cdot 10^{-6} \exp(-41135/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was obtained. For  $k_{\infty}$ , the results from

this study were combined with those from the studies of Liu and Laidler,<sup>1</sup> and Colket *et al.*<sup>2</sup> to obtain the value of  $k_{\infty}$  cited in the Table.

- (d) Expression of Colket *et al.*<sup>2</sup> accepted but recommendation limited to a pressure of 1 bar.

### Preferred Values

$$k_{\infty} = 2.1 \cdot 10^{16} \exp(-41135/T) \text{ s}^{-1} \text{ over the range } 750\text{--}1700 \text{ K.}$$

### Reliability

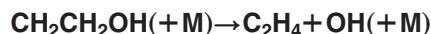
$$\Delta \log k_{\infty} = \pm 0.4 \text{ over the range } 750\text{--}1700 \text{ K.}$$

*Comments on Preferred Values*

The preferred expression for  $k$  is that derived by Ernst *et al.*<sup>3</sup> from the results of their own studies and those of Liu and Laidler<sup>1</sup> and of Colket *et al.*<sup>2</sup> The results of these studies are in good agreement but they are all carried out in the fall-off region and substantial extrapolation is required to obtain the expression for  $k_\infty$ . Fairly large error limits are therefore suggested.

**References**

- <sup>1</sup>T. H. Lui and K. J. Laidler, Can. J. Chem. **46**, 479 (1968).
- <sup>2</sup>M. B. Colket, D. W. Naegeli, and I. Glassman, Int. J. Chem. Kinet. **7**, 223 (1975).
- <sup>3</sup>J. Ernst, K. Spindler, and H. Gg. Wagner, Ber. Bunsenges. Phys. Chem. **80**, 645 (1976).
- <sup>4</sup>CEC, 1992; Supplement I, 1994 (see references in Introduction).

*Thermodynamic Data*

$$\begin{aligned}\Delta H^\circ_{298} &= 127.8 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298} &= 127.85 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 6.3 \cdot 10^{32} T^{-2.388} \exp(-15990/T) \text{ molecule cm}^{-3} \\ &(300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$6.2 \cdot 10^{11} \exp(-11900/T)$	544–673	Diau and Lee, 1996 <sup>1</sup>	(a)

**Comments**

- (a) Pulsed laser photolysis at 193 nm of  $\text{CH}_2\text{CH}_2/\text{H}_2\text{O}/\text{N}_2\text{O}$  mixtures in He bath gas at pressures in the range 366–811 mbar.  $[\text{OH}]$  was monitored by LIF excited at 282.0 nm. The establishment of the equilibrium  $\text{OH} + \text{C}_2\text{H}_4 \rightleftharpoons \text{C}_2\text{H}_4\text{OH}$  was followed and values of the forward and reverse rate constant were derived.

**Preferred Values**

$$k = 6.2 \cdot 10^{11} \exp(-11900/T) \text{ s}^{-1} \text{ over the range } 500\text{--}800 \text{ K.}$$

*Reliability*

$\Delta \log k = \pm 0.3$  over the range 500–800 K.

*Comments on Preferred Values*

There is only one study of this reaction.<sup>1</sup> The expression obtained for  $k$  is accepted as our preferred expression but with substantial error limits until confirmatory studies are carried out. The values of  $k$  obtained were found to be only slightly pressure dependent over the range studied (366–811 mbar) suggesting that at these pressures  $k$  is close to its high pressure limit. There is some support for the value of  $k$  from the work of Hess and Tully,<sup>2</sup> who found in their study of the  $\text{OH} + \text{C}_2\text{H}_5\text{OH}$  reaction that  $\text{C}_2\text{H}_4\text{OH}$  decomposed rapidly on the time scale of their experiments (milliseconds) at temperatures greater than  $\sim 520$  K.

**References**

- <sup>1</sup>E. W-G. Diau and Y-P. Lee, J. Chem. Phys. **96**, 377 (1992).
- <sup>2</sup>W. P. Hess and F. P. Tully, Chem. Phys. Lett. **152**, 183 (1988).



### Rate Coefficient Data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$3.0 \cdot 10^{-12}$	293	Miyoshi, Matsui, and Washida, 1989 <sup>1</sup>	(a)
<i>Reviews and Evaluations</i>			
$3.0 \cdot 10^{-12}$	298	IUPAC, 1998 <sup>2</sup>	(b)

### Comments

- (a) Pulsed laser photolysis of  $\text{ClCH}_2\text{CH}_2\text{OH}$  and  $\text{BrCH}_2\text{CH}_2\text{OH}$  in He bath gas at pressures in the range 2.7–9.3 mbar.  $[\text{CH}_2\text{CH}_2\text{OH}]$  monitored by photoionization mass spectrometry in the presence of excess  $\text{O}_2$ .
- (b) Accepts the value of Miyoshi *et al.*<sup>1</sup>

### Preferred Values

$$k = 3 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

### Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

### Comments on Preferred Values

Miyoshi *et al.*<sup>1</sup> have obtained consistent results using two different radical sources and their technique appears to give reliable data for the analogous reaction of  $\text{CH}_3\text{CHOH}$ . Their value of  $k$  at 298 K is therefore accepted as the preferred value but with large error limits until confirmatory studies are available.

There are no data on the temperature dependence of  $k$ . In their study of the reaction of OH radicals with  $\text{C}_2\text{H}_5\text{OH}$  Hess and Tully<sup>3</sup> found that  $\text{CH}_2\text{CH}_2\text{OH}$  decomposes rapidly on the time scale of their experiments (milliseconds) at temperatures  $> 520$  K and pressures close to 1 bar. Under most combustion conditions such decomposition is likely to predominate over the reaction with  $\text{O}_2$ .

In low temperature studies the UV absorption spectrum of  $\text{O}_2\text{CH}_2\text{CH}_2\text{OH}$  has been observed<sup>4,5</sup> suggesting that at  $\sim 300$  K the reaction proceeds mainly by formation of the peroxy adduct.

### References

- <sup>1</sup> A. Miyoshi, H. Matsui, and N. Washida, Chem. Phys. Lett. **160**, 291 (1989).
- <sup>2</sup> IUPAC, Supplement VII, 1999 (see references in Introduction).
- <sup>3</sup> W. P. Hess and F. P. Tully, Chem. Phys. Lett. **152**, 183 (1988).
- <sup>4</sup> C. Anastasi, D. J. Muir, V. J. Simpson, and P. Pagsberg, J. Phys. Chem. **95**, 5791 (1991).
- <sup>5</sup> T. P. Murells, M. E. Jenkin, S. J. Shalliker, and D. G. Hayman, J. Chem. Soc. Faraday Trans. **87**, 2351 (1991).



### Rate Coefficient Data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$8.3 \cdot 10^{-11} \exp(-10999/T)$	1300–1700	Natarajan and Bhaskaran, 1982 <sup>1</sup>	(a)

### Comments

- (a) Shock tube study on  $\text{C}_2\text{H}_5\text{OH}$  decomposition, products monitored by UV-visible emission and rate coefficient derived by fitting to a complex mechanism.

rived by modeling a complex system making the expression for  $k$  obtained of uncertain reliability. At this stage no recommendation is made.

### Preferred Values

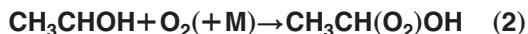
No recommendation.

### Comments on Preferred Values

The only available data come from a shock tube study of the decomposition of  $\text{C}_2\text{H}_5\text{OH}$ . The values of  $k$  were de-

### References

- <sup>1</sup> K. Natarajan and K. H. Bhaskaran, Proc. 13th Int. Symp. on Shock Tubes and Waves, 1982, p. 834.



#### Thermodynamic Data

$$\begin{aligned}\Delta H_{298}^{\circ}(1) &= -100.0 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ}(1) &= 7.03 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c(1) &= 2.23 T^{-0.017} \exp(+12080/T) \\ (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$1.4 \cdot 10^{-8} T^{-1.2} + 8.0 \cdot 10^{-10} \exp(-2525/T)$	300–682	Grotheer <i>et al.</i> , 1988 <sup>1</sup>	(a)
$1.3 \cdot 10^{-11}$	300	Anastasi <i>et al.</i> , 1989 <sup>2</sup>	(b)
$2.8 \cdot 10^{-11}$	293	Miyoshi, Matsui, and Washida, 1989 <sup>3</sup>	(c)
<i>Reviews and Evaluations</i>			
$1.9 \cdot 10^{-11}$	298	IUPAC, 1998 <sup>4</sup>	(d)

#### Comments

- (a) Fast flow discharge system with CH<sub>3</sub>CHOH generated by Cl+C<sub>2</sub>H<sub>5</sub>OH reaction. [CH<sub>3</sub>CHOH] monitored by low electron energy mass spectrometry in the presence of a large excess of O<sub>2</sub>. Total pressure ~1 mbar.
- (b) Pulse radiolysis of Ar/SF<sub>6</sub>/HCl/C<sub>2</sub>H<sub>5</sub>OH mixtures at a total pressure of 1 bar with [SF<sub>6</sub>]>[HCl]>[C<sub>2</sub>H<sub>5</sub>OH]>[O<sub>2</sub>]. CH<sub>3</sub>CHOH was generated by the Cl+C<sub>2</sub>H<sub>5</sub>OH reaction and its concentration monitored by UV absorption spectroscopy at 260 nm.
- (c) Pulsed laser photolysis of CH<sub>3</sub>COCH(OH)CH<sub>3</sub> mixtures in He bath gas at total pressures in the range 2.7–9.3 mbar. [CH<sub>3</sub>CHOH] monitored by photoionization mass spectrometry.
- (d) Mean of the  $k$ (298 K) values of Grotheer *et al.*,<sup>1</sup> Anastasi *et al.*,<sup>2</sup> and Miyoshi *et al.*<sup>3</sup>

#### Preferred Values

$$k = [1.4 \cdot 10^{-8} T^{-1.2} + 8.0 \cdot 10^{-10} \exp(-2525/T)] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the range } 300\text{--}1000 \text{ K.}$$

#### Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 300 \text{ K, rising to } \pm 0.5 \text{ at } 1000 \text{ K.}$$

#### Comments on Preferred Values

The values of  $k$  at 300 K from the studies of Grotheer *et al.*<sup>1</sup> and of Anastasi *et al.*<sup>2</sup> are in good agreement. That of

Miyoshi *et al.*<sup>3</sup> is substantially higher and may be due to the different source of CH<sub>3</sub>CHOH radicals used in their study. The sole determination of the temperature dependence of  $k$ , from the study of Grotheer *et al.*,<sup>1</sup> suggests that with increase in temperature  $k$  goes through a minimum at ~420 K. The expression obtained by Grotheer *et al.*<sup>1</sup> is provisionally accepted as our preferred expression for  $k$ , but substantial error limits are suggested until confirmatory studies are available. Grotheer *et al.*<sup>1</sup> suggest that the two terms in the expression for  $k$  are associated with two reaction channels, that at lower temperature, corresponding to the first term, associated with adduct formation, with the second being due to an abstraction channel, which predominates at high temperatures. Analogous behavior is observed for the CH<sub>2</sub>OH+O<sub>2</sub> reaction.

Studies of the photo-oxidation of ethanol by Carter *et al.*<sup>5</sup> provide evidence that CH<sub>3</sub>CHO is the major product at 300 K.

#### References

- <sup>1</sup> H.-H. Grotheer, G. Riekert, D. Walter, and Th. Just, 22nd Symp.(Int.) Combustion, 1988, p. 963.
- <sup>2</sup> A. Anastasi, V. Simpson, J. Munk, and P. Pagsberg, Chem. Phys. Lett. **164**, 18 (1989).
- <sup>3</sup> A. Miyoshi, H. Matsui, and N. Washida, Chem. Phys. Lett. **160**, 291 (1989).
- <sup>4</sup> IUPAC, Supplement VII, 1999 (see references in Introduction).
- <sup>5</sup> W. P. L. Carter, K. R. Darnall, R. A. Graham, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **83**, 2305 (1979).

*Thermodynamic Data*

$$\Delta H^0_{298}(1) = 53.0 \text{ kJ mol}^{-1}$$

$$\Delta S^0_{298}(1) = 138.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 5.42 \cdot 10^{32} T^{-2.109} \exp(-4040/T) \text{ molecule cm}^{-3}$$

(300 ≤  $T/\text{K}$  ≤ 5000)

$$\Delta H^0_{298}(2) = 67.0 \text{ kJ mol}^{-1}$$

$$\Delta S^0_{298}(2) = 104.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 9.99 \cdot 10^{26} T^{-0.795} \exp(-8230/T) \text{ molecule cm}^{-3}$$

(300 ≤  $T/\text{K}$  ≤ 5000)

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data ( $k = k_1 + k_2$ )**

$k/\text{s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Reviews and Evaluations</i>			
$8 \cdot 10^{13} \exp(-10830/T)$	300–600	CEC, 1992; 1994 <sup>1</sup>	(a)
$2 \cdot 10^{14} \exp(-10170/T)$	298–500	Atkinson, 1996 <sup>2</sup>	(b)

**Comments**

- (a) Preferred values based on the high pressure rate coefficient recommended by Batt.<sup>3</sup>
- (b) Recommended value based on the experimental data for the decomposition of C<sub>2</sub>-C<sub>5</sub> alkoxy radicals, converting relative rate coefficients to absolute values with  $k(\text{C}_2\text{H}_5\text{O} + \text{NO}) = 2.3 \cdot 10^{-11} \exp(150/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .<sup>5</sup> The A factor is the mean value of the re-evaluated data accounting for reaction path degeneracy, and  $E/R$  adjusted to yield the same decomposition rate coefficient at the mid point of the temperature range employed in the experimental study of Batt and Milne<sup>4</sup> conducted over the temperature range 435–491 K and at total pressures of 910 mbar in CF<sub>4</sub> bath gas.

**Preferred Values**

$k = 2 \cdot 10^{14} \exp(-10170/T) \text{ s}^{-1}$  over the range 300–600 K at 900 mbar.

**Reliability**

$\Delta \log k = \pm 1.0$  over the range 300–600 K.

*Comments on Preferred Values*

The recommended expression of Atkinson<sup>2</sup> is adopted as the preferred expression. The results of Batt and Milne,<sup>4</sup> which were used in deriving the expression, were obtained in the fall-off region. On thermodynamic grounds Channel (1) would be expected to dominate.

**References**

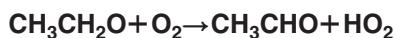
<sup>1</sup> CEC, 1992; Supplement I, 1994 (see references in Introduction).

<sup>2</sup> R. Atkinson, Int. J. Chem. Kinet. **29**, 99 (1997).

<sup>3</sup> L. Batt, Int. Rev. Phys. Chem. **6**, 53 (1987).

<sup>4</sup> L. Batt and R. T. Milne, Int. J. Chem. Kinet. **9**, 549 (1977).

<sup>5</sup> IUPAC, Supplement VII, 1999 (see references in Introduction).

*Thermodynamic Data*

$$\begin{aligned}\Delta H^\circ_{298} &= -137.4 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{298} &= 13.45 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 3.09 \cdot 10^2 T^{-0.596} \exp(+16300/T) \\ &(300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$8.0 \cdot 10^{-15}$	296	Gutman, Sanders, and Butler, 1982 <sup>1</sup>	(a)
$9.8 \cdot 10^{-15}$	353		
$7.1 \cdot 10^{-14} \exp(-552/T)$	295–411	Hartmann <i>et al.</i> , 1990 <sup>2</sup>	(b)
$2.4 \cdot 10^{-14} \exp(-325/T)$	295–354	Fittschen <i>et al.</i> , 1999 <sup>3</sup>	(c)
<i>Reviews and Evaluations</i>			
$1.0 \cdot 10^{-13} \exp(-830/T)$	300–1000	CEC, 1992; 1994 <sup>4</sup>	(d)
$6.3 \cdot 10^{-14} \exp(-550/T)$	295–411	NASA, 1997 <sup>5</sup>	(e)
$6.0 \cdot 10^{-14} \exp(-550/T)$	290–420	IUPAC, 1999 <sup>6</sup>	(e)

**Comments**

- (a) Pulsed laser photolysis at 266 nm of  $\text{C}_2\text{H}_5\text{ONO}/\text{O}_2/\text{He}$  mixtures at a total pressure of 53 mbar, with  $\text{O}_2$  in large excess.  $[\text{CH}_3\text{CH}_2\text{O}]$  was monitored by time resolved LIF.
- (b) Pulsed laser photolysis at 248 nm of  $\text{C}_2\text{H}_5\text{ONO}/\text{O}_2/\text{He}$  mixtures at a total pressure of 35 mbar with  $\text{O}_2$  in large excess.  $[\text{C}_2\text{H}_5\text{O}]$  was monitored by time resolved LIF excited at 328.8 nm. The yield of  $\text{HO}_2$  was determined by titration with NO and detection of the OH produced by LIF.
- (c) Pulsed laser photolysis at 248 nm of  $\text{C}_2\text{H}_5\text{ONO}/\text{O}_2/\text{He}$  mixtures at a total pressure of 100 mbar with  $\text{O}_2$  in large excess.  $[\text{C}_2\text{H}_5\text{O}]$  was monitored by time resolved LIF using an excitation wavelength of 323 nm. In some experiments the  $\text{C}_2\text{H}_5\text{O}$  radicals were generated by the reaction of F atoms with  $\text{C}_2\text{H}_5\text{OH}$ .
- (d) Based on the studies of Gutman *et al.*<sup>1</sup> and Zabarnick and Heicklen<sup>7</sup> together with an A factor assumed to be the same as that for the reaction  $\text{CH}_3\text{O} + \text{O}_2$ .
- (e) Based on the studies of Gutmann *et al.*<sup>1</sup> and Hartmann *et al.*<sup>2</sup>

Heicklen<sup>7</sup> which gives a value of  $k$  at 298 K compatible with values from the other studies, within the fairly wide error limits involved. However, there are substantial uncertainties associated with the reference reaction ( $\text{C}_2\text{H}_5\text{O} + \text{NO}$ ) used in the relative rate measurement<sup>7</sup> and our evaluation here is based on the absolute measurements of Gutman *et al.*,<sup>1</sup> Hartmann *et al.*,<sup>2</sup> and Fittschen *et al.*<sup>3</sup>

The values of  $k(298 \text{ K})$  from the three studies are in reasonable agreement. The temperature dependence obtained by Hartmann *et al.*<sup>2</sup> is significantly higher than observed by Gutman *et al.*<sup>1</sup> and Fittschen *et al.*<sup>3</sup> but the scatter on the data is large. The preferred temperature dependence is taken as the mean of the values of  $E/R$  obtained by Hartmann *et al.*<sup>1</sup> and Fittschen *et al.*<sup>3</sup> To obtain the A factor, this value of  $E/R$  is combined with a value of  $k$  at 298 K which is the mean of the values from the studies of Gutmann *et al.*,<sup>1</sup> Hartmann *et al.*,<sup>2</sup> and Fittschen *et al.*<sup>3</sup>

Measurements of the  $\text{HO}_2$  yield by Hartmann *et al.*<sup>2</sup> show that the production of  $\text{CH}_3\text{CHO} + \text{HO}_2$  is the dominant reaction channel at 298 K.

**Preferred Values**

$k = 3.8 \cdot 10^{-14} \exp(-440/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 290–1000 K.

*Reliability*

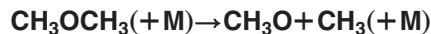
$\Delta \log k = \pm 0.2$  at 290 K, rising to  $\pm 0.5$  at 1000 K.

*Comments on Preferred Values*

As well as the absolute determinations of  $k$  cited in the Table, there is a relative rate measurement by Zabarnick and

**References**

- <sup>1</sup>D. Gutman, N. Sanders, and J. E. Butler, *J. Phys. Chem.* **86**, 66 (1982).
- <sup>2</sup>D. Hartmann, J. Karthäuser, J. P. Sawerysyn, and R. Zellner, *Ber. Bunsenges. Phys. Chem.* **94**, 639 (1990).
- <sup>3</sup>C. Fittschen, A. Frenzel, K. Imrik, and P. Devolder, *Int. J. Chem. Kinet.* **31**, 860 (1999).
- <sup>4</sup>CEC, 1992; Supplement I, 1994 (see references in Introduction).
- <sup>5</sup>NASA Evaluation No. 12, 1997 (see references in Introduction).
- <sup>6</sup>IUPAC, Supplement VII, 1999 (see references in Introduction).
- <sup>7</sup>S. Zabarnick and J. Heicklen, *Int. J. Chem. Kinet.* **7**, 455 (1985).

*Thermodynamic Data*

$$\Delta H_{298}^{\circ} = 347.7 \text{ kJ mol}^{-1}$$

$$\Delta S_{298}^{\circ} = 156.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c = 4.91 \cdot 10^{30} T^{-1.094} \exp(-42160/T) \text{ molecule cm}^{-3}$$

(200 ≤  $T/\text{K}$  ≤ 6000)

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{s}^{-1}$	$T/\text{K}$	[M]/molecule $\text{cm}^{-3}$	Reference	Comments
<i>Rate Coefficient Measurements</i>				
<i>High Pressure Range</i>				
$1.0 \cdot 10^{15} \exp(-38246/T)$	782–936	$(2.6\text{--}49) \cdot 10^{17}(\text{CH}_3\text{OCH}_3)$	Pacey, 1975 <sup>1</sup>	(a)
$2.1 \cdot 10^{15} \exp(-38546/T)$	1063–1223	$6.4 \cdot 10^{18}(\text{CH}_3\text{OCH}_3)$	Aronowitz and Naegeli, 1977 <sup>2</sup>	(b)
$3.1 \cdot 10^{-2}$	1005	$(9.6\text{--}77) \cdot 10^{17}(\text{CH}_3\text{OCH}_3)$	Held <i>et al.</i> , 1977 <sup>3</sup>	(c)
$3.2 \cdot 10^{16} \exp(-41767/T)$	680–850	$(4.5\text{--}11.4) \cdot 10^{18}(\text{CH}_3\text{OCH}_3)$	Batt <i>et al.</i> , 1982 <sup>4</sup>	(d)
$3.9 \cdot 10^{14} \exp(-37750/T)$	1250–1650	$(8.3\text{--}9.5) \cdot 10^{18}(\text{Ar})$	Hidaka, Sato, and Yamane, 2000 <sup>5</sup>	(e)

**Comments**

- (a) Pyrolysis of  $\text{CH}_3\text{OCH}_3$  in a flow system with conversion from 0.2% to 10%. Products analyzed by gas chromatography.
- (b) Pyrolysis of  $\text{CH}_3\text{OCH}_3$  in an adiabatic flow reactor. Products analyzed by gas chromatography.
- (c) Thermal decomposition of  $\text{CH}_3\text{OCH}_3$  in a flow system. Average  $[\text{CH}_3]$  in the reactor measured by UV absorption spectroscopy and the product yields measured by gas chromatography. Results were interpreted by computer simulation with a 19-reaction mechanism.
- (d) Pyrolysis of  $\text{CH}_3\text{OCH}_3$  in absence and presence of  $\text{CH}_4$  in a static system. Both sets of experiments are in very good agreement.
- (e) Shock tube study of pyrolysis of  $\text{CH}_3\text{OCH}_3/\text{Ar}$  mixtures. Three different shock tubes were used, one for time resolved and single pulse studies with provision for GC analysis of products, the other two for time resolved optical studies on reactants and products. The determination of  $k$  was based mainly on measurements of laser absorption at  $3.39 \mu\text{m}$  and simulation of the absorption profiles using a detailed reaction mechanism.

**Preferred Values**

$$k_{\infty} = 2.6 \cdot 10^{15} \exp(-39080/T) \text{ s}^{-1} \text{ over the range } 700\text{--}1700 \text{ K.}$$

*Reliability*

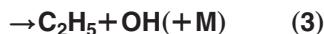
$$\Delta \log k_{\infty} = \pm 0.5 \text{ over the range } 700\text{--}1700 \text{ K.}$$

*Comments on Preferred Values*

The most recent study using shock tube pyrolysis is in quite good agreement with the earlier flow reactor studies. Under all experimental conditions the reaction is very close to the high pressure limit. We recommend a value for  $k_{\infty}$  based on an average of the experimental data of Pacey,<sup>1</sup> Aronowitz and Naegeli,<sup>2</sup> Held *et al.*,<sup>3</sup> Batt *et al.*,<sup>4</sup> and Hidaka *et al.*<sup>5</sup> but with substantial error limits.

**References**

- <sup>1</sup> P. D. Pacey, Can. J. Chem. **53**, 2742 (1979).
- <sup>2</sup> D. Aronowitz and D. Naegeli, Int. J. Chem. Kinet. **9**, 471 (1977).
- <sup>3</sup> A. M. Held, K. C. Manthorne, P. D. Pacey, and H. P. Reinholdt, Can. J. Chem. **55**, 4128 (1977).
- <sup>4</sup> L. Batt, G. Alvarado-Salinas, I. A. B. Reid, C. Robinson, and D. B. Smith, 19th Symp. (Int.) Combust., 1982, p. 81.
- <sup>5</sup> Y. Hidaka, K. Sato, and M. Yamane, Combust. Flame **123**, 1 (2000).



