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ESTIMATION OF HYDROXYL RADICAL REACTION RATE CONSTANTS FOR GAS-PHASE ORGANIC COMPOUNDS USING A STRUCTURE-REACTIVITY RELATIONSHIP: AN UPDATE

ERIC S. C. KWOK and ROGER ATKINSON*†

Statewide Air Pollution Research Center, University of California, Riverside, CA 92521, U.S.A.

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Abstract—The structure–reactivity approach proposed by Atkinson (1986, *Chem. Rev.* **86**, 69–201) and extended by Atkinson (1987, *Int. J. Chem. Kinet.* **19**, 799–828) for the calculation of rate constants for the gas-phase reactions of the OH radical with organic compounds has been re-investigated using the presently available database. Substituent group factors for several new groups are derived, including those for fluorinated ethers. Using a large fraction of the available database to derive the parameters needed to calculate the OH radical reaction rate constants, the 298 K rate constants of ~90% of approximately 485 organic compounds are predicted to within a factor of 2 of the experimental values. Disagreements between calculated and experimental rate constants most commonly occur for halogen-containing compounds, and in particular for haloalkanes, haloalkenes and halogenated ethers. Disagreements also arise for ethers, especially for polyethers and cycloethers. The present estimation technique is reasonably reliable when used within the database used in its derivation, but extrapolation to organic compounds outside of this database results in a lack of assurance of its reliability, and its use for organic compounds which belong to classes other than those used in its development is discouraged.

Key word index: Hydroxyl radical, reaction rate constants, organic compounds, estimation method.

INTRODUCTION

Organic chemicals are emitted into the atmosphere from a wide variety of anthropogenic and biogenic sources (Graedel *et al.*, 1986), and can also be formed *in situ* in the atmosphere by transformations of directly emitted precursor compounds (Atkinson, 1988a, 1994). In the atmosphere, chemical compounds with liquid-phase vapor pressures of $> 10^{-6}$ Torr at the ambient atmospheric temperature exist, at least partially, in the gas phase (Bidleman, 1988). Gas-phase organic chemicals are removed from the atmosphere by wet and dry deposition (Bidleman, 1988), photolysis (Atkinson, 1988a, 1994), and chemical reaction (Atkinson, 1988a, 1994), primarily with hydroxyl (OH) radicals, nitrate (NO₃) radicals, and ozone (O₃).

For the majority of gas-phase organic chemicals present in the troposphere, reaction with the OH radical is the dominant loss process (Atkinson, 1988a). The tropospheric lifetime of a chemical is the most important factor in determining the relative importance of transport, to both remote regions of the globe (Bidleman *et al.*, 1990) and to the stratosphere (WMO,

1992), and in determining the possible buildup in its atmospheric concentration and therefore its potential to be an absorber of infrared radiation. There is therefore a need to know, through either direct experimental measurements or reliable estimation methods, the rate constants for the gas-phase reactions of organic compounds with the OH radical.

To date, OH radical reaction rate constants have been measured for ~500 organic chemicals (Atkinson, 1989, 1994). There are, however, many more organic chemicals emitted into the atmosphere or formed in the atmosphere from photolysis or chemical reactions of precursor compounds (Graedel *et al.*, 1986; Atkinson, 1994) for which OH radical reaction rate constants are not experimentally available. A number of methods for the estimation of gas-phase OH radical reaction rate constants for organic compounds have been proposed, ranging from estimation methods for single classes of organic compounds to generalized estimation methods for the complete range of organic compounds (see, for example, Gaffney and Levine, 1979; Heicklen, 1981; Güsten *et al.*, 1981, 1984; Zetzsch, 1982; Klöpffer *et al.*, 1985; Jolly *et al.*, 1985; Walker, 1985; Atkinson, 1986, 1987, 1988b; Güsten and Klasinc, 1986; Cohen and Benson, 1987a, b; Dilling *et al.*, 1988; Hodson, 1988; Cooper *et al.*, 1990;

* To whom correspondence should be addressed.

† Also at Department of Soil and Environmental Sciences.

Grosjean and Williams, 1992; Klamt, 1993). Many of these estimation methods utilize molecular properties of the chemical, such as ionization energy (Gaffney and Levine, 1979; Güsten *et al.*, 1984; Güsten and Klasinc, 1986; Grosjean and Williams, 1992), NMR chemical shifts (Hodson, 1988), molecular orbitals (Cooper *et al.*, 1990; Klamt, 1993), bond-dissociation energies (Heicklen, 1981) and infrared absorption frequencies (Jolly *et al.*, 1985), or involve transition state calculations (Cohen and Benson, 1987a,b). Other estimation methods utilize correlations between gas- and liquid-phase OH radical reaction rate constants (Güsten *et al.*, 1981; Klöpffer *et al.*, 1985; Dilling *et al.*, 1988; Grosjean and Williams, 1992).

However, most of these estimation methods are restricted in their use because of the limited database concerning molecular properties such as ionization potentials, bond-dissociation energies and infrared absorption frequencies. An often-used estimation method is that developed and tested by Atkinson (1986, 1987, 1988b) and which uses structure-reactivity relationships. This estimation method has been shown to provide good agreement (generally to within a factor of 2) between experimentally measured and calculated rate constants for 300–450 chemicals (Atkinson, 1987, 1988b; Müller and Klein, 1991; Meylan and Howard, 1993) and is the basis of the Syracuse Research Corporation's "Atmospheric Oxidation Program" (Meylan and Howard, 1993). However, it does not perform well for fluoroethers (Zhang *et al.*, 1992), ethers (including polyethers and cyclic ethers) (Atkinson, 1987; Wallington *et al.*, 1988; Dagaut *et al.*, 1989, 1990), certain haloalkenes (Atkinson, 1987), and haloalkanes containing $-\text{CF}_3$ groups (Atkinson, 1986).

In this work, we have used the presently available database (Atkinson, 1989, 1994) to update this estimation method, and to assess the utility of this approach and to determine those classes of organic compounds (if any) for which its use is not appropriate.

