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## DIRECT MEASUREMENTS OF THE RATE COEFFICIENT FOR THE REACTION $\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O}$ OVER 300–1500 K

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The flash photolysis/resonance fluorescence technique for studying OH radical kinetics was extended to temperatures above 1500 K using the High Temperature Photochemistry reactor. In this application to combustion related processes, direct measurements of the rate coefficient for the benchmark reaction,



were obtained over the widest temperature range to date on this reaction and are described by the expression:

$$k(T) = 10^{-16.59 \pm 0.68} T^{1.83 \pm 0.17} \exp[-1396 \pm 134/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (298–1512 K)}$$

This expression ties together previous low and high temperature data, and allows use of the rate coefficient over the measurement temperatures to an estimated accuracy of 10% or better. It also provides a firmer basis for the extrapolation of  $k(T)$  to higher temperatures, and allows critical comparison with theoretical calculations.

The experimental methods employed are applicable, with minor modifications, to the study of many OH reactions over the temperature range 300–1500 K. An upper limit of  $\approx 1600$  K was found on the use of  $\text{H}_2\text{O}$  as a photolytic source of OH radicals for kinetic studies, due to the thermal dissociation of  $\text{H}_2\text{O}$  at higher temperatures.

### Introduction

The current rate coefficient data base for elementary reactions falls well behind the needs of models which are being developed to understand hydrocarbon combustion and pollutant formation and destruction processes. To see why this is so, one needs only to look at the large number of chemical reactions which have been used to model such diverse systems as, for example, ethylene flames (e.g., Refs. 1, 2), photochemical smog (e.g., Ref. 3), and chlorocarbons in the stratosphere (e.g., Ref. 4). Since most of these reactions are also temperature dependent, experimental determination of all relevant data is an enormous task.<sup>5,6</sup> The realistic experimental approach to this problem is to study a selected number of reactions, especially those believed to be most important in the mechanisms to be modeled and those which fairly represent a large class of similar reactions.<sup>7</sup>

There is also considerable effort (e.g., Refs. 8–11) directed at filling many of the experimental gaps by theoretically derived rate coefficients. In recent

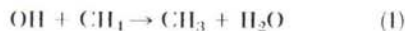
years significant progress in the calculational methods has narrowed the distinction between chemical reactions of practical importance and those of theoretical interest. Such calculational advances require "benchmark" experimental measurements against which their success is to be judged.

For elementary bimolecular reactions, the variation of the rate coefficient with temperature is of crucial importance both to the extrapolation of experimental data to temperatures of interest, and as a test of the predictive capability of theoretical models. This is particularly true for the usual case of rate coefficient deviation from simple Arrhenius behavior.

An additional practical problem in the determination of the temperature dependence of rate coefficients is the practice of "connecting" low temperature measurements with those obtained by different techniques at high temperatures. The actual temperature dependence (e.g., the Arrhenius slope) is often distorted by systematic errors in the data obtained using one or both of the techniques. This problem can be minimized by employing a single,

direct measurement technique in which the reaction of interest can be studied in isolation over a wide temperature range.

With these considerations in mind, we measured the rate coefficient  $k(T)$  for the reaction



over a wide temperature range. This reaction fulfills most of the above criteria; it has practical importance at ambient temperatures (hydrocarbon degradation in the atmosphere) and at elevated temperatures (initiation of methane combustion), is strongly temperature dependent, and is of current theoretical interest.

In this paper, we report direct measurements of the rate coefficient  $k(T)$  for Reaction (1) over the temperature range 298–1512 K, the widest temperature range for any single OH kinetic study to date. The experimental methods discussed are applicable, with only minor modifications, to the study of many OH reactions over a comparable temperature range. In addition to providing the first direct high temperature measurements of  $k(T)$ , the temperature dependence obtained by this single technique is of a precision amenable to future theoretical examination.

### Experimental

The flash photolysis/resonance fluorescence (FP/RF) technique has been used extensively to study OH radical kinetics. A major part of recent experimental efforts (e.g., Refs. 12–16) has been devoted to obtaining such kinetic data over wide temperature ranges. Measurements up to temperatures of about 1100 K have been previously reported by other workers.<sup>16,17</sup> The High Temperature Photochemistry (HTP) technique discussed here permits OH kinetic measurements up to at least 1500 K.

### Apparatus

The construction details of the HTP reactor have been described elsewhere.<sup>18</sup> Briefly, it consists of an alumina reaction tube, suitably heated and insulated. Reaction zone temperature, pressure, and concentrations of reagents can be varied independently. Metered flows of gases are admitted near the base of the reactor, and/or through a movable cooled inlet at any axial position within the reactor. The cooled inlet was used to vary the residence time of the reagents in the hot reactor tube. In these studies, no functional dependence of the kinetic data on residence time was observed when one or more of the reagents were added via the cooled inlet. At high temperatures, the cooled inlet minimized  $\text{H}_2\text{O}$  thermal dissociation (see below).

All experiments were performed in Ar diluent (boil-off from the liquid). The  $\text{H}_2\text{O}$  vapor was produced by bubbling Ar through distilled  $\text{H}_2\text{O}$  at atmospheric pressure and temperatures. UHP grade methane (Matheson) was used for experiments below 500 K; at higher temperatures, 5.1% methane in Ar (MG Scientific, calibrations standard) was used.

The temperature in the reaction zone was measured before and after each set of experiments using a shielded thermocouple.<sup>18</sup> The reported value is the average of these two measurements. The uncertainty in these measurements was estimated<sup>19</sup> as  $\pm 1\%$ , plus any drift observed over the time of the experiments.