#### Thermodynamic Data

$$\Delta H^{\circ}_{298}(1) = 45.6 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298}(1) = 127.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 5.55 \cdot 10^{30} T^{-1.651} \exp(-5930/T) \text{ molecule cm}^{-3}$$

(300 ≤  $T/\text{K}$  ≤ 5000)

$$\Delta H^{\circ}_{298}(2) = 363.6 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298}(2) = 157.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 1.90 \cdot 10^{32} T^{-1.562} \exp(-44330/T) \text{ molecule cm}^{-3}$$

(200 ≤  $T/\text{K}$  ≤ 6000)

$$\Delta H^{\circ}_{298}(3) = 393.0 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298}(3) = 150.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 1.21 \cdot 10^{31} T^{-1.346} \exp(-47650/T) \text{ molecule cm}^{-3}$$

(300 ≤  $T/\text{K}$  ≤ 5000)

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2 + k_3$ )

$k/\text{s}^{-1}$	T/K	[M]/molecule cm <sup>-3</sup>	Reference	Comments
<i>Rate Coefficient Measurements</i>				
<i>Intermediate Fall-off Range</i>				
$k_2 = 2.5 \cdot 10^{16} \exp(-42500/T)$	1085–1165	$(3.3\text{--}4.5) \cdot 10^{18}$ (Ar)	Tsang, 1976 <sup>1</sup>	(a)
$k_2 = 3.0 \cdot 10^{18} \exp(-38000/T)$	1300–1700	$(4.3\text{--}11.3) \cdot 10^{19}$ (Ar)	Natarajan and Bhaskaran, 1981 <sup>2</sup>	(b)
$(k_1 + k_2) = 8.5 \cdot 10^{13} \exp(-33372/T)$	1160–1285	$9 \cdot 10^{18}$ (Ar)	Herzler, Manion, and Tsang, 1997 <sup>3</sup>	(c)
<i>Reviews and Evaluations</i>				
$k_1 = 1.0 \cdot 10^{14} \exp(-38600/T)$	1000–1600		Dagaut, Boettner, and Cathonnet, 1992 <sup>4</sup>	(d)
$k_2 = 2.51 \cdot 10^{16} \exp(-42400/T)$				
$k_3 = 5.0 \cdot 10^{16} \exp(-45900/T)$				
$k_1^0 [\text{Ar}] = [\text{Ar}] 4.3 \cdot 10^{59} T^{-18.85} \exp(-43510/T)$	1000–1700		Marinov, 1998 <sup>5</sup>	(e)
$k_1^\infty = 2.8 \cdot 10^{13} T^{0.09} \exp(-33284/T)$				
$F_{c,1}(\text{Ar}) = 0.3 \exp(-T/350) + 0.7 \exp(-T/800) + \exp(-3800/T)$				
$k_2^0 [\text{Ar}] = [\text{Ar}] 4.8 \cdot 10^{61} T^{-18.9} \exp(-55320/T)$				
$k_2^\infty = 5.9 \cdot 10^{23} T^{-1.68} \exp(-45800/T)$				
$F_{c,2}(\text{Ar}) = 0.5 \exp(-T/200) + 0.5 \exp(-T/890) + \exp(-4600/T)$				

#### Comments

- (a) Single-pulse shock tube study of the dissociation of 3,3-dimethyl-2-butanol and 2,3-dimethyl-2-butanol. Analysis of hydrocarbon products by gas chromatography with flame ionization detection.
- (b) Shock tube study; products monitored by UV-visible emission and rate coefficient derived by fitting to a complex mechanism.
- (c) Single-pulse shock tube experiments of the decomposition of the tetraethoxysilane. Analysis of reactants and products by gas chromatography. Decomposition of  $\text{C}_2\text{H}_5\text{OH}$  probably in the pressure-dependent region. A branching ratio for elimination of  $\text{H}_2\text{O}$  [Channel (1)] versus C-C bond fission [Channel (2)] of 0.75 is estimated.
- (d) Kinetic modeling of  $\text{C}_2\text{H}_5\text{OH}$  pyrolysis and oxidation with a reaction mechanism comprising 452 reactions and 61 species. Analysis based on the results of Refs. 2, 6–9.
- (e) Kinetic modeling of  $\text{C}_2\text{H}_5\text{OH}$  oxidation with a mecha-

nism of 369 reactions. Analysis based on an RRKM treatment between 1 and 4.5 bar from Ref. 10.

#### Preferred Values

No recommendation.

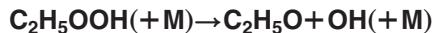
#### Comments on Preferred Values

No detailed studies of the temperature and pressure dependences of the rate coefficients have been carried out. This prevents us from recommending limiting rate coefficients. The experimental evidence<sup>3</sup> suggests that the reaction is in the intermediate fall-off range under all the experimental conditions so far investigated.

Marinov<sup>5</sup> has successfully modeled details of ethanol oxidation on the basis of the estimates for  $k_1$  and  $k_2$  cited in the Table. Therefore, it is suggested that, provisionally, these results may be used until more direct measurements become available.

## References

- <sup>1</sup> W. Tsang, Int. J. Chem. Kinet. **8**, 173 (1976).  
<sup>2</sup> K. Natarajan and K. A. Bhaskaran, Proc. 13th Int. Symp. Shock Tubes and Waves, 1981, p. 834.  
<sup>3</sup> J. Herzler, J. A. Manion, and W. Tsang, J. Phys. Chem. **101**, 5500 (1997).  
<sup>4</sup> P. Dagaut, J. C. Boettner, and M. Cathonnet, J. Chem. Phys. **89**, 867 (1992).  
<sup>5</sup> N. M. Marinov, Int. J. Chem. Kinet. **31**, 183 (1998).  
<sup>6</sup> Ö. L. Gülder, 19th Symp. (Int.) Combustion, 1982, p. 275.  
<sup>7</sup> G. Rotzoll, J. Anal. Appl. Pyrol. **9**, 43 (1985).  
<sup>8</sup> M. P. Dunphy and J. M. Simmie, J. Chem. Soc. Faraday Trans. **87**, 1691 (1991).  
<sup>9</sup> M. P. Dunphy, P. M. Patterson, and J. M. Simmie, J. Chem. Soc. Faraday Trans. **87**, 2549 (1991).  
<sup>10</sup> G. P. Smith and D. M. Golden, Int. J. Chem. Kinet. **10**, 489 (1978).



### Thermodynamic Data

$$\begin{aligned}\Delta H_{298}^{\circ} &= 194.0 \text{ kJ mol}^{-1} \\ \Delta S_{298}^{\circ} &= 139.3 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 1.51 \cdot 10^{31} T^{-1.630} \exp(-23680/T) \text{ molecule cm}^{-3} \\ &\quad (300 \leq T/\text{K} \leq 5000)\end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

### Rate Coefficient Data

$k/\text{s}^{-1}$	T/K	Reference	Comments
<i>Reviews and Evaluations</i>			
$4.0 \cdot 10^{15} \exp(-21600/T)$	400–1000	CEC, 1992; 1994 <sup>1</sup>	(a)

### Comments

(a) Derived by analogy with the estimated high pressure limit for decomposition of methyl hydroperoxide,  $k(\text{CH}_3\text{OOH} + \text{M})$  based on decomposition of  $\text{C}_7$  hydroperoxides.

### Preferred Values

$k_{\infty} = 4 \cdot 10^{15} \exp(-21600/T) \text{ s}^{-1}$  over the range 400–800 K.

### Reliability

$\Delta \log k_{\infty} = \pm 0.3$  over the range 400–800 K.

### Comments on Preferred Values

The only experimental study is that of Kirk and Knox<sup>2</sup> in which the pyrolysis of  $\text{C}_2\text{H}_5\text{OOH}$  was studied in a gas flow

apparatus with benzene carrier over the temperature range 553–653 K at total pressure of 13–26 mbar. The reported Arrhenius parameters [ $k = 2.5 \cdot 10^{13} \exp(-19000/T) \text{ s}^{-1}$ ] are substantially lower than measured recently for  $\text{CH}_3\text{OOH}$  decomposition,<sup>3</sup> [ $k(\text{CH}_3\text{OOH} + \text{M}) = 6.3 \cdot 10^{14} \times \exp(-21300/T) \text{ s}^{-1}$ ] although at 650 K the rate coefficient values are comparable. There is a strong possibility that the reaction is in the fall-off region at the low pressures employed by Kirk and Knox,<sup>2</sup> which would account for the low  $A$  factor. The uncertainties do not allow a firm recommendation but the expression recommended previously<sup>1</sup> for  $k_{\infty}$  is consistent with the data.

### References

- <sup>1</sup> CEC, 1992; Supplement I, 1994 (see references in Introduction).  
<sup>2</sup> A. D. Kirk and J. H. Knox, Trans. Faraday Soc. **56**, 1296 (1960).  
<sup>3</sup> P. D. Lightfoot, P. Roussel, F. Caralp, and R. Lesclaux, J. Chem. Soc. Faraday Trans. **87**, 3213 (1990).

**CHCCH<sub>2</sub>+CHCCH<sub>2</sub>→Products****Rate Coefficient Data**

<i>k</i> /cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
5.6·10 <sup>-11</sup>	623–673	Alkemade and Homann, 1989 <sup>1</sup>	(a)
1.2·10 <sup>-10</sup>	298	Morter <i>et al.</i> , 1994 <sup>2</sup>	(b)
4.3·10 <sup>-11</sup>	295	Atkinson and Hudgens, 1999 <sup>3</sup>	(c)
(7.5–15)·10 <sup>-12</sup>	1000–1250	Scherer, Just, and Frank, 2000 <sup>4</sup>	(d)
4·10 <sup>-11</sup>	298	Fahr and Nayak, 2000 <sup>5</sup>	(e)

**Comments**

- (a) Propargyl radicals were generated from the respective chloride or bromide by the reaction  $\text{Na} + \text{C}_3\text{H}_3\text{X} \rightarrow \text{C}_3\text{H}_3 + \text{NaX}$  in a flow reactor fed by a multi-jet diffusion burner. The carrier gas was He or N<sub>2</sub> at total pressures in the range 2.3–4.6 mbar. Products were monitored by quadrupole mass spectrometry and batch samples by gas chromatography.
- (b) C<sub>3</sub>H<sub>3</sub> radicals were produced by 193 nm pulsed laser photolysis of C<sub>3</sub>H<sub>3</sub>Cl/He/CO<sub>2</sub> mixtures. [C<sub>3</sub>H<sub>3</sub>] and [HCl] were monitored by IR absorption using a color center laser spectrometer. Total pressures were typically 35 mbar. Quantum yield of 0.07 obtained for production of HCl. Similar experiments with C<sub>3</sub>H<sub>3</sub>Br give higher values of *k*, attributed to secondary reactions generated by C<sub>3</sub>H<sub>2</sub> and HBr which are produced with a substantial quantum yield in the photolysis of C<sub>3</sub>H<sub>3</sub>Br.
- (c) C<sub>3</sub>H<sub>3</sub> radicals were produced by 193 nm pulsed laser photolysis of C<sub>3</sub>H<sub>3</sub>Cl/He mixtures over the pressure range 3–132 mbar. [C<sub>3</sub>H<sub>3</sub>] was monitored by cavity ring down laser spectroscopy at 332.5 nm. Absolute concentrations were derived using  $\sigma_{332.5} = 413 \cdot 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$ , determined in the same study. End products were analyzed by GC and detailed modeling was carried out to correct for secondary chemistry. The rate constant was independent of pressure over the range studied.
- (d) Shock tube study on pyrolysis of 3-iodo-propyne/Ar mixtures with [H] monitored by ARAS behind reflected shock waves at pressures in the range 1.5–2.2 bar. GC analysis carried out on the post shock gases showed that the vast majority of products were C<sub>6</sub>H<sub>6</sub> species. The absorption cross section for the C<sub>6</sub>H<sub>6</sub> products was determined and used in the determination of the rate constant cited in the Table for the reaction 2C<sub>3</sub>H<sub>3</sub> → C<sub>6</sub>H<sub>6</sub>, which is the dominant process.
- (e) Propargyl and methyl radicals were produced by laser photolysis at 193 nm of C<sub>3</sub>H<sub>3</sub>Cl/CH<sub>3</sub>N<sub>2</sub>CH<sub>3</sub>/He mixtures in a flow system at 65 mbar. GC/MS analysis was carried out on the products. Separate experiments were carried out on C<sub>3</sub>H<sub>3</sub>Cl/He mixtures to identify products from the propargyl radical self-reactions. The yields of C<sub>2</sub>H<sub>6</sub>, C<sub>4</sub>H<sub>6</sub>, and C<sub>6</sub>H<sub>6</sub> were modeled using a detailed mechanism to derive values of *k*.

**Preferred Values**

$k = 6.5 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 298–1000 K.

*Reliability*

$\Delta \log k = \pm 0.5$  over the range 298–1000 K.

*Comments on Preferred Values*

Recent theoretical studies of Miller and Klippenstein<sup>6</sup> have served to demonstrate the complex temperature and pressure dependence of the rate constant and product distribution of this reaction. For the behavior of the rate constant they identify three distinct temperature regions: (i)  $T < 500 \text{ K}$ ; the rate constant is pressure independent and has only a small temperature coefficient. (ii)  $500 \text{ K} < T < 2000 \text{ K}$ ; the overall rate constant and those of the various product channels are functions of temperature and pressure and, over this region, the overall rate constant falls by a factor of  $\sim 1000$  from its room temperature value. (iii)  $T > 2000 \text{ K}$ ; the rate constant becomes pressure independent. There are insufficient experimental data to test these predictions. At 298 K the values obtained by Fahr and Nayak<sup>5</sup> and by Atkinson and Hudgens<sup>3</sup> are in good agreement but Morter *et al.*<sup>2</sup> obtain a value higher by approximately a factor of 3. The value at 623–673 K obtained by Alkemade and Homann<sup>1</sup> is also close to that of Atkinson and Hudgens<sup>3</sup> and Fahr and Nayak<sup>5</sup> suggesting little temperature dependence of *k* over the range 298–650 K. Our preferred value over this range is a mean of the values of Alkemade and Homann,<sup>1</sup> Atkinson and Hudgens,<sup>3</sup> Fahr and Nayak,<sup>5</sup> and Morter *et al.*<sup>2</sup> At higher temperatures there have been no definitive studies. The shock tube study of Scherer *et al.*<sup>4</sup> at 1100–1250 K was carried out under conditions where the theoretical treatment<sup>6</sup> predicts strong temperature and pressure dependence of *k* and until this is investigated we limit our recommendations to lower temperatures.

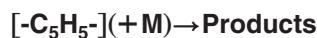
The theoretical treatment of Miller and Klippenstein<sup>6</sup> suggests that above  $\sim 2000 \text{ K}$  the sole reaction channel leads to phenyl+H but at lower temperatures a number of product channels are open and the branching ratios are both temperature and pressure dependent. For combustion temperatures the main products are predicted to be fulvene, benzene, and phenyl+H. The limited experimental data come from end

product analysis. At 298 K Fahr and Nayak<sup>5</sup> found the main products to be 1,5-hexadiyne, 1,2-hexadiene-5-yne, and an unidentified C<sub>6</sub>H<sub>6</sub> compound. At 623–673 K Alkemade and Homann<sup>1</sup> find 1,2-hexadiene-5-yne, benzene, 1,3-hexadiene-5-yne, 1,5-hexadiyne, and 1,2,4,5-hexatetraene while over the range 1150–1600 K Scherer *et al.*<sup>4</sup> find the products to be a range of C<sub>6</sub>H<sub>6</sub> compounds the distribution of which shifts, as the temperature rises, from aliphatic C<sub>6</sub>H<sub>6</sub> products towards benzene, and with only a small contribution (~5%) from H atom producing channels at 1600 K. Stein *et al.*,<sup>7</sup> from the results of a flow reactor study, have also suggested a route from propargyl *via* 1,5-hexadiyne to ben-

zene. At this stage we make no recommendations for branching ratios.

## References

- <sup>1</sup> U. Alkemade and K. H. Homann, Z. Phys. Chem. N. F. **161**, 19 (1989).
- <sup>2</sup> C. L. Morter, S. K. Farhat, J. D. Adamson, G. P. Glass, and R. F. Curl, J. Phys. Chem. **98**, 7029 (1994).
- <sup>3</sup> D. B. Atkinson and J. W. Hudgens, J. Phys. Chem. A **103**, 4242 (1999).
- <sup>4</sup> S. Scherer, Th. Just, and P. Frank, 28th Symp. (Int.) Combustion, 2000, p. 1522.
- <sup>5</sup> A. Fahr and A. Nayak, Int. J. Chem. Kinet. **32**, 118 (2000).
- <sup>6</sup> J. A. Miller and S. J. Klippenstein, J. Phys. Chem. A **105**, 7254 (2001).
- <sup>7</sup> S. E. Stein, J. A. Walker, M. M. Suryan, and A. Fahr, 23rd Symp. (Int.) Combustion, 1990, p. 85.



### Rate Coefficient Data

<i>k</i> /s <sup>-1</sup>	<i>T</i> /K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
5.0 · 10 <sup>13</sup> exp(−16757/T)	1080–1550	Burcat and Dvinyaninov, 1997 <sup>1</sup>	(a)

### Comments

(a) Single-pulse shock tube study of cyclopentadiene pyrolysis at pressures in the range 1.7–9.6 bar in Ar bath gas. Product analysis by gas chromatography. Rate coefficient extracted by fitting product concentration profiles with a reaction mechanism comprising 36 reactions.

### Preferred Values

$k = 5 \cdot 10^{13} \exp(-16760/T)$  s<sup>-1</sup> over the range 1000–1600 K.

### Reliability

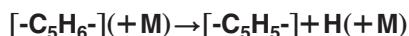
$\Delta \log k = \pm 0.5$  over the range 1000–1600 K.

### Comments on Preferred Values

For the preferred expression for *k* we accept the only published rate coefficient for this reaction. Burcat and Dvinyaninov<sup>1</sup> found that this reaction was essential to the mechanism of cyclopentadiene pyrolysis to achieve agreement between the predicted and experimental product distributions. The authors suggest the most probable product is the pent-2-ene-4-yne-1-yl radical. However, for this radical to be formed an H atom must perform a two carbon displacement. The pent-2-ene-4-yne-1-yl radical would most likely decompose to yield C<sub>2</sub>H<sub>2</sub> + C<sub>3</sub>H<sub>3</sub>.

## References

- <sup>1</sup> A. Burcat and M. Dvinyaninov, Int. J. Chem. Kinet. **29**, 505 (1997).



#### Thermodynamic Data

$$\Delta H^\circ_{298} = 345.2 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298} = 105.6 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c = 7.1 \cdot 10^{23} T^{0.312} \exp(-41330/T) \text{ molecule cm}^{-3}$$

(300 ≤ T/K ≤ 2000)

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data

##### Rate Coefficient Data

$k/\text{s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$1.1 \cdot 10^{15} \exp(-38760/T)$	1250–1550	Roy <i>et al.</i> , 1997 <sup>1</sup>	(a)
$4.0 \cdot 10^{14} \exp(-38760/T)$	1250–1600	Roy <i>et al.</i> , 1998 <sup>2</sup>	(a)

#### Comments

- (a) Measurements behind reflected shock waves at 0.7–5.6 bar total pressure. Low concentrations, 1–8 ppm, cyclopentadiene in Ar were employed. H atoms were monitored by ARAS. In the early stages (up to 250  $\mu\text{s}$ ) the observed [H] profiles depend only on the dissociation of cyclopentadiene and the reaction cyclopentadiene + H → products. Roy *et al.*<sup>2</sup> extended the temperature range of the study of Roy *et al.*<sup>1</sup> The expression cited above is a fit to their data<sup>2</sup> and that derived from a re-evaluation of the data of Roy *et al.*<sup>1</sup> with an improved ARAS calibration curve.

#### Preferred Values

$$k = 4.0 \cdot 10^{14} \exp(-38760/T) \text{ s}^{-1} \text{ over the range } 1250\text{--}1600 \text{ K.}$$

#### Reliability

$$\Delta \log k = \pm 0.3 \text{ over the range } 1250\text{--}1600 \text{ K.}$$

#### Comments on Preferred Values

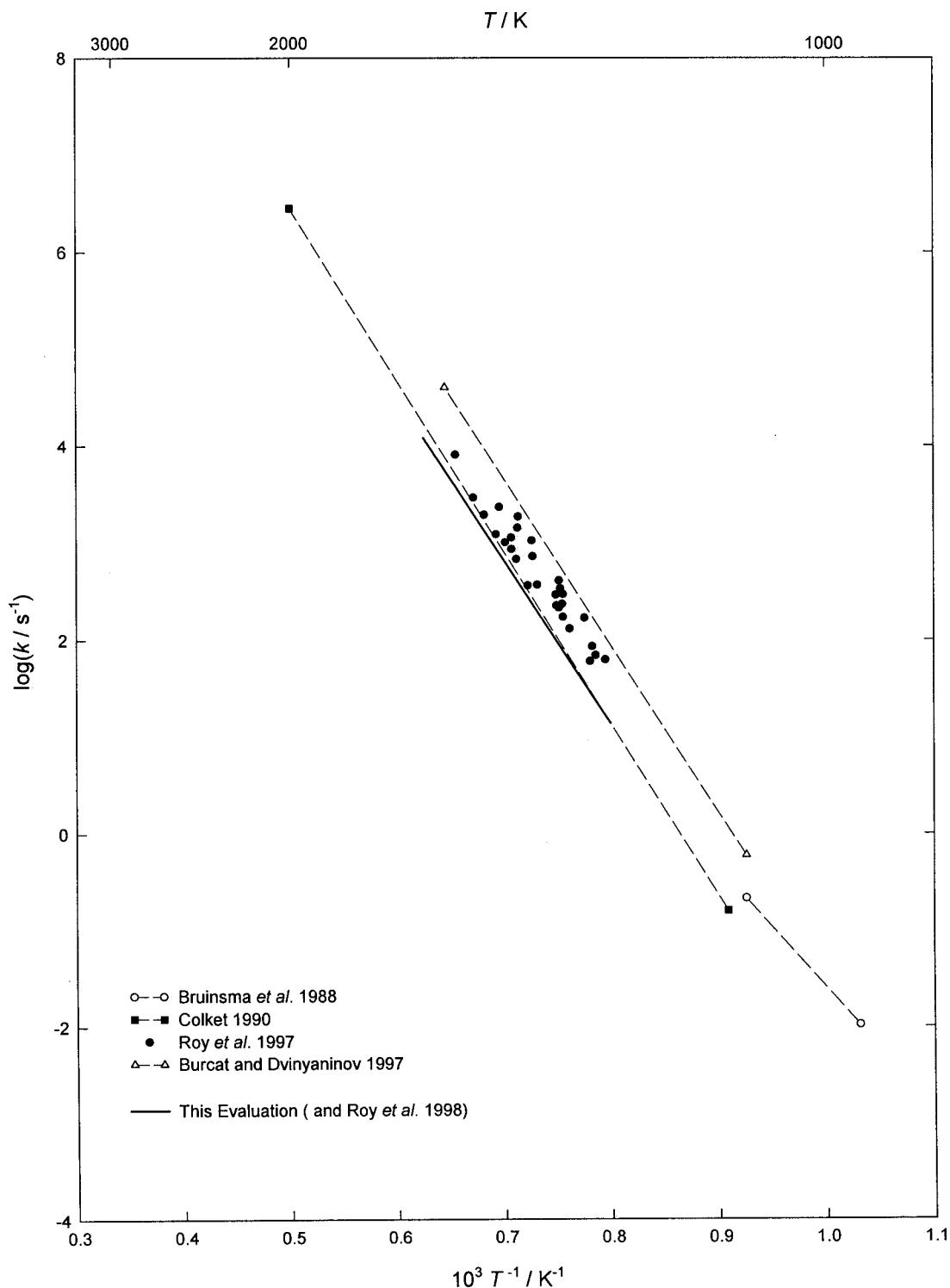
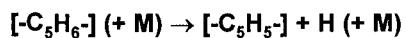
The data of Roy *et al.*,<sup>1,2</sup> which represent the only direct measurements of cyclopentadiene dissociation, have been obtained by using highly diluted mixtures of cyclopentadiene in the ppm range. This strongly reduces the influence of secondary reactions. Single-pulse shock tube experiments, with end product analysis by gas chromatography, have been carried out by Colket,<sup>3</sup> Burcat and Dvinyaninov,<sup>4</sup> and Kern *et al.*<sup>5</sup> In each study the rate coefficient was extracted by fitting observed concentration profiles with a large kinetic mechanism. Bruinsma *et al.*<sup>6</sup> also studied cyclopentadiene dissociation in a flow reactor with GC analysis. We have based our recommendation on the analysis of Roy *et al.*<sup>2</sup> as these are the most direct studies and least likely to be influenced by secondary chemistry. The results of Colket<sup>3</sup> are in full agreement with the recommendation.

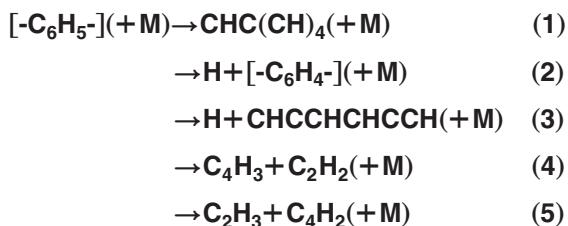
Roy *et al.*<sup>7</sup> have also studied the H + C<sub>5</sub>H<sub>5</sub> reaction over the range 1150–1500 K. Combining their measurements of  $k_{-1}$  with the values of  $k$  from their earlier work,<sup>1,2</sup> Roy *et al.*<sup>7</sup> derived values of the enthalpy of formation of the cyclopentadienyl radical in excellent agreement with values derived from other studies. Using a simple fall-off analysis they also derived the expressions  $k_\infty = 7.65 \cdot 10^{19} T^{-1.183} \exp(-42513/T) \text{ s}^{-1}$  and  $k_0(\text{Ar}) = 1.07 \cdot 10^{80} T^{-16.788} \exp(-8547.9/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Comparison of the values of  $k$  calculated from our preferred expression and those from this expression for  $k_\infty$  suggests that the reaction is not too far from its high pressure limit at the pressures and temperatures used in the experimental studies, a finding supported by other, RRKM calculations.<sup>2,5</sup>

It has usually been assumed that the products of C<sub>5</sub>H<sub>6</sub> decomposition are C<sub>5</sub>H<sub>5</sub> + H. Theoretical calculations by Backsay and Mackie<sup>8</sup> have suggested that there may also be other channels leading to molecular products coming from open chains formed by C-C fission following hydrogen shifts in the cyclopentadiene. The lowest barrier found in their calculations was for formation of CH<sub>2</sub>CHCHCCH<sub>2</sub>, which subsequently decomposes into acetylene and methylacetylene.

