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Chemical
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Monograph No. 2

Gas-phase Tropospheric Chemistry of Organic Compounds

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Jean W. Gallagher, Editor

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Foreword

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The regular issues of the *Journal of Physical and Chemical Reference Data* are published bimonthly and contain compilations and critical data reviews of moderate length. Longer works, volumes of collected tables, and other material unsuited to a periodical format have previously been published as *Supplements to the Journal*. Beginning in 1989 the generic title of these works has been changed to *Monograph*, which reflects their character as independent publications. This volume, "Gas-Phase Tropospheric Chemistry of Organic Compounds" by Roger Atkinson, is presented as *Monograph No. 2* of the *Journal of Physical and Chemical Reference Data*.

Jean W. Gallagher, Editor
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Gas-Phase Tropospheric Chemistry of Organic Compounds

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The gas-phase reactions of selected classes of organic compounds (alkanes, alkenes (including isoprene and monoterpenes), alkynes, aromatic hydrocarbons and oxygen-containing organic compounds and their degradation products) under tropospheric conditions are reviewed and evaluated. The recommendations of the most recent IUPAC evaluation [J. Phys. Chem. Ref. Data **21**, 1125 (1992)] are used for the $\leq C_3$ organic compounds, unless more recent data necessitates reevaluation. In addition to the review of the gas-phase tropospheric chemistry of these classes of organic compounds, the previous reviews and evaluations of Atkinson [J. Phys. Chem. Ref. Data, Monograph 1 (1989)] for OH radical reactions, Atkinson [J. Phys. Chem. Ref. Data **20**, 459 (1991)] for NO_3 radical reactions and Atkinson and Carter [Chem. Rev. **84**, 437 (1984)] for O_3 reactions with organic compounds are updated.

Keywords: atmospheric chemistry; hydroxyl radical; nitrate radical; organic compounds; ozone; reaction kinetics; reaction mechanisms.

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1. Introduction

Organic chemicals are introduced into the atmosphere in large quantities from a variety of anthropogenic and biogenic sources,[1–4] with estimated biogenic and anthropogenic non-methane organic compound emissions of ~1000 million ton yr^{-1} and ~100 million ton yr^{-1}, respectively.[4] These emissions of organic compounds lead to a complex series of chemical and physical transformation and removal processes in the atmosphere which result in such effects as ozone formation in urban[5,6] and rural[7,8] areas and in the global troposphere,[9] stratospheric ozone depletion,[4] long range transport of chemicals,[10] acid deposition,[11] and global climate change.[12] A large amount of experimental data concerning the chemical and physical processes of emitted organic compounds has been obtained from laboratory and ambient air studies over the past two decades, and there is now an understanding, at varying levels of detail, of the atmospheric chemistry of the various classes of organic compounds emitted into the troposphere.[13–19] Because of the complexity of the physical and chemical processes involved and the often non-linear response of the parameters of interest to changes in the input(s), the use of computer models incorporating the emissions, atmospheric chemistry and atmospheric transport processes is generally necessary to elucidate the effects of emissions of chemicals of anthropogenic and biogenic origin on the atmosphere.

Chemical mechanisms of varying levels of detail have been formulated and used as components of these computer modeling studies. For the more complex non-methane organic compounds, the chemical mechanisms are often compared with experimental data obtained from environmental chambers during their development (see, for example, references 20–24) and hence under the concentration conditions of these experimental data the predictions of the chemical mechanisms are constrained to be in reasonable agreement with experimental data. However, these environmental chamber data are of somewhat limited utility due to the difficulties of working at the low reactant concentrations characteristic of the ambient atmosphere and of monitoring product species which are present in low concentrations and/or readily deposit at the chamber walls. The accuracies of chemical mechanisms used in the computer models designed to simulate the troposphere and/or stratosphere are then dependent on the accuracy of the individual rate constants, reaction mechanisms and product distributions for the multitude of elementary reactions which actually occur in the atmosphere.