The optical plane (reaction zone) of the reactor, as used for the OH kinetic experiments, is shown in Fig. 1. The OH radicals were produced from the vacuum ultraviolet photodissociation of  $\text{H}_2\text{O}$  vapor using a flashlamp (ca. 0.5–1.5 atm Ar, 10–100 J, LiF window, self-triggered, about 1 flash per second). Flash pulsewidths (less than 50  $\mu\text{s}$ ) were always much shorter than the chemical time scales of the OH/ $\text{CH}_4$  kinetic studies. The initial rise in the output of a photodiode placed near the flashlamp was used to trigger the detection electronics (see below).  $\text{OH}(^2\Sigma^+ \rightarrow ^2\Pi)$  resonance radiation was provided by a microwave excited diagnostic flow lamp (3%  $\text{H}_2\text{O}$  in He, 1 Torr total pressure).

The OH resonance fluorescence was viewed at right angles to the flow and flashlamps through light collection optics and an interference filter (310 nm, 20% peak transmission, 10 nm bandwidth) by a cooled photomultiplier tube (EMI 9558QA). Several light collection optics configurations were used, with a two lens geometry (not shown in Fig. 1) giving the highest signal to noise ratio, although with high background light levels. Some of the data re-

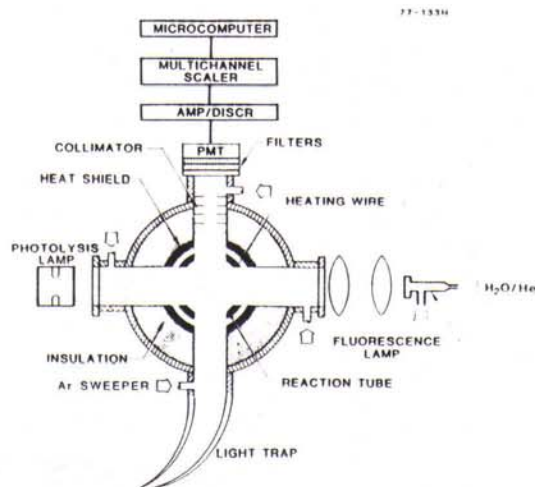


FIG. 1. Optical plane of the HTP reactor.



ported below were obtained with geometric collimation only (no lenses).

To eliminate PMT overload from scattered flashlamp radiation and from fluorescence by  $\text{OH}(\text{A}^2\Sigma^+)$  produced during the flash, a variable delay circuit was used to gate the cathode to first dynode voltage only during the period over which kinetic measurements were performed (typically 1–100 ns after the flash). This permitted measurements of first order rate coefficients as high as ca.  $1000 \text{ s}^{-1}$ .

The time dependent fluorescence intensity,  $I(t)$ , which is directly proportional to the OH concentration,  $[\text{OH}]_t$ , was measured by accumulating signal over 500–2000 flashes using a multichannel scaler (100  $\mu\text{s}$ /channel); the accumulated signal was then transferred to a microcomputer for analysis.

#### Detection of OH at Temperatures above 1000 K

The effect of temperature on the production and detection of OH was found in this work to be relatively small. Wagner and Zellner<sup>20</sup> have proposed that a large reduction of OH detection sensitivity may be anticipated in resonance absorption measurements at high temperatures, due to the difference in the rotational temperature of OH radicals in the reactor and in the resonance lamp. We did not observe such a reduction in our resonance fluorescence measurements. Similarly, no significant changes were observed in the efficiency of photolytic production of OH with temperature. Note that water cooling of the flashlamp window prevented any temperature induced reduction of window transmission.

On the other hand, a large increase in background (i.e., time independent signal) was observed at high temperatures, and resulted in a deterioration of the signal to noise ratio. A small part of this background resulted from scattered thermal radiation from the reactor walls, which at 1500 K is significant even at the OH detection wavelengths ( $\approx 310 \text{ nm}$ ). The larger component of the increased background level observed at high temperatures resulted from the continuous generation of OH by thermal dissociation of  $\text{H}_2\text{O}$ , possibly at the hot reactor walls. The relative concentration of this background OH was measured as a function of the  $[\text{H}_2\text{O}]$  at several reactor temperatures. At each temperature, the measured OH background was found to be proportional to  $[\text{H}_2\text{O}]^{2/3}$ , as shown in Fig. 2. This dependence is in good agreement with the results of an equilibrium calculation for an initial mixture of  $\text{H}_2\text{O}$  in Ar which considered formation of the species H, OH,  $\text{H}_2\text{O}_2$ ,  $\text{H}_2$ ,  $\text{H}_2\text{O}$ , O,  $\text{O}_2$ , and  $\text{O}_3$ . The measured increase in the background OH concentration with increasing temperature was also found to agree with the equilibrium calculation at all but the lowest temperatures (ca. 1200 K) for which the background OH was detected. On the basis of

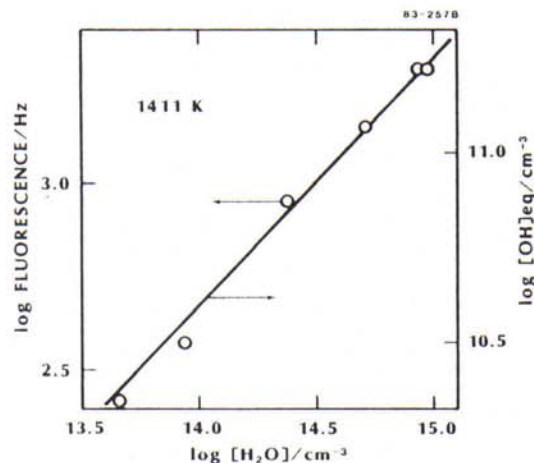


FIG. 2. Comparison of observed OH fluorescence intensity (Hz) with calculated equilibrium  $[\text{OH}]$  for  $\text{H}_2\text{O}$  thermal dissociation at 1411 K; collimating light collection optics.

the equilibrium calculation, we estimate that at 1600 K the OH concentration resulting from  $\text{H}_2\text{O}$  thermal dissociation is sufficiently high that this temperature is an upper limit to the use of  $\text{H}_2\text{O}$  photodissociation to produce OH for kinetic studies (e.g., due to consumption of the  $\text{CH}_4$  by OH upstream of the optical plane, and to the high background signal).