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*Thermodynamic Data*

$$\Delta H^{\circ}_{298}(1) = 253.8 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298}(1) = 50.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 55.9 T^{0.537} \exp(-30870/T) \quad (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^{\circ}_{298}(3) = 392.6 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298}(3) = 147.5 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 1.19 \cdot 10^{27} T^{0.200} \exp(-47650/T) \text{ molecule cm}^{-3} \quad (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^{\circ}_{298}(5) = 429.1 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298}(5) = 195.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(5) = 3.07 \cdot 10^{33} T^{-1.156} \exp(-52400/T) \text{ molecule cm}^{-3} \quad (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^{\circ}_{298}(2) = 321.5 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298}(2) = 117.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 8.11 \cdot 10^{26} T^{-0.495} \exp(-38820/T) \text{ molecule cm}^{-3} \quad (300 \leq T/\text{K} \leq 5000)$$

$$\Delta H^{\circ}_{298}(4) = 422.0 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298}(4) = 197.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(4) = 1.70 \cdot 10^{33} T^{-1.059} \exp(-51470/T) \text{ molecule cm}^{-3} \quad (300 \leq T/\text{K} \leq 5000)$$

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data ( $k = k_1 + k_2 + k_3 + k_4 + k_5$ )**

$k/\text{s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$5.0 \cdot 10^{13} \exp(-36736/T)$	1500–1900	Rao and Skinner, 1988 <sup>1</sup>	(a)
$k_1 = 3.0 \cdot 10^{13} \exp(-36736/T)$	1500–1900		(b)
$k_1 = 4.5 \cdot 10^{13} \exp(-36500/T)$	1450–1730	Braun-Unkhoff, Frank, and Just, 1988 <sup>2</sup>	(c)
<i>Reviews and Evaluations</i>			
$k_1 = 4.0 \cdot 10^{13} \exp(-36700/T)$	1450–1900	CEC, 1992; 1994 <sup>3</sup>	(d)

**Comments**

- (a) Pyrolysis of highly dilute mixtures of  $\text{C}_6\text{D}_6$ ,  $\text{C}_6\text{H}_5\text{Cl}$ ,  $\text{C}_6\text{H}_5\text{Br}$ , and  $\text{C}_6\text{H}_5\text{I}$  behind incident shock waves at 0.4 bar total pressure. Formation of H and D atoms monitored by ARAS. RRKM calculations were carried out to evaluate unimolecular fall-off rate expressions. Rate expressions for the dissociation of phenyl radicals were deduced from the pyrolysis of chloro- and bromobenzene. From these experiments it was found that about 18% of the phenyl radicals dissociate in some way without formation of H atoms, while the remainder produce H atoms, presumably via the  $\text{CHC}(\text{CH})_4$  radical.
- (b) See Comment (a). To interpret the results from iodo-benzene pyrolysis it is necessary to introduce additional reactions to the model. In particular the dissociation of iodobenzene to phenyl radicals and I atoms which has been measured by Robaugh and Tsang.<sup>4</sup> RRKM calculations indicate that the phenyl radical dissociation rate coefficient should be near the high pressure limit.
- (c) Dissociation of phenyl radicals studied behind reflected

shock waves. Phenyl radicals were generated from pyrolysis of 1–100 ppm nitrosobenzene in Ar at total pressures of 1.2–2.4 bar. [H] determined by ARAS. In the early stages of reaction a first-order rate with an activation energy of  $(306 \pm 8) \text{ kJ mol}^{-1}$  was found. From the thermodynamic data for the heat of formation of o-benzene, available to the authors at the time of their study, together with the experimental value for the activation energy, it was concluded that it is not possible to attribute the high temperature H-atom production to a direct decomposition pathway of the phenyl radical. Therefore, a 2-step reaction mechanism was assumed in which the first step is isomerization to generate linear  $\text{C}_6\text{H}_5$  structure which immediately dissociates to form products including H atoms. A re-evaluation of their data, with a new reaction scheme based upon a lower enthalpy of reaction for Channel (2) by Wang *et al.*,<sup>11</sup> showed that a more satisfactory interpretation of the experimental data is possible by assuming that Channel (2) is the dominant decay channel.

(d) See Comments on Preferred Values.

### Preferred Values

$k_2 = 4.0 \cdot 10^{13} \exp(-36700/T) \text{ s}^{-1}$  over the range 1450–1900 K.

#### Reliability

$\Delta \log k_2 = \pm 0.4$  over the range 1450–1900 K.

#### Comments on Preferred Values

There have been several experimental studies of this reaction in which the reaction was probed by monitoring H-atom production<sup>1,2,5,6</sup> and also a shock-tube laser Schlieren density gradient study.<sup>7</sup> The data of Rao and Skinner<sup>1</sup> and Braun-Unkhoff, Frank, and Just<sup>2</sup> are in good agreement and form the basis for the preferred value, which is numerically unchanged from our previous evaluation.<sup>3</sup> As well, there is an indirect study by Colket,<sup>8</sup> who investigated the pyrolysis of acetylene and vinylacetylene over the temperature range 1100–2400 K in a single pulse shock tube, and deduced forward and reverse rate coefficients for the reaction  $\text{CHC(CH}_4\text{)}_4 \rightarrow [-\text{C}_6\text{H}_5\text{-}] \rightarrow n\text{-C}_4\text{H}_3(+\text{C}_2\text{H}_2)$ , obtaining an expression for  $k_1$  in reasonable numerical agreement with the preferred expression for  $k_2$ . However, the work of Colket<sup>8</sup> was not aimed to study this reaction explicitly. Reaction (1) is only one in a rather large reaction system used by Colket.

The experimentally determined activation energy is compatible with the heat of reaction for isomerization [Channel (1)], as well as with the direct C-H split to form o-benzene and H [Channel (2)], the heats of reaction for the dissociation [Channels (3) and (4)] being too endothermic. The recommended rate coefficient is for Channel (2). This conclusion is different from the earlier recommendation.<sup>3</sup> RRKM,<sup>1,9–11</sup> calculations indicate that at temperatures around 1500 K, and at total pressures of about 1 bar,  $k_1$  as well as  $k_2$  are not far from the high pressure limit.

The H-atom production observed in many studies was believed to arise following decomposition of  $\text{CHC(CH}_4\text{)}_4$ . A theoretical study<sup>9</sup> indicates that while ring opening to form  $\text{CHC(CH}_4\text{)}_4$ , Channel (1) is the energetically most favorable reaction with a calculated barrier of 267 kJ mol<sup>-1</sup>, decomposition to form o-benzene+ H, Channel (2), which is calculated to be 318 kJ mol<sup>-1</sup>, endothermic is predicted to be the major product channel. According to the calculations recy-

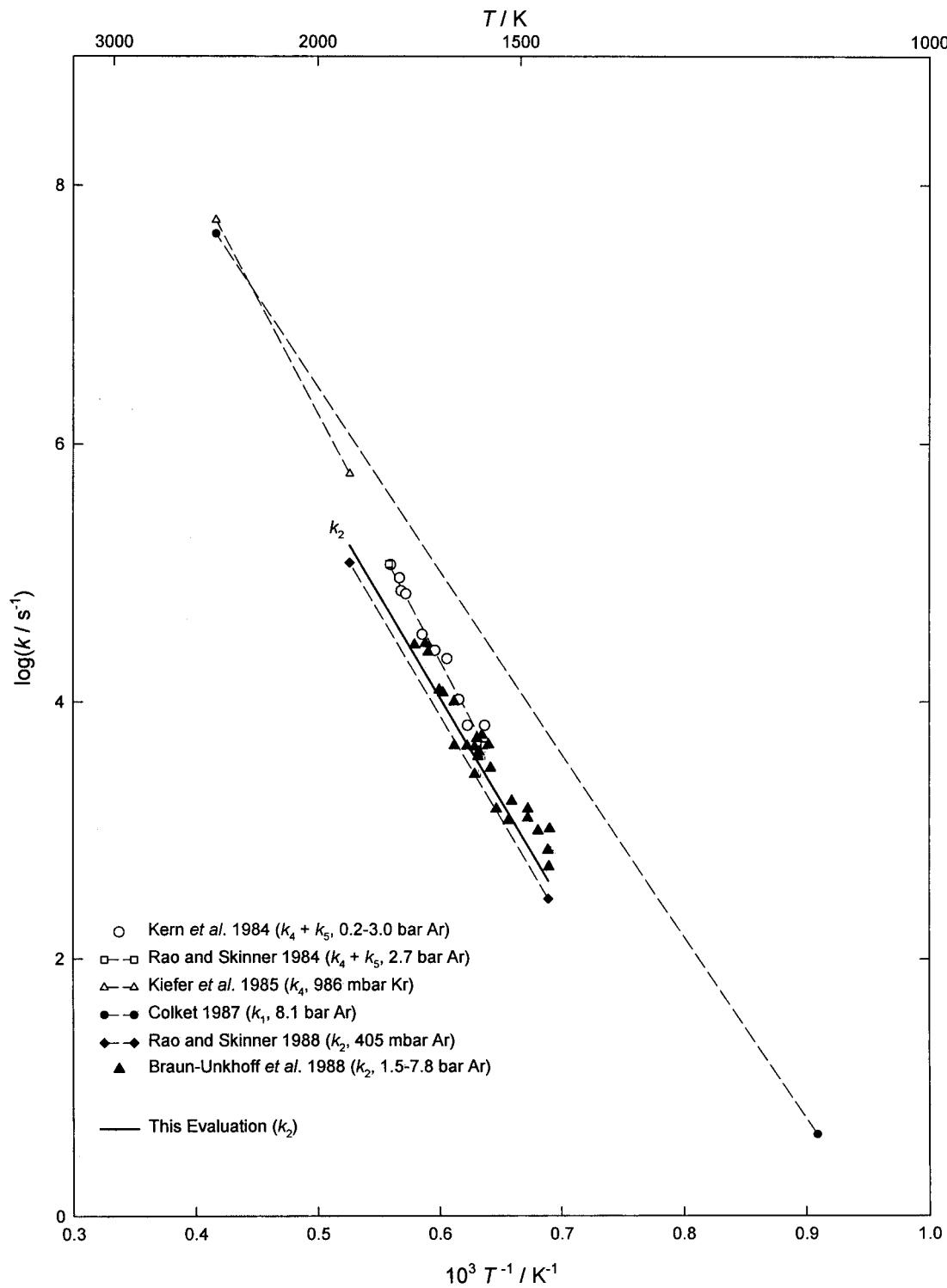
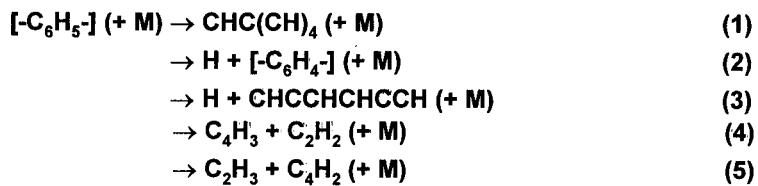
culation of  $\text{CHC(CH}_4\text{)}_4$  proceeds with a barrier of only 23 kJ mol<sup>-1</sup>, whereas the barrier for  $\text{CHC(CH}_4\text{)}_4$  decomposition to form H+  $\text{C}_6\text{H}_4$  [Channel (3)] is 150 kJ mol<sup>-1</sup>, and to form  $\text{C}_4\text{H}_3 + \text{C}_2\text{H}_2$  [Channel (4)] is 180 kJ mol<sup>-1</sup>. A recent theoretical study by Wang *et al.*<sup>11</sup> confirmed in principle the results of Madden *et al.*,<sup>9</sup> but the former authors derived rate coefficients at a considerable higher level of computational accuracy. With these new data Wang *et al.*<sup>11</sup> could model the experimental results of Braun-Unkhoff *et al.*<sup>2</sup> as well as the data from a study on benzene decay performed by Laskin and Lifshitz.<sup>12</sup>

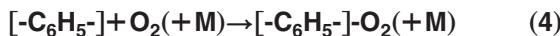
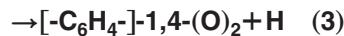
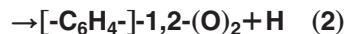
Rao and Skinner<sup>6</sup> used a similar experimental method to that of Braun-Unkhoff *et al.*<sup>2</sup> and arrived at practically the same rate coefficient for the H-atom producing channel. It is likely that their data can be interpreted by a dominating Channel (2) as well.

In conclusion, since the barrier for the recyclization of  $\text{CHC(CH}_4\text{)}_4$  was found to be very low<sup>9,11</sup> and more recently determined experimental values for the enthalpy of formation,  $\Delta_f H^\circ_{298}$ , for o-benzene cluster around 446 kJ mol<sup>-1</sup>,<sup>13</sup> it seems reasonable to ascribe the available experimental results to a mechanism with the dominant path forming o-benzene+ H in the first step. Contributions of Channels (3) and (4) can be neglected at typical combustion conditions.

### References

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#### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = -41.1 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = -19.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 7.566 \cdot 10^{-6} T^{1.475} \exp(+5250/T) \\ (300 \leq T/K \leq 4000)$$

$$\Delta H^\circ_{298}(3) = -242.9 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = -45.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 2.06 \cdot 10^{-7} T^{1.555} \exp(+29510/T) \\ (300 \leq T/K \leq 4000)$$

$$\Delta H^\circ_{298}(2) = -224.6 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = -42.5 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 1.42 \cdot 10^{-7} T^{1.671} \exp(+27330/T) \\ (300 \leq T/K \leq 4000)$$

$$\Delta H^\circ_{298}(4) = -177.3 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(4) = -144.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(4) = 6.13 \cdot 10^{-32} T^{1.703} \exp(+21380/T) \text{ cm}^3 \text{ molecule}^{-1} \\ (300 \leq T/K \leq 4000)$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2 + k_3 + k_4$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$k_1 = 4.3 \cdot 10^{-11} \exp(-3080/T)$	1050–1500	Frank <i>et al.</i> , 1994 <sup>1</sup>	(a)
$(k_2 + k_3) = 5.0 \cdot 10^{-11} \exp(-4520/T)$	1050–1500		
$k_4 = 1.0 \cdot 10^{-11} \exp(+161/T)$	297–473	Yu and Lin, 1994 <sup>2</sup>	(b)
$k_1 = 1.7 \cdot 10^{-11} \exp(-1802/T)$	1100–1350	Kumaran and Michael, 1997 <sup>3</sup>	(c)
$(k_2 + k_3) = 7.5 \cdot 10^{-12} \exp(-1814/T)$	1100–1350		
<i>Branching Ratios</i>			
$k_1/k = 0.75 \pm 0.1$	1200	Frank <i>et al.</i> , 1994 <sup>1</sup>	(a)
$(k_2 + k_3)/k = 0.25 \pm 0.1$	1200		
$k_1/k = 0.7 \pm 0.05$	1100–1350	Kumaran and Michael, 1997 <sup>3</sup>	(c)
$(k_2 + k_3)/k = 0.3 \pm 0.05$	1100–1350		

#### Comments

- (a) Measurements behind reflected shock waves at total pressures of 1.3–2.5 bar. Phenyl radicals generated from mixtures containing 5–45 ppm nitrosobenzene in Ar with 5–20 fold excess O<sub>2</sub>. [H] and [O] monitored simultaneously by ARAS. The branching ratios  $k_1/k$  and  $(k_2 + k_3)/k$  were found to be slightly temperature dependent, with  $k_1/k \approx 0.70$  at 1500 K and  $k_1/k \approx 0.78$  at 1050 K.
- (b) Flow reactor study in the pressure range 27–107 mbar Ar. Phenyl radicals generated by photolysis of C<sub>6</sub>H<sub>5</sub>NO at  $\lambda = 248$  nm. Formation of the peroxy radical was monitored at 496.4 nm by the cavity-ring-down technique. The possible product,  $[-\text{C}_6\text{H}_5\cdot]\text{-O}$ , was not detected by absorption at  $\lambda = 575.4$  nm.
- (c) Measurements behind reflected shock waves at total pressures of about 0.45 bar. Phenyl radicals generated from mixtures containing 2.6 ppm iodobenzene with 250 fold excess O<sub>2</sub>. [H] and [O] determined by ARAS in separate experiments. The branching ratios were found to be constant over the temperature range investigated.

#### Preferred Values

$k_1 = 1.7 \cdot 10^{-11} \exp(-1802/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 1050–1500 K.

$(k_2 + k_3) = 7.5 \cdot 10^{-12} \exp(-1814/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 1100–1400 K.

$k_4 = 1.0 \cdot 10^{-11} \exp(161/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 297–500 K.

#### Reliability

$\Delta \log k_1 = \pm 0.2$  over the range 1050–1500 K.

$\Delta \log (k_2 + k_3) = \pm 0.3$  over the range 1100–1400 K.

$\Delta \log k_4 = \pm 0.2$  over the range 297–500 K.

#### Comments on Preferred Values

The data of Frank *et al.*<sup>1</sup> and Kumaran and Michael<sup>3</sup> clearly show that under the experimental conditions employed ( $P > 0.5$  bar,  $T > 1000$  K) phenyl radicals react with molecular oxygen to generate O atoms [Channel (1)] or H atoms [Channels (2) and (3)]. The data of Kumaran and Michael<sup>3</sup> for  $k_1$  and  $(k_2 + k_3)$  are preferred over those of Frank *et al.*<sup>1</sup> as the experiments were conducted with lower phenyl radical precursor concentrations and are less likely to

be influenced by subsequent reactions. The data of Baldwin *et al.*<sup>4</sup> are preliminary.

The good agreement of the data of Kumaran and Michael<sup>3</sup> and Frank *et al.*<sup>1</sup> for  $k_1$  over the common temperature range of the studies (1100–1350 K) allows us to recommend the preferred values over the combined temperature range of the two studies. Values of  $(k_2 + k_3)$  from the two studies agree well at the upper limit of the common temperature range, but differ by a factor of 2 at the lower limit (the data of Frank *et al.*<sup>1</sup> being lower). We therefore restrict the temperature range of the preferred value for  $(k_2 + k_3)$  to that studied by Kumaran and Michael.<sup>3</sup> The measured branching ratios are comparable with the recommended expressions for the rate coefficients.

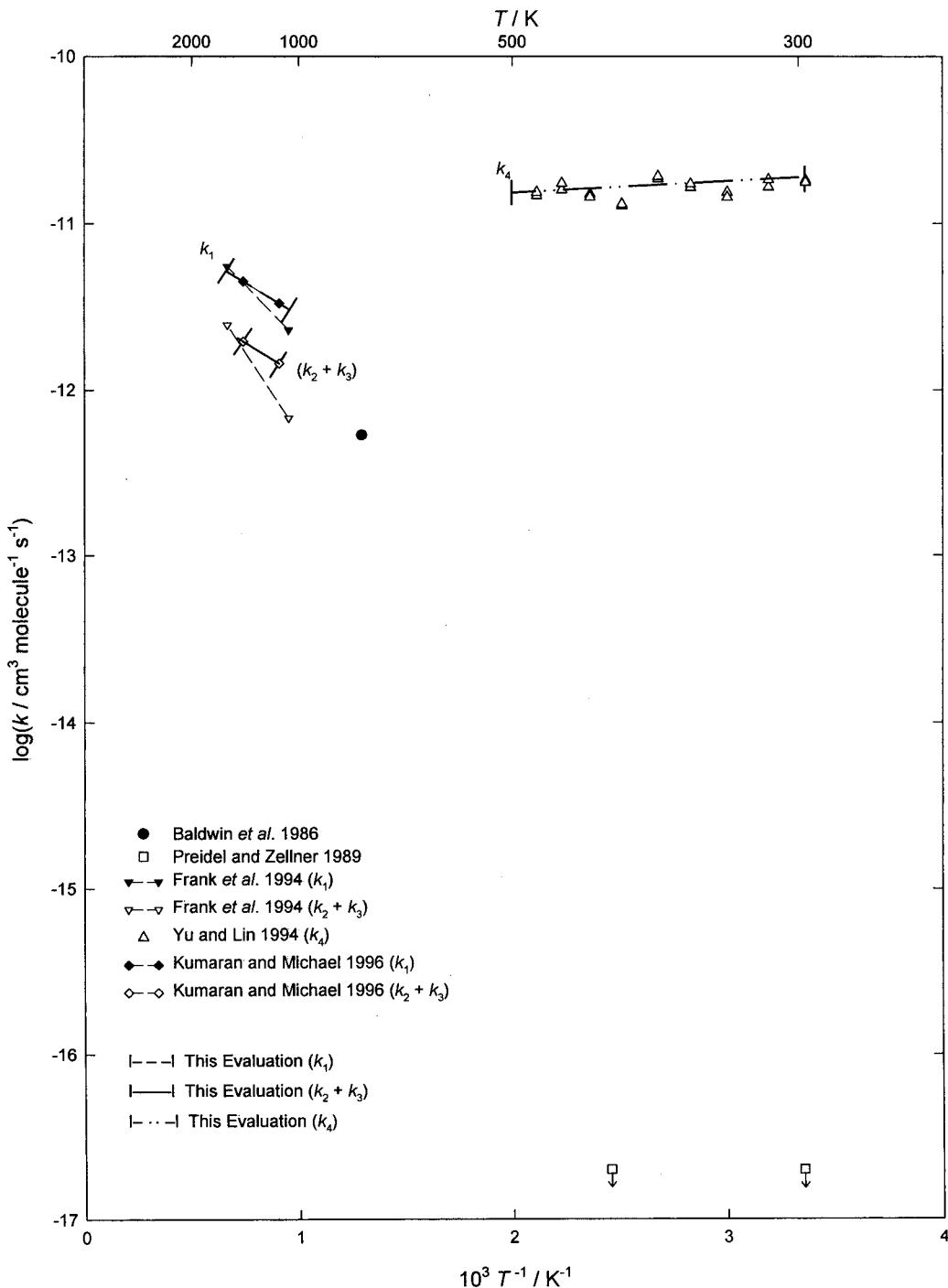
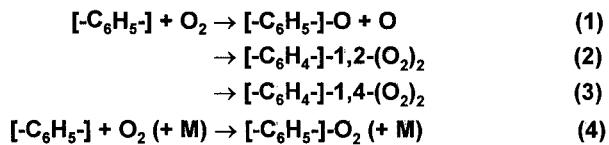
At temperatures below 500 K adduct formation predominates. The study of Yu and Lin<sup>2</sup> clearly shows the production of the peroxy radical under the experimental conditions studied. The reaction was found to be close to the high pressure limit, and no pressure dependence of the rate coefficients could be observed. In a preliminary study Yu and Lin<sup>5</sup> monitored phenyl by its absorption at 505 nm, and Preidel and

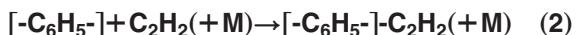
Zellner<sup>6</sup> monitored phenyl by its absorption at 488 nm. In both cases strong contamination from co-absorption by phenyl peroxy radicals resulted in reported rate coefficients that are too low.<sup>2</sup>

Quantum chemical calculations<sup>7</sup> suggest that the reaction is complex, the reactants forming an initial adduct which may either decompose to yield an O atom and a phenoxy radical or, following internal rearrangement, decay to form an H atom and a quinone. The computed barrier heights are compatible with the experimental results.

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#### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = -28.2 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = -52.6 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 1.04 \cdot 10^{-8} T^{1.799} \exp(+3700/T) \\ (300 \leq T/\text{K} \leq 2000)$$

$$\Delta H^\circ_{298}(2) = -177.5 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = -144.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 1.59 \cdot 10^{-38} T^{3.171} \exp(+22170/T) \text{ cm}^3 \text{ molecule}^{-1} \\ (300 \leq T/\text{K} \leq 3000)$$

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$k_1 = 1 \cdot 10^{-11} \exp(-3550/T)$	900–1230	Fahr, Mallard, and Stein, 1986 <sup>1</sup>	(a)
$k_1 = 6.6 \cdot 10^{-11} \exp(-5083/T)$	1043–1330	Fahr and Stein, 1988 <sup>2</sup>	(b)
$4.1 \cdot 10^{-18} T^{1.77} \exp(-1152/T)$	297–523	Yu <i>et al.</i> , 1994 <sup>3</sup>	(c)
$1.7 \cdot 10^{-11} \exp(-3849/T)$	1130–1430	Heckmann, Hippler, and Troe, 1996 <sup>4</sup>	(d)

#### Comments

- (a) Very-low-pressure-pyrolysis experiments in a Knudsen cell flow reactor. Phenyl radicals generated from nitrobenzene pyrolysis at pressures in the range 1–13  $\mu\text{bar}$ . Formation of products monitored by mass spectrometry. Rate coefficient measured relative to phenyl recombination rate coefficient. Value in table based on  $k([-\text{C}_6\text{H}_5^-] + [-\text{C}_6\text{H}_5^-] \rightarrow [-\text{C}_6\text{H}_5^-]_2) = 9.5 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .<sup>3</sup>
- (b) Same technique as in Comment (a) with generation of phenyl radicals from phenylvinylsulphone pyrolysis.
- (c) Flow reactor measurements at 27 mbar total pressure of Ar bath gas. Phenyl radicals generated by laser photolysis of nitrosobenzene at  $\lambda = 248 \text{ nm}$  in the presence of a large excess of acetylene.  $[-\text{C}_6\text{H}_5^-]$  monitored by cavity-ring-down spectroscopy at  $\lambda = 504.8 \text{ nm}$ ; total rate coefficient determined. RRKM analysis was applied to determine the individual channel rate coefficients:  $k_1 = 9.5 \cdot 10^{-42} T^{9.33} \exp(-1713/T)$  and  $k_2 = 1.8 \cdot 10^{-7} T^{-1.63} \exp(-2711/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at atmospheric pressure in  $\text{N}_2$  or Ar bath gas.
- (d) Shock tube study behind reflected shock waves at pressures in the range 2.7–3.6 bar Ar. Phenyl generated from pyrolysis of nitrosobenzene. Formation of phenylethyne monitored by UV absorption at 240 nm.

#### Preferred Values

$k = 4.0 \cdot 10^{-18} T^{1.77} \exp(-1152/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 297–550 K.

$k_1 = 6.6 \cdot 10^{-11} \exp(-5080/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 900–1500 K.

#### Reliability

$\Delta \log k = \pm 0.3$  over the range 297–550 K.

$\Delta \log k_1 = \pm 0.3$  over the range 900–1500 K.