PROCEDURES

The general approach has been described by Atkinson (1986, 1987, 1988b), and is based on the observations that gas-phase OH radical reactions with organic compounds proceed by four reaction pathways which are assumed to be additive: H-atom abstraction from C–H and O–H bonds; OH radical addition to $>\text{C}=\text{C}<$ and $-\text{C}\equiv\text{C}-$ bonds; OH radical addition to aromatic rings; and OH radical interaction with N-, S-, and P- atoms [and with more complex structural units such as $-\text{>P}=\text{S}$ (Goodman *et al.*, 1988a; Atkinson, 1988b) and >NC(O)S- groups (Kwok *et al.*, 1992)]. The total rate constant is then given by

$$k_{\text{total}} = k(\text{H-atom abstraction from C-H and O-H bonds}) + k(\text{OH addition to } >\text{C}=\text{C}< \text{ and } -\text{C}\equiv\text{C}- \text{ bonds})$$

$$+ k(\text{OH addition to aromatic rings}) + k(\text{OH interaction with N-, S- and P-containing groups}).$$

The OH radical reactions with many, if not most, organic compounds proceed by more than one of these pathways. The four OH radical reaction pathways are dealt with separately in the sections below.

RESULTS AND DISCUSSION

H-atom abstraction from C–H and O–H bonds

As discussed by Atkinson (1986), the calculation of H-atom abstraction rate constants from C–H and O–H bonds is based on the estimation of group rate constants for H-atom abstraction from $-\text{CH}_3$, $-\text{CH}_2-$, $>\text{CH}-$ and $-\text{OH}$ groups. The rate constants for H-atom abstraction from $-\text{CH}_3$, $-\text{CH}_2-$ and $>\text{CH}-$ groups depend on the identity of the substituents attached to these groups, with

$$k(\text{CH}_3\text{-X}) = k_{\text{prim}}F(\text{X})$$

$$k(\text{X-CH}_2\text{-Y}) = k_{\text{sec}}F(\text{X})F(\text{Y})$$

$$k\left(\text{X-CH}\begin{array}{c} \nearrow \text{Y} \\ \searrow \text{X} \end{array}\right) = k_{\text{tert}}F(\text{X})F(\text{Y})F(\text{Z})$$

where k_{prim} , k_{sec} and k_{tert} are the group rate constants for H-atom abstraction from $-\text{CH}_3$, $-\text{CH}_2-$ and $>\text{CH}-$ groups, respectively, for a "standard" substituent, and $F(\text{X})$, $F(\text{Y})$ and $F(\text{Z})$ are the substituent factors for the substituent groups X, Y and Z, respectively. The standard substituent group is chosen to be $\text{X}(\text{Y}=\text{Z}) = -\text{CH}_3$, with $F(-\text{CH}_3) = 1.00$ by definition (Atkinson, 1986). For example, for *n*-butane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$, $k_{\text{total}} = \{k_{\text{prim}}F(-\text{CH}_2-) + k_{\text{sec}}F(-\text{CH}_3)F(-\text{CH}_2-) + k_{\text{sec}}F(-\text{CH}_3)F(-\text{CH}_2-) + k_{\text{prim}}F(-\text{CH}_2-)\}$.

As previously (Atkinson, 1987), we have assumed that the temperature dependence of the substituent factors $F(\text{X})$ can be expressed in the form

$$F(\text{X}) = e^{E_{\text{X}}/T} \quad (1)$$

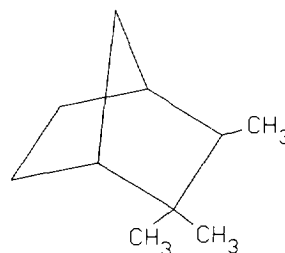
and hence that the effect of the substituent groups X, Y and Z is manifested solely in the temperature dependence of the group rate constants and that the pre-exponential factors for H-atom abstraction from $-\text{CH}_3$, $-\text{CH}_2-$ or $>\text{CH}-$ groups are independent of the substituent groups.

Group rate constants k_{prim} , k_{sec} and k_{tert} were obtained from the available database for the alkanes. Since kinetic data are available for many of the alkanes over a wide temperature range (exceeding 250–1000 K in certain cases), temperature-dependent values of the group rate constants k_{prim} , k_{sec} and k_{tert} were derived using the expression $k = CT^2e^{-D/T}$ (Atkinson, 1987). The available alkane rate constants were taken from the reviews and evaluations of Atkinson (1989, 1994), and fall into three classes: alkanes for which rate constants are recommended over a temper-

ature range; alkanes for which a rate constant is recommended at room temperature; and alkanes for which rate constants have been measured (generally at room temperature) but for which no recommendation is made (generally due to only a single study having been carried out). For those alkanes for which recommendations are available over a temperature range, recommended rate constants were calculated at temperatures of 231, 250, 272, 298, 333, 375, 429, 500, 599, 752 and 1000 K [i.e. in equal increments of $1000/T(\text{K})$ of 0.33]. (Obviously, only temperatures which fall within the range for which rate constants are recommended were used.) Preliminary analyses showed no obvious trend of the substituent factors, F , for the $-\text{CH}_2-$, $>\text{CH}-$ and $>\text{C}<$ groups and, as previously (Atkinson, 1986, 1987), we set $F(-\text{CH}_2-) = F(>\text{CH}-) = F(>\text{C}<)$ for the derivation of the group rate constants and substituent factors.

A nonlinear least-squares analysis of the rate constant data for acyclic alkanes and the essentially non-ring-strained cycloalkanes cyclohexane, methylcyclohexane, *cis*- and *trans*-bicyclo [4.4.0] decane and tricyclo[3.3.1.1] decane (adamantane), as a function of temperature where available, was carried out minimizing $\{(k_{\text{exp}} - k_{\text{calc}})/k_{\text{exp}}\}^2$, where k_{exp} and k_{calc} are the experimental (or recommended) and calculated rate constants, respectively. The group rate constants and substituent factors obtained are given in Tables 1 and 2, respectively. Ring-strain effects for cycloalkanes with other than six-member rings were taken into account through ring-strain factors F_{ring} (Atkinson, 1986, 1987), using the 298 K recommended or measured rate constants for cyclopropane, cyclobutane, cyclopentane, isopropylcyclopropane, bicyclo[2.2.1]heptane, *cis*- and *trans*-bicyclo[4.3.0]nonane, bicyclo[3.3.0]octane, tricyclo[5.2.1.0^{2,6}]decane and 1,1,3-trimethylbicyclo[3.1.1]heptane (*trans*-pinane). As discussed by Atkinson and As-