An estimate for the OH detection sensitivity at high temperature can be obtained by directly comparing the observed count rate resulting from the  $\text{H}_2\text{O}$  thermal dissociation with the equilibrium OH concentration calculated from the thermochemical data (cf. Fig. 2). Thus, for the collimator light collection optics, we estimate a detection response of  $1 \times 10^{-8} \text{ Hz cm}^3 \text{ molecule}^{-1}$ , while for the two-lens collection optics, a value of  $4 \times 10^{-7} \text{ Hz cm}^3 \text{ molecule}^{-1}$  is obtained. On the basis of these values, we estimate that the initial  $[\text{OH}]_0$  produced by the flash photolysis of  $\text{H}_2\text{O}$ , ranged from 1 to  $10 \times 10^{10} \text{ molecule cm}^{-3}$ . Similar values of  $[\text{OH}]_0$  have been reported<sup>13,15,17</sup> in lower temperature analogs of the ITP reactor.

Methane concentrations,  $[\text{CH}_4]$ , ranged from 1 to  $5 \times 10^{13} \text{ molecule cm}^{-3}$  at 1512 K and from 0.6 to  $5 \times 10^{16} \text{ molecule cm}^{-3}$  at 298 K, and were thus at least a factor of 100 higher than the  $[\text{OH}]_0$  estimated above. Under these conditions, only pseudo first order kinetics are expected to affect the temporal variation of the OH concentrations, with radical-radical reactions occurring at negligible rates. In the absence of complicating secondary reactions, the relaxation of  $[\text{OH}]_t$  is then given by the expression,

$$[\text{OH}]_t = [\text{OH}]_0 \exp [-(p + k[\text{CH}_4])t] \quad (\text{A})$$

where  $p$  is the approximately first order rate coefficient for the removal of OH from the viewing zone by flow and diffusion.

#### Measurements and Data Reduction

A typical fluorescence intensity profile,  $I(t) \propto [\text{OH}]_t$ , obtained at 1396 K, is shown in Fig. 3. The decay is accurately described by a single exponential function, of the form

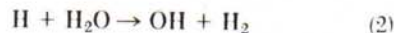
$$I(t) = a e^{(-t/\tau)} + b \quad (\text{B})$$

as were all decays obtained in the presence of significant amounts of  $\text{CH}_4$ . Equation (B) is identical in form to the kinetic expression, Eq. (A), except that a constant term,  $b$ , has been added to account for the presence of the scattered light background. The kinetic information is contained in the characteristic decay time,  $\tau$ , which by comparison with Eq. (A) is given as:

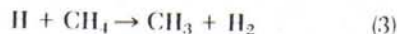
$$\tau^{-1} = p + k[\text{CH}_4] \quad (\text{C})$$

For very low or zero  $[\text{CH}_4]$  some slight deviations from simple exponential behavior were observed, particularly at temperatures higher than about 1000 K. Some such deviations can result from the only approximate validity of first order flow and diffusion loss models. In addition, at temperatures

above about 1000 K, we have previously shown<sup>14</sup> that the reaction



can be a significant secondary source of OH, and can result in the appearance of maxima in  $[\text{OH}]$ , several ms after the flash. The OH profiles are then properly described by the superposition of two exponential terms, one for the removal of OH, the other for the removal of H atoms. In the previous work,<sup>14</sup> this secondary OH generation was used to measure the rate coefficient  $k_2$  for the  $\text{H} + \text{H}_2\text{O}$  reaction. For the purposes of the present study, it should be noted that H atoms diffuse out of the observation zone much more rapidly than OH radicals, so that the  $[\text{OH}]$  produced via Reaction (2) is significantly smaller than the  $[\text{OH}]_0$ , which therefore accounts for most of the observed OH fluorescence signal. Furthermore, in the presence of  $\text{CH}_4$  the H atoms produced by photolysis are rapidly scavenged by the reaction



so that only the decay of the photolytically produced OH is observed.

Because the photolytic OH dominates the secondary OH, the OH profiles obtained at low or zero  $[\text{CH}_4]$  were also fitted with single exponential functions (Eq. (B)), as were the higher  $[\text{CH}_4]$  data. The forced single exponential fitting resulted in somewhat larger uncertainties for the first order decay rate coefficient at low  $[\text{CH}_4]$ , with consequently lower statistical weight in the determination of the slope of the first order decay rate coefficient vs.  $[\text{CH}_4]$  plots (vide infra) used to determine the rate coefficient  $k$ .

Data reduction was implemented by fitting the decays (cf. Fig. 3) with Eq. (B) using the gradient-expansion least squares algorithm given by Bevington.<sup>21</sup> Data points were weighted by the square of the reciprocal of their uncertainties, which were estimated by propagating the counting uncertainties (square root of the number of counts) through Eq. (B) according to the prescriptions given by Cveticanovic et al.<sup>22</sup> The fitting procedure yielded values of  $a$ ,  $b$ , and  $\tau^{-1}$  (cf. Eqs. (B) and (C)) with their relative uncertainties. Values of the reduced fit variance  $\chi^2$  ranged between 0.7 to 1.3, indicating the appropriateness of the functional form of Eq. (B) to represent the data.