It is evident that, together with experimental laboratory, ambient air and theoretical studies of the kinetics, mechanisms and products of the atmospheric reactions of organic compounds, there must also be an ongoing parallel effort to critically review and evaluate these data. These evaluation efforts serve to present the current status of knowledge of atmospheric chemistry, in part for modelers, and to point out the areas of uncertainty for designing future experimental and/or theoretical studies. The reactions of interest for modeling the chemistry occurring in the stratosphere have been reviewed and evaluated for several years by the National Atmospheric and Space Administration (NASA) Panel for Data Evaluation [with the most recent evaluation being Number 10, published in 1992[18]] and by the IUPAC (formerly CODATA) Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry (with the most recent evaluation being Supplement IV[19]). While these two data evaluation panels were originally concerned largely with stratospheric chemistry, due to the potential for stratospheric ozone depletion by inputs of ClO_x and NO_x into the stratosphere, tropospheric chemistry is now being included to an increasing degree in both evaluations through the tropospheric chemistry of the hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) proposed as alternatives to the chlorofluorocarbons and, especially in the more recent IUPAC evaluations,[19,25] by the inclusion of the reactions of $\leq C_3$ alkanes, alkenes, alkynes, aldehydes, ketones, alcohols, carboxylic acids and organosulfur species. The gas-phase atmospheric reactions of the HFCs and HCFCs have been dealt with in detail recently,[14,18,19] and the atmospheric chemistry of reduced organosulfur compounds has been reviewed by Tyndall and Ravishankara.[17]

However, the troposphere contains at least several hundred organic compounds, with the vast majority of them being $\geq C_4$ species, and there is an obvious need for the review and evaluation of the chemical reactions which occur in the troposphere for these chemicals. To date, several critical reviews and evaluations of the kinetics and mechanisms of the gas-phase reactions of organic compounds with OH radicals,[26–28] NO_3 radicals[15,16] and O_3[29] have been carried out, with the most recent of these being those of Atkinson and Carter[29] for O_3 reactions and Atkinson[16,28] for OH and NO_3 radical reactions. In addition to these reviews of specific (and important) reaction pathways, the tropospheric chemistry of selected organic compounds has been reviewed by Atkinson and Lloyd,[30] Atkinson[13] and Roberts.[31] The review of Atkinson and Lloyd[30] focused on the tropospheric reactions of eight hydrocarbons (*n*-butane, 2,3-dimethylbutane, ethene, propene, 1-butene, *trans*-2-butene, toluene and *m*-xylene) and their degradation products, while that of Atkinson[13] dealt in a more global sense with the tropospheric chemistry of the alkanes, alkenes, alkynes, oxygenates (including those formed during the atmospheric degradations of the hydrocarbon species), nitrogen-containing organics, and aromatic hydrocarbons.

The present article serves to update and extend the Atkinson[13] review to take into account more recent data. In the previous article,[13] the reactions of alkyl, alkyl peroxy and alkoxy radicals, and their substituted analogs, were dealt with as single entities, regardless of the chemical structure of the alkyl radical, alkyl peroxy radical, or alkoxy radical. A somewhat different approach than used by Atkinson[13] is employed here, since recent data for organic radicals indicate that there are significant differences between the reaction pathways occurring in the troposphere, depending on the structures of the radicals.

The reactions of organic compounds under tropospheric conditions are dealt with in Sec. 2:

2.1. Alkanes
2.2. Alkenes
2.3. Alkynes
2.4. Aromatic hydrocarbons and aromatic compounds formed during the tropospheric photooxidations of the aromatic hydrocarbons.
2.5. Oxygen-containing organic compounds, including those formed as photooxidation products of the alkanes, alkenes, alkynes and aromatic hydrocarbons.
2.6. Nitrogen-containing organic compounds formed as photooxidation products of the alkanes and alkenes.