#### Comments on Preferred Values

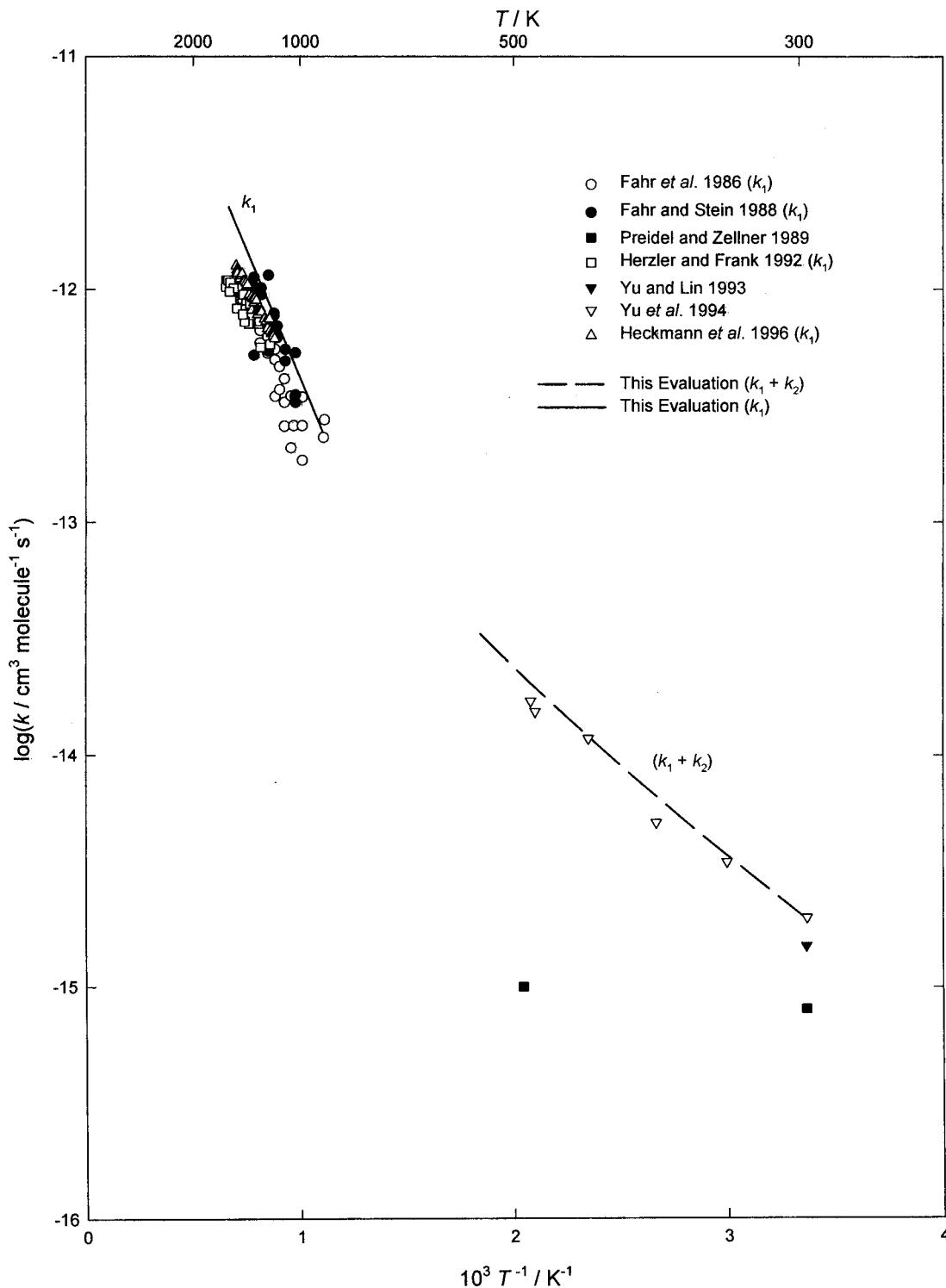
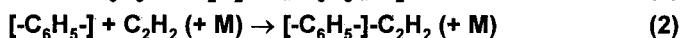
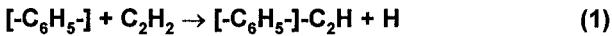
At  $T > 1000 \text{ K}$  and pressures up to at least 2 bar contributions from Channel (2) are unimportant. Thus the direct measurements of  $k_1$  by Heckmann, Hippler, and Troe<sup>4</sup> are in excellent agreement with the relative rate determinations of Fahr *et al.*<sup>1,4</sup> when converted to absolute values of  $k_1$  using the value of  $k([-\text{C}_6\text{H}_5^-] + [-\text{C}_6\text{H}_5^-] \rightarrow [-\text{C}_6\text{H}_5^-]_2)$  determined by Heckmann, Hippler, and Troe.<sup>4</sup> The preferred value is based on the determination of Ref. 4, applied over the combined temperature range of Refs. 1, 2, and 4. Herzler and Frank<sup>5</sup> have studied the reverse reaction,  $\text{H} + [-\text{C}_6\text{H}_5^-]\text{-C}_2\text{H}$ , in reflected shock waves in the temperature range 1190–1500 K. The value of  $k_{-1}$  found agrees well with the preferred value when converted to  $k_1$  applying  $K_c(1)$  above, as shown on the accompanying plot.

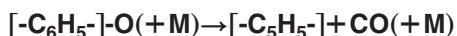
At  $T < 1000 \text{ K}$ , Yu *et al.*<sup>3</sup> have measured the overall rate coefficient,  $(k_1 + k_2)$ , over a substantial temperature range. The room temperature rate coefficient agrees with that from an earlier study from the same group employing the same techniques.<sup>6</sup> An RRKM analysis, based on BAC-MP4 data, indicates that, under the experimental conditions used, the values are close to the high pressure limit and any contribution from Channel (1) is negligible. The RRKM calculations indicate that, while the overall reaction is pressure independent, the channel branching ratios are highly pressure dependent; at 1000 K, for example,  $k_1/(k_1 + k_2)$  ranges from 1.0 at 1  $\mu\text{bar}$  to 0.14 at 1 bar. The experimental determinations<sup>1,2,4</sup> of  $k_1$ , which span the pressure range 1  $\mu\text{bar}$ –4 bar, however, show no pressure dependence. We recommend experimental values of  $(k_1 + k_2)$  determined by Yu *et al.*<sup>4</sup> over the range 297–550 K. The upper limits determined by Preidel and Zellner<sup>7</sup> at 50 mbar  $\text{N}_2$  total pressure, monitoring the absorption of 488 nm radiation, attributed to phenyl radicals, are lower than the recommended values.

## References

- <sup>1</sup> A. Fahr, W. G. Mallard, and S. E. Stein, 21st Symp. (Int.) Combustion, 1986, p. 825.  
<sup>2</sup> A. Fahr and S. E. Stein, 22nd Symp. (Int.) Combustion, 1988, p. 1023.  
<sup>3</sup> T. Yu, M. C. Lin, and C. F. Melius, Int. J. Chem. Kinet. **26**, 1095 (1994).

- <sup>4</sup> E. Heckmann, H. Hippler, and J. Troe, 26th Symp. (Int.) Combustion, 1996, p. 543.  
<sup>5</sup> J. Herzler and P. Frank, Ber. Bunsenges. Phys. Chem. **96**, 1333 (1992).  
<sup>6</sup> T. Yu and M. C. Lin, J. Am. Chem. Soc. **115**, 4371 (1993).  
<sup>7</sup> M. Preidel and R. Zellner, Ber. Bunsenges. Phys. Chem. **93**, 1417 (1989).



*Thermodynamic Data*

$$\Delta H_{298}^{\circ} = 103.3 \text{ kJ mol}^{-1}$$

$$\Delta S_{298}^{\circ} = 149.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c = 9.9 \cdot 10^{33} T^{-2.368} \exp(-13070/T) \text{ molecule cm}^{-3}$$

(300  $\leq T/\text{K} \leq 2000$ )

See Section 3 for the source of the Thermodynamic Data.

**Rate Coefficient Data**

$k/\text{s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$1.0 \cdot 10^{12} \exp(-24000/T)$	1000–1430	Lin and Lin, 1985 <sup>1</sup>	(a)
$2.5 \cdot 10^{11} \exp(-22100/T)$	1000–1580	Lin and Lin, 1986 <sup>2</sup>	(b)
$7.4 \cdot 10^{11} \exp(-22070/T)$	1000–1200	Frank <i>et al.</i> , 1994 <sup>3</sup>	(c)
<i>Reviews and Evaluations</i>			
$2.5 \cdot 10^{11} \exp(-22100/T)$	1000–1580	CEC, 1992; 1994 <sup>4</sup>	(d)

**Comments**

- (a) Pyrolysis of phenyl methyl ether (anisole) in a shock tube. Initial precursor concentrations in the range 0.1%–0.5% in Ar at total pressures of 0.5–0.9 bar. [CO] determined by resonance absorption using a cw CO laser.  $k$  deduced from [CO] profiles, assuming anisole and phenoxy decomposition were the only relevant reactions.
- (b) See Comment (a). The kinetic mechanism is extended and the deduction of  $k$  is based on computer simulation.
- (c) Reaction studied behind reflected shock waves at reaction pressures around 2 bar Ar. Phenoxy generated from pyrolysis of methyl phenyl ether and allyl phenyl ether with precursor concentrations in the range 20–70 ppm. [CO] was monitored by molecular resonance absorption in the wavelength region 121–165 nm. CO production above 1300 K was practically instantaneous with final [CO] equal to the initial precursor concentration.
- (d) Based on the work of Lin and Lin.<sup>2</sup>

**Preferred Values**

$k = 7.4 \cdot 10^{11} \exp(-22070/T) \text{ s}^{-1}$  over the range 1000–1600 K.

*Reliability*

$\Delta \log k = \pm 0.2$  over the range 1000–1600 K.

*Comments on Preferred Values*

The data of Frank *et al.*<sup>3</sup> are preferred as they were obtained at much lower initial concentrations than those from the previous work of Lin and Lin.<sup>1,2</sup> Under the conditions employed by Lin and Lin<sup>1,2</sup> secondary reactions are of considerable influence, in particular the reaction,  $\text{CH}_3 + \text{phenoxy} \rightarrow o\text{- or } p\text{-cresol}$ , had to be taken into account; the rate and products of this reaction are not well known. The activation energies found by Lin and Lin<sup>1,2</sup> and Frank *et al.*<sup>3</sup> are in close agreement. We therefore extend the temperature range for the preferred value up to the highest values used by Lin and Lin.<sup>2</sup> In a pyrolysis study of methoxy benzene decomposition, Mackie *et al.*<sup>5</sup> determined  $k/k(\text{CH}_3 + \text{C}_6\text{H}_5\text{O}) = 5 \cdot 10^{-2} \exp(-21140/T)$ . Assuming  $k(\text{CH}_3 + \text{C}_6\text{H}_5\text{O}) = 1.7 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,<sup>5</sup> independent of temperature, values of  $k$  were obtained which are in good agreement with the recommended values. The value reported from an earlier, very-low-pressure-pyrolysis study,<sup>6</sup> is only approximate, and is too low.

**References**

<sup>1</sup>C.-Y. Lin and M. C. Lin, Int. J. Chem. Kinet. **9**, 1025 (1985).

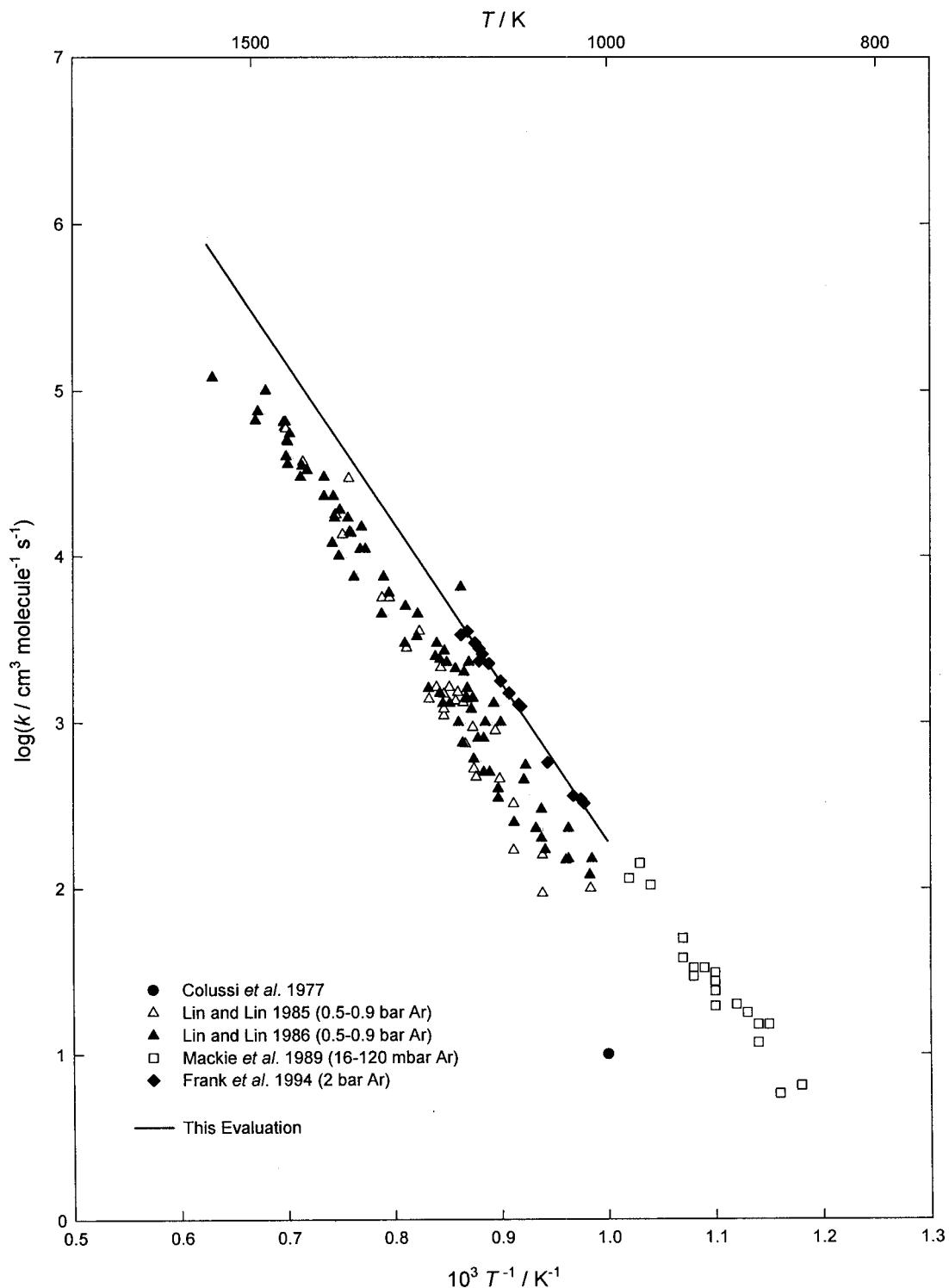
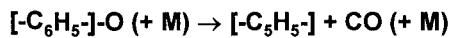
<sup>2</sup>C.-Y. Lin and M. C. Lin, J. Phys. Chem. **90**, 425 (1986).

<sup>3</sup>P. Frank, J. Herzler, Th. Just, and C. Wahl, 25th Symp. (Int.) Combustion, 1994, p. 833.

<sup>4</sup>CEC, 1992; Supplement I, 1994 (see references in Introduction).

<sup>5</sup>J. C. Mackie, K. R. Doolan, and P. F. Nelson, J. Phys. Chem. **93**, 664 (1989).

<sup>6</sup>A. J. Colussi, F. Zabel and S. W. Benson, Int. J. Chem. Kinet. **9**, 161 (1977).





#### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = 281.8 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = 147.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 7.27 \cdot 10^{31} T^{-1.72} \exp(-34260/T) \text{ molecule cm}^{-3}$$

(300 ≤ T/K ≤ 5000)

$$\Delta H^\circ_{298}(3) = 495.1 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(3) = 153.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 4.93 \cdot 10^{28} T^{-0.332} \exp(-59950/T) \text{ molecule cm}^{-3}$$

(300 ≤ T/K ≤ 5000)

$$\Delta H^\circ_{298}(2) = 377.8 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = 118.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 3.28 \cdot 10^{26} T^{-0.717} \exp(-45570/T) \text{ molecule cm}^{-3}$$

(300 ≤ T/K ≤ 5000)

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2 + k_3$ )

$k/\text{s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$(k_2 + k_3) = 3.4 \cdot 10^{15} \exp(-42900/T)$	1400–1750	Braun-Unkhoff, Frank, and Just, 1990 <sup>1</sup>	(a)
$(k_2 + k_3) = 2 \cdot 10^{15} \exp(-42100/T)$	1200–1500	Hippler, Reihls, and Troe, 1990 <sup>2</sup>	(b)
<i>Reviews and Evaluations</i>			
$5.1 \cdot 10^{13} \exp(-36370/T)$	1350–1900	CEC, 1992; 1994 <sup>3</sup>	(c)

#### Comments

- (a) Measurements of H-atom concentrations behind reflected shock waves in Ar bath gas at ~2 bar containing benzyl iodide at concentration in the range 0.3–3.5 ppm. ARAS was employed to detect H atoms at 121.5 nm and I atoms at 164.2 nm. The initial concentration of benzyl iodide was determined by measuring [I] behind the shock front.  $k$  was obtained by computer simulation of H atom profile with a 4-reaction mechanism.
- (b) Re-evaluation of data of Müller-Markgraf and Troe,<sup>4</sup> obtained by monitoring benzyl radical UV absorption measured behind reflected shock waves in mixtures of Ar and benzyl iodide, benzyl chloride, or methyl benzyl ketene. The reinterpretation included the revised rate constants:  $k(\text{toluene} \rightarrow \text{H} + \text{benzyl}) = 1 \cdot 10^{15} \exp(-43300/T) \text{ s}^{-1}$ ,  $k(\text{H} + \text{benzyl} \rightarrow \text{toluene}) = 4.3 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k(\text{H} + \text{toluene} \rightarrow \text{H}_2 + \text{benzyl}) = 2.1 \cdot 10^{-10} \exp(-4209/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .
- (c) Preferred value is based on the direct determinations of Müller-Markgraf and Troe<sup>4,5</sup> [see Comment (b)] and of Braun-Unkhoff *et al.*<sup>1</sup> [see Comment (a)].

#### Preferred Values

$$(k_2 + k_3) = 3.4 \cdot 10^{15} \exp(-42900/T) \text{ s}^{-1} \text{ over the range } 1200\text{--}1750 \text{ K.}$$

#### Reliability

$$\Delta \log(k_2 + k_3) = \pm 0.3 \text{ over the range } 1200\text{--}1750 \text{ K.}$$

#### Comments on Preferred Values

There is considerable scatter in the experimental data, as can be seen in the accompanying Arrhenius plot. There have been three experimental studies<sup>6,7,11</sup> of this reaction since our previous evaluations.<sup>3</sup> Colket and Seery<sup>6</sup> conducted single-pulse shock tube experiments in which the products from the pyrolysis of 1% toluene mixtures in 10 bar Ar at 1200–1850 K were analyzed by gas chromatography. The expression  $k_1 = 6 \cdot 10^{13} \exp(-35230/T) \text{ s}^{-1}$  was obtained indirectly by modeling the formation of  $\text{C}_2\text{H}_2$  and species arising from the decomposition of 5-membered ring compounds. The model did not include benzyl decomposition via Channels (2) or (3), but did include decomposition to give  $\text{C}_4\text{H}_4 + \text{C}_3\text{H}_3$ . Jones *et al.*<sup>7</sup> pyrolyzed mixtures of 4–160 mbar benzylbromide in 10–12 bar Ar at 1450–1650 K. The concentrations of benzylbromide, benzyl radicals, and benzyl radical fragment products were monitored by time-resolved absorption spectra in the range  $\lambda = 270\text{--}330 \text{ nm}$ . The experimentally determined rate coefficients are scattered, but agree with a theoretically derived rate expression for the decomposition of benzyl;  $k = 4 \cdot 10^{16} \exp(-48817/T) \text{ s}^{-1}$ . Of all the studies of this rate coefficient,<sup>1,2,4–9,12,13</sup> that of Braun-Unkhoff *et al.*<sup>1</sup> is least likely to have been influenced by secondary reactions and is taken as the basis for the preferred values. The preferred expression agrees with the rate expression obtained by Hippler *et al.*<sup>2</sup> from a re-evaluation of the data of Müller-Markgraf and Troe.<sup>4</sup> The agreement between the studies allows us to extend the lower temperature limit of the preferred value to 1200 K. Other studies are probably influenced by the occurrence of secondary reactions, particularly in the studies of ethylbenzyne decomposition,<sup>8</sup> and uncer-

tainties in the assumed reaction mechanism used to interpret laser Schlieren signals.<sup>9,10</sup>

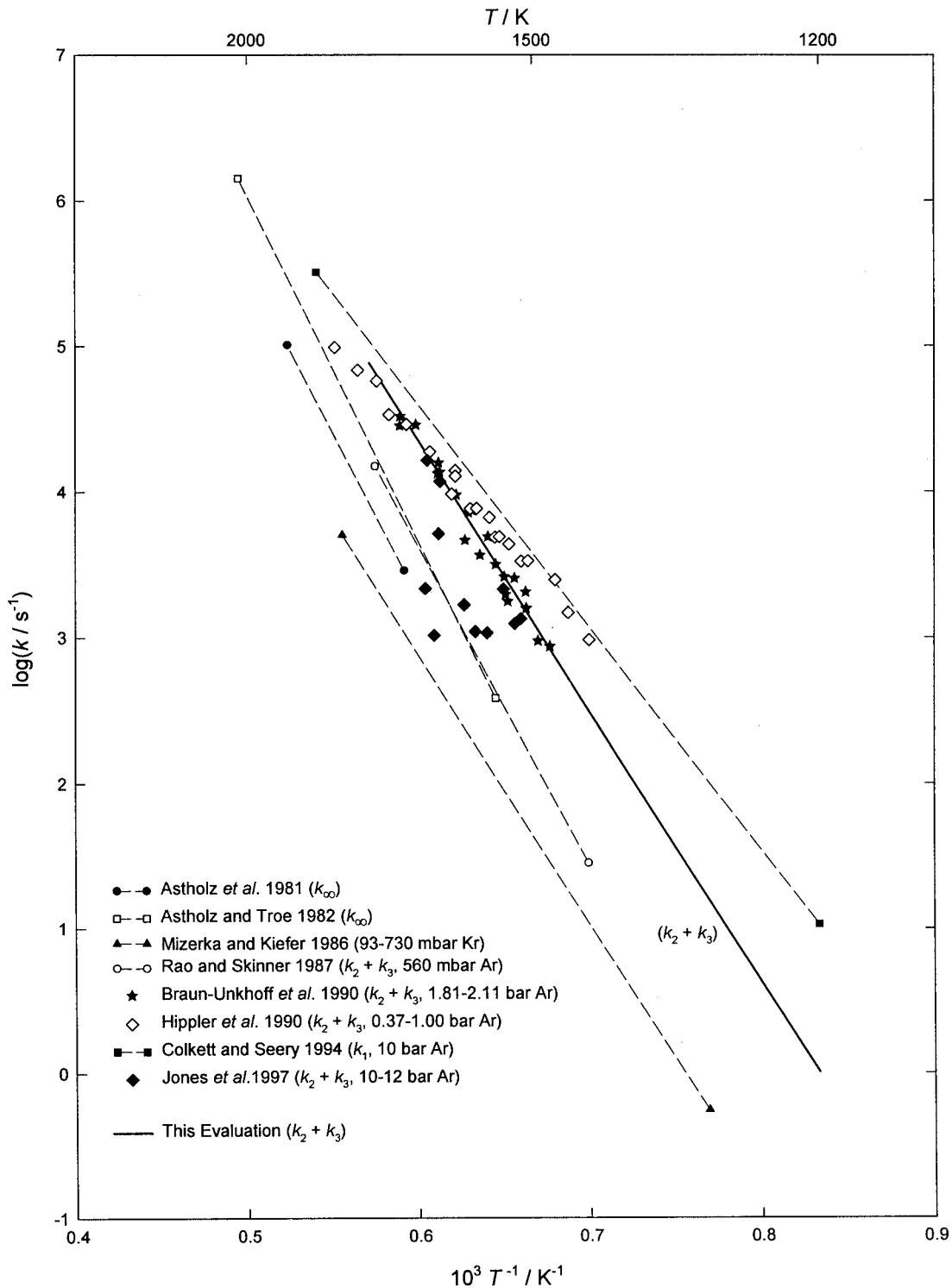
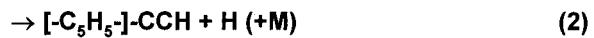
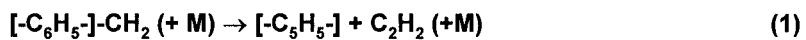
Rao and Skinner<sup>8</sup> and Braun-Unkhoff *et al.*<sup>1</sup> have shown that benzyl decomposition leads predominantly to H atom production. The low activation energy recorded by Braun-Unkhoff *et al.*<sup>1</sup> and high H-atom yields precludes significant benzyl decomposition via Channel (1) and channels producing  $C_4H_4 + C_3H_3$  and  $C_4H_3 + C_3H_4$ , (H atom production following decomposition of  $C_5H_5$ ,  $C_4H_4$  or  $C_4H_3$ ). The reaction enthalpies and additional barrier to ring opening would lead to higher activation energies than observed experimentally. The most probable initial step is isomerization of benzyl, followed by rapid decomposition of the isomer and H atom production.<sup>1,8</sup> Braun-Unkhoff *et al.*<sup>1</sup> concluded, on thermodynamic grounds that the most likely pathway is via isomerization to 6-methylenecyclo[3.1.0]hexenyl and subsequent decomposition to 5-ethynylcyclopenta-1,3-diene + H [Channel (2)]. Based upon quantum chemical calculations of several possible reaction paths for benzyl decay, Jones *et al.*<sup>7</sup> concluded that the energetically most probable channels are direct ring opening to the 1,3,5,6-heptatetrenyl radical and isomerization of benzyl to the 6-methylenecyclo[3.1.0]hexenyl radical followed by further decay to H + cyclopentadienylacetylene. The products of the decomposition of benzyl have been studied in a molecular beam.<sup>11</sup> Highly excited benzyl radicals, well above their dissociation limit, were generated by 2-photon photolysis of toluene ( $\lambda = 193$  nm) or cycloheptatriene ( $\lambda = 248$  and  $\lambda = 193$  nm). Förchtenicht *et al.*<sup>11</sup> have shown by soft ioniza-

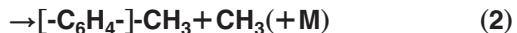
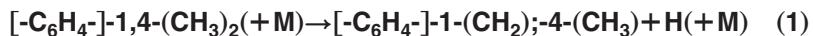
tion in a quadrupole mass spectrometer that the only reaction products of the benzyl decay were  $C_7H_6 + H$ , however, they could not identify the chemical structure of  $C_7H_6$ . This result is contrary the hypothesis of Colket and Seery<sup>6</sup> that benzyl decomposes via norbornadienyl to acetylene and cyclopentadienyl [Channel (1)].