Figure 4 shows the first order decay coefficients ( $\tau^{-1}$ ) obtained as a function of  $[\text{CH}_4]$  at several temperatures. The slopes of these plots, which are the bimolecular rate coefficients for the  $\text{OH} + \text{CH}_4$

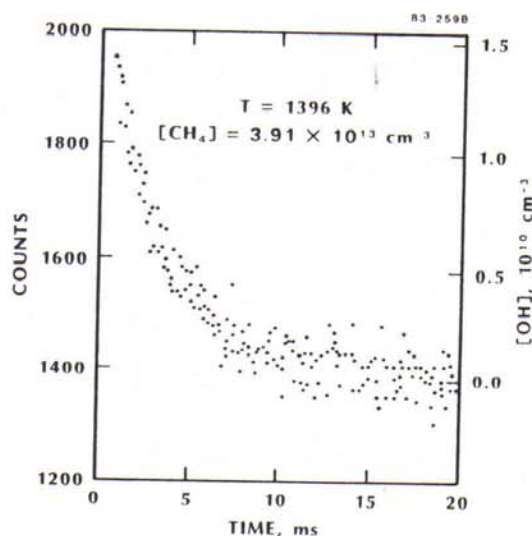


FIG. 3. Typical OH fluorescence intensity profile; two-lens optics, 0.1 ms/channel, 1000 flashes. Estimated OH concentrations (not required for the determination of  $k(T)$ ) are indicated.



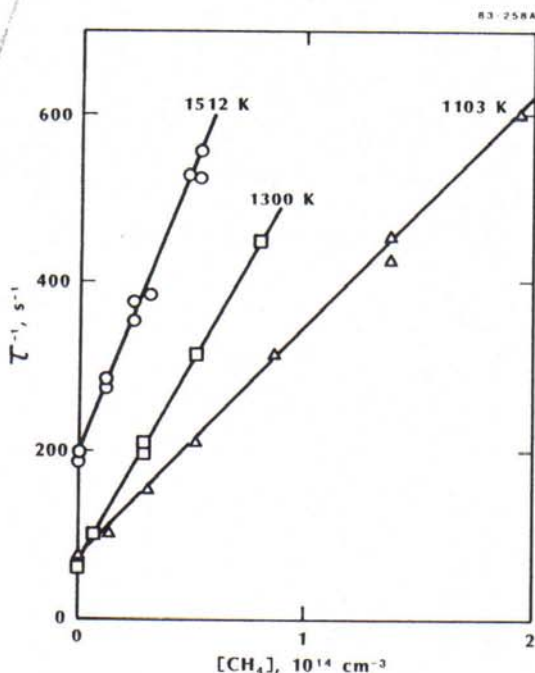


FIG. 4. Pseudo first order rate coefficients for OH removal vs.  $[\text{CH}_4]$ . Lines shown are best fits to data. The slope of each line is  $k(T)$ .

reaction (cf. Eq. (C)), were computed from a linear least squares fit weighted by the squares of the reciprocals of the uncertainties of the individual points. These weights included a contribution from an estimated 5% uncertainty in the measurement of  $[\text{CH}_4]$ .

### Results and Discussion

Table I lists the measured values for the rate coefficient  $k(T)$  and the experimental conditions under which they were obtained. No systematic variation of  $k$  could be detected with pressure, flash-lamp energy, flow velocity, or  $[\text{H}_2\text{O}]$ . The uncertainties represent one standard deviation, and include the effect of the uncertainty in temperature measurements on  $k$ ,  $(\partial k/\partial T)dT$ , calculated<sup>22</sup> from the estimated temperature dependence of  $k$ . The values of  $k(T)$  are also plotted in Fig. 5, where distinct curvature of the Arrhenius plot is noted. Our measurements were fitted with the modified Arrhenius expression:

$$k(T) = 10^{-16.59 \pm 0.68} T^{1.83 \pm 0.17} \exp[-1396 \pm 134/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (298-1512 \text{ K}) \quad (\text{D})$$

This expression was obtained by weighted nonlinear least squares fitting of the  $k(T)$  vs.  $T$  data, and represents our data with an average deviation of less than 10% over the entire 298–1512 K temperature range.

The data were also fitted with an expression in which the curvature is represented as a second order correction to the linear Arrhenius form, i.e.,  $\ln k(T) = A_\infty - E_\infty/RT + C/(RT)^2$ , where  $A_\infty$ ,  $E_\infty$ , and  $C$  are fitting parameters. The resulting expression,  $k(T) = 6.54 \times 10^{-11} \exp[-3.75 \times 10^3/T + 3.26 \times 10^5/T^2]$ , did not fit the data as well as Eq. (D) in which the multiplicative factor  $T^n$  is used to describe the curvature.