Only gas-phase reactions are discussed, since while highly important under many tropospheric conditions, the reactions occurring in the particle and/or aqueous phase (for example, in fog, cloud and rain droplets), on surfaces (heterogeneous reactions) and gas-to-particle conversion (see, for example, Refs. 32–38) are beyond the scope of the present article. As in the previous review,[13] the most recent NASA[18] and, especially, IUPAC[19] evaluations are used for the $\leq C_3$ reactions, generally without reevaluation or detailed discussion. The present article is in essence an extension of the IUPAC evaluation[19] to more complex organic compounds characteristic of the lower troposphere and, in particular, polluted air masses. Thus the present article and the most recent IUPAC evaluation[19] are complementary and both are necessary for an in-depth coverage of the chemistry of organic compounds in the troposphere. In addition, the previous articles[16,28,29] dealing with the kinetics and mechanisms of the gas-phase reactions of OH and NO_3 radicals and O_3 with organic compounds have been updated, with the data reported since these reviews[16,28,29] being tabulated, discussed and evaluated in Secs. 3, 4 and 5. In these sections, discussion is limited to those organic compounds for which new information has become available since these previous review articles[16,28,29] were prepared. Previous data are not included in the tables of rate constants, and hence the previous reviews[16,28,29] must be consulted for rate constant and mechanistic information available and used at the times of their finalization. The literature through mid-1992 has been included in this article. (See Addendum, Sec. 6 for data through early/mid-1993.)

Rate constants k determined as a function of temperature are generally cited using the Arrhenius expression, $k = A\,e^{-B/T}$, where A is the Arrhenius pre-exponential factor and B is in K. In some cases rate constants have been obtained over extended temperature ranges and the simple Arrhenius expression, as expected, does not hold, with curvature in the Arrhenius plots being observed.[28] In these cases, a three-parameter equation, $k = CT^n e^{-D/T}$ has been used,[28] generally with $n = 2$ ($k = CT^2 e^{-D/T}$). The equation, $k = CT^n e^{-D/T}$, can be transformed into the Arrhenius expression, $k = A\,e^{-B/T}$, centered at a temperature T, with $A = Ce^nT^n$ and $B = D + nT$.

Reactions which are in the fall-off region between second- and third-order kinetics or between first- and second-order kinetics are dealt with by using the Troe fall-off expression,[39] with

$$k = \left(\frac{k_0[M]}{1 + \dfrac{k_0[M]}{k_\infty}}\right) F^{\{1 + (\log_{10}k_0[M]/k_\infty)^2\}^{-1}} \qquad (1)$$

where k_0 is the limiting low-pressure rate constant, k_∞ is the limiting high-pressure rate constant, M is the concentration of the third-body gas (generally air in this article) and F is the broadening coefficient. In general, the rate constants k_0 and k_∞ have T^n temperature dependencies. The temperature dependence of F is given by $F \simeq e^{-T/T^*}$ for temperatures appropriate to the troposphere, where T^* is a constant for a given reaction.[19,40] All rate constants are given in cm molecule s units, and pressure are given in Torr (1 Torr = 133.3 Pa).

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2. Gas-Phase Tropospheric Chemistry of Organic Compounds

2.1. Alkanes

The atmospheric chemistry of the alkanes has been reviewed and discussed previously,[1,2] and the kinetics and mechanisms of the reactions with OH and NO_3 radicals and with O_3 have been reviewed and evaluated[3–5] and these reviews and evaluations are updated in Secs. 3, 4, and 5, respectively. The gas-phase reactions of the alkanes with O_3 are of negligible importance as an atmospheric loss process, since the available data[5] show that the room temperature rate constants for these reactions are $<10^{-23}$ cm^3 molecule^{-1} s^{-1}. Under atmospheric conditions, the potential loss processes for the alkanes involve gas-phase reactions with OH and NO_3 radicals.

OH Radical Reactions

The kinetics and mechanisms of the reactions of the OH radical with alkanes have been reviewed and evaluated by Atkinson,[3] and that evaluation is updated in Sec. 3.1. Rate constants have been determined over significant temperature ranges for a number of alkanes and, as expected from theoretical considerations, the Arrhenius plots exhibit curvature. Accordingly, the three-parameter expression $k = C\,T^2\,e^{-D/T}$ was generally used[3] (see also Sec. 3.1). The 298 K rate constants and the parameters C and D recommended [from Ref. 3 and Sec. 3.1] are given in Table 1 for alkanes of relevance to tropospheric chemistry. Room temperature rate constants for other alkanes for which recommendations have not been given (generally due to only single studies being carried out) are also given in Table 1.