chmann (1992), only those rings containing the $-\text{CH}_2-$ or $>\text{CH}-$ groups were considered in accounting for ring strain. For example, for *iso*-camphane (2,2,3-trimethylbicyclo[2.2.1]heptane)



$$k_{\text{total}} = \{2k_{\text{sec}}F(-\text{CH}_2-)F(>\text{CH}-)F_5F_6 \\ + k_{\text{tert}}[F(-\text{CH}_2-)]^2F(>\text{CH}-)F_5F_5F_6 \\ + k_{\text{tert}}[F(-\text{CH}_2-)]^2F(>\text{C}<)F_5F_5F_6 \\ + k_{\text{sec}}[F(>\text{CH}-)]^2F_5F_5 \\ + k_{\text{tert}}F(>\text{C}<)F(>\text{CH}-)F(-\text{CH}_3)F_5F_6 \\ + 2k_{\text{prim}}F(>\text{C}<) + k_{\text{prim}}F(>\text{CH}-)\}$$

where F_5 and F_6 are the factors for five- and six-membered rings, respectively. The ring-strain factors F_{ring} at 298 K are given in Table 2.

For the acyclic alkanes, the agreement between the calculated and experimentally measured rate constants is excellent, with agreement to within a factor of 1.37 over the entire temperature ranges for which experimental data are available. Larger discrepancies occur for the two strained-ring polycyclic alkanes *trans*-pinane and quadricyclo[2.2.0^{2,6}.0^{3,5}]heptane, with the calculated 298 K rate constants for these cycloalkanes being factors of 1.5 and 2.5 lower than the experimentally measured values, respectively.

Table 1. Temperature-dependent parameters C and D in $k = CT^2e^{-D/T}$ for the group rate constants for H-atom abstraction from $-\text{CH}_3$, $-\text{CH}_2-$, $>\text{CH}-$ and $-\text{OH}$ groups, together with 298 K group rate constants for H-atom abstraction from $-\text{CH}_3$, $-\text{CH}_2-$, $>\text{CH}-$, $-\text{OH}$ groups and initial OH radical addition to $-\text{C}(\text{O})\text{OH}$, $-\text{ONO}_2$ and $-\text{NO}_2$ groups

Group	$10^{18} \times C^a$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	$D(\text{K})^a$	$10^{12} \times k(298 \text{ K})$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
$-\text{CH}_3$	4.49 (4.47)	320 (303)	0.136 (0.144)
$-\text{CH}_2-$	4.50 (4.32)	-253 (-233)	0.934 (0.838)
$>\text{CH}-$	2.12 (1.89)	696 -711	1.94 (1.83)
$k_{\text{abst}}(-\text{OH})$	2.1 ^b (1.89) ^b	85 (460)	0.14 (0.036)
$k_{\text{add}}(\text{R}-\text{C}(\text{O})\text{OH})$			0.52
$k_{\text{add}}(\text{R}-\text{ONO}_2)$			0.36
$k_{\text{add}}(\text{R}-\text{NO}_2)$			0.13

^a Data in parentheses are the previous values of Atkinson (1987).

^b Assumed equal to the value for H-atom abstraction from the $>\text{CH}-$ group (see text).

Table 2. Substituent factors $F(X)$ at 298 K^a

X	$F(X)$ at 298 K ^b
-CH ₃	1.00 (1.00)
$\left. \begin{array}{l} -\text{CH}_2- \\ >\text{CH}- \\ >\text{C}< \end{array} \right\}$	1.23 (1.29)
-F	0.094 (0.099)
-Cl	0.38 (0.38)
-Br	0.28 (0.30)
-I	0.53
$\left. \begin{array}{l} -\text{CH}_2\text{Cl} \\ -\text{CHCl}_2 \\ -\text{CHCl}- \\ >\text{CCl}- \end{array} \right\}$	0.36 (0.57) ^c
$\left. \begin{array}{l} -\text{CHBr} \\ -\text{CHBr}- \end{array} \right\}$	0.46 (0.57) ^c
-CCl ₃	0.069 (0.090)
-CF ₃	0.071 (0.075)
-CHF ₂	0.13 (~ 0.10)
-CH ₂ F	0.61 (~ 0.85)
-CF ₂ Cl	0.031 (~ 0.025)
-CFCI ₂	0.044
-CHF-	0.21
-CF ₂ -	0.018
= O	8.7 (8.8)
$\left. \begin{array}{l} -\text{CHO} \\ >\text{CO} \end{array} \right\}$	0.75 (0.76)
$\left. \begin{array}{l} -\text{CH}_2\text{C(O)}- \\ >\text{CHC(O)}- \\ \rightarrow \text{CC(O)}- \end{array} \right\}$	3.9 (4.4)
$\left. \begin{array}{l} -\text{C}_6\text{H}_5 \\ >\text{C} = \text{C} \\ -\text{C} \equiv \text{C}- \end{array} \right\}$	~ 1.0 (~ 1.0)
-OH	3.5 (3.4)
-OR (R = alkyl)	8.4 (6.1)
$\left. \begin{array}{l} -\text{OCF}_3 \\ -\text{OCF}_2- \\ -\text{OCHF}_2 \\ -\text{OCH}_2\text{F} \end{array} \right\}$	0.17
-C(O)Cl	0.067 (~ 0.5)
$\left. \begin{array}{l} -\text{OCH}_2\text{CF}_3 \\ -\text{OCH}(\text{CF}_3)_2 \\ -\text{OCHClCF}_3 \end{array} \right\}$	0.44
-C(O)OR (R = alkyl)	0.74 (0.0)
-OC(O) (R = alkyl)	1.6 (1.5)
-C(O)OH	0.74
-C(O)CF ₃	0.11
$\left. \begin{array}{l} -\text{CH}_2\text{ONO}_2 \\ >\text{CHONO}_2 \\ \rightarrow \text{CONO}_2 \end{array} \right\}$	0.20 (0.21)
-ONO ₂	0.04 (0.10)
-CN	0.19 (0.14)
-CH ₂ CN	~ 0.12 (0.5)
-NO ₂	0.0

Table 2. (Continued)

X	$F(X)$ at 298 K ^b
-CH ₂ NO ₂	0.14
3-member ring	0.020 (0.017)
4-member ring	0.28 (0.22)
5-member ring	0.64 (0.80)
7- and 8-member rings	~ 1.0 (~ 1.0)

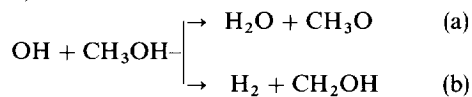
^a Values of E_X can be calculated from $F(X) = e^{E_X/T}$ [equation (1)].