While each benzyl radical decays to yield an H atom, identification of the accompanying hydrocarbon products remains unclear. We therefore recommend only a rate coefficient for the sum of Channels (2) and (3).

## References

- <sup>1</sup> M. Braun-Unkhoff, P. Frank, and Th. Just, Ber. Bunsenges. Phys. Chem. **94**, 1417 (1990).
- <sup>2</sup> H. Hippler, C. Reihs, and J. Troe, Z. Physik. Chem. N. F. **167**, 1 (1990).
- <sup>3</sup> CEC, 1992; Supplement I, 1994 (see references in Introduction).
- <sup>4</sup> W. Müller-Markgraf and J. Troe, J. Phys. Chem. **92**, 4899 (1988).
- <sup>5</sup> W. Müller-Markgraf and J. Troe, 21st Symp. (Int.) Combustion, 1987, p. 875.
- <sup>6</sup> M. B. Colket and D. J. Seery, 25th Symp. (Int.) Combustion, 1994, p. 883.
- <sup>7</sup> J. J. Jones, G. B. Bacska, and J. C. Mackie, J. Phys. Chem. A **101**, 7105 (1997).
- <sup>8</sup> V. S. Rao and G. B. Skinner, 21st Symp. (Int.) Combustion, 1987, p. 809.
- <sup>9</sup> L. J. Mizerka and J. H. Kiefer, Int. J. Chem. Kinet. **18**, 363 (1986).
- <sup>10</sup> K. M. Pamidimukkala, R. D. Kern, M. R. Patel, H. C. Wei, and J. H. Kiefer, J. Phys. Chem. **91**, 2148 (1987).
- <sup>11</sup> H. Förchtenicht, H. Hippler, J. Troe, and J. P. Toennies, J. Photochem. Photobiol. A Chem. **80**, 33 (1994).
- <sup>12</sup> D. C. Astholz, J. Durant, and J. Troe, 18th Symp. (Int.) Combustion, 1981, p. 885.
- <sup>13</sup> D. C. Astholz and J. Troe, J. Chem. Soc. Faraday Trans. 2 **78**, 1413 (1982).





#### Thermodynamic Data

$$\Delta H^\circ_{298}(1) = 375.8 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(1) = 103.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 4.26 \cdot 10^{19} T^{1.592} \exp(-44310/T) \text{ molecule cm}^{-3}$$

(300 ≤  $T/\text{K}$  ≤ 5000)

$$\Delta H^\circ_{298}(2) = 434.1 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298}(2) = 165.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 5.80 \cdot 10^{29} T^{-0.767} \exp(-52080/T) \text{ molecule cm}^{-3}$$

(300 ≤  $T/\text{K}$  ≤ 5000)

See Section 3 for the source of the Thermodynamic Data.

#### Rate Coefficient Data ( $k = k_1 + k_2$ )

$k/\text{s}^{-1}$	$T/\text{K}$	[M]/molecule $\text{cm}^{-3}$	Reference	Comments
<i>Rate Coefficient Measurements</i>				
<i>High Pressure Range</i>				
$5 \cdot 10^{15} \exp(-42700/T)$	1000–1800	$(4.0–90.5) \cdot 10^{17}$	Hippler, Seisel, and Troe, 1994 <sup>1</sup>	(a)
$k_1 = 1 \cdot 10^{16} \exp(-45700/T)$	1300–1800	$(9–16) \cdot 10^{18}$	Da Costa <i>et al.</i> , 2000 <sup>2</sup>	(b)
<i>Branching Ratios</i>				
$k_2/k = 0.10$	1000	$(4.1–7.2) \cdot 10^{10}$	Lange <i>et al.</i> , 1994 <sup>3</sup>	(c)
$k_2/k = 0.15$	1500			
$k_2/k = 0.20$	1750			
<i>Reviews and Evaluations</i>				
$k_\infty = 4 \cdot 10^{15} \exp(-42600/T)$	1400–1800		CEC, 1992; 1994 <sup>4</sup>	(d)

#### Comments

- (a) Shock tube study; measurements behind reflected shock waves in Ar bath gas. The reaction was monitored by measuring UV absorption over the range  $\lambda = 210$ –350 nm. Both *p*-xylene and 4-methylbenzyl radicals absorb in this region. At  $\lambda = 265$  nm absorption is due to 4-methylbenzyl; at shorter wavelengths *p*-xylene absorption dominates. Supersedes the earlier study of Brouwer, Müller-Markgraf, and Troe,<sup>5</sup> in which the absorption spectra of *p*-xylene and the 4-methylbenzyl radical could not be resolved.
- (b) Shock tube study on *o*-, *m*-, and *p*-xylene/Ar mixtures at total pressures of 1.6–4.0 bar. [H] was monitored behind reflected shock waves by ARAS at 121.6 nm. Values of  $k$  were derived by fitting [H] profiles using a simplified mechanism incorporating the parallel C-C dissociation channel and secondary reactions. It was concluded that  $k$  values were close to their high pressure limit.
- (c) Photodissociation of *p*-xylene at 193 nm. Production of CH<sub>3</sub> radicals monitored by resonantly enhanced multi-photon ionization (REMPI) spectroscopy and VUV single-photon ionization coupled with mass spectroscopic ion analysis. Results combined with those from an earlier study<sup>6</sup> of the photodissociation of *p*-xylene at 193 nm, in which *p*-xylene and 4-methyl benzyl radicals were monitored by absorption in the spectral region 220–320 nm. Conversion to thermal branching ratios with SACM unimolecular reaction rate theory.<sup>7</sup>
- (d) Preferred value based on the data of Brouwer, Müller-

Markgraf, and Troe,<sup>5</sup> which has been superseded by that of Hippler, Seisel, and Troe;<sup>1</sup> see Comment (a).

#### Preferred Values

$k_\infty = 5 \cdot 10^{15} \exp(-42700/T) \text{ s}^{-1}$  over the range 1000–1800 K.

$k_1/k = 0.85$ ;  $k_2/k = 0.15$  at 1500 K.

#### Reliability

$\Delta \log k_\infty = \pm 0.3$  over the range 1000–1800 K.

$\Delta(k_1/k) = \Delta(k_2/k) = \pm 0.10$  at 1500 K.

#### Comments on Preferred Values

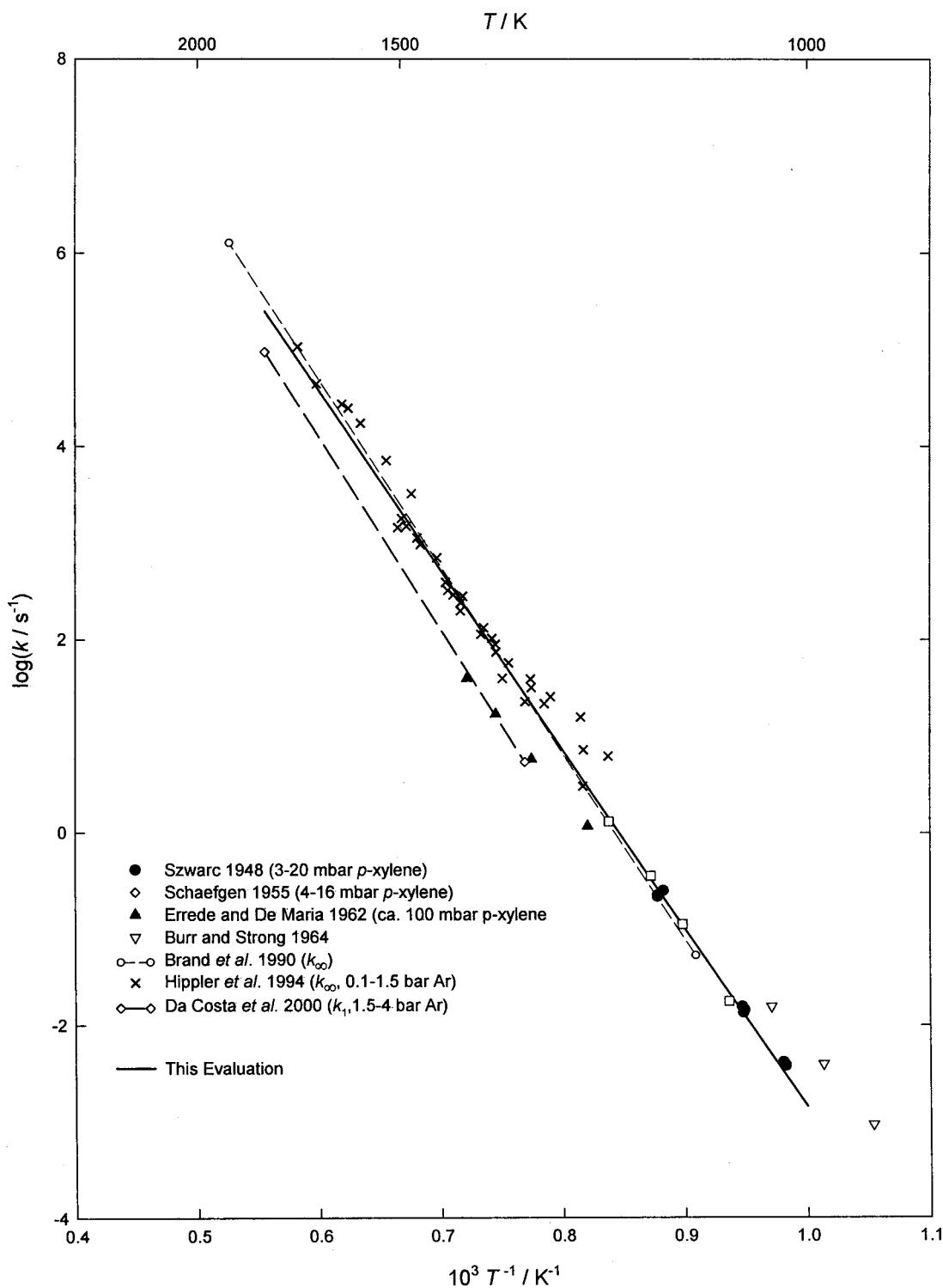
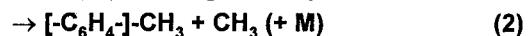
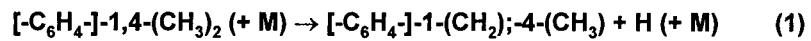
The data of Hippler, Seisel, and Troe<sup>1</sup> are close to the high pressure limit and their expression is adopted. The results of the *p*-xylene pyrolysis studies of Swarc,<sup>8</sup> Schaefgen,<sup>9</sup> and Errede and DeMaria<sup>10</sup> conducted at lower pressures (<100 mbar) agree well with the preferred value. Burr and Strong<sup>11</sup> studied the pyrolysis in H<sub>2</sub> and obtained values slightly above the preferred value. Brand *et al.*<sup>6</sup> derived an expression for the limiting high pressure rate coefficient from a study of the pressure dependent photodissociation of *p*-xylene at  $\lambda = 193$  nm, extrapolating the results to the high and low pressure limits by SACM<sup>7</sup> calculations. The expression obtained,  $k_\infty = 1.8 \cdot 10^{16} \exp(-44380/T) \text{ s}^{-1}$ , is in excellent agreement with our expression. The measurements of

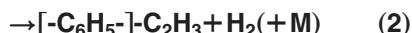
Da Costa *et al.*,<sup>2</sup> who determined  $k_1$  by monitoring H atom production, are also in good agreement with our recommended expression for  $k$ .

The branching ratios are derived from experiments in which the products of the photodissociation of *p*-xylene were measured and the thermal branching ratios obtained from these results using SACM theory. They are therefore semi-empirical. However, the *p*-xylene photodissociation studies show that the energetically favorable channel, Channel (1), is indeed dominant. Results of similar experiments,<sup>12</sup> employing 158 nm radiation to photodissociate *p*-xylene, are fully compatible with the results of the SACM calculations. Furthermore, from their study in which  $k_1$  was measured, Da Costa *et al.*<sup>2</sup> conclude that Channel (2) contributes  $\sim 15\%$  to the overall rate of decomposition, supporting our preferred values.

## References

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### Thermodynamic Data

$$\Delta H^{\circ}_{298}(1) = 105.1 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298}(1) = 128.6 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(1) = 1.43 \cdot 10^{31} T^{-1.863} \exp(-12940/T) \text{ molecule cm}^{-3} \\ (300 \leqslant T/\text{K} \leqslant 3000)$$

$$\Delta H^{\circ}_{298}(3) = 324.3 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298}(3) = 153.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(3) = 9.56 \cdot 10^{28} T^{-0.546} \exp(-39200/T) \text{ molecule cm}^{-3} \\ (300 \leqslant T/\text{K} \leqslant 3000)$$

$$\Delta H^{\circ}_{298}(5) = 423.0 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298}(5) = 129.6 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(5) = 3.24 \cdot 10^{26} T^{-0.190} \exp(-50820/T) \text{ molecule cm}^{-3} \\ (300 \leqslant T/\text{K} \leqslant 3000)$$

$$\Delta H^{\circ}_{298}(2) = 118.0 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298}(2) = 125.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(2) = 4.37 \cdot 10^{25} T^{-0.110} \exp(-14160/T) \text{ molecule cm}^{-3} \\ (300 \leqslant T/\text{K} \leqslant 3000)$$

$$\Delta H^{\circ}_{298}(4) = 359.4 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298}(4) = 93.5 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(4) = 1.22 \cdot 10^{23} T^{0.352} \exp(-43040/T) \text{ molecule cm}^{-3} \\ (300 \leqslant T/\text{K} \leqslant 3000)$$

$$\Delta H^{\circ}_{298}(6) = 428.9 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ}_{298}(6) = 175.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c(6) = 2.13 \cdot 10^{34} T^{-2.073} \exp(-52030/T) \text{ molecule cm}^{-3} \\ (300 \leqslant T/\text{K} \leqslant 3000)$$

See Section 3 for the source of the Thermodynamic Data.

### Rate Coefficient Data ( $k = k_1 + k_2 + k_3 + k_4 + k_5 + k_6$ )

$k/\text{s}^{-1}$	$T/\text{K}$	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$k_3 = 1.0 \cdot 10^{13} \exp(-31800/T)$	888–1018	Szwarc, 1949 <sup>1</sup>	(a)
$k_3 = 4.0 \cdot 10^{14} \exp(-35300/T)$	876–1000	Esteban, Kerr, and Trotman-Dickenson, 1963 <sup>2</sup>	(b)
$k_3 = 5.0 \cdot 10^{14} \exp(-34800/T)$	906–1010	Crowne, Grigulis, and Throssell, 1969 <sup>3</sup>	(c)
$k_3 = 5.0 \cdot 10^{14} \exp(-35300/T)$	910–1089	Clark and Price, 1970 <sup>4</sup>	(d)
$k_1 = 1.1 \cdot 10^9 \exp(-26000/T)$	910–1089		
$k_2 = 5.0 \cdot 10^{12} \exp(-32200/T)$	910–1089		
$k_3 = 2.0 \cdot 10^{15} \exp(-36700/T)$	800–1100	Ebert, Erderer, and Schmidt, 1978 <sup>5</sup>	(e)
$k_6 = 1.0 \cdot 10^{16} \exp(-41800/T)$	800–1100		
$k_3 = 7.1 \cdot 10^{15} \exp(-37400/T)$	990–1190	McMillen, Trevor, and Golden, 1980 <sup>6</sup>	(f)
$k_3 = 2.0 \cdot 10^{15} \exp(-36600/T)$	1053–1234	Robaugh and Stein, 1981 <sup>7</sup>	(g)
$k_3 = 2.5 \cdot 10^{14} \exp(-35200/T)$	770–820	Brooks, Peacock, and Reuben, 1982 <sup>8</sup>	(h)
$k_3 = 5.0 \cdot 10^{15} \exp(-37500/T)$	873–998	Davis, 1983 <sup>9</sup>	(i)
$k_3 = 1.3 \cdot 10^{17} \exp(-40900/T)$	1250–1600	Brouwer, Müller-Markgraf, and Troe, 1983 <sup>10</sup>	(j)
$k_4 = 2.5 \cdot 10^{12} \exp(-30100/T)$	1250–1600		(k)
$k_3 = 2.0 \cdot 10^{15} \exp(-36600/T)$	1000–1110	Grela and Colussi, 1985 <sup>11</sup>	(l)
$k_3 = 3.1 \cdot 10^{13} \exp(-30200/T)$	1300–1800	Mizerka and Kiefer, 1986 <sup>12</sup>	(m)
$k_3 = 3.5 \cdot 10^{15} \exp(-36900/T)$	1200–1600	Müller-Markgraf and Troe, 1988 <sup>13</sup>	(n)
<i>Reviews and Evaluations</i>			
$k_3 = 7.1 \cdot 10^{15} \exp(-37800/T)$	770–1800	CEC 1992; 1994 <sup>14</sup>	(o)

### Comments

- (a) Pyrolysis of ethylbenzene in the presence of excess toluene in a flow reactor at pressures between 10 and 22 mbar. Products condensed and pressure of products, evaporated at controlled temperatures, measured.
- (b) Pyrolysis of ethylbenzene in the presence of excess aniline in a flow reactor at pressures between 12.5 and

- 17.9 mbar.  $\text{H}_2$  and  $\text{CH}_4$  product yield determined with a gas burette; other products by gas chromatography.
- (c) Stirred flow reactor at pressures between 8 and 18 mbar. Reactant and product analysis by gas chromatography.
- (d) Toluene carrier flow system at pressures between 26 and 48 mbar. Reactant and product analysis by gas chromatography.

- (e) Flow reactor study at pressures between 0.13 and 1.3 mbar and at 1 bar. Product analysis by gas chromatography and time-of-flight mass spectrometry.
- (f) Very low pressure pyrolysis in a Knudsen cell reactor at pressures between 0.013 and 1.3  $\mu$ bar. Mass spectrometric analysis of reaction products. Rate expression for high pressure limit.
- (g) Very low pressure pyrolysis at pressures lower than 1.3  $\mu$ bar in a stirred flow reactor. Rate expression given in Table is for high pressure limit. Gas analysis by mass spectrometry.
- (h) Static reactor study at pressures between 10 and 65 mbar. Gas analysis by gas chromatography.
- (i) Flow reactor study at 1 bar total pressure. Analysis of rate of formation of toluene by gas chromatography.
- (j) Shock tube study; dissociation of ethylbenzene and product formation monitored by UV absorption spectroscopy. Experimental pressure range 0.3–33 bar Ar bath gas; rate expression obtained for gas densities in the range  $4.2 \cdot 10^{19}$ – $1.5 \cdot 10^{20}$  molecule cm $^{-3}$ .
- (k) See Comment (j); experimental pressure range 0.4–32 bar Ar bath gas; rate expression given is for gas densities in the range  $4.8 \cdot 10^{19}$ – $1.4 \cdot 10^{20}$  molecule cm $^{-3}$ .
- (l) Very low pressure pyrolysis in a stirred reactor. Reaction products determined by mass spectrometry. Rate expression given is for high pressure limit.
- (m) Shock tube study in which the density gradient was monitored by laser Schlieren technique. Density range  $4.3 \cdot 10^{17}$ – $4.2 \cdot 10^{18}$  molecule cm $^{-3}$ ; Kr bath gas.
- (n) Shock tube study; reaction monitored by UV absorption measurements in the spectral region 190–330 nm. Density range  $1.2 \cdot 10^{19}$ – $1.4 \cdot 10^{20}$  molecule cm $^{-3}$ ; Ar bath gas.
- (o) See Comments on Preferred Value.

### Preferred Values

$k_3 = 7.1 \cdot 10^{15} \exp(-37800/T)$  s $^{-1}$  over the range 770–1800 K.

### Reliability

$\Delta \log k_3 = \pm 0.1$  at 770 K, increasing to  $\pm 0.4$  at 1800 K.

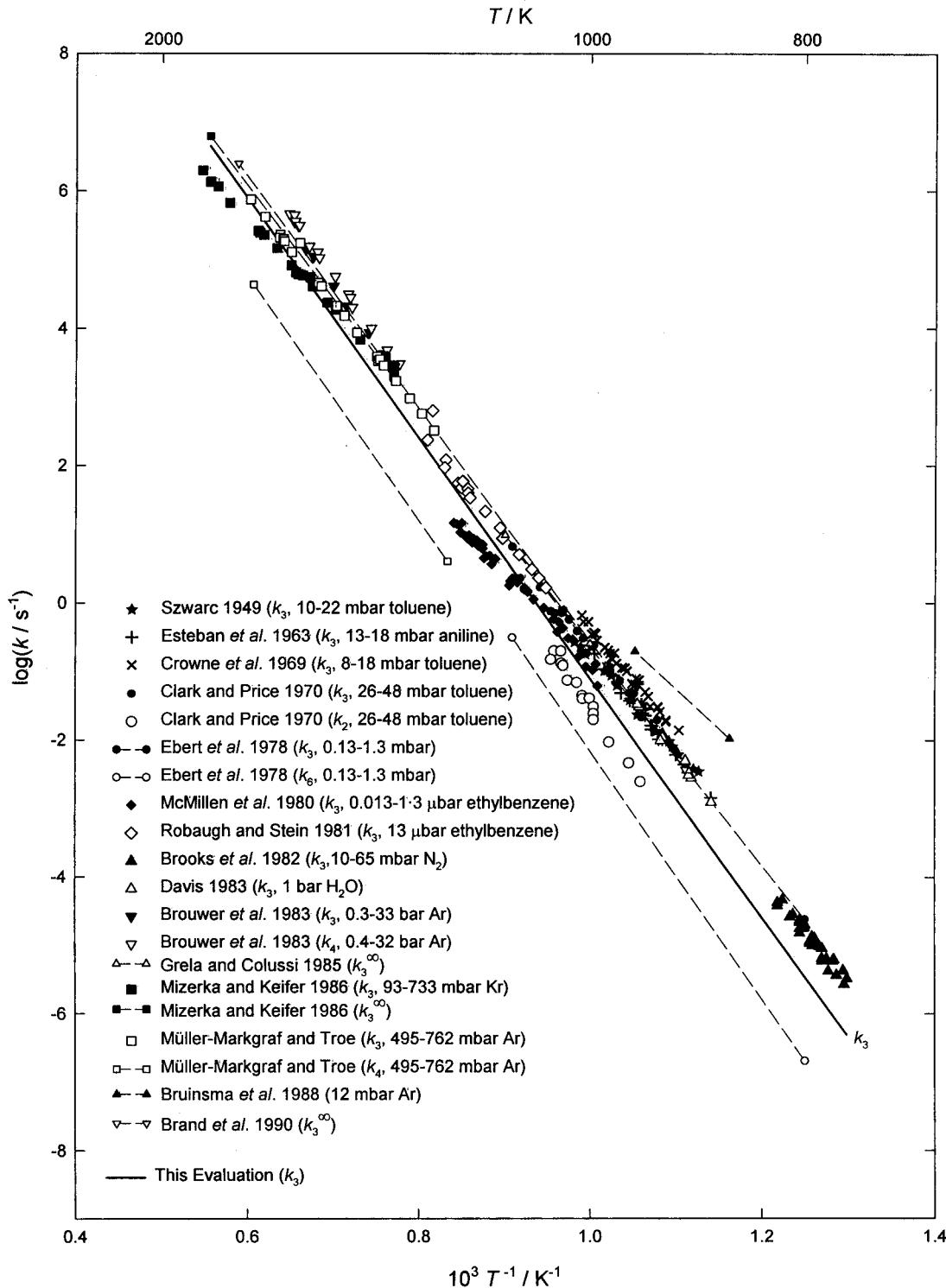
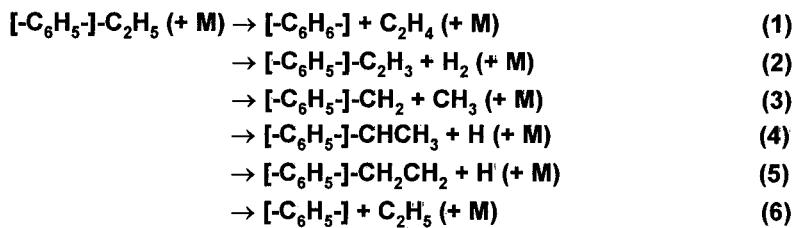
### Comments on Preferred Values

The preferred values remain unchanged from our previous evaluation<sup>14</sup> and are based on the data of Szwarc,<sup>1</sup> Esteban *et al.*,<sup>2</sup> Crowne *et al.*,<sup>3</sup> Clark and Price,<sup>4</sup> Ebert *et al.*,<sup>5</sup> McMillen *et al.*,<sup>6</sup> Robaugh and Stein,<sup>7</sup> Brooks *et al.*,<sup>8</sup> Davis,<sup>9</sup> Brouwer *et al.*,<sup>10</sup> Grela and Colussi,<sup>11</sup> Mizerka and Kiefer,<sup>12</sup> and Müller-Markgraf and Troe.<sup>13</sup> The values reported by Brand *et al.*<sup>15</sup> from a pressure dependence photodissociation study, taking pressure effects into account, also agree with the preferred values. As well, Bruinsma *et al.*<sup>16</sup> report a value for ( $k_1 + k_2 + k_3$ ) from a flow tube study with end product analysis.

It can be assumed that the given expression for  $k_3$  represents values close to the high pressure limit. Insufficient experimental data are available for the other channels to allow recommended rate expressions to be given.

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## 6. Tables of Rate Data for C, C<sub>2</sub>, Ethyl, *i*-Propyl, *t*-Butyl, and Allyl

### 6.1. Other Reactions of Atomic Carbon [C(<sup>3</sup>P)]

#### Introduction to the Data Sheet

The data for the reaction of ground state atomic carbon, C(<sup>3</sup>P), with O<sub>2</sub>, N<sub>2</sub>, and NO, are evaluated on separate data sheets. The very limited data available on reactions of C(<sup>3</sup>P) with other species are summarized, without evaluation, in this Table.