These OH radical reactions proceed via H-atom abstraction from the C-H bonds

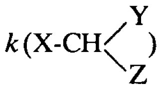
$$OH + RH \rightarrow H_2O + R\cdot$$

to generate an alkyl radical and, as discussed previously,[3,6] the rate constants for these OH radical reactions with alkanes can be fit to within a factor of ~2 over the temperature range 250–1000 K from consideration of the CH_3–, –CH_2– and >CH– groups in the alkane, and the neighboring substituent groups. Thus

$$k(CH_3\text{–}X) = k_{\text{prim}}\,F(X)$$

$$k(X\text{–}CH_2\text{–}Y) = k_{\text{sec}}\,F(X)\,F(Y)$$

and



$$k\left(X\text{–}CH\!\begin{smallmatrix}Y\\ Z\end{smallmatrix}\right) = k_{\text{tert}}\,F(X)\,F(Y)\,F(Z)$$

where k_{prim}, k_{sec} and k_{tert} are the OH radical rate constants per –CH_3, –CH_2– and >CH– group, respectively, for $X = Y = Z =$ –CH_3 as the standard substituent group, and $F(X)$, $F(Y)$ and $F(Z)$ are the substituent factors for X, Y and Z substituent groups. As derived by Atkinson,[6]

$$k_{\text{prim}} = 4.47 \times 10^{-18}\,T^2\,e^{-303/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1},$$

$$k_{\text{sec}} = 4.32 \times 10^{-18}\,T^2\,e^{233/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1},$$

$$k_{\text{tert}} = 1.89 \times 10^{-18}\,T^2\,e^{711/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1},$$

$F(\text{–}CH_3) = 1.00$, and $F(\text{–}CH_2\text{–}) = F(>CH\text{–}) = F(>C<) = e^{76/T}$. For cycloalkanes, the effects of ring strain are taken into account by means of ring factors.[6–8] This estimation technique not only allows the calculation of OH radical reaction rate constants for alkanes for which experimental data do not exist, but also allows the initially formed isomeric alkyl radical distribution to be calculated for a given alkane.[2]

NO_3 Radical Reactions

The NO_3 radical reacts with the alkanes with rate constants at room temperature in the 10^{-17} to 10^{-16} cm^3 molecule^{-1} s^{-1} range (Ref. 4 and Sec. 4.1). The recommended 298 K rate constants and temperature

TABLE 1. Rate constants k at 298 K and parameters C and D in $k = CT^2e^{-D/T}$ for the reaction of OH radicals with alkanes (from Ref. 3 and Sec. 3.1)

Alkane	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1})	$10^{18} \times C$ (cm^3 molecule^{-1} s^{-1})	D (K)
Methane	0.00686	7.44	1361
Ethane	0.257	15.1	492
Propane	1.15	15.0	44
n-Butane	2.54	15.1	−190
2-Methylpropane	2.33	11.1	−256
n-Pentane	3.94	21.0	−223
2-Methylbutane	3.9		
2,2-Dimethylpropane	0.849	17.9	187
n-Hexane	5.61		
2-Methylpentane	5.6		
3-Methylpentane	5.7		
2,2-Dimethylbutane	2.32	a	a
2,3-Dimethylbutane	5.99	12.1	−512
n-Heptane	7.15		
2,2-Dimethylpentane	3.4		
2,4-Dimethylpentane	5.2		
2,2,3-Trimethylbutane	4.23	9.04	−495
n-Octane	8.68	b	b
2,2-Dimethylhexane	4.8		
2,2,4-Trimethylpentane	3.59	20.6	−201
2,3,4-Trimethylpentane	7.0		
2,2,3,3-Tetramethylbutane	1.06	19.0	139
n-Nonane	10.2		
2-Methyloctane	10.1		
4-Methyloctane	9.7		
2,3,5-Trimethylhexane	7.9		
n-Decane	11.6		
n-Undecane	13.2		
n-Dodecane	14.2		
n-Tridecane	16		
n-Tetradecane	19		
n-Pentadecane	22		
n-Hexadecane	25		
Cyclopropane	0.084		
Cyclobutane	1.5		
Cyclopentane	5.08	25.5	−241
Cyclohexane	7.49	26.6	−344
Cycloheptane	12.5		
Methylcyclohexane	10.4		
cis- and *trans*-Bicyclo[4.4.0]decane	20		