^b Values in parentheses are those of Atkinson (1987).

^c Values of $F(X)$ for X = -CH₂Cl, -CHCl₂ and -CH₂Br only obtained previously.

For compound classes other than the alkanes, substituent factors $F(X)$ were derived using the rate constants given in the reviews of Atkinson (1989, 1994), as updated with those from the recent studies of Schmoltner *et al.* (1993) for haloalkanes and Scollard *et al.* (1993) for halogenated aldehydes. The substituent factors $F(X)$ were derived from nonlinear least-squares analyses (Atkinson, 1986, 1987), using only the room temperature rate constants since the determination of the factor $F(X)$ at 298 K defines the temperature dependence of $F(X)$ through equation (1). Based on the presently available experimental data (Atkinson, 1989, 1994), initial OH radical addition to -ONO₂ groups in alkyl nitrates, -NO₂ groups in nitroalkenes and -C(O)OH groups in carboxylic acids was assumed and these initial addition rate constants at room temperature and atmospheric pressure of air are given in Table 1. While Hynes and Wine (1991) have shown that OH radical reaction with CH₃CN proceeds by both H-atom abstraction and initial OH radical addition at room temperature and atmospheric pressure of air, only H-atom abstraction has been assumed here in order to fit the data for CH₃CN and C₂H₅CN.

H-atom abstraction from O-H bonds is almost always a minor reaction pathway. The group rate constant k_{OH} was obtained from the branching ratio for the two pathways in the OH radical reaction with methanol,



of $k_a/(k_a + k_b) = 0.15$ at 298 K (Atkinson, 1989), combined with an assumed value of C in the temperature-dependent expression $k_{\text{OH}} = CT^2 e^{-D/T}$ identical to that for H-atom abstraction from the >CH- group. This leads to the group rate constant given in Table 1. This rate constant for H-atom abstraction from -OH groups is significantly higher than previously derived (Atkinson, 1987, 1988b) (the difference being due to the lower rate constant ratio k_a/k_b obtained from the previously available data), but

this has little effect since H-atom abstraction from O-H bonds is of minor importance.

The substituent factors $F(X)$ obtained for the various α and β substituent groups X are given in Table 2. Because of previously known problems in obtaining agreement between calculated and experimentally measured rate constants for ethers, and especially fluoroethers, polyethers and cyclic ethers (Atkinson, 1987; Zhang *et al.*, 1992; Wallington *et al.*, 1988; Dagaut *et al.*, 1989, 1990), the fluoroethers were dealt with separately from nonhalogen-containing ethers, and a number of different substituent factors were investigated, ranging from a single α substituent group factor $F(-O-)$ to both α and β substituent group factors, including separate β substituent group factors $F(-CH_2O-)$, $F(>CHO-)$ and $F(-\rightarrow CO-)$. These various attempts to obtain good agreement between experimental and calculated data were not judged successful, in part because the use of an increased number of substituent factors led to only a minimally better agreement. Therefore, it was decided to use only the α substituent group factor $F(-O-)$, and empirically deal with those cases of two ether groups bonded to the same carbon atom by assuming that $[F(-O-)]^2 = F(-O-)$, as is also assumed in the Syracuse Research Corporation's AOP. It should be noted that, because of the low reactivities of the fluorinated ethers, the possibility of errors in the experimentally measured rate constants exists. Similarly, the use of a larger range of substituent group factors than previously was explored to fit the experimental database for the haloalkanes; however, problems were still encountered for a number of haloalkanes containing $-CF_3$ and $-CF_2Cl$ groups.

For the 290 organic compounds that react with the OH radical by H-atom abstraction from C-H and O-H bonds for which experimental data are available, the calculated 298 K rate constants disagree with the recommended values or experimental data by more than a factor of 2 for 36 compounds (12%) (Table 3).

Among the oxygenates, rate constants are available for formaldehyde, acetone, methanol and ethanol over large temperature ranges (~ 270 – 1200 K), and Figs 1 and 2 show Arrhenius plots of the calculated and recommended rate constants for these OH radical reactions. The agreement is good throughout the temperature ranges for which experimental data are available and for which recommendations have been made [note that the recommendation for the formaldehyde reaction (Atkinson, 1994) uses the expression $k = CT e^{-D/T}$ rather than $k = CT^2 e^{-D/T}$].

Because of the generally greater reactivity of $>C=C<$ and $-C\equiv C-$ bonds and aromatic rings towards OH radical addition, H-atom abstraction from alkyl or substituted alkyl groups in the alkenes, alkynes and aromatic compounds is generally of minor importance and the substituent group factors $F(>C=C<)$, $F(-C\equiv C-)$ and $F(-C_6H_5)$ are not well defined. While the rate constant per $-CH_3$ group obtained by Atkinson (1989) from toluene, toluene- d_5

and the xylenes of $6.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K implies a value of $F(-C_6H_5) = 4.6$, the room temperature rate constants for ethylbenzene, propylbenzene, isopropylbenzene and the ethyltoluenes suggest that a value of $F(-C_6H_5) \sim 1.0$ is more appropriate. As previously (Atkinson, 1986, 1987), the substituent group factors $F(>C=C<)$ and $F(-C\equiv C-)$ were also set equal to unity.