Previous measurements of  $k(T)$  have recently been reviewed by Cohen and Westberg.<sup>10</sup> Room temperature measurements ranging from  $6.3$  to  $10.7 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  have been reported. Our 298 K value of  $(8.5 \pm 0.6) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  lies nearly exactly at the midpoint of this range, and is in good agreement with the 298 K value recommended by Cohen and Westberg,  $(8.1 \pm 1.7) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . For temperatures up to about 500 K, all of the recent studies reviewed by Cohen and Westberg are in excellent agreement with our data. In the temperature range 500–1000 K, the measurements of Tully and Ravishankara<sup>16</sup> agree well with the present measurements, while the data of Zellner and Steinert<sup>23</sup> lie significantly higher. It now seems certain that the lower values are correct.<sup>16</sup>

Figure 6 summarizes the high temperature data. Above 1020 K, the only previous direct measurements are the shock tube/flash photolysis/resonance absorption data of Ernst et al.<sup>24</sup> and the laser pyrolysis/laser fluorescence data of Fairchild et al.<sup>25</sup> While the absolute agreement with our measurements appears to be good, the precision of the data of Ernst et al. is insufficient to compare the temperature dependence of  $k(T)$  in this temperature region. The data of Fairchild et al. are some 30–40% lower than our measurements, but have uncertainties comparable to this discrepancy. More recent laser pyrolysis/laser fluorescence measurements appear to be in better agreement with our measurements.<sup>26</sup> A relative rate shock tube measurement by Bradley et al.<sup>27</sup> at 1300 K falls about a factor of 2 lower than our data. All other previously reported high temperature data were deduced from measurements in flames,<sup>28–33</sup> and are subject to complex mechanistic interpretations. Measurements by Dixon-Lewis and Williams<sup>28</sup> at 1285 K and by Peeters and Mahnen<sup>29</sup> over 1100–1900 K are in agreement with our results, although the expression given by Peeters and Mahnen appears to underestimate the temperature dependence of  $k(T)$ . The other flame measurements appear to overestimate  $k(T)$  by as much as a factor of 5.

Table II shows the  $k(T)$  Arrhenius parameters

TABLE I  
Measured rate coefficients for  $\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O}$

Temperature, K	Pressure, torr	$[\text{H}_2\text{O}]$ , $10^{15} \text{ molecule cm}^{-3}$	$k$ , $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
298 $\pm$ 3	99	6.0	0.0085 $\pm$ 0.0006
362 $\pm$ 10	100	4.2	0.0228 $\pm$ 0.0043
407 $\pm$ 5	97	4.4	0.0463 $\pm$ 0.0034
410 $\pm$ 14	83	0.2	0.0629 $\pm$ 0.009
510 $\pm$ 10	200	1.1	0.154 $\pm$ 0.014
525 $\pm$ 10	180	0.6	0.177 $\pm$ 0.017
546 $\pm$ 5	95	1.7	0.202 $\pm$ 0.010
626 $\pm$ 16	100	3.6	0.439 $\pm$ 0.038
698 $\pm$ 22	98	3.3	0.478 $\pm$ 0.07
900 $\pm$ 12	95	2.5	1.48 $\pm$ 0.08
967 $\pm$ 35	170	3.6	2.12 $\pm$ 0.23
1005 $\pm$ 15	95	2.4	2.16 $\pm$ 0.11
1103 $\pm$ 17	95	2.1	2.72 $\pm$ 0.15
1164 $\pm$ 17	180	2.5	3.34 $\pm$ 0.20
1174 $\pm$ 22	180	2.2	2.41 $\pm$ 0.22
1176 $\pm$ 17	95	2.1	3.18 $\pm$ 0.17
1196 $\pm$ 17	200	0.2	3.89 $\pm$ 0.25
1196 $\pm$ 37	360	0.6	4.26 $\pm$ 0.39
1238 $\pm$ 18	346	2.5	3.77 $\pm$ 0.32
1244 $\pm$ 17	180	2.4	3.68 $\pm$ 0.23
1261 $\pm$ 23	95	1.1	3.58 $\pm$ 0.27
1261 $\pm$ 18	178	5.2	3.80 $\pm$ 0.37
1300 $\pm$ 18	197	0.4	4.74 $\pm$ 0.20
1307 $\pm$ 18	180	2.3	4.20 $\pm$ 0.21
1314 $\pm$ 23	95	1.2	4.84 $\pm$ 0.50
1345 $\pm$ 18	180	1.2	5.32 $\pm$ 0.31
1365 $\pm$ 19	170	2.7	5.61 $\pm$ 0.34
1396 $\pm$ 19	200	0.5	6.44 $\pm$ 0.53
1455 $\pm$ 20	170	2.3	5.98 $\pm$ 0.69
1510 $\pm$ 20	200	0.4	6.52 $\pm$ 1.15
1512 $\pm$ 20	100	0.8	6.74 $\pm$ 0.35

recommended by various workers, and the values of  $k(T)$  obtained when these expressions are evaluated at selected temperatures. Extrapolations of simple Arrhenius expressions<sup>12,29</sup> result in large discrepancies between high and low temperature data. Curvature of Arrhenius plots for the  $\text{OH} + \text{CH}_4$  reaction was first recognized by Zellner and Steinert,<sup>23</sup> and was subsequently confirmed by Tully and Ravishankara<sup>16</sup> and by Jeong and Kaufman.<sup>34</sup> The data of the latter two studies, obtained over narrower temperature ranges than the present experiments, are in excellent agreement with our data over the temperature range of overlap, but only one<sup>16</sup> of the reported modified Arrhenius expressions extrapolates well to the present high temperature data. The modified Arrhenius expression reported<sup>35</sup> for the data of Jeong and Kaufman<sup>34</sup> over 278–473 K, if extrapolated to 1500 K, overestimates

our measurements by about a factor of 6. This discrepancy is due to the large reported value of the temperature exponent ( $n$  in Table II), which is notoriously difficult to estimate accurately from studies covering narrow temperature ranges. This example reiterates the need for measurements over as wide a temperature range as possible, if empirically determined modified Arrhenius parameters are to be used for (a) comparisons with, and evaluations of, theoretical predictions, and (b) reliable extrapolations to temperatures where no direct measurements are available. (Several flame measurements<sup>30,31</sup> and the high temperature data of Zellner and Steinert<sup>23</sup> also argue for a stronger upward curvature of the Arrhenius plot, but for the reasons discussed above, these measurements are believed to be less reliable.)