[a] Arrhenius expression of $k = 2.84 \times 10^{-11} e^{-747/T}$ cm^3 molecule^{-1} s^{-1} recommended (245–330 K).
[b] Arrhenius expression of $k = 3.15 \times 10^{-11} e^{-384/T}$ cm^3 molecule^{-1} s^{-1} recommended (300–500 K).

dependent parameters, taken from Ref. 4 and Sec. 4.1, are given in Table 2, which also includes the room temperature rate constants for alkanes for which only a single study has been carried out and for which no recommendations are given. Under atmospheric conditions, the nighttime reactions of the alkanes with the NO_3 radical can be calculated to be typically two orders of magnitude less important as an atmospheric loss process than are the daytime OH radical reactions (although the relative importance of the NO_3 radical reactions may vary widely, depending on the OH and NO_3 radical concentrations[4]).

Similar to the OH radical reactions, these NO_3 radical reactions proceed via H-atom abstraction from the C–H bonds

$$NO_3 + RH \rightarrow HONO_2 + \dot{R}$$

For alkanes for which no experimental data presently exist, the overall 298 K rate constants and the distribution of initially formed alkyl radical isomers can be calculated by the use of $-CH_3$, $-CH_2-$ and $>CH-$ group rate constants and substituent factors, as discussed above for the corresponding OH radical reactions. Atkinson[4] derived group rate constants (in cm^3 molecule^{-1} s^{-1} units) at 298 K of $k_{prim} = 7.0 \times 10^{-19}$, $k_{sec} = 1.5 \times 10^{-17}$, and $k_{tert} = 8.2 \times 10^{-17}$, and substituent factors at 298 K of $F(-CH_3) = 1.00$ and $F(-CH_2-) = F(>CH-) = F(>C<) = 1.5$, and these can be used to calculate the room tem-

TABLE 2. Rate constants k at 298 K and temperature dependent parameters, $k = Ae^{-B/T}$, for the reaction of NO_3 radicals with alkanes (from Ref. 4 and Sec. 4.1)

Alkane	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	$10^{17} \times k$ (cm^3 molecule^{-1} s^{-1})
Methane			<0.1
Ethane			0.14[a]
Propane			1.7[a]
n-Butane	2.76	3279	4.59
2-Methylpropane	3.05	3060	10.6
n-Pentane			8.1
2-Methylbutane			16
n-Hexane			10.5
2,3-Dimethylbutane			43
Cyclohexane			13.5
n-Heptane			14.5
n-Octane			18.2
n-Nonane			24.1

[a]Estimated from group rate constants, see text.

perature rate constants for the NO_3 radical reactions with the alkanes and the distribution of alkyl radicals formed.

Reactions of Alkyl ($\dot{R}$) Radicals

The available kinetic and mechanistic data show that under tropospheric conditions the alkyl radicals react with O_2 to form an alkyl peroxy radical.

$$R^{\cdot} + O_2 \xrightarrow{M} RO_2^{\cdot}$$

The room temperature kinetic data presently available for O_2 addition to alkyl radicals are given in Table 3. For methyl and ethyl radicals at room temperature, these reactions are in the fall-off region at and below atmospheric pressure, and the IUPAC recommended values of k_o, k_∞ and F for these O_2 reactions are:[9] methyl, $k_o = 1.0 \times 10^{-30} (T/300)^{-3.3}$ cm^6 molecule^{-2} s^{-1} (200–300 K), $k_\infty = 2.2 \times 10^{-12} (T/300)$ cm^3 molecule^{-1} s^{-1} (200–300 K) and $F = 0.27$ at 298 K; ethyl, $k_o = 5.9 \times 10^{-29} (T/300)^{-3.8}$ cm^6 molecule^{-2} s^{-1} (200–300 K), $k_\infty = 7.8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (200–300 K) and $F = 0.54$ at 298 K. In addition, Xi *et al.*[12] have determined a rate constant of $k_\infty = 2.1 \times 10^{-12} (T/300)^{-2.1}$ cm^3 molecule^{-1} s^{-1} for the reaction of O_2 with the 2,2-dimethyl-1-propyl (neopentyl) radical over the temperature range 266–374 K.