OH radical addition to $>C=C<$ and $-C\equiv C-$ bonds

The calculation of rate constants for OH radical addition to $>C=C<$ and $-C\equiv C-$ bonds used the same approach as previously (Atkinson, 1986, 1987, 1988b) in that the rate constant for OH radical addition to these carbon-carbon unsaturated bonds depends on the number, identity and position of substituent groups around the $>C=C<$ or $-C\equiv C-$ bond(s). Conjugated double bond systems are dealt with by considering the entire conjugated $>C=C-C=C<$ system as a single unit (Atkinson, 1986), rather than as conjugated $>C=C<$ sub-units as done by Ohta (1983). Thus, for *cis*-2-butene and myrcene $[(CH_3)_2C=CHCH_2CH_2C(=CH_2)CH=CH_2]$ the overall OH radical reaction rate constants are given by

$$\begin{aligned} k_{\text{total}}(\text{cis-2-butene}) &= k(\text{cis-CH=CH-}) \\ &\quad + 2k_{\text{prim}}F(>C=C<), \\ k_{\text{total}}(\text{myrcene}) &= k(>C=CH-) \\ &\quad + k(CH_2=CHC=CH_2) \\ &\quad + 2k_{\text{prim}}F(>C=C<) \\ &\quad + k_{\text{sec}}F(>C=C<)F(-CH_2-) \\ &\quad + k_{\text{sec}}F(-CH_2-)F(>C=C<) \end{aligned}$$

where for myrcene $k(>C=CH-)$ refers to OH radical addition to the $>C=C<$ bond in the $(CH_3)_2C=CH-$ unit and $k(CH_2=CHC=CH_2)$ refers to OH radical addition to the $>C=C<$ bonds in the $CH_2=CHC(=CH_2)-$ unit. The 298 K rate constants for addition to the $CH_2=CH-$, $CH_2=C<$, *cis*- and *trans*- $-CH=CH-$, $-CH=C<$ and $>C=C<$ nonconjugated carbon-carbon double bond units and the various $-C\equiv C-$ and conjugated $>C=C-C=C<$ units are given in Table 4. The rate constants for addition to $CH_2=CH-$, $CH_2=C<$, *cis*- and *trans*- $-CH=CH-$, $-CH=C<$ and $>C=C<$ groups are based on those for OH radical addition to propene, 2-methylpropene, *cis*-2-butene, *trans*-2-butene, 2-methyl-2-butene and 2,3-dimethyl-2-butene, respectively (Atkinson, 1986). It should be noted that there is no evidence for ring-strain effects on OH radical addition to cycloalkenes.

For alkenes containing substituent groups, X , other than alkyl groups, group substituent factors $C(X)$ are used. For example, for $CH_2=CHX$ and $XCH=CYZ$, the rate constants are given by

$$k(CH_2=CHX) = k(CH_2=CH-)C(X)$$

Table 3. Organic compounds for which the experimental and calculated 298 K rate constants disagree by a factor of > 2

Organic compound	$10^{12} \times k$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	
	Calculated	Experimental ^a
<i>H-atom abstraction</i>		
Quadricyclo[2.2.0 ^{2,6} .0 ^{3,5}]heptane	0.69	1.83
Cyclobutanone	4.5	0.87
Cyclopentanone	6.8	2.94
3,3-Dimethylbicyclo[2.2.1]heptan-2-one	12.3	5.15
Glyoxal	25.3	11.4
Pentane-1,5-dial	57.4	23.8
Glycolaldehyde	23.4	9.9
Di-isopropyl ether	33.3	10.2
Epoxycyclohexane	0.39	0.076
1,3-Dioxane	28.6	9.15
1,4-Dioxane	38.6	10.9
4-Methyl-1,3-dioxane	39.1	11.3
1,3,5-Trioxane	23.5	6.2
1,1-Dimethoxyethane	18.7	8.9
1,2-Dimethoxypropane	32.1	14.3
1,1,3-Trimethoxypropane	34.5	16.7
2-Methoxyethyl ether	40.9	17.5
2-Ethoxyethyl ether	54.6	26.8
CH ₃ CH(ONO ₂)C(O)CH ₃	0.55	1.27
CHF ₃	0.00161	0.00031
CH ₃ CF ₃	0.00966	0.0046
CHFBrCF ₃	0.00363	0.0167
CHClBrCF ₃	0.0147	0.0463
CHFClCF ₂ Cl	0.00215	0.0123
CHCl ₂ CF ₂ Cl	0.00868	0.053
CHCl ₂ CCl ₃	0.0193	0.233
CHCl ₂ CF ₂ CF ₃	0.00504	0.025
CHFClCF ₂ CF ₂ Cl	0.00125	0.00885
(CH ₃) ₃ CCl	0.147	0.412
CHF ₂ CF ₂ CF ₂ CHF ₂	0.00062	0.0046
CHF ₂ OCHF ₂	0.00583	0.0247
CHF ₂ OCF ₂ CHFCl	0.00416	0.017
CH ₂ ClCHO	6.34	3.1
CHCl ₂ CHO	6.29	2.5
CF ₃ C(O)OCH ₃	0.218	0.052
2,2,2-Trifluoroethanol	0.372	0.0955
<i>OH Radical addition to >C = < bonds</i>		
Sabinene	55.8	117
CH ₂ = CCl ₂	2.67	10.9
CHCl = CCl ₂	0.805	2.36
CFCl = CCl ₂	0.214	7.6
CF ₂ = CCl ₂	0.214	7.5
CF ₂ = CFCF ₃	0.214	7
<i>OH radical addition to aromatic rings</i>		
<i>o</i> -Xylene	6.51	13.7
<i>p</i> -Xylene	6.51	14.3
β -Dimethylstyrene	92.3	33
Acetophenone	0.74	2.74
Fluorobenzene	2.44	0.69
Benzyl alcohol	$\sim 8.5^b$	22.9
N,N-Dimethylaniline	438	148
<i>o</i> -Nitrophenol	6.6	0.90
3,5-Dimethylphenol	230	113
2,3-Dichlorophenol	9.2	1.66
2,4-Dichlorophenol	5.2	1.06
Tetralin	11.4	34.3

^a Data from Atkinson (1989, 1994).^b Assuming that $\sigma_{o,p}^+(\text{-CH}_2\text{OH}) = \sigma_{o,p}^+(\text{-CH}_3)$.

and

$$k(\text{XCH} = \text{CYZ}) = k(\text{-CH} = \text{C<})C(\text{X})C(\text{Y})C(\text{Z})$$

respectively [for alkyl substituent groups, $C(\text{alkyl})$]

$= 1.00$]. The group factors $C(\text{X})$ derived from the available database for haloalkenes, nitriles and oxygenated organic compounds containing $>\text{C} = \text{C}<$ bonds (Atkinson, 1989, 1994) are given in Table 5.