It should be noted that if the data of Jeong and



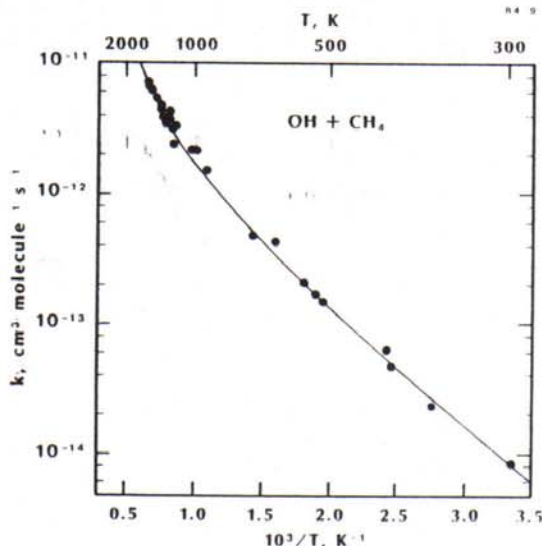


FIG. 5. Arrhenius plot for  $k(T)$ . For clarity, error bars have been omitted, but see Table I.

Kaufman<sup>34</sup> are fitted using "theoretically guided" values of  $n$  (e.g., in the range 1.5–2.5) rather than the empirical value of 4.23, extrapolation to 1500 K gives significantly better agreement with our measurements. Accuracy from such theoretically guided extended extrapolations, although gratifying in the present case, should not be generally expected for other  $\text{OH} + \text{RH}$  reactions (particularly if reaction mechanisms change with temperature). Furthermore, extrapolation using empirical values of  $n$  should be preferred whenever the uncertainty of these (e.g.,  $\pm 0.17$  for our measurements) is smaller than the estimated confidence interval of the theoretical values.

The conclusions of several recent evaluations, as well as the result of a transition state theory (TST) calculation, are shown in the second part of Table II. The older recommendations of Wilson<sup>37</sup> and of Shaw<sup>36</sup> overestimate  $k(T)$  at all temperatures, as they emphasize the high  $k(T)$  values from the early flame data. The expression of Ernst et al.,<sup>24</sup> based primarily on low temperature data and their shock tube/flash photolysis measurements, agrees reasonably well with our measurements. Cohen and Westberg<sup>10</sup> recommend a slightly higher temperature exponent ( $n = 2.4$ ), and predict  $k(T)$  values which are some 10% below our measurements in the intermediate (ca. 1000 K) region. These differences are most likely a result of their inclusion of the Zellner and Steinert data.

The TST calculation by Cohen and Westberg<sup>10</sup> and Cohen<sup>38</sup> falls about 10% lower than our values at 1500 K, a satisfactory agreement even consider-

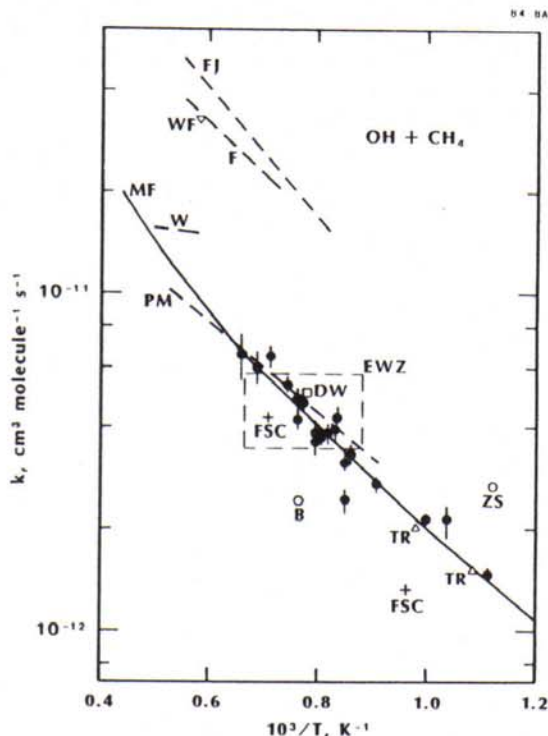


FIG. 6. Arrhenius plot for  $k(T)$  at elevated temperatures: (●) this work, data; (MF) this work, fit; (PM) Ref. 29; (EWZ) Ref. 24; (○) Ref. 23; (△) Ref. 16; (□) Ref. 28; (▽) Ref. 31; (◇) Ref. 30; (F) Ref. 32; (W) Ref. 33; (ZS) Ref. 25.

ing that the calculated  $k(T)$  is scaled to the experimental data at 300 K. An earlier TST calculation<sup>39,40</sup> largely overestimated high temperature  $k(T)$  data. Interestingly, the temperature exponent obtained by the TST calculation is closer to our experimentally derived value than to that of any of the earlier, narrower temperature range studies.

Table II also gives our evaluation obtained by combining our  $k(T)$  data with those of Tully and Ravishankara<sup>16</sup> and of Jeong and Kaufman.<sup>34</sup> The fit to the combined data,

$$k(T) = 9.50 \times 10^{-18} T^{1.96} \exp[-1328/T] \quad (278-1512 \text{ K}) \quad (\text{E})$$

deviates at most 6% from the fitted expression of each individual experimental study over the temperature range relevant to that study. Even if allowance is made for some small systematic errors in each study, it appears fairly certain that Eq. (E) predicts values of  $k(T)$  to an accuracy of 10% or better over 278–1512 K.