At elevated temperatures, these reactions of alkyl radicals with O_2 have been assumed to also occur by an H-atom abstraction pathway, for example

$$^{\cdot}C_2H_5 + O_2 \rightarrow CH_2{=}CH_2 + HO_2$$

However, this is now recognized not to be a parallel reaction route, but to occur from the activated $RO_2^{\cdot}$ radical[13]

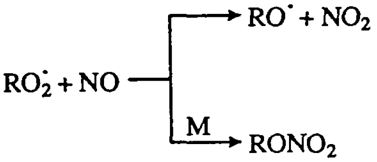
$$\begin{tikzcd} R^{\cdot} + O_2 \arrow[r, shift left] & \arrow[l, shift left] [RO_2^{\cdot}]^* \arrow[r] \arrow[d, "M"] & HO_2 + \text{alkene} \\ & RO_2^{\cdot} & \end{tikzcd}$$

At the high pressure limit, peroxy radical formation is therefore the sole reaction process. At 760 Torr and 298 K, the formation yield of $C_2H_4 + HO_2$ from the reaction of the ethyl radical with O_2 is $\sim 0.05\%$.[9]

Hence, for the alkyl radicals studied to date, under atmospheric conditions the reactions with O_2 proceed via addition to form a peroxy radical, with a room temperature rate constant of $\gtrsim 10^{-12}$ cm^3 molecule^{-1} s^{-1} at atmospheric pressure. For the smaller alkyl radicals these reactions are in the fall-off regime between second- and third-order kinetics, but are reasonably close to the high-pressure rate constant at 760 Torr of air. Under atmospheric conditions, these reactions with O_2 are the sole loss process of these alkyl radicals, and other reactions need not be considered.

Alkyl Peroxy ($RO_2^{\cdot}$) Radicals

As discussed above, these radicals are formed from the addition of O_2 to the alkyl radicals. Under tropospheric conditions, $RO_2^{\cdot}$ radicals react with NO (by two pathways),



with HO_2 radicals,

$$RO_2^{\cdot} + HO_2 \rightarrow ROOH + O_2$$

with $RO_2^{\cdot}$ radicals (either self-reaction or reaction with other alkyl peroxy radicals),

$$RO_2^{\cdot} + RO_2^{\cdot} \rightarrow \text{products}$$

and with NO_2.

TABLE 3. High-pressure rate constants k_∞ for the addition reactions of alkyl radicals ($\dot{R}$) with O_2 at around room temperature

$\dot{R}$	$10^{12} \times k_\infty$ (cm^3 molecule^{-1} s^{-1})	T (K)	Reference
Methyl	$2.2^{+2.2}_{-1.1}$	298	Atkinson *et al.*[9]
	1.0[a]	298	
Ethyl	$7.8^{+4.6}_{-2.9}$	298	Atkinson *et al.*[9]
	7.0[a]	298	
1-Propyl	8^{+5}_{-3}	298	Atkinson *et al.*[9]
2-Propyl	$11^{+11}_{-5.5}$	298	Atkinson *et al.*[9]
1-Butyl	7.5 ± 1.4	300	Lenhardt *et al.*[10]
2-Butyl	16.6 ± 2.2	300	Lenhardt *et al.*[10]
2-Methyl-2-propyl	23.4 ± 3.9	300	Lenhardt *et al.*[10]
2-Methyl-1-propyl	2.9 ± 0.7	298 ± 3	Wu and Bayes[11]
2,2-Dimethyl-1-propyl	2.4 ± 0.4	293 ± 1	Xi *et al.*[12]
Cyclopentyl	17 ± 3	293	Wu and Bayes[11]
Cyclohexyl	14 ± 2	298 ± 3	Wu and Bayes[11]

[a]Value at 760 Torr total pressure calculated from the fall-off expression.

$$RO_2^{\cdot} + NO_2 \xrightarrow{M} RO_2NO_2$$

The reaction pathways which occur depend on the NO to HO_2 and/or $RO_2^{\cdot}$ radical concentration ratios, and in the troposphere the reaction with NO is expected to dominate for NO concentrations ≳7 × 10^8 molecule cm^{-3}.[14,15] The reaction of $RO_2^{\cdot}$ radicals with NO_2 to form alkyl peroxynitrates is generally unimportant under lower tropospheric conditions due to the rapid thermal decomposition of the alkyl peroxynitrates back to reactants (see Sec. 2.6).