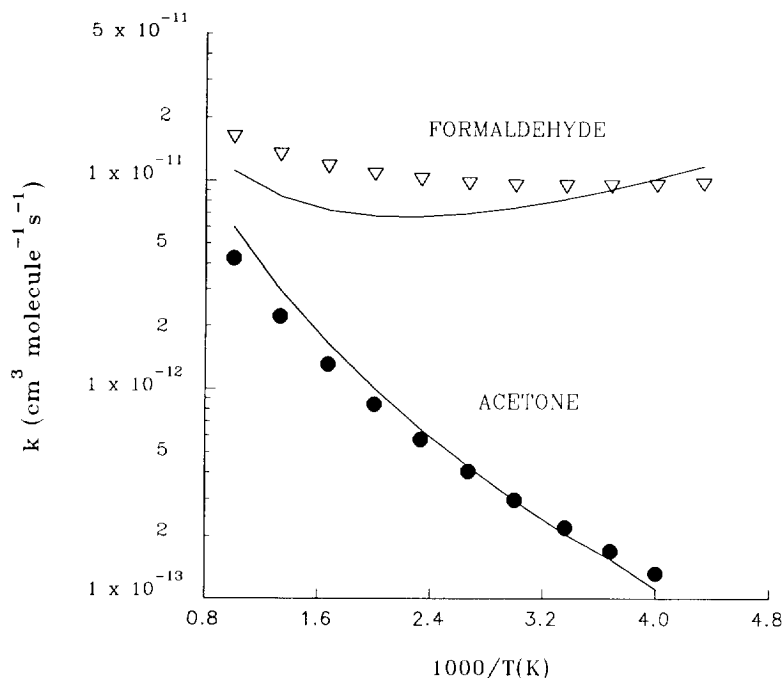


Fig. 1. Arrhenius plots of recommended (Atkinson, 1989, 1994) (∇ , \bullet) and calculated (—) rate constants for the gas-phase reactions of the OH radical with formaldehyde and acetone.

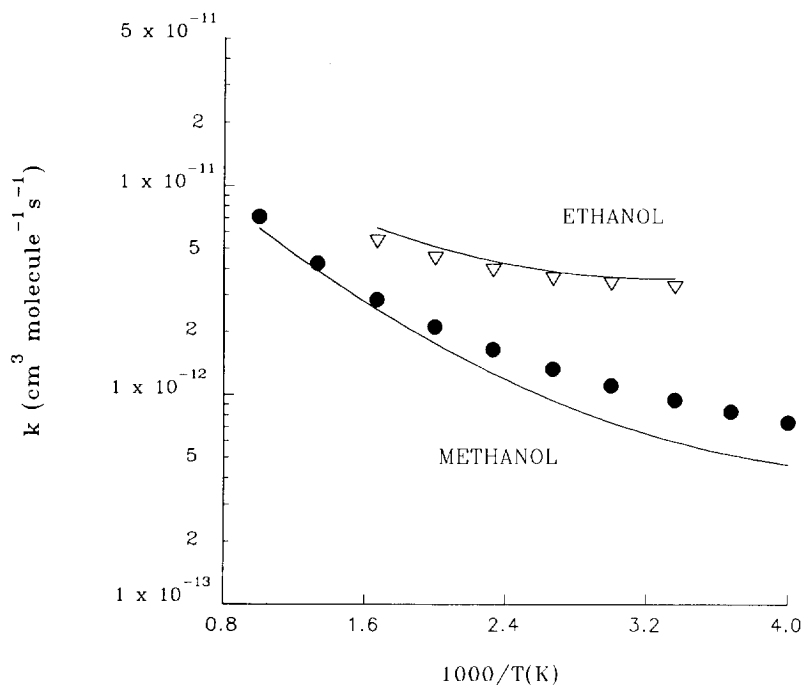


Fig. 2. Arrhenius plots of recommended (Atkinson, 1989, 1994) (∇ , \bullet) and calculated (—) rate constants for the gas-phase reactions of the OH radical with methanol and ethanol.

For reactions that involve OH radical addition to $>\text{C}=\text{C}<$ and $-\text{C}\equiv\text{C}-$ bonds the calculated 298 K rate constants disagree with the experimental rate constants by a factor of >2 for six of a total of 98 compounds (6%) (Table 3).

OH radical addition to aromatic rings. The rate constants for OH radical addition to aromatic rings are calculated using the correlation between the OH radical addition rate constant and the sum of the electrophilic substituent constants $\sum\sigma^+$ (Zetzsch,

Table 4. 298 K group rate constants for OH radical addition to $>C=C<$, $-C\equiv C-$ and $>C=C-C=C<$ structural units

Structural unit	$10^{12} \times k$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
$\text{CH}_2 = \text{CH}-$	26.3
$\text{CH}_2 = \text{C} <$	51.4
<i>cis</i> - $-\text{CH} = \text{CH}-$	56.4
<i>trans</i> - $-\text{CH} = \text{CH}-$	64.0
$-\text{CH} = \text{C} <$	86.9
$>C = \text{C} <$	110
$\left. \begin{array}{l} \text{H}_2\text{C} = \text{CHCH} = \text{CH}- \\ \text{H}_2\text{C} = \text{CHC} = \text{CH}_2 \end{array} \right\}$	105
$\left. \begin{array}{l} \text{H}_2\text{C} = \text{CHCH} = \text{C} < \\ \text{H}_2\text{C} = \text{CHC} = \text{CH}- \\ \text{H}_2\text{C} = \text{CCH} = \text{CH}- \\ -\text{CH} = \text{CHCH} = \text{CH}- \\ \text{H}_2\text{C} = \text{CC} = \text{CH}_2 \end{array} \right\}$	142
$\left. \begin{array}{l} \text{H}_2\text{C} = \text{CHC} = \text{C} < \\ \text{H}_2\text{C} = \text{CCH} = \text{C} < \\ -\text{CH} = \text{CHCH} = \text{C} < \\ \text{H}_2\text{C} = \text{CC} = \text{CH}- \\ -\text{CH} = \text{CCH} = \text{CH}- \end{array} \right\}$	~ 190
$\left. \begin{array}{l} >C = \text{CHCH} = \text{C} < \\ \text{H}_2\text{C} = \text{CC} = \text{C} < \\ -\text{CH} = \text{CC} = \text{CH}- \\ -\text{CH} = \text{CHC} = \text{C} < \\ -\text{CH} = \text{CCH} = \text{C} < \end{array} \right\}$	~ 260
$\text{HC} \equiv \text{C}-$	7.0
$-\text{C} \equiv \text{C}-$	27

1982; Atkinson, 1986, 1987, 1991). As discussed by Zetzsch (1982), $\sum\sigma^+$ is calculated by assuming that (a) steric hindrance can be neglected, (b) $\sum\sigma^+$ is the sum of all of the substituent constants of the substituent groups attached to the aromatic ring, (c) the OH radical adds to the position yielding the most negative value of $\sum\sigma^+$, and (d) if all positions on the ring are occupied, the *ipso* position is treated as a *meta* position.