TABLE II  
Temperature dependence for  $\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O}$

Reference	A <sup>a</sup>	n	E <sup>o</sup> /R, K	Temperature range, K	k(298 K) × 10 <sup>15a,b</sup>	k(1000 K) × 10 <sup>12a,b</sup>	k(1500 K) × 10 <sup>12a,b</sup>
Experimental:							
This Work	$2.57 \times 10^{-17}$	1.83	1396	298–1512	8.0	1.97	6.6
JK(1982) <sup>11,35</sup>	$1.28 \times 10^{-24}$	4.23	453	268–473	8.2	4.0	25.8
TR(1980) <sup>16</sup>	$1.32 \times 10^{-17}$	1.92	1355	298–1020	7.9	1.96	6.7
ZS(1976) <sup>21</sup>	$5.76 \times 10^{-21}$	3.08	1010	300–892	8.1	3.65	17.8
DFS(1974) <sup>12</sup>	$2.36 \times 10^{-12}$	0	1711	240–373	7.6	0.4	0.75
PM(1973) <sup>29</sup>	$5.0 \times 10^{-11}$	0	3020	1100–1900	2.0	2.4	6.7
Evaluations: <sup>c</sup>							
This Work	$9.50 \times 10^{-18}$	1.96	1328	278–1512	7.8	1.91	6.6
CW(1983) <sup>10</sup>	$3.2 \times 10^{-19}$	2.4	1060	240–3000	7.9	1.76	6.6
CW(1983) <sup>10,d</sup>	$2.8 \times 10^{-16}$	1.5	1560	"	7.7	1.86	5.7
EWZ(1978) <sup>24</sup>	$2.57 \times 10^{-18}$	2.13	1234	"	7.6	1.84	6.6
S(1978) <sup>36</sup>	$1.41 \times 10^{-17}$	2.0	1485	"	8.6	3.2	11.8
W(1972) <sup>17</sup>	$4.7 \times 10^{-11}$	0	2500	300–2000	10.7	3.8	8.9

<sup>a</sup>Units in  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

<sup>b</sup>Calculated from parameters in preceding columns.

<sup>c</sup>Evaluations based on a single set of measurements have been omitted.

<sup>d</sup>Transition state theory calculation scaled to measurements at 300 K.

<sup>e</sup>Not specified.

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## COMMENTS

K. Brezinsky, Princeton University, USA. Is the mechanism of methane oxidation so sensitive to the rate constant of  $\text{OH} + \text{CH}_4$  that further work is necessary or are the results of your experiments definitive enough for modeling purposes?

*Authors' Reply.* The expression

$$k(T) = 10^{-16.59 + 0.68 T^{-1.83 + 0.17}} \exp [-1396 \pm 134/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (298\text{--}1512 \text{ K})$$

predicts statistical uncertainties in  $k(T)$ , calculated from the full covariance matrix, smaller than 3, 4, 6, and 10% at 1000, 1500, 2000, and 2500 K, respectively. Such small uncertainties should not be surprising, because a large number of points, each measured with an estimated experimental error of 5–20% (see Table I in text) was obtained over a wide temperature range. Allowing for unrecognized systematic errors (which must be assumed to be small because of the excellent overlap of the present measurements with lower temperature data), it seems unlikely that the true value of  $k(T)$  differs from our fit by more than 10% over the 300–1500

K range of measurements. The accuracy of the extrapolated values also depends on how suitable the modified Arrhenius function is to represent  $k(T)$  over the extended temperature range. Since Cohen's TST<sup>1</sup> calculations up to 3000 K indicate no obvious deviation of  $k(T)$  from the modified Arrhenius form, it seems likely that the above statistical uncertainties, even when conservatively doubled (e.g., 20% at 2500 K) are sufficiently small for most current modeling uses.

Clearly measurements similar to those reported here would be quite useful for other, less well-characterized reactions, and should be made.

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N. Cohen, Aerospace Corporation, USA. I have two comments. First: Dr. J. F. Bott and I have been looking at reactions of OH radicals with hy-



drocarbons and other reagents behind incident shock waves. The reaction rate coefficient for  $\text{OH} + \text{CH}_4$  was measured at 1220 K to be  $3 \times 10^{-12} \text{ cm}^3/\text{molecule} \cdot \text{s}^{-1}$ , in excellent agreement with the very impressive work presented by Madronich and Felder. The revised Transition State Theory calculations referred to by Dr. Madronich and described previously<sup>1</sup> also agree with the Aerochemi experimental results within the error limits of the calculations.

Second, Dr. Madronich stresses rightly the importance of error limits on these parameters in the expression  $k = AT^n \exp(-E/RT)$ . In our own data evaluation<sup>2</sup> we have taken the view that in both experiments and the calculations the values of  $k$  precede those of  $A$ ,  $n$ , and  $E$ ; therefore it is certainly justified—and probably preferable—to attach uncertainties to the values of  $k$  directly rather than to  $A$ ,  $n$ , and  $E$ .

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#### Authors' Reply.