There have been very few studies at high temperatures. The vast majority of the studies consist of a determination of the rate constant at a single temperature, close to ambient, carried out by discharge flow or pulsed photolysis, and monitoring [C] under pseudo first order conditions. Only in a few cases have products been identified.

TABLE 6.1. Reaction of C atoms

<i>k/cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup></i>	<i>T/K</i>	Reference	Comments
		C+H <sub>2</sub> (+M)→CH <sub>2</sub> (+M)	
7.1·10 <sup>-32</sup> cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup> (M=He)	300	Husain and Kirsch, 1971 <sup>3</sup>	(c) (h)
6.9·10 <sup>-32</sup> cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup> (M=He)	300	Husain and Young, 1975 <sup>4</sup>	(d)
<6.7·10 <sup>-18</sup> exp(160/T)	298	Martinotti, Welch, and Wolf, 1968 <sup>1</sup>	(a)
6.6·10 <sup>-10</sup> exp(-11700/T)	1525–2540	Dean, Davidson, and Hanson, 1991 <sup>5</sup>	(e)
		C+H <sub>2</sub> O→Products	
<3.6·10 <sup>-13</sup>	300	Husain and Kirsch, 1971 <sup>3</sup>	(c)
<1.0·10 <sup>-12</sup>	300	Husain and Young, 1975 <sup>4</sup>	(d)
		C+CO(+M)→C <sub>2</sub> O(+M)	
6.3·10 <sup>-32</sup> cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup> (M=He)	300	Husain and Kirsch, 1971 <sup>3</sup>	(c) (h)
		C+CO <sub>2</sub> →Products	
<1·10 <sup>-14</sup>	300	Husain and Kirsch, 1971 <sup>3</sup>	(c)
<1·10 <sup>-15</sup>	300	Husain and Young, 1975 <sup>4</sup>	(d)
		C+N <sub>2</sub> O→Products	
2.5·10 <sup>-11</sup>	300	Husain and Kirsch, 1971 <sup>3</sup>	(c)
1.3·10 <sup>-11</sup>	300	Husain and Young, 1975 <sup>4</sup>	(d)
8.5·10 <sup>-12</sup>	298	Dorthe <i>et al.</i> , 1991 <sup>6</sup>	(f)
		C+CH <sub>4</sub> →Products	
<5·10 <sup>-15</sup>	298	Braun <i>et al.</i> , 1969 <sup>2</sup>	(b)
<2·10 <sup>-15</sup>	300	Husain and Kirsch, 1971 <sup>3</sup>	(c)
		C+C <sub>2</sub> H <sub>2</sub> →Products	
<6·10 <sup>-17</sup>	298	Martinotti, Welch, and Wolf, 1968 <sup>1</sup>	(a)
2.0·10 <sup>-10</sup>	300	Haider and Husain, 1992 <sup>7</sup>	(g)
2.1·10 <sup>-10</sup>	300	Haider and Husain, 1993 <sup>8</sup>	(g)
5.7·10 <sup>-10</sup> <i>T</i> <sup>-0.12</sup>	15–295	Chastaing <i>et al.</i> , 2001 <sup>15,16</sup>	(j)
2.4·10 <sup>-10</sup>	300	Bergeat and Loison, 2001 <sup>13</sup>	(k)
		C+C <sub>2</sub> H <sub>4</sub> →Products	
<6.3·10 <sup>-17</sup>	298	Martinotti, Welch, and Wolf, 1968 <sup>1</sup>	(a)
2.0·10 <sup>-10</sup>	300	Haider and Husain, 1993 <sup>8,9</sup>	(g)
5.6·10 <sup>-10</sup> <i>T</i> <sup>-0.11</sup>	15–295	Chastaing <i>et al.</i> , 2001 <sup>15,16</sup>	(j)
2.1·10 <sup>-10</sup>	300	Bergeat and Loison, 2001 <sup>13</sup>	(k)
		C+CH <sub>3</sub> CCH→Products	
3.9·10 <sup>-10</sup>	300	Haider and Husain, 1992 <sup>7</sup>	(g)
5.1·10 <sup>-10</sup> <i>T</i> <sup>-0.11</sup>	15–295	Chastaing <i>et al.</i> , 2000 <sup>14,15</sup>	(l)
		C+CH <sub>2</sub> CCH <sub>2</sub> →Products	
8.0·10 <sup>-10</sup>	300	Husain and Ioannou, 1997 <sup>11</sup>	(g)
3.7·10 <sup>-10</sup> <i>T</i> <sup>-0.01</sup>	15–295	Chastaing <i>et al.</i> , 2000 <sup>14,15</sup>	(l)
		C+C <sub>3</sub> H <sub>6</sub> →Products	
4.0·10 <sup>-10</sup>	300	Haider and Husain, 1993 <sup>9</sup>	(g)
		C+[-C <sub>6</sub> H <sub>6</sub> -]→Products	
4.9·10 <sup>-10</sup>	300	Haider and Husain, 1993 <sup>10</sup>	(g)
2.8·10 <sup>-10</sup>	300	Bergeat and Loison, 2001 <sup>13</sup>	(k)
		C+[-C <sub>6</sub> H <sub>5</sub> -]-CH <sub>3</sub> →Products	
5.5·10 <sup>-10</sup>	300	Haider and Husain, 1993 <sup>10</sup>	(g)

### Comments

- (a) Fast flow discharge system with C atoms produced by a discharge in a  $\text{C}_3\text{O}_2/\text{He}$  stream. Products analyzed by gas chromatography. Results from this study are in very poor agreement with those from other studies and are not considered reliable.
- (b) Single shot flash photolysis of  $\text{C}_3\text{O}_2$ . [C] monitored by light absorption in the 166 nm region and photographic plate photometry. Total pressure 200 mbar.
- (c) Single shot flash photolysis of  $\text{C}_3\text{O}_2$ . [C] monitored by resonance absorption at 166 nm.
- (d) Repetitive flash photolysis of  $\text{C}_3\text{O}_2$ . [C] monitored by resonance absorption at 166 nm with signal averaging.
- (e) Shock tube study. C atoms produced by pyrolysis of  $\text{C}_3\text{O}_2/\text{Ar}$  mixtures at temperatures in the range 2327–2538 K, and by laser photolysis at 193 nm of  $\text{C}_3\text{O}_2/\text{Ar}$  mixtures in the range 1504–2042 K. [C] monitored by ARAS using peaks in the range 115–180 nm. The observed activation energy is in good agreement with the reaction endothermicity and the reaction is assumed to be the bimolecular process giving  $\text{CH}+\text{H}$  rather than the thermolecular reaction observed at low temperatures.
- (f) Fast flow discharge study using a discharge in a dilute  $\text{CO}/\text{He}$  mixture as the C atom source. [C] monitored by observation of CS chemiluminescence from the  $\text{C}+\text{OCS}$  reaction. Experiments at fixed [OCS] and varying [ $\text{N}_2\text{O}$ ] were used to derive  $k$ . Corrections were made for deviations from plug flow in the system.
- (g) Technique as in (d) but with improved signal analysis.
- (h) Pseudo-first order rate constant for decay of  $\text{C}(\text{P}^3)$  in excess  $\text{H}_2$  or CO was shown to vary linearly with total pressure (He bath gas) over the range 1340–525 mbar.
- (i) Exothermic reaction channels open to  $\text{C}+\text{N}_2\text{O}$  produce either  $\text{CO}+\text{N}_2$  or  $\text{NO}+\text{CN}$ . In both cases electronic excitation of one or both of the product species is possible. Crossed beam studies and observations of the chemiluminescence have demonstrated the formation of NO and CN.<sup>12</sup> No evidence has been found for the alternative channel.
- (j) Low temperatures were achieved by isentropic expansion of gas mixtures through a Laval nozzle. The mixtures consisted of the carrier gas (He, Ar, or  $\text{N}_2$ ) containing a small concentration of  $\text{C}_3\text{O}_2$  and varying amounts of  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{CH}_3\text{CCH}$ , or  $\text{CH}_2\text{CCH}_2$ .  $\text{C}(\text{P}_J^3)$  atoms were produced in the flow by laser photolysis at 193 nm of the  $\text{C}_3\text{O}_2$ .  $[\text{C}(\text{P}_J^3)]$  was monitored by time-resolved vacuum-ultraviolet laser-induced fluorescence. The expression for  $k$  is a fit to data from this study and data from an earlier study<sup>16</sup> in which the [C] was monitored by chemiluminescence from the  $\text{C}+\text{NO}_2$  reaction.
- (k) Fast flow system using He as the carrier gas at pressures of a few mbar and with C atoms produced by the reaction of  $\text{CBr}_4$  with K atoms in a furnace at 473–493 K. [C] was monitored by resonance fluorescence at 156.1 nm or 165.7 nm. The relative yields of H atoms from the C atom reactions with  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ , and  $\text{C}_6\text{H}_6$  were determined by detecting H by resonance fluorescence at 121.6 nm. Absolute yields were estimated by comparing the signals with those from  $\text{C}+\text{H}_2\text{S}$  which gives a yield close to unity. The absolute yield of H from the  $\text{C}_2\text{H}_4$  reaction was estimated to be 0.92, and the relative yields were  $\text{C}_2\text{H}_4:\text{C}_2\text{H}_2:\text{C}_6\text{H}_6 = 1.0:0.58:0.17$ .
- (l) Rate constants were determined using the technique described in Comment (k). Crossed molecular studies were also carried out over a range of relative translational energies of the reactants and measurement of the H atom production. The results were consistent with the reactions  $\text{C}+\text{CH}_3\text{CCH} \rightarrow \text{C}_4\text{H}_3+\text{H}$  and  $\text{C}+\text{CH}_2\text{CCH}_2 \rightarrow \text{C}_4\text{H}_3+\text{H}$  being the sole reaction channels with methylacetylene and allene, respectively, as suggested by Kaiser *et al.*<sup>17,18</sup>
- (m) Crossed molecular beam studies,<sup>17</sup> together with theoretical calculations,<sup>18</sup> have shown that under single collision conditions  $\text{C}(\text{P}^3)$  adds to unsaturated hydrocarbons and the complex so formed rapidly decomposes solely, or predominantly, by C-H bond rupture. Thus  $\text{C}+\text{C}_2\text{H}_2 \rightarrow \text{C}_3\text{H}+\text{H}$ ,  $\text{C}+\text{C}_2\text{H}_4 \rightarrow \text{C}_3\text{H}_3+\text{H}$ ,  $\text{C}+\text{CH}_3\text{CCH} \rightarrow \text{C}_4\text{H}_3+\text{H}$ , and  $\text{C}+\text{CH}_3\text{CHCH}_2 \rightarrow \text{C}_4\text{H}_5+\text{H}$ . For the  $\text{C}+\text{C}_2\text{H}_2$  reaction the channel giving  $\text{C}_3\text{H}_2$  has also been detected in molecular beam studies,<sup>19</sup> but the corresponding channel for  $\text{C}+\text{C}_2\text{H}_4$  could not be detected. Various isomeric structures of the products are possible. At higher gas densities collisions may affect the outcome of these processes but product studies under bulk gas conditions are lacking.

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## 6.2. Reactions of C<sub>2</sub> Species

### Introduction to the Data Sheet

The kinetics of the ground state species C<sub>2</sub>(X  $^1\Sigma_g^+$ ), are complicated by the proximity of the first excited triplet state, C<sub>2</sub>(a  $^3\Pi_u$ ), which lies some 7.3 kJ mol<sup>-1</sup> above it. The equilibrium constant for singlet triplet has a value of  $\sim 0.3$  at 300 K rising to  $\sim 4$  at 2500 K. Thus, if equilibrium is established, there are always significant concentrations of both species present. Since the reactivity of the two states can differ

markedly the rate of intersystem crossing may be relevant to the kinetics of the system under study. This is particularly so because the vast majority of rate constant measurements for C<sub>2</sub> in a specific state have been carried out by following the decay in concentration of that state, the rate of which will include contributions from both chemical reaction and intersystem crossing. In a few cases rate constants for intersystem crossing have been measured. Crossing is not readily induced by many lighter, singlet species such as N<sub>2</sub>, CO<sub>2</sub>, CF<sub>4</sub>, Ar, and their interaction with both states can be studied, but rapid crossing is induced by O<sub>2</sub>, to a lesser degree by heavy species such as Xe or Kr, and possibly also by NO.

Data on the kinetics of C<sub>2</sub>(X  $^1\Sigma_g^+$ ) and C<sub>2</sub>(a  $^3\Pi_u$ ) are tabulated including rate constants for intersystem crossing. In some experiments, particularly with O<sub>2</sub>, it has not been possible to distinguish the specific state involved and, in most of the experiments performed at high temperatures, no attempt has been made to do so even though the concentration of the triplet state has been monitored. In such cases the reactant is specified in the table as C<sub>2</sub>(X  $^1\Sigma_g^+$ /a  $^3\Pi_u$ ) and the rate constants are listed in a separate section.

No attempt has been made to evaluate the data since most of it refers to the 300 K region and there is fair agreement amongst the few available studies.

TABLE 6.2. Reactions of C<sub>2</sub> molecules (X  $^1\Sigma_g^+$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
		C <sub>2</sub> (X $^1\Sigma_g^+$ ) + O <sub>2</sub> → Products	
2.8 · 10 <sup>-12</sup>	298	Paternack and McDonald, 1979 <sup>4</sup>	(a)
3.0 · 10 <sup>-12</sup>	300	Reisler, Mangir, and Wittig, 1980 <sup>5</sup>	(b)
1.5 · 10 <sup>-11</sup> exp(-493/T)	298–1300	Baugham and Oldenborg, 1984 <sup>11</sup>	(c)
		C <sub>2</sub> (X $^1\Sigma_g^+$ ) + H <sub>2</sub> → Products	
1.4 · 10 <sup>-12</sup>	298	Paternack and McDonald, 1979 <sup>4</sup>	(a)
1.4 · 10 <sup>-12</sup>	300	Reisler, Mangir, and Wittig, 1980 <sup>6</sup>	(d)
1.8 · 10 <sup>-10</sup> exp(-1470/T)	300–600	Pitts, Paternack, and McDonald, 1982 <sup>10</sup>	(e)
		C <sub>2</sub> (X $^1\Sigma_g^+$ ) + H <sub>2</sub> O → Products	
<3 · 10 <sup>-14</sup>	300	Reisler, Mangir, and Wittig, 1980 <sup>6</sup>	(d)
		C <sub>2</sub> (X $^1\Sigma_g^+$ ) + N <sub>2</sub> → Products	
<3 · 10 <sup>-14</sup>	300	Reisler, Mangir, and Wittig, 1980 <sup>6</sup>	(d)
		C <sub>2</sub> (X $^1\Sigma_g^+$ ) + NO → Products	
2.1 · 10 <sup>-10</sup>	300	Reisler, Mangir, and Wittig, 1980 <sup>6</sup>	(d)
		C <sub>2</sub> (X $^1\Sigma_g^+$ ) + CO <sub>2</sub> → Products	
No apparent reaction	298	Paternack and McDonald, 1979 <sup>4</sup>	(a)
<3 · 10 <sup>-14</sup>	300	Reisler, Mangir, and Wittig, 1980 <sup>6</sup>	(d)
		C <sub>2</sub> (X $^1\Sigma_g^+$ ) + CH <sub>4</sub> → Products	
1.9 · 10 <sup>-11</sup>	298	Paternack and McDonald, 1979 <sup>4</sup>	(a)
1.7 · 10 <sup>-11</sup>	300	Reisler, Mangir, and Wittig, 1980 <sup>6</sup>	(d)
5.0 · 10 <sup>-11</sup> exp(-297/T)	300–600	Pitts, Paternack, and McDonald, 1982 <sup>10</sup>	(e)
		C <sub>2</sub> (X $^1\Sigma_g^+$ ) + C <sub>2</sub> H <sub>2</sub> → Products	
4.3 · 10 <sup>-10</sup>	300	Reisler, Mangir, and Wittig, 1980 <sup>6</sup>	(d)
		C <sub>2</sub> (X $^1\Sigma_g^+$ ) + C <sub>2</sub> H <sub>4</sub> → Products	
3.3 · 10 <sup>-10</sup>	298	Paternack and McDonald, 1979 <sup>4</sup>	(a)
		C <sub>2</sub> (X $^1\Sigma_g^+$ ) + C <sub>2</sub> H <sub>6</sub> → Products	
1.6 · 10 <sup>-10</sup>	298	Paternack and McDonald, 1979 <sup>4</sup>	(a)
		C <sub>2</sub> (X $^1\Sigma_g^+$ ) + C <sub>3</sub> H <sub>8</sub> → Products	
3.3 · 10 <sup>-10</sup>	300	Reisler, Mangir, and Wittig, 1980 <sup>6</sup>	(d)
		C <sub>2</sub> (X $^1\Sigma_g^+$ ) + [-C <sub>6</sub> H <sub>6</sub> -] → Products	
5.2 · 10 <sup>-10</sup>	300	Reisler, Mangir, and Wittig, 1980 <sup>6</sup>	(d)

TABLE 6.2. Reactions of C<sub>2</sub> molecules ( $X^1\Sigma_g^+$ )—Continued.

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
Reactions of C <sub>2</sub> (a <sup>3</sup> Π <sub>u</sub> )			
2.7·10 <sup>-11</sup> (M=O <sub>2</sub> )	300	C <sub>2</sub> (a <sup>3</sup> Π <sub>u</sub> )(+M)→C <sub>2</sub> (X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> )(+M) Mangir, Reisler, and Wittig, 1980 <sup>7</sup>	(h)
2.0·10 <sup>-13</sup> (M=Kr)	300	Reisler, Mangir, and Wittig, 1980 <sup>6</sup>	(d)
4.5·10 <sup>-12</sup> (M=Xe)	300	Reisler, Mangir, and Wittig, 1980 <sup>6</sup>	(d)
5.5·10 <sup>-12</sup> exp(+24/T)(M=Xe)	300–500	Pasternack, Pitts, and McDonald, 1981 <sup>9</sup>	(k)
3.4·10 <sup>-12</sup>	300	C <sub>2</sub> (a <sup>3</sup> Π <sub>u</sub> ) + O <sub>2</sub> →Products Filseth <i>et al.</i> , 1979 <sup>3</sup>	(f)
3.0·10 <sup>-12</sup>	298	Donnelly and Pasternack, 1979 <sup>1</sup>	(g)
3.0·10 <sup>-12</sup>	300	Reisler, Mangir, and Wittig, 1980 <sup>5</sup>	(b)
1.5·10 <sup>-11</sup> exp(-493/T)	298–1300	Baughcum and Oldenborg, 1984 <sup>11</sup>	(c)
<5·10 <sup>-15</sup>	298	C <sub>2</sub> (a <sup>3</sup> Π <sub>u</sub> ) + H <sub>2</sub> →Products Pasternack and McDonald, 1979 <sup>4</sup>	(a)
<3·10 <sup>-14</sup>	300	Reisler, Mangir, and Wittig., 1980 <sup>6</sup>	(d)
1.6·10 <sup>-11</sup> exp(-3012/T)	370–600	Pasternack, Pitts, and McDonald, 1981 <sup>9</sup>	(k)
1.8·10 <sup>-11</sup> exp(-3710/T)	475–604	C <sub>2</sub> (a <sup>3</sup> Π <sub>u</sub> ) + D <sub>2</sub> →Products Pasternack, Pitts, and McDonald, 1981 <sup>9</sup>	(k)
<3·10 <sup>-14</sup>	300	C <sub>2</sub> (a <sup>3</sup> Π <sub>u</sub> ) + H <sub>2</sub> O→Products Reisler, Mangir, and Wittig, 1980 <sup>6</sup>	(d)
<3·10 <sup>-14</sup>	300	C <sub>2</sub> (a <sup>3</sup> Π <sub>u</sub> ) + N <sub>2</sub> →Products Reisler, Mangir, and Wittig, 1980 <sup>6</sup>	(d)
7.5·10 <sup>-11</sup>	300	C <sub>2</sub> (a <sup>3</sup> Π <sub>u</sub> ) + NO→Products Reisler, Mangir, and Wittig, 1979 <sup>2</sup>	(i)
1.7·10 <sup>-11</sup> exp(-2805/T)	337–605	C <sub>2</sub> (a <sup>3</sup> Π <sub>u</sub> ) + CH <sub>4</sub> →Products Pasternack, Baronavski, and McDonald, 1980 <sup>8</sup>	(j)
<3·10 <sup>-14</sup>	300	Reisler, Mangir, and Wittig, 1980 <sup>6</sup>	(d)
<3·10 <sup>-16</sup>	298	Donnelly and Pasternack, 1979 <sup>1</sup>	(g)
9.6·10 <sup>-11</sup>	298	C <sub>2</sub> (a <sup>3</sup> Π <sub>u</sub> ) + C <sub>2</sub> H <sub>2</sub> →Products Donnelly and Pasternack, 1979 <sup>1</sup>	(g)
1.7·10 <sup>-10</sup>	298	C <sub>2</sub> (a <sup>3</sup> Π <sub>u</sub> ) + C <sub>2</sub> H <sub>4</sub> →Products Reisler, Mangir, and Wittig, 1980 <sup>6</sup>	(i)
1.4·10 <sup>-11</sup>	298	Donnelly and Pasternack, 1979 <sup>1</sup>	(g)
1.2·10 <sup>-10</sup> exp(5/T)	300–600	Pasternack, Pitts, and McDonald, 1981 <sup>9</sup>	(k)
1.3·10 <sup>-12</sup>	298	C <sub>2</sub> (a <sup>3</sup> Π <sub>u</sub> ) + C <sub>2</sub> H <sub>6</sub> →Products Donnelly and Pasternack 1979 <sup>1</sup>	(g)
2.4·10 <sup>-11</sup> exp(-920/T)	300–600	Pasternack, Pitts, and McDonald, 1981 <sup>9</sup>	(k)
1.7·10 <sup>-12</sup>	298	C <sub>2</sub> (a <sup>3</sup> Π <sub>u</sub> ) + C <sub>3</sub> H <sub>8</sub> →Products Reisler, Mangir, and Wittig, 1980 <sup>6</sup>	(d)
1.8·10 <sup>-11</sup> exp(97/T)	300–600	Pasternack, Pitts, and McDonald, 1981 <sup>9</sup>	(k)
4.9·10 <sup>-11</sup> exp(-71/T)	300–600	C <sub>2</sub> (a <sup>3</sup> Π <sub>u</sub> ) + n-C <sub>4</sub> H <sub>10</sub> →Products Pasternack, Pitts, and McDonald, 1981 <sup>9</sup>	(k)
7.6·10 <sup>-11</sup>	300	C <sub>2</sub> (a <sup>3</sup> Π <sub>u</sub> ) + [-C <sub>6</sub> H <sub>6</sub> ]→Products Reisler, Mangir, and Wittig, 1980 <sup>6</sup>	(d)
<2.10 <sup>-15</sup>	300	C <sub>2</sub> (a <sup>3</sup> Π <sub>u</sub> ) + Ar→Products Filseth <i>et al.</i> , 1979 <sup>3</sup>	(f)
<3.10 <sup>-14</sup>	300	Reisler, Mangir, and Wittig, 1980 <sup>6</sup>	(d)
Reactions of C <sub>2</sub> (X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> /a <sup>3</sup> Π <sub>u</sub> )			
2.5·10 <sup>-8</sup> exp(-71650/T)	2580–4650	C <sub>2</sub> (X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> /a <sup>3</sup> Π <sub>u</sub> )(+M)→C+C(+M) Kruse and Roth, 1997 <sup>12</sup>	(l)
1.1·10 <sup>-11</sup> exp(-337/T)	300–600	C <sub>2</sub> (X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> /a <sup>3</sup> Π <sub>u</sub> ) + O <sub>2</sub> →Products Pitts, Pasternack, and McDonald, 1982 <sup>10</sup>	(e)
2.8·10 <sup>-10</sup> exp(-4070/T)	2750–3950	Kruse and Roth, 1998 <sup>13</sup>	(m)
1.1·10 <sup>-11</sup> exp(-381/T)	298–711	Fontijn <i>et al.</i> , 2001 <sup>14</sup>	(n)
1.1·10 <sup>-10</sup> exp(-4000/T)	2580–4650	C <sub>2</sub> (X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> /a <sup>3</sup> Π <sub>u</sub> ) + H <sub>2</sub> →C <sub>2</sub> H+H Kruse and Roth, 1997 <sup>12</sup>	(l)
2.5·10 <sup>-11</sup> exp(-21000/T)	2896–3420	C <sub>2</sub> (X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> /a <sup>3</sup> Π <sub>u</sub> ) + N <sub>2</sub> →2CN Sommer <i>et al.</i> , 1997 <sup>15</sup>	(o)
5.3·10 <sup>-10</sup>	2580–4650	C <sub>2</sub> (X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> /a <sup>3</sup> Π <sub>u</sub> ) + C <sub>2</sub> →C+C <sub>3</sub> Kruse and Roth, 1997 <sup>12</sup>	(l)