Monocyclic aromatic compounds and biphenyls. The correlation between the OH radical addition rate constants and $\sum\sigma^+$ has recently been updated by Atkinson (1991), and no new kinetic data which would affect that correlation have appeared since that update. Thus (Atkinson, 1991)

$$\log_{10} k_{\text{add}} (\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = -11.71 - 1.34 \sum\sigma^+ \quad (2)$$

The electrophilic substituent factors used for the $-\text{C}_6\text{H}_5-x\text{Cl}_x$ groups in the mono- and dichlorobiphenyls are those derived by Atkinson (1991), which are consistent with the recent data of Kwok *et al.* (1995) for 2,2', 3,3'- and 3,5-dichlorobiphenyl. The agreement between the experimental and calculated OH radical reaction rate constants for monocyclic aromatic compounds and biphenyls is reasonably good (the calculated rate constants include the calculated contributions due to H-atom abstraction

Table 5. Group substituent factors, $C(X)$, at 298 K for OH radical addition to $>C=C<$ and $-C\equiv C-$ bonds

Substituent group	$C(X)$ at 298 K ^a
$-\text{F}$	0.21 (~ 0.4)
$-\text{Cl}$	0.21 (0.20)
$-\text{Br}$	0.26 (0.26)
$-\text{CH}_2\text{Cl}$	0.76 (0.76)
$-\text{CHO}$	0.34 (0.26)
$-\text{C}(\text{O})\text{CH}_3$	0.90 (0.91)
$\left. \begin{array}{l} -\text{CH}_2\text{ONO}_2 \\ >\text{CHONO}_2 \end{array} \right\}$	0.47
$-\text{C}(\text{O})\text{OR}$ (R = alkyl)	0.25
$-\text{OR}$ (R = alkyl)	1.3 (1.3)
$-\text{CN}$	0.16 (0.15)
$-\text{CH}_2\text{OH}$	~ 1.6

^a Values in parentheses are those of Atkinson (1987).

from, or OH radical addition to or interaction with, the substituent groups in these compounds), with a disagreement of a factor of > 2 occurring for 12 out of the 66 compounds (18%) (Table 3). N,N-Dimethylaniline and 3,5-dimethylphenol are calculated to have rate constants $> 2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and it is possible that a "maximum rate constant" of $\sim 2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ should be used when the calculated values exceed this value.

Polycyclic and heteroatom-containing aromatic compounds. Kinetic data are now available for dibenzo-*p*-dioxin, 1-chlorodibenzo-*p*-dioxin and dibenzofuran (Kwok *et al.*, 1994a, 1995). The approach used to calculate the rate constants for polychlorodibenzo-*p*-dioxins (PCDDs) and polychlorodibenzofurans (PCDFs), in which dibenzo-*p*-dioxin is viewed as two benzene rings substituted by two $-\text{OPh}$ groups and dibenzofuran is viewed as two benzene rings substituted by a $-\text{Ph}$ and an $-\text{OPh}$ group (Kwok *et al.*, 1995), is recommended.

The room temperature rate constants for the reactions of the OH radical with phenanthrene and anthracene recently measured by Kwok *et al.* (1994b) are lower by factors of 2.5–8 than the previous recommendations and rate data (Biermann *et al.*, 1985; Atkinson, 1989), casting doubt on the previously proposed correlation between the OH radical addition rate constants and ionization potential (Biermann *et al.*, 1985). Therefore, at this time the estimation of rate constants for the PAH and alkyl-substituted PAH is uncertain. For substituted PAH, the enhancement of the rate constant over that for the parent PAH may be approximately estimated using the correlation between the rate constant and $\sum\sigma^+$ discussed above for the monocyclic aromatic compounds, with the enhancement factor being $e^{1.34\sum\sigma^+}$, as also proposed by

Atkinson (1987). This approach may also work for heteroatom-containing aromatic compounds such as the pyridines and triazines.

OH radical interaction with N-, S- and P-containing groups. The OH radical reactions with a number of nitrogen-, sulfur- and phosphorus-containing organic compounds appear to proceed, at least in part, by an initial addition reaction (Atkinson, 1989, 1994), although the products observed may in some cases be those expected from H-atom abstraction. The reaction of the OH radical with methyl mercaptan (CH_3SH) is one example, with the CH_3S radical being formed in essentially unit yield despite the fact that the initial reaction proceeds by OH radical addition (Atkinson, 1994). The available information is briefly discussed below.

Nitrogen-containing organic compounds. The situation as far as the available database is concerned is unchanged since the previous discussion of Atkinson (1987). Rate constants are available for seven amines and substituted amines and for N-nitrosodimethylamine and dimethylnitramine (Atkinson, 1989). The group rate constants and substituent group factors are given in Tables 6 and 7, respectively; these should only be used for homologs of the compounds from which these factors were derived. For example, the group rate constants $k_{>\text{N-}}$, $k_{>\text{NH}}$ and $k_{-\text{NH}_2}$ and the substituent group factors $F(-\text{NH}_2)$, $F(>\text{NH})$ and $F(>\text{N-})$ are only appropriate for *alkyl*-substituted amines.

Sulfur-containing organic compounds. As for the nitrogen-containing organic compounds, the situation has not changed appreciably since the Atkinson (1987) article, although a somewhat larger database is now available (Atkinson, 1989, 1994). The group rate constants and substituent group factors are given in Tables 6 and 7, respectively.

Table 6. Group rate constants at 298 K for the reactions of OH radicals with N-, S- and P-containing organic compounds

Group (R = alkyl)	$10^{12} \times k$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
RNH_2	21
R_2NH	63
R_3N	66
R_2NNO	0
R_2NNO_2	1.3
RSH	32.5
RSR	1.7 ^a
RSSR	225
$-\text{>P}=\text{O}$	0
$-\text{>P}=\text{S}$	53
$>\text{NC}(\text{O})\text{S-}$	11.9

^aBased on the data for OH radical addition to CH_3SCH_3 at 298 K and 760 Torr total pressure of air (Atkinson, 1989).