1. Your recent shock tube measurement at 1220 K is ca. 20% lower than our measurements and the extrapolated value of Tully and Ravishankara,<sup>1</sup> and about 10% below the TST calculation,<sup>2</sup> and the Cohen and Westberg evaluation.<sup>3</sup> Considering the different techniques involved, we concur that the agreement seems reasonable.
2. A distinction must be made between using the Arrhenius parameters in their own right, and using them to simply provide a convenient analytical expression for  $k(T)$ . In the former case, the experimental value of the individual parameters (e.g., activation energy, Arrhenius  $A$  factor, curvature exponent) is of primary interest, often to compare with theoretical calculations or to predict the behavior of a large class of similar reactions. The success of such calculations and predictions can be judged only if the uncertainties of the experimentally determined parameters are known. In the latter case, the main interest is to estimate the uncertainty in  $k(T)$  when this is calculated from the analytical expression. As reiterated in the comment by Vidoczy, only the specification of the entire covariance matrix gives a statistically valid procedure to estimate this uncertainty. Over temperature ranges where measurements are available, the uncertainty in  $k(T)$  may be roughly inferred from the "scatter" of the measurements, but this procedure is highly

questionable when extrapolating outside the measurement ranges, e.g., to combustion temperatures.

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*T. Vidoczy, Central Research Institute, Hungary.*

You have stressed the importance of error limits of estimated parameters—I propose to go further, stressing the importance of the full covariance matrix. Though unfortunately uncommon in the literature, giving the full covariance matrix and the number of points the fit was made to has two distinctive benefits:

1) At extrapolation, one can calculate the true confidence interval of the estimated value (knowing only the error limits of the parameters, and applying the law of error propagation, one usually grossly overestimates the error limits of the extrapolated values).

2) One cannot avoid noticing the usually very heavy correlation between the parameters—this might have an impact on the interpretation of the individual parameters.

*Authors' Reply.* We agree that the three off-diagonal elements of the (symmetric) covariance matrix for the  $AT^n e^{-E/RT}$  fit should also be reported. The complete matrix is indeed required for estimating the error in  $k(T)$  (see, for example, the discussion by Cvetanović et al.<sup>1</sup> in the context of linear Arrhenius fits). A statistically valid estimation of error is especially important when  $k(T)$  is extrapolated outside the temperature range of measurements.

The parameter correlation which you mention is certainly present—as in all least squares problems—but this should not interfere with the interpretation of the individual parameters, since the uncertainty of each parameter (obtained from properly calculated diagonal elements of the covariance matrix) already accounts for the correlation. This is why the uncertainties tend to be rather large. So the reporting of the off-diagonal matrix elements is really not helpful here.

The omission of the off-diagonal elements is, in our opinion, relatively minor compared to the still common practice of not reporting uncertainties for  $A$ ,  $n$ , and  $E$ . Perhaps one of the reasons that this

- 6 practice remains tacitly tolerated is that many of the nonlinear least squares computer routines in common use are plagued by very slow convergence, local (false) minima leading to incorrect parameter estimates, and erratic and unreliable uncertainty computations. The development of a standard routine specifically optimized for the  $\text{AT}^m e^{-E/\text{RT}}$  function would certainly be useful.

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A. Fontijn, *Rensselaer Polytechnic Institute, USA*. As an originator of the High-Temperature Photochemistry (HTP) technique (while also at AeroChem)<sup>1,2</sup> I think that you have understated its capability in one respect. The particular upper limit of 1500–1600 K you mention for OH studies is dependent on the sensitivity(?) of the detection technique and on residence time, hence is not an absolute limit.

I agree with you that in work with HTP, or its older brother the HTFFR (high-temperature fast-flow reactor), there is no need to work up to the maximum temperature of 1800–1900 K when trends are sufficiently unambiguous or good agreement with published data exists. However, such is frequently not the case.

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*Authors' Reply.* HTP studies of OH kinetics are quite different from O atom studies with which you are perhaps more familiar.<sup>1,2</sup> For O atoms, kinetic measurements up to 1670 K have been achieved.<sup>3</sup> For OH, the lower detection sensitivity, the possible interference of the  $\text{H} + \text{H}_2\text{O}$  reaction which we discussed in a separate paper,<sup>4</sup> and the thermal dissociation of  $\text{H}_2\text{O}$  which we discuss in the present paper, show that high temperature kinetic data are

more difficult to obtain. The upper limit of ca. 1600 K on flash photolysis/resonance fluorescence studies of OH kinetics, which we established in the present work using  $\text{H}_2\text{O}$  as the parent molecule for OH photolytic production, is based on already generous estimates of OH detection sensitivity and short residence time, so we do not share your optimism for measurements at higher temperatures in the near future.

A serious deterioration of the signal to noise ratio (S/N) results from the high background fluorescence by OH produced when the  $\text{H}_2\text{O}$  pyrolyzes. At 1500 K and  $[\text{H}_2\text{O}] = 2 \times 10^{14} \text{ cm}^{-3}$ , the concentration of thermally produced OH is comparable ( $[\text{OH}]_{th} = 1 \times 10^{10} \text{ cm}^{-3}$ ) to the OH concentration produced by the photolytic flash, in spite of the short residence time achieved by use of a cooled inlet (see main text). Consider only the temperature dependence of the equilibrium.

$$[\text{OH}]_{th} \propto [\text{H}_2\text{O}]^{2/3} \exp[-24,200/T].$$

A simple but instructive calculation shows that the OH detection sensitivity must be at least doubled for every 30 K increase in temperature, if the same S/N ratio is to be maintained.

Further reduction of residence time does not offer a viable solution either, since it may affect mixing and heating of the gases, and will in any case be less useful at high temperatures where both the rate of approach to equilibrium and the final (equilibrium) OH concentration are much higher.

Finally, we have not implied that extension of measurements to higher temperatures is not useful, for this or any other reaction. However, efforts to extend the high temperature limit in such OH kinetics studies are opposed by rather severe constraints.

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