### Comments

- (a)  $C_2(X^1\Sigma_g^+)$  produced by multiphoton UV excimer laser photodissociation of hexafluorobutyne-2 and monitored by laser induced fluorescence at 691 nm. The authors explain the faster reaction rates of  $C_2(X^1\Sigma_g^+)$  with  $H_2$  and hydrocarbons by a hydrogen atom exchange reaction to form ground state  $C_2H$ , which is forbidden for  $C_2(a^3\Pi_u)$ .
- (b) IR multiphoton dissociation of  $C_2H_3CN$ . Radical depletion monitored by laser induced fluorescence and CO formation by chemiluminescence. Total pressures 1–5 mbar. The authors conclude that CO in highly excited triplet states is the primary product.
- (c) Multiphoton photolysis of  $CF_3CCF_3$  at 193 nm to produce both  $C_2(X^1\Sigma_g^+)$  and  $C_2(a^3\Pi_u)(v=0,1,2)$ . Radical disappearance monitored by laser induced fluorescence in the 516 nm region.  $C_2(X^1\Sigma_g^+)$  monitored by double resonance laser induced fluorescence using excitation wavelengths at 771 nm and 404 nm. Intersystem crossing is fast at 300 K but results suggest that it becomes slower at higher temperatures. Rate constants for  $O_2$  removal of singlet and triplet states appear to be identical within experimental error.
- (d) IR multiple photon dissociation of  $C_2H_3CN$  or  $C_2HCl_3$ .  $C_2$  monitored by laser induced fluorescence. Total pressures 1–7 mbar Ar or He. Measurements of intersystem crossing rates with  $C_2Cl_4$  as scavenger. Considerable intersystem crossing with heavy collision partners or with non-singlet partners.
- (e) Production of  $C_2(X^1\Sigma_g^+)$  by photolysis of hexafluorobutyne-2 in 13 mbar He.  $C_2$  monitored by time resolved laser induced fluorescence. In the case of  $O_2$  as reactant laser induced fluorescence is used at low temperatures and at high temperatures [ $^1C_2$ ] is monitored by chemiluminescence of excited CO from the  $C_2+O_2$  reaction. Insertion mechanism proposed for reaction of  $C_2(X^1\Sigma_g^+)$  with H-H and C-H bonds. Very fast equilibration between  $C_2(X^1\Sigma_g^+)$  and  $C_2(a^3\Pi_u)$  in the presence of  $O_2$ . Different sets of Arrhenius parameters for  $C_2+O_2$  under the assumptions that (i)  $k(^1C_2+O_2)\approx k(^3C_2+O_2)$ , and (ii)  $k(^1C_2+O_2)\gg k(^3C_2+O_2)$ .
- (f) IR multiple photon dissociation of acrylonitrile  $C_2H_3CN$ ; laser induced fluorescence detection of  $C_2(a^3\Pi_u)$ ; total pressures up to 65 mbar. A VUV chemiluminescence signal was observed when  $O_2$  was present in the mixture and attributed to electronically excited  $CO(A^1\Pi)$ .
- (g)  $C_2(a^3\Pi_u)$  formed by multiphoton UV photolysis of  $C_2H_2$  or  $C_2H_4$  at 193 nm and monitored by laser induced fluorescence. Total pressures 0–525 mbar.
- (h) IR-MPD of vinylcyanide or trichloroethylene.  $C_2(a^3\Pi_u)$  and  $C_2(X^1\Sigma_g^+)$  observed by laser induced fluorescence. The intersystem crossing rates were obtained by increasing the concentration of  $O_2$  in the sample and comparing the removal rates of  $^1C_2$  and  $^3C_2$ . At 300 K the intersystem crossing is much faster than chemical reactions; therefore it is possible only to measure the rate of equilibrated  $^1C_2/ ^3C_2$  mixtures.
- (i)  $C_2(a^3\Pi_u)$  produced by IR multiple photon dissociation of either vinylcyanide or ethylene in the presence of NO or Ar. Decay of  $C_2(a^3\Pi_u)$  monitored by laser induced fluorescence under slow flow conditions. CN formation observed by chemiluminescence.
- (j)  $C_2$  produced by 193 nm excimer laser photolysis of hexafluorobutyne-2 and monitored by laser induced fluorescence. Total pressure 17–300 mbar  $CH_4$ .
- (k)  $C_2(a^3\Pi_u)$  produced by multiphoton UV excimer laser photodissociation of hexafluorobutyne-2 or benzene.  $C_2$  depletion measured by laser induced fluorescence. Authors suggest that the reactions of  $^3C_2$  with  $H_2$  and saturated hydrocarbons proceed via H atom abstraction (supported by BEBO techniques, linear free energy correlation, and Evans-Polanyi plots), whereas with unsaturated hydrocarbons faster insertion reactions take place.
- (l)  $C_2H_2$  pyrolysis studied using reflected shock waves in Ar/ $C_2H_2$  mixtures. Reaction progress monitored by detection of  $C_1$ ,  $C_2$ , and  $C_3$  species.  $[C_2]$  monitored by laser absorption at two wavelengths in the  $d^3\Pi_g \leftarrow a^3\Pi_u$  system. Atomic resonance absorption spectrometry used to monitor [C].  $[C_3]$  monitored in emission in the range 330–600 nm. Similar experiments carried out with added  $H_2$ . Rate constants obtained by fitting  $[C_1]$ ,  $[C_2]$ ,  $[C_3]$  profiles with a detailed reaction mechanism. A theoretical treatment<sup>16</sup> of the  $C_2+H_2$  reaction gives significantly higher values of  $k$  than the experimental values (by factors of 2–9).
- (m) Pyrolysis of Ar/ $C_2H_2/O_2$  mixtures in reflected shock waves building on the experiments described in Comment (l).  $[C_2]$  was monitored by ring-dye-laser absorption spectroscopy at 516.646 nm. Authors observe that the rate parameters obtained are very different from the low temperature values previously reported and suggest that at high temperature the channels forming  $C_2O+O$  or  $CO_2+C$  may be important, rather than the channel forming 2CO.
- (n) Pulsed laser photolysis at 193 nm of slowly flowing mixtures of Ar/ $C_2Cl_4/O_2$  mixtures at total pressures in the range 26.7–373 mbar. The reaction progress was followed by time-resolved monitoring in both the visible and vacuum-UV of the chemiluminescence (CO emissions) from the reaction. Values of  $k$  calculated from the two emission regimes were in good agreement. Quenching experiments suggest that the reaction proceeds through formation of  $C_2O_2$  which may dissociate to produce 2CO.
- (o) Reflected shock waves in  $C_{60}/Ar/N_2$  mixtures.  $[C_2]$  monitored by absorption spectroscopy using the  $d^3\Pi_g \leftarrow a^3\Pi_u$  transition and simultaneously CN emissions monitored over the range 377–392 nm.  $[C_2]$  and [CN] profiles fitted using a mechanism of 5 reactions.

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### 6.3. Evaluated Rate Data for Some Reactions of Ethyl, *i*-Propyl, and *t*-Butyl Radicals

TABLE 6.3. Reactions of ethyl, *i*-propyl, and *t*-butyl radicals

Reaction	$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	$\pm \Delta \log k$	Note >
<i>Ethyl Radicals</i>				
$\text{C}_2\text{H}_5(+\text{M}) \rightarrow \text{C}_2\text{H}_4 + \text{H}(+\text{M})$	$k^\infty = 8.2 \cdot 10^{13} \exp(-20070/T) \text{ s}^{-1}$ $k^0 = [\text{C}_2\text{H}_6] 1.71 \cdot 10^{-6} \exp(-16800/T) \text{ s}^{-1}$	700–1100	0.3	A1
$\text{C}_2\text{H}_5 + \text{O}_2 \rightarrow \text{C}_2\text{H}_4 + \text{HO}_2$	$F_c(\text{C}_2\text{H}_6) = 0.25 \exp(-T/97) + 0.75 \exp(-T/1379)$	700–1000	$\Delta F_c = \pm 0.1$	A1
$\text{C}_2\text{H}_5 + \text{H}_2 \rightarrow \text{C}_2\text{H}_6 + \text{H}$	$1.0 \cdot 10^{-13}$	700–1200	0.2 at 700 K rising to 0.4 at 1200 K	A2
$\text{C}_2\text{H}_5 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_4 + \text{CH}_4$	$5.1 \cdot 10^{-24} T^{3.6} \exp(-4250/T)$	700–1200	0.2 at 700 K rising to 0.6 at 1200 K	A3
$\rightarrow \text{C}_3\text{H}_8$	$1.5 \cdot 10^{-12}$	300–2000	0.4 at 300 K rising to 0.7 at 2000 K	A4
$\text{C}_2\text{H}_5 + \text{C}_2\text{H}_2 \rightarrow \text{C}_2\text{H}_5\text{CH}=\text{CH}$	$k^\infty = 6.1 \cdot 10^{-11}$	300–2000	0.3	A4
$\text{C}_2\text{H}_5 + \text{C}_2\text{H}_4 \rightarrow n\text{-C}_4\text{H}_9$	$5.6 \cdot 10^{-14} \exp(-3520/T)$	300–600	0.5	A5
$\rightarrow \text{C}_2\text{H}_6 + \text{C}_2\text{H}_3$	$1.8 \cdot 10^{-13} \exp(-3670/T)$	300–600	0.5	A6
$\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5 \rightarrow n\text{-C}_4\text{H}_{10}$	$8.1 \cdot 10^{-31} T^{5.82} \exp(-6000/T)$	600–900	0.5	A7
$\rightarrow \text{C}_2\text{H}_6 + \text{C}_2\text{H}_4$	$k^\infty = 1.9 \cdot 10^{-11}$	295–1200	0.3	A8
$\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5\text{CHO} \rightarrow \text{C}_2\text{H}_6 + \text{C}_2\text{H}_5\text{CO}$	$2.9 \cdot 10^{-13} \exp(-3660/T)$	300–700	0.3	A9
$\text{C}_2\text{H}_5 + \text{C}_3\text{H}_5 \rightarrow \text{CH}_2=\text{C}=\text{CH}_2 + \text{C}_2\text{H}_6$	$1.6 \cdot 10^{-12} \exp(66/T)$	500–1200	0.3	A10
$\rightarrow \text{C}_3\text{H}_6 + \text{C}_2\text{H}_4$	$4.3 \cdot 10^{-12} \exp(66/T)$	500–1200	0.4	
$\rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CHCH}_2$	$k^\infty = 3.3 \cdot 10^{-10} \exp(66/T)$	500–1200	0.4	
<i>i</i> -Propyl Radicals				
$i\text{-C}_3\text{H}_7(+\text{M}) \rightarrow \text{C}_3\text{H}_6 + \text{H}(+\text{M})$	$k^\infty = 8.76 \cdot 10^7 T^{1.76} \exp(-17870/T) \text{ s}^{-1}$ $k^0 = [\text{He}] 3.56 \cdot 10^{-7} \exp(-14200/T) \text{ s}^{-1}$	170–1000	0.3	B1
	$F_c(\text{He}) = 0.35$	750–830	0.3	B1
$i\text{-C}_3\text{H}_7 + \text{O}_2 \rightarrow \text{C}_3\text{H}_6 + \text{HO}_2$	$3.3 \cdot 10^{-14} \exp(1290/T)$	650–800	0.5	B2
$i\text{-C}_3\text{H}_7 + \text{H}_2 \rightarrow \text{C}_3\text{H}_8 + \text{H}$	$1.3 \cdot 10^{-23} T^{3.28} \exp(-4360/T)$	300–1200	0.5	B3
$i\text{-C}_3\text{H}_7 + \text{C}_2\text{H}_2 \rightarrow (\text{CH}_3)_2\text{CHCH}=\text{CH}$	$5.3 \cdot 10^{-14} \exp(-3470/T)$	300–600	0.5	B4
$i\text{-C}_3\text{H}_7 + \text{C}_2\text{H}_4 \rightarrow (\text{CH}_3)_2\text{CHCH}_2=\text{CH}_2$	$7.5 \cdot 10^{-14} \exp(-3470/T)$	300–600	0.5	B5
$i\text{-C}_3\text{H}_7 + i\text{-C}_3\text{H}_7 \rightarrow \text{C}_6\text{H}_{14}$	$k^\infty = 6.8 \cdot 10^{-12}$	300–1000	0.1 at 300 K, rising to 0.3 at 1000 K	B6
$\rightarrow \text{C}_3\text{H}_8 + \text{C}_3\text{H}_6$	$4.2 \cdot 10^{-12}$	300–1000	0.1 at 300 K, rising to 0.5 at 1000 K	B6
$i\text{-C}_3\text{H}_7 + i\text{-C}_3\text{H}_7\text{CHO} \rightarrow \text{C}_3\text{H}_8 + (\text{CH}_3)_2\text{CHCO}$ (a)	$(k_a + k_b) = 6.6 \cdot 10^{-14} \exp(-3170/T)$	300–650	0.5	B7
$\rightarrow \text{C}_3\text{H}_8 + (\text{CH}_3)_2\text{CCHO}$ (b)				
$\rightarrow \text{C}_3\text{H}_8 + \text{CH}_2\text{CH}(\text{CH}_3)\text{CHO}$ (c)	$k_c = 5.3 \cdot 10^{-14} \exp(-4780/T)$	500–650	0.5	B7
<i>t</i> -Butyl Radicals				
$t\text{-C}_4\text{H}_9(+\text{M}) \rightarrow i\text{-C}_4\text{H}_8 + \text{H}(+\text{M})$	$k^\infty = 8.3 \cdot 10^{13} \exp(-19200/T) \text{ s}^{-1}$	300–800	0.5	C1
$t\text{-C}_4\text{H}_9 + \text{O}_2 \rightarrow i\text{-C}_4\text{H}_8 + \text{HO}_2$	$1.0 \cdot 10^{-13} \exp(1590/T)$	298–800	0.5	C2
$t\text{-C}_4\text{H}_9 + \text{H}_2 \rightarrow i\text{-C}_4\text{H}_{10} + \text{H}$	$3.1 \cdot 10^{-26} T^{4.24} \exp(-4510/T)$	300–1200	0.5	C3
$t\text{-C}_4\text{H}_9 + \text{C}_2\text{H}_2 \rightarrow (\text{CH}_3)_3\text{CCH}=\text{CH}$	$1.2 \cdot 10^{-13} \exp(-4320/T)$	300–600	0.5	C4
$t\text{-C}_4\text{H}_9 + \text{C}_2\text{H}_4 \rightarrow (\text{CH}_3)_3\text{CCH}_2\text{CH}_2$	$3.3 \cdot 10^{-14} \exp(-4020/T)$	300–650	0.5	C5
$t\text{-C}_4\text{H}_9 + t\text{-C}_4\text{H}_9 \rightarrow \text{C}_8\text{H}_{18}$	$k^\infty = 5.2 \cdot 10^{-8} T^{-1.73}$	300–1000	0.15 at 300 K, rising to 0.3 at 1000 K	C6
$\rightarrow i\text{-C}_4\text{H}_{10} + i\text{-C}_4\text{H}_8$	$1.2 \cdot 10^{-7} T^{-1.73}$	300–1000	0.15 at 300 K, rising to 0.5 at 1000 K	C6
$t\text{-C}_4\text{H}_9 + t\text{-C}_4\text{H}_9\text{CHO} \rightarrow i\text{-C}_4\text{H}_{10} + t\text{-C}_4\text{H}_9\text{CO}$	$1.0 \cdot 10^{-14} \exp(-3200/T)$	300–700	0.5	C7
$\rightarrow i\text{-C}_4\text{H}_{10} + \text{CH}_2\text{C}(\text{CH}_3)\text{CHO}$	$3.9 \cdot 10^{-14} \exp(-5540/T)$	500–700	0.5	C7

## Notes

- A1.  $\text{C}_2\text{H}_5 + \text{M}$ . See separate data sheet for a discussion of this reaction.
- A2.  $\text{C}_2\text{H}_5 + \text{O}_2$ . See separate data sheet for a discussion of this reaction.
- A3.  $\text{C}_2\text{H} + \text{H}_2$ . The available literature data have been reviewed by Tsang,<sup>1</sup> and we have adopted his recommendation here.
- A4.  $\text{C}_2\text{H}_5 + \text{CH}_3$ . See separate data sheet for the reaction  $\text{CH}_3 + \text{C}_2\text{H}_5$ .
- A5.  $\text{C}_2\text{H}_5 + \text{C}_2\text{H}_2$ . For the addition reaction we have recommended the rate expression given by Kerr and Parsonage,<sup>4</sup> with adjustment to allow for the change in  $k$  of the reference reaction,  $k(\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5 \rightarrow \text{n-C}_4\text{H}_{10}) = 1.9 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (see Note A8).
- A6.  $\text{C}_2\text{H}_5 + \text{C}_2\text{H}_4$ . For the addition reaction we have recommended the rate expression given by Kerr and Parsonage,<sup>4</sup> with adjustment to allow for the change in  $k$  of the reference reaction,  $k(\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5 \rightarrow \text{n-C}_4\text{H}_{10}) = 1.9 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (see Note A8). The recommended value for the addition reaction is consistent with direct kinetic data<sup>29</sup> for the reverse decomposition reaction,  $\text{n-C}_4\text{H}_9 \rightarrow \text{C}_2\text{H}_5 + \text{C}_2\text{H}_4$  and is in reasonable agreement with the expression derived by Roscoe *et al.*<sup>30</sup> from the results of an earlier experimental study by Bossard and Back<sup>31</sup> on the pyrolysis of  $\text{C}_2\text{H}_4$ .
- A7. Based on an analysis of the data of Halstead and Quinn,<sup>5,6</sup> Mackenzie *et al.*,<sup>7</sup> Ayrancı and Back,<sup>8</sup> and Zhang and Back.<sup>9</sup>
- A8.  $\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5$ . See separate data sheet for a discussion of this reaction.
- A9.  $\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5\text{CHO}$ . The available literature data have been evaluated by McAdam and Walker<sup>10</sup> and we have adopted their recommendation, with adjustment to allow for the change in  $k$  of the reference reaction,  $k(\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5 \rightarrow \text{n-C}_4\text{H}_{10}) = 1.9 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (see Note A8).
- A10. Based on the measured value of  $k(298 \text{ K}) = 1.0 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  determined by Garland and Bayes<sup>36</sup> together with the disproportion/combination ratios<sup>27</sup> and Tsang's<sup>28</sup> recommendations for the various paths.
- B1.  $i\text{-C}_3\text{H}_7 + \text{M}$ . Taken from the recent direct study of Seakins *et al.*<sup>11</sup> using laser flash photolysis coupled with photoionization mass spectrometry; rate expressions derived from a transition state model including literature data<sup>12–16</sup> for the forward and reverse reactions. Yamauchi *et al.*<sup>33</sup> conclude from a shock tube study at  $\sim 1$  bar and temperatures of 900–1400 K that C-C bond fission and isomerization do not compete with C-H bond rupture under these conditions.
- B2.  $i\text{-C}_3\text{H}_7 + \text{O}_2$ . Calculated from the ratio  $k(i\text{-C}_3\text{H}_7 + i\text{-C}_3\text{H}_7\text{CHO} \rightarrow \text{C}_3\text{H}_8 + \text{C}_4\text{H}_7\text{O})/k(i\text{-C}_3\text{H}_7 + \text{O}_2 \rightarrow \text{C}_3\text{H}_6 + \text{HO}_2) = 2.57 \exp(-4580/T)$ , as

determined by Gulati and Walker<sup>17</sup> over the temperature range 653–773 K, from measurements of the yields of  $\text{C}_3\text{H}_8$  and  $\text{C}_3\text{H}_6$  in the oxidation of  $i\text{-C}_3\text{H}_7\text{CHO}$ . Recommended  $k$  based on  $k(i\text{-C}_3\text{H}_7 + \text{C}_3\text{H}_7\text{CHO} \rightarrow \text{C}_3\text{H}_8 + \text{C}_4\text{H}_7\text{O}) = 8.47 \cdot 10^{-14} \times \exp(-3290/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , as calculated for the temperature range 653–773 K from the data of Kerr and Trotman-Dickenson<sup>23</sup> (see Note B7). DeSain *et al.*<sup>32</sup> have studied the rate of  $\text{HO}_2$  production and find that it has two components, a prompt component corresponding to direct production of  $\text{HO}_2$ , and a slower component corresponding to the decomposition of the propylperoxy radical adduct.

B3.  $i\text{-C}_3\text{H}_7 + \text{H}_2$ . The only experimental data for this reaction were measured at 713 K, where the ratio  $k(i\text{-C}_3\text{H}_7 + \text{O}_2 \rightarrow \text{C}_3\text{H}_6 + \text{HO}_2)/k(t\text{-C}_4\text{H}_9 + \text{H}_2 \rightarrow i\text{-C}_4\text{H}_{10} + \text{H}) = 3.06 \cdot 10^3$  has been determined by Baldwin *et al.*<sup>18</sup> from measurements of the yields of  $\text{C}_3\text{H}_8$  and  $\text{C}_3\text{H}_6$  in the oxidation of  $i\text{-C}_3\text{H}_7\text{CHO}$  in the presence of added  $\text{H}_2$ . This gives  $k = 6.5 \cdot 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  based on  $k(i\text{-C}_3\text{H}_7 + \text{O}_2 \rightarrow \text{C}_3\text{H}_6 + \text{HO}_2) = 2.0 \cdot 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 713 K (see Note B2). To obtain a temperature dependence of  $k$ , we have taken the recommendation of Tsang,<sup>2</sup>  $k = 5.8 \cdot 10^{-23} T^{3.28} \exp(-4363/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (based on his evaluated data for the reverse reaction and the equilibrium constant) and adjusted the pre-exponential factor to fit the above value of  $k$  at 713 K.

B4.  $i\text{-C}_3\text{H}_7 + \text{C}_2\text{H}_2$ . For the addition reaction we have recommended the rate expression given by Kerr and Parsonage,<sup>4</sup> with adjustment to allow for the change in  $k$  of the reference reaction,  $k(i\text{-C}_3\text{H}_7 + i\text{-C}_3\text{H}_7 \rightarrow \text{C}_6\text{H}_{14}) = 6.8 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (see Note B6).

B5.  $i\text{-C}_3\text{H}_7 + \text{C}_2\text{H}_4$ . For the addition reaction we have recommended the rate expression as evaluated by Kerr and Parsonage,<sup>4</sup> with allowance for the change in  $k$  of the reference reaction,  $k(i\text{-C}_3\text{H}_7 + i\text{-C}_3\text{H}_7 \rightarrow \text{C}_6\text{H}_{14}) = 6.8 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (see Note B6).

B6.  $i\text{-C}_3\text{H}_7 + i\text{-C}_3\text{H}_7$ . There is good agreement on the room temperature total rate coefficient of the combination reaction ( $k_c$ ) plus the disproportionation reaction ( $k_d$ ) as measured by molecular modulation studies.<sup>19</sup> The preferred value is the mean of the results of Anastasi and Arthur,<sup>19</sup> Parkes and Quinn,<sup>20</sup> and Arrowsmith and Kirsch,<sup>21</sup> i.e.,  $k_c + k_d = 1.1 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The recommended values of  $k_c$  and  $k_d$  were then derived from the ratio  $k_d/k_c = 0.62$  at room temperature.<sup>19</sup> The value of  $k_c = 5 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , over the temperature range 683–808 K from very-low-pressure-pyrolysis studies,<sup>22</sup> is in good agreement with the molecular modulation studies.

B7.  $i\text{-C}_4\text{H}_7 + i\text{-C}_3\text{H}_7\text{CHO}$ . The preferred data are from the study of Kerr and Trotman-Dickenson,<sup>23</sup> with allowance for the change in  $k$  of the reference

reaction,  $k(i\text{-C}_3\text{H}_7 + i\text{-C}_3\text{H}_7 \rightarrow \text{C}_6\text{H}_{14}) = 6.8 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (see Note B6).