Table 7. Substituent group factors $F(X)$ at 298 K for the reactions of OH radicals with N-, S- and P-containing organic compounds

Substituent group X	$F(X)$ at 298 K
$\left. \begin{array}{l} -\text{NH}_2 \\ >\text{NH} \\ >\text{N-} \\ >\text{NNO} \\ >\text{NNO}_2 \end{array} \right\}$	9.3
$\left. \begin{array}{l} -\text{SH} \\ -\text{S-} \\ -\text{SS-} \end{array} \right\}$	7.8
$\left. \begin{array}{l} -\text{OP<-} \\ -\text{SP<-} \end{array} \right\}$	20.5
$\left. \begin{array}{l} >\text{NC}(\text{O})\text{S-} \\ -\text{SC}(\text{O})\text{N<} \end{array} \right\}$	4.1

Phosphorus-containing organic compounds. Rate constants have been measured for six compounds containing $-\text{>P}=\text{O}$ and $-\text{>P}=\text{S}$ groups, and for four compounds containing $-\text{>P}(=\text{X})\text{N<}$ groups, with $\text{X}=\text{O}$ or S (Atkinson, 1989, 1994). Group rate constants and substituent group factors have been derived for the $-\text{>P}=\text{O}$ and $-\text{>P}=\text{S}$ containing compounds (Atkinson, 1988b), and these are changed only slightly (Tables 6 and 7). For the phosphorothioamides and phosphoramidates, the P and N portions of the molecules were dealt with separately (Goodman *et al.*, 1988b); this is probably not appropriate although an insufficient database exists for this class of compound for any meaningful estimation method to be derived (apart from the observation that they are all "reactive").

Thiocarbamates. Rate constants for three thiocarbamates containing the structural unit $>\text{NC}(\text{O})\text{S-}$ have been determined at room temperature (Kwok *et al.*, 1992) and a group rate constant $k_{>\text{NC}(\text{O})\text{S-}}$ and substituent group factors $F(>\text{NC}(\text{O})\text{S-})$ and $F(-\text{SC}(\text{O})\text{N<})$ derived (Kwok *et al.*, 1992). The group rate constant and substituent group factors are given in Tables 6 and 7, respectively.

The calculated 298 K rate constants for these 34 N-, S- and P-containing organic compounds agree with the experimental values to within a factor of 2, not surprisingly since the entire database was used to derive the group rate constants and substituent factors.

CONCLUSIONS

A re-investigation of the Atkinson (1986, 1987, 1988b) empirical estimation method allowing the calculation of OH radical reaction rate constants, using the presently available kinetic database, shows that in general terms the situation has not changed markedly

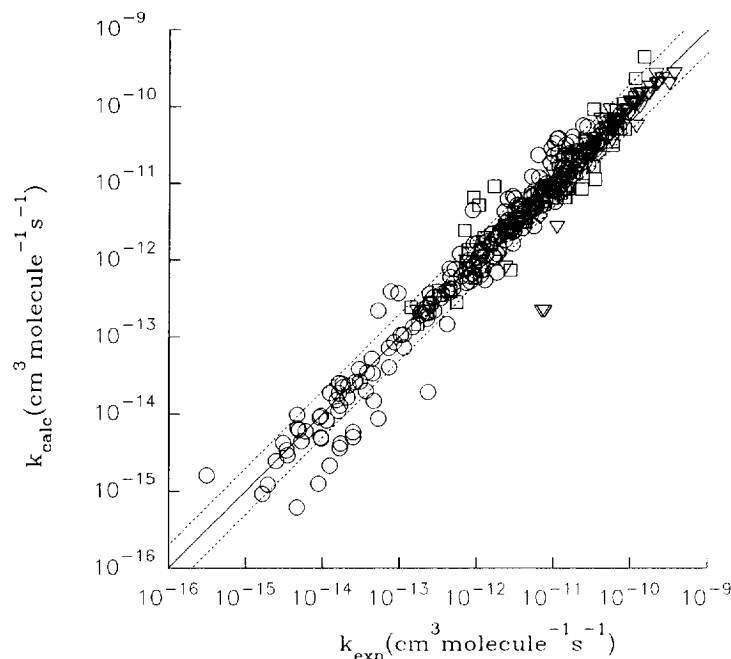


Fig. 3. Comparison of the experimental (k_{exp}) and calculated (k_{calc}) 298 K rate constants for the reactions of the OH radical with ~ 485 organic compounds. Reactions involve: \circ , H-atom abstraction; ∇ , OH radical addition to $>\text{C}=\text{C}<$ and $-\text{C}\equiv\text{C}-$ bonds; \square , OH radical addition to aromatic rings; \diamond , OH radical interaction with N-, S- and P-atoms. The solid line denotes perfect agreement, and the dashed lines denote disagreement by a factor of 2.

since 1986. Using a large fraction of the available database to derive the parameters needed to calculate the OH radical reaction rate constants, the 298 K rate constants of $\sim 90\%$ of approximately 485 organic compounds are predicted to within a factor of 2 of the experimental values (Fig. 3). Disagreements between calculated and measured rate constants most commonly occur for halogen-containing organic compounds, and especially for the haloalkanes, haloalkenes and halogenated ethers (Table 3). Problems also arise for the ethers, in particular for the polyethers and cycloethers (Table 3). In addition to the uncertainties in the ability to correctly estimate the reaction rate constants, the uncertainties in the ambient atmospheric concentrations of the OH radical, both as a function of time and place, must be recognized, since the lifetime, τ , of a chemical with respect to gas-phase reaction with the OH radical is given by $\tau = (k_{\text{OH}}[\text{OH}])^{-1}$.

The present estimation technique is reasonably reliable when used within the database used in its derivation, but *extrapolation* to organic compounds outside of the database used for its development and testing results in a lack of assurance of its reliability. Thus, while the present estimation method appears to be reliable to well within a factor of 2 for calculating the rate constants for reactions of the OH radical reactions with alkanes and alkenes (including over wide temperature ranges for the alkanes), the calculation of room temperature rate constants for organic compound classes other than the alkanes or alkenes is

prone to significant error. In particular, its use for organic compounds which belong to classes other than those tested is discouraged.

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