- C1.  $t\text{-C}_4\text{H}_9 + \text{M}$ . The available literature data have been reviewed by Tsang<sup>3</sup> and we have adopted his recommendations here.
- C2.  $t\text{-C}_4\text{H}_9 + \text{O}_2$ . The rate coefficient at 753 K,  $k = 8.3 \cdot 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was calculated from the ratio  $k(t\text{-C}_4\text{H}_9 + \text{O}_2 \rightarrow t\text{-C}_4\text{H}_8 + \text{HO}_2)/k(t\text{-C}_4\text{H}_9 + \text{H}_2 \rightarrow t\text{-C}_4\text{H}_{10} + \text{H}) = 6.89 \cdot 10^3$  at 753 K, as determined by Evans and Walker,<sup>24</sup> from measurements of yields of  $i\text{-C}_4\text{H}_8$  and  $i\text{-C}_4\text{H}_{10}$  in the decomposition of 2,2,3,3-tetramethylbutane in the presence of  $\text{O}_2$  and  $\text{H}_2$ , by taking  $k(t\text{-C}_4\text{H}_9 + \text{H}_2 \rightarrow i\text{-C}_4\text{H}_{10} + \text{H}) = 1.1 \cdot 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 753 K (see Note C3). This value was used together with the values of  $k$  at 298 K measured by Dilger *et al.*<sup>34</sup> and Lenhardt *et al.*<sup>35</sup> to obtain the Arrhenius expression.
- C3.  $t\text{-C}_4\text{H}_9 + \text{H}_2$ . There are no experimental data on the rate coefficient of this reaction, but we have accepted the recommendation of Tsang,<sup>3</sup> which is based on reliable data for the reverse reaction  $k(\text{H} + i\text{-C}_4\text{H}_{10})$  together with thermochemical data which now appear to be established.
- C4.  $t\text{-C}_4\text{H}_9 + \text{C}_2\text{H}_2$ . We have accepted the evaluation of Kerr and Parsonage<sup>4</sup> on the addition reaction, with adjustment of the rate coefficient of the reference reaction,  $k(t\text{-C}_4\text{H}_9 + t\text{-C}_4\text{H}_9 \rightarrow \text{C}_8\text{H}_{18}) = 2.7 \cdot 10^{-12}(T/300)^{-1.73} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (see Note C6).
- C5.  $t\text{-C}_4\text{H}_9 + \text{C}_2\text{H}_4$ . We have accepted the evaluation of Kerr and Parsonage<sup>4</sup> on the addition reaction, with adjustment of the rate coefficient of the reference reaction,  $k(t\text{-C}_4\text{H}_9 + t\text{-C}_4\text{H}_9 \rightarrow \text{C}_8\text{H}_{18}) = 2.7 \cdot 10^{-12}(T/300)^{-1.73} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (see Note C6).
- C6.  $t\text{-C}_4\text{H}_9 + t\text{-C}_4\text{H}_9$ . There is good agreement on the room temperature rate coefficient of the combination reaction ( $k_c$ ), as measured by molecular modulation studies. The preferred data are from the evaluation of all the experimental data by Arthur,<sup>25</sup> which differs slightly from the recommendation of Tsang,<sup>3</sup> based on the earlier data of Parkes and Quinn.<sup>20</sup> The rate coefficient of the disproportionation reaction ( $k_d$ ) has been calculated from the ratio  $k_d/k_c = 2.3$  at room temperature.<sup>25</sup>
- C7.  $t\text{-C}_4\text{H}_9 + t\text{-C}_4\text{H}_9\text{CHO}$ . The preferred data are from the study of Birrell and Trotman-Dickenson,<sup>26</sup> with allowance for the change in the  $k$  of the reference reaction,  $k(t\text{-C}_4\text{H}_9 + t\text{-C}_4\text{H}_9 \rightarrow \text{C}_8\text{H}_{18}) = 2.7 \cdot 10^{-12}(T/300)^{-1.73} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (see Note C6). For the reaction  $t\text{-C}_4\text{H}_9 + t\text{-C}_4\text{H}_9\text{CHO} \rightarrow t\text{-C}_4\text{H}_{10} + t\text{-C}_4\text{H}_9\text{CO}$ , the data of Birrell and Trotman-Dickenson<sup>26</sup> yield the value  $k = 1.9 \cdot 10^{-15} \exp(-2540/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , which would appear to be a serious underestimation of the

Arrhenius parameters, in relation to data for the analogous reactions,  $\text{R} + \text{RCHO} \rightarrow \text{RH} + \text{RCO}$ . Accordingly, we have calculated the preferred rate equation from the experimental value of  $k$  at 550 K and an assumed value of  $A = 1.0 \cdot 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

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## 6.4. Evaluated Rate Data for Some Reactions of Allyl Radicals

TABLE 6.4. Reactions of allyl radicals

Reaction	$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	$\pm \Delta \log k$	Note
$\text{C}_3\text{H}_5(+\text{M}) \rightarrow \text{CH}_2=\text{C}=\text{CH}_2 + \text{H}(+\text{M})$	$k^\infty = 1.5 \cdot 10^{11} T^{0.84} \exp(-30050/T) \text{ s}^{-1}$	800–1500	0.3	A1
$\text{C}_3\text{H}_5 + \text{O}_2 \rightarrow \text{CH}_2=\text{C}=\text{CH}_2 + \text{HO}_2$	$1.71 \cdot 10^{-12} \exp(-11400/T)$	600–1200	0.3 at 600 K, rising to 0.5 at 1200 K	A2
$\rightarrow \text{CO} + \text{products}$	$7.6 \cdot 10^{-12} \exp(-9450/T)$	600–1200	0.3	
$\text{C}_3\text{H}_5 + \text{H}_2 \rightarrow \text{C}_3\text{H}_6 + \text{H}$	$1.8 \cdot 10^{-19} T^{2.4} \exp(-9550/T)$	300–1100	0.7 at 300 K, falling to 0.3 at 1100 K	A3
$\text{C}_3\text{H}_5 + \text{CH}_4 \rightarrow \text{C}_3\text{H}_6 + \text{CH}_3$	$6.6 \cdot 10^{-23} T^{3.4} \exp(-11670/T)$	300–1200	0.4	A4
$\text{C}_3\text{H}_5 + \text{C}_2\text{H}_6 \rightarrow \text{C}_3\text{H}_6 + \text{C}_2\text{H}_5$	$3.9 \cdot 10^{-22} T^{3.3} \exp(-9990/T)$	300–1200	0.4	A5
$\text{C}_3\text{H}_5 + \text{C}_3\text{H}_8 \rightarrow \text{C}_3\text{H}_6 + \text{CH}_3\text{CH}_2\text{CH}_2$ (a)	$3.9 \cdot 10^{-22} T^{3.3} \exp(-9990/T)$	300–1200	0.4 over the range 600–1000 K, rising to 0.7	A6
$\rightarrow \text{C}_3\text{H}_6 + \text{CH}_3\text{CHCH}_3$ (b)	$1.3 \cdot 10^{-22} T^{3.3} \exp(-8660/T)$	300–1200	at other temperatures	
$\text{C}_3\text{H}_5 + i\text{-C}_4\text{H}_{10} \rightarrow \text{C}_3\text{H}_6 + (\text{CH}_3)_2\text{CHCH}_2$ (a)	$5.9 \cdot 10^{-22} T^{3.3} \exp(-9990/T)$	300–1200	0.4 over the range 600–1000 K, rising to 0.7	A7
$\rightarrow \text{C}_3\text{H}_6 + (\text{CH}_3)_3\text{C}$ (b)	$7.0 \cdot 10^{-23} T^{3.3} \exp(-7800/T)$	300–1200	at other temperatures	
$\text{C}_3\text{H}_5 + \text{HCHO} \rightarrow \text{C}_3\text{H}_6 + \text{HCO}$	$1.2 \cdot 10^{-16} T^{1.8} \exp(-9155/T)$	300–1000	0.4	A8
$\text{C}_3\text{H}_5 + \text{C}_6\text{H}_5\text{CH}_3 \rightarrow \text{C}_3\text{H}_6 + \text{C}_6\text{H}_5\text{CH}_2$	$1.8 \cdot 10^{-11} \exp(-8660/T)$	600–1000	1.0	A9
$\text{C}_3\text{H}_5 + \text{C}_2\text{H}_4 \rightarrow \text{C}_3\text{H}_6 + \text{C}_2\text{H}_3$ (a)	$6.6 \cdot 10^{-23} T^{3.4} \exp(-13120/T)$	600–1200	0.5	A10
$\rightarrow c\text{-C}_5\text{H}_8 + \text{H}$ (b)	$1.0 \cdot 10^{-13} \exp(-9620/T)$	600–1200	0.7	
$\text{C}_3\text{H}_5 + 2\text{-C}_4\text{H}_8 \rightarrow \text{C}_3\text{H}_6 + \text{CH}_2\text{CH}=\text{CHCH}_3$ (a)	$3.6 \cdot 10^{-11} \exp(-8180/T)$	600–1000	1.0	A11
$\rightarrow \text{C}_3\text{H}_6 + \text{CH}_3\text{C}=\text{CHCH}_3$ (b)	$3.3 \cdot 10^{-23} T^{3.4} \exp(-12160/T)$	600–1000	0.5	
$\rightarrow \text{CH}_2=\text{CHCH}_2\text{CH}(\text{CH}_3)\text{CHCH}_3$ (c)	$k_c^\infty = 1.0 \cdot 10^{-13} \exp(-9620/T)$	600–1200	0.7	
$\text{C}_3\text{H}_5 + \text{H} \rightarrow \text{C}_3\text{H}_6$ (a)	$(k_a^\infty + k_b) = 2.8 \cdot 10^{-10}$	300–1000	0.2 at 300 K, rising to 0.5 at 1000 K	A12
$\rightarrow \text{C}_2\text{H}_3 + \text{CH}_3$ (b)				
$\rightarrow \text{C}_3\text{H}_4 + \text{H}_2$ (c)				
$\text{C}_3\text{H}_5 + \text{O} \rightarrow \text{H} + \text{CH}_2\text{-CHCHO}$ (a)	$k_c = 3 \cdot 10^{-11}$	300–1000	0.5	
$\rightarrow \text{C}_2\text{H}_3 + \text{HCHO}$ (b)	$3.0 \cdot 10^{-10}$	300–1000	0.2 over the range 300–600 K and 0.4 over the range 600–1000 K	A13
$\text{C}_3\text{H}_5 + \text{OH} \rightarrow \text{C}_3\text{H}_4 + \text{H}_2\text{O}$ (a)	$< 3 \cdot 10^{-11}$	300–1000		
$\rightarrow \text{CH}_2=\text{CHCHO} + 2\text{H}$ (b)	$k_a = 1.0 \cdot 10^{-11}$	300–1000	0.5	A14
$\rightarrow \text{CH}_2=\text{CHCH}_2\text{OH}$ (c)	$(k_b + k_c^\infty) = 2.5 \cdot 10^{-11}$	300–1000	0.3	
$\text{C}_3\text{H}_5 + \text{HO}_2 \rightarrow \text{C}_3\text{H}_6 + \text{O}_2$ (a)	$4.4 \cdot 10^{-12}$	300–1000	0.3 over the range 600–800 K, rising to 0.5 at 1000 K	A15
$\rightarrow \text{CO} + \text{products}$ (b)	$1.1 \cdot 10^{-11}$	500–900	0.3	
$\text{C}_3\text{H}_5 + \text{CH}_3 \rightarrow \text{CH}_4 + \text{CH}_2=\text{C}=\text{CH}_2$ (a)	$6.0 \cdot 10^{-13}$	500–800	0.2	A16
$\rightarrow \text{C}_2\text{H}_5\text{CH}=\text{CH}_2$ (b)				
$\text{C}_3\text{H}_5 + \text{CH}_3\text{O}_2 \rightarrow \text{CH}_2=\text{CHCH}_2\text{O} + \text{CH}_3\text{O}$	$k_b^\infty = 1.55 \cdot 10^{-9} T^{-0.54} \exp(117/T)$	300–800	0.2 at 300 K, rising to 0.5 at 800 K	
$\text{C}_3\text{H}_5 + \text{C}_2\text{H}_5 \rightarrow \text{CH}_2=\text{C}=\text{CH}_2 + \text{C}_2\text{H}_6$ (a)	$2.0 \cdot 10^{-11}$	500–1200	0.5	A17
$\rightarrow \text{C}_3\text{H}_6 + \text{C}_2\text{H}_4$ (b)	$1.6 \cdot 10^{-12} \exp(66/T)$	500–1200	0.3	A18
$\rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$ (c)	$4.3 \cdot 10^{-12} \exp(66/T)$	500–1200	0.4	
$\text{C}_3\text{H}_5 + \text{C}_3\text{H}_5 \rightarrow \text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}=\text{CH}_2$ (a)	$k_c^\infty = 3.3 \cdot 10^{-11} \exp(66/T)$	500–1200	0.4	
$\rightarrow \text{C}_3\text{H}_6 + \text{CH}_2=\text{C}=\text{CH}_2$ (b)	$k_a^\infty = 2.3 \cdot 10^{-11}$	300–1000	0.2	A19
	$k_b = 1.0 \cdot 10^{-13}$	300–1000	0.7	

## Notes

- A1.  $\text{C}_3\text{H}_5 + \text{M}$ . Tsang and Walker<sup>1</sup> obtained the high pressure value  $k^\infty = 40 \pm 10 \text{ s}^{-1}$  at 1080 K from single pulse shock tube studies of 1,7-octadiene decomposition. Combination with low temperature data on H atom addition to allene to form allyl gave the recommended expression for  $k^\infty$ . No other high temperature data are available, but Walker<sup>2</sup> recommended  $k^\infty = 10^{14.0} \exp(-31270/T) \text{ s}^{-1}$ , based on thermochemical estimates, which gives  $k^\infty = 27 \text{ s}^{-1}$  at 1080 K in excellent agreement with Tsang's experimental value. Tsang<sup>3</sup> gives data for fall-off effects in his review.
- A2.  $\text{C}_3\text{H}_5 + \text{O}_2$ . Walker *et al.*<sup>4-6</sup> used the decomposition of 4,4-dimethylpent-1-ene in the presence of  $\text{O}_2$  and the direct oxidation of  $\text{C}_3\text{H}_6$  to study the reactions of allyl radicals with  $\text{O}_2$  between 673 and 773 K. Analysis for allene and CO was used to monitor the reactions. All of the reactions have an energy barrier. Rate constants were determined as  $k/k_r^{1/2}$  where  $k_r = 2.3 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the recombination of allyl radicals. Reactions to give CO probably involve the formation of a cyclic peroxy intermediate, so that alternative pathways may occur outside the temperature range studied. Stothard and Walker<sup>7</sup> also found evidence for a radical branching reaction ( $\text{C}_3\text{H}_5 + \text{O}_2 \rightarrow 2 \text{ radicals} + \text{products}$ ) for which they give  $k = 2.7 \cdot 10^{-13} \exp(-8720/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Formation of allylperoxy radicals is possible at low temperatures but will not be important under combustion conditions.<sup>8</sup>
- A3.  $\text{C}_3\text{H}_5 + \text{H}_2$ . This rate constant has not been measured experimentally. We accept Tsang's<sup>3</sup> recommendation which is based on a thermochemical calculation involving  $k = 2.87 \cdot 10^{-19} T^{2.5} \exp(-1255/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the reverse reaction, which is itself based on the experimental value for  $k(\text{H} + 2\text{-C}_4\text{H}_8 \rightarrow \text{H}_2 + \text{CH}_3\text{CHCHCH}_2)$ .<sup>3</sup>
- A4.  $\text{C}_3\text{H}_5 + \text{CH}_4$ . No experimental data are available. We accept Tsang's<sup>3</sup> recommendation which is based on a thermochemical calculation with  $k(\text{CH}_3 + \text{C}_3\text{H}_6 \rightarrow \text{CH}_4 + \text{CH}_2\text{CHCH}_2) = 3.7 \cdot 10^{-24} T^{3.5} \exp(-2860/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .
- A5.  $\text{C}_3\text{H}_5 + \text{C}_2\text{H}_6$ . No experimental data are available. We accept Tsang's<sup>3</sup> recommendation which is based on a thermochemical calculation with  $k(\text{C}_2\text{H}_5 + \text{C}_3\text{H}_6 \rightarrow \text{C}_2\text{H}_6 + \text{CH}_2\text{CHCH}_2) = 3.7 \cdot 10^{-24} T^{3.5} \exp(-3340/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  which itself is based on Tsang's<sup>3</sup> recommendation for  $k(\text{CH}_3 + \text{C}_3\text{H}_6)$  (see above). A simple check supports the recommendations for allyl+ $\text{CH}_4$  and allyl+ $\text{C}_2\text{H}_6$ . At 750 K,  $k(\text{C}_3\text{H}_5 + \text{C}_2\text{H}_6)/k(\text{C}_3\text{H}_5 + \text{CH}_4) = 29$  compared with  $k(\text{HO}_2 + \text{C}_2\text{H}_6)/k(\text{HO}_2 + \text{CH}_4) = 23$  from Walker's<sup>9,10</sup> experimental  $\text{HO}_2$  data. As the allyl reactions are only marginally more endothermic than the  $\text{HO}_2$  reactions, the allyl ratio should be comparable with the  $\text{HO}_2$  value, as observed.
- A6.  $\text{C}_3\text{H}_5 + \text{C}_3\text{H}_8$ . No experimental data are available. We accept Tsang's<sup>3</sup> recommendation for abstraction at a primary position [equal to  $k(\text{C}_3\text{H}_5 + \text{C}_2\text{H}_6)$ , see Note

A5]. For abstraction at the secondary position, Tsang recommends the same  $A$  factor (per C-H bond) and a reduction in activation energy of 7 kJ mol<sup>-1</sup>. However, at 750 K,  $k(\text{C}_3\text{H}_5 + \text{CH}_3\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_3\text{CHCH}_3)/k(\text{C}_3\text{H}_5 + \text{C}_2\text{H}_6) = 1.0$  compared with the analogous  $\text{HO}_2$  reaction ratio of 1.7. A difference of 11 kJ mol<sup>-1</sup> in the allyl activation energies is therefore recommended giving  $k_b = 1.3 \cdot 10^{-22} T^{3.3} \times \exp(-8660/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for abstraction by allyl at the secondary C-H positions.

- A7.  $\text{C}_3\text{H}_5 + i\text{-C}_4\text{H}_{10}$ . No experimental data are available. The expression for primary abstraction is the same as for allyl+ $\text{C}_2\text{H}_6$  with allowance for path degeneracy, i.e.,  $3/2k(\text{allyl} + \text{C}_2\text{H}_6)$ . The expression for attack at the tertiary position is derived by comparison with  $\text{HO}_2$  data<sup>9,10</sup> (see Note A6) and we recommend  $k_b = 0.7 \cdot 10^{-22} T^{3.3} \exp(-7800/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .
- A8.  $\text{C}_3\text{H}_5 + \text{HCHO}$ . No experimental data are available. Tsang<sup>3</sup> gives  $k = 2.4 \cdot 10^{-16} T^{1.8} \exp(-9154/T)$ , calculated thermochemically from an estimate of  $k$  for the reverse reaction. In combination with the recommended value of  $k(\text{allyl} + \text{C}_2\text{H}_6)$ , then  $k/k(\text{allyl} + \text{C}_2\text{H}_6) = 84$  at 770 K compared with  $k(\text{HO}_2 + \text{HCHO})/k(\text{HO}_2 + \text{C}_2\text{H}_6) = 29$  from Walker's  $\text{HO}_2$  data.<sup>9-11</sup> The difference in the ratios is a little larger than expected (see Note A6) and we recommend a reduction in Tsang's  $A$  factor for allyl+HCHO by a factor of 2.
- A9.  $\text{C}_3\text{H}_5 + \text{C}_6\text{H}_5\text{CH}_3$ .  $\log(k/k_1) = -0.55 - 3760/T$  was obtained by Throssell<sup>12</sup> from the measurement of propene and but-1-ene in the decomposition of 4-phenylbut-1-ene and hexa-1,5-diene between 850 and 950 K, where reaction (1) is  $\text{CH}_3 + \text{C}_3\text{H}_5 \rightarrow 1\text{-C}_4\text{H}_8$ . If the present recommended value of  $k_1 = 6.5 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  is used to calculate  $k$  the value obtained at 725 K is a factor of 18 higher than the only other experimental value of  $6.6 \cdot 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  obtained by Louw<sup>13</sup> from studies of the decomposition of diallyloxalate, as a source of allyl radicals, in the presence of toluene. Provisionally, the recommended expression is based on the results of Throssel<sup>12</sup> and the present recommendations for  $k_1$  but it should be noted that use of this and the recommended data for allyl+HCHO (see Note A8) gives  $k(\text{C}_3\text{H}_5 + \text{HCHO})/k(\text{C}_3\text{H}_5 + \text{C}_6\text{H}_5\text{CH}_3) = 0.6$  at 770 K compared with the analogous  $\text{HO}_2$  ratio from Walker's data<sup>9,10</sup> equal to 10. Comparable values are expected from the similar thermochemistry involved (see Notes A5 and A6 above) suggesting that the expression for  $k$  may give high values. Substantial error limits are suggested.
- A10.  $\text{C}_3\text{H}_5 + \text{C}_2\text{H}_4$ . There are no experimental data for the addition and abstraction paths. The recommended expression for abstraction is based on  $k(\text{C}_3\text{H}_5 + \text{CH}_4)$  with an increase of 12 kJ mol<sup>-1</sup> in the activation energy on thermochemical grounds. For the addition path, which will be reversed at combustion

- temperatures, the recommendation is based<sup>14</sup> on the  $A$  factors for addition of  $C_2H_5$ ,  $n\text{-}C_3H_7$  and  $i\text{-}C_3H_7$  to  $C_2H_4$  ( $A = 1 \cdot 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) and an increase in the activation energy ( $E = 30 \text{ kJ mol}^{-1}$ ) by  $50 \text{ kJ mol}^{-1}$ , the delocalization energy of allyl radicals.<sup>1</sup> Tsang<sup>3</sup> reports evidence that the decomposition of 4-pentenyl radicals at 1100 K leads to 2.5% conversion to cyclopentane. It is possible, therefore, that addition of allyl to  $C_2H_5$  may lead to cyclopentane through the sequence  $C_3H_5 + C_2H_4 \rightarrow 4\text{-pentenyl} \rightarrow \text{cyclopentyl} \rightarrow \text{cyclopentane} + H$ .
- A11.  $C_3H_5 + 2\text{-}C_4H_8$ . No experimental data are available for any path. The recommended value for abstraction at the allyl position is based on  $k(C_3H_5 + C_6H_5CH_3)$  with adjustments due to path degeneracy (3 to 6) and to a slight weakening of the C-H bond in  $2\text{-}C_4H_8$  ( $\sim 6 \text{ kJ mol}^{-1}$ ). For the alternative abstraction, the recommendation is based on  $k(C_3H_5 + C_2H_4)$  with adjustments for path degeneracy (4 to 2) and for the weaker C-H bond ( $E$  lower by  $12 \text{ kJ mol}^{-1}$ ). The recommended expression for addition is based on kinetic data for alkyl+alkene<sup>14</sup> with  $E$  increased by  $50 \text{ kJ mol}^{-1}$  delocalization energy.
- A12.  $C_3H_5 + H$ . The only experimental data were obtained by Hanning-Lee and Pilling<sup>15</sup> who used laser flash photolysis of hexa-1,5-diene at 291 K, measuring  $[H]$  and  $[C_3H_5]$  by resonance fluorescence and absorption spectroscopy, respectively. The rate coefficient showed no significant variation between 170 and 680 mbar. The value is consistent with the theoretical treatment of Harding and Klippenstein<sup>27</sup> and an estimate by Tsang,<sup>3</sup> who has calculated fall-off values for  $k_a/(k_a+k_b)$ . Allera and Shaw's<sup>16</sup> estimate of  $k_c/(k_a^\infty+k_b+k_c) \approx 0.1$ , is the basis of the recommended value of  $k_c$ . A negligible temperature coefficient is expected between 300 and 1000 K.
- A13.  $C_3H_5 + O$ . Studied directly by Slagle *et al.*<sup>17</sup> between 300 and 600 K using laser flash photolysis and detection first by photoionization mass spectrometry and second by absorption spectroscopy and resonance fluorescence for  $C_3H_5$  and O, respectively. The mass spectrometry results suggest a slight decrease in  $k$  with temperature [ $2.3 \cdot 10^{-10} \exp(120/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ] but no such trend is observed from absorption spectroscopy. The only product detectable by mass spectrometry was acrolein suggesting that the major channel is  $O + C_3H_5 \rightarrow C_3H_4O + H$ . In particular, no  $C_2H_3$  or  $HCHO$  was observed and  $k_b < 3 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  is recommended.
- A14.  $C_3H_5 + OH$ . There are no experimental data. Tsang<sup>3</sup> recommends  $k_a = 1 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the abstraction process (based on comparable reactions) and  $(k_b^\infty + k_c) = 2.5 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the high pressure limit for the addition channel. Tsang<sup>3</sup> has carried out RRKM calculations for the fall-off effects which are unimportant below about 1200 K.
- A15.  $C_3H_5 + HO_2$ . There is only one, indirect, study<sup>4</sup>. Measurement of propene and CO yields in the decomposition of 4,4-dimethylpent-1-ene in the presence of  $O_2$  gives  $k_a/k_b = 0.38 \pm 0.18$  between 670 and 750 K, and further studies<sup>5</sup> with added propene give  $k_b$ .  $[C_3H_5]$  is determined from the rate of formation of hexa-1,5-diene and  $[HO_2]$  from the rate of formation of propene oxide in the reaction  $HO_2 + C_3H_6 \rightarrow C_3H_6O + OH$  ( $k$  is accurately known). Small corrections are made for the formation of propene in the molecular decomposition of 4,4-dimethylpent-1-ene.<sup>4</sup> Original values modified first by use of the value of  $k$  for allyl recombination recommended in this table and, second, (5%) for the formation of CO in the reaction  $C_3H_5 + O_2$ . The mechanism of (b) almost certainly involves addition followed by rapid loss of OH and further decomposition to form  $HCHO + C_2H_3$  radicals which react uniquely with  $O_2$  under the conditions used to form CO. Other paths, including formation of acrolein, may be possible.
- A16.  $C_3H_5 + CH_3$ . The expression for  $k_\infty$  is that obtained by Stoliarov *et al.*<sup>26</sup> from a direct laser photolysis/photoionization mass spectrometry study of the reaction. Over the range of pressures (3–40 mbar He) and temperatures (300–800 K) used, the reaction appeared to be at, or close to, its high pressure limit. The value of  $k(300 \text{ K})$  is  $1.0 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  which is slightly higher than the value of  $6.5 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  obtained by Garland and Bayes<sup>18</sup> and substantially larger than the value of  $2.3 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 1000 K calculated thermochemically by Throssell<sup>12</sup> from the kinetics of but-1-ene homolysis into  $C_3H_5$  and  $CH_3$  radicals. However, the expression for  $k$  is compatible with the use of the cross-combination rule and data for  $CH_3$  radical combination and  $C_3H_5$  recombination over its whole temperature range. Tsang<sup>3</sup> has carried out RRKM calculations for the fall-off in  $k_b$ . Based on data<sup>19</sup> for the disproportionation/combination ratio of methylallyl+ $CH_3$  ( $= 0.02$ ).  $k_a = 6.0 \cdot 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  is recommended for the disproportionation path.
- A17.  $C_3H_5 + CH_3O_2$ . There are no experimental data or suggested mechanisms for this reaction. The main path almost certainly involves combination followed by rapid loss of  $CH_3O$  radicals to give  $CH_2=CHCH_2O$  radicals which will undergo homolysis and react with  $O_2$  to give a variety of products such as CO,  $HCHO$ , and acrolein. A value of  $k = 2 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  is recommended for the overall reaction, based on the specific rate constant for CO formation in the reaction  $C_3H_5 + HO_2$  (see recommendation).
- A18.  $C_3H_5 + C_2H_5$ . Based on the measured value of  $k(298 \text{ K}) = 1.0 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  determined by Garland and Bayes<sup>18</sup> together with the

- disproportion/combination ratios<sup>20</sup> and Tsang's<sup>3</sup> recommendations for the various paths.
- A19.  $\text{C}_3\text{H}_5 + \text{C}_3\text{H}_5$ . There have been a number of recent direct measurements<sup>21–23</sup> of  $k$  over a range of temperatures and at pressures up to 1 bar. Earlier studies (see Tsang<sup>3</sup>) were either indirect or involved low pressure pyrolysis with extensive extrapolation to high pressure. All of the recent studies employed pulsed laser photolysis of hexa-1,5-diene as the allyl radical source and monitored the second order decay of  $[\text{C}_3\text{H}_5]$  by UV absorption spectroscopy. The values of  $k$  obtained in these studies are in excellent agreement. Tulloch *et al.*<sup>21</sup> find  $k$  to have a very small negative temperature dependence between 295 K and 571 K but Boyd *et al.*<sup>22</sup> find negligible change in  $k$  in the range 403–540 K. On the basis of these studies a temperature independent value of  $k_a^\infty = 2.3 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  is recommended. A shock tube study on cyclopentadiene decomposition<sup>24</sup> suggests a slightly higher value at 1080–1550 K but the determination is very indirect. The recombination rate constant appears to have reached its high pressure limit by 1 mbar at low temperatures but fall-off is expected to be important above about 1200 K.<sup>3</sup> James and Kambanis<sup>25</sup> give  $k_b k_a^\infty = 0.008$  between 400 and 460 K, but Tsang and Walker<sup>1</sup> found a value below 0.005 above 1000 K. A value of  $k_b = 1.0 \cdot 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  is recommended.
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