Reaction with NO

The recommended NASA[16] and IUPAC[9] room temperature rate constants for the reactions of alkyl peroxy radicals with NO and the absolute literature data of Peeters *et al.*[17] and Anastasi *et al.*[18] for the $(CH_3)_2CHO_2^{\cdot}$[17] and $(CH_3)_3CO_2^{\cdot}$[17,18] radicals are given in Table 4. Both the NASA[16] and IUPAC[9] evaluations recommend a rate constant for the reaction of $CH_3O_2^{\cdot}$ radicals with NO of $k(CH_3O_2^{\cdot} + NO) = 4.2 \times 10^{-12}\ e^{(180 \pm 180)/T}$ cm^3 molecule^{-1} s^{-1}, with $k(CH_3O_2^{\cdot} + NO) = 7.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K. The NASA and IUPAC recommended rate constants for the reaction of the $C_2H_5O_2^{\cdot}$ radical with NO[9,16] are both based on the measurement of Plumb *et al.*[19] Although no experimental temperature-dependent data are available, the NASA evaluation[16] recommends a temperature independent rate constant for the reaction of the $C_2H_5O_2^{\cdot}$ radical with NO. Furthermore, the IUPAC[9] recommendations for the reactions of the $CH_3CH_2CH_2O_2^{\cdot}$ and $(CH_3)_2CHO_2^{\cdot}$ radicals with NO assume that the overall rate constants for these reactions are identical to that for the corresponding $C_2H_5O_2^{\cdot}$ radical reaction. Recently, however, Peeters *et al.*[17] have measured significantly lower rate constants for the reactions of the $(CH_3)_2CHO_2^{\cdot}$ and $(CH_3)_3CO_2^{\cdot}$ radicals with NO at 290 K of (5.0 ± 1.2) × 10^{-12} cm^3 molecule^{-1} s^{-1} and (4.0 ± 1.1) × 10^{-12} cm^3 molecule^{-1} s^{-1}, respectively. Unfortunately, no measurements for the $CH_3O_2^{\cdot}$ or $C_2H_5O_2^{\cdot}$ radical reactions were carried out by Peeters *et al.*[17] for comparison with the previous literature data.

Hence, it is recommended that the rate constant for the reaction of the $CH_3O_2^{\cdot}$ radical with NO is given by

$$k(CH_3O_2^{\cdot} + NO) = 4.2 \times 10^{-12}\ e^{180/T}\ cm^3\ molecule^{-1}\ s^{-1}$$
$$= 7.6 \times 10^{-12}\ cm^3\ molecule^{-1}\ s^{-1} \text{ at 298 K}$$

and that the overall rate constants for the higher ($\geq C_2$) alkyl peroxy radicals with NO are identical, with

$$k(RO_2^{\cdot} + NO) = 4.9 \times 10^{-12}\ e^{180/T}\ cm^3\ molecule^{-1}\ s^{-1}$$
$$= 8.9 \times 10^{-12}\ cm^3\ molecule^{-1}\ s^{-1} \text{ at 298 K.}$$

The reaction of $CH_3O_2^{\cdot}$ with NO has been shown to proceed primarily by[9,16,20,21]

$$CH_3O_2^{\cdot} + NO \rightarrow CH_3O^{\cdot} + NO_2$$

and Plumb *et al.*[19] have shown from direct measurements that the reaction of $C_2H_5O_2^{\cdot}$ radicals with NO forms NO_2 with a yield of ≥0.80.

However, for the larger alkyl peroxy radicals, Darnall *et al.*,[22] Takagi *et al.*,[23] Atkinson *et al.*[24–27] and Harris and Kerr[28] have shown that the reaction pathway to form the alkyl nitrate becomes important. At room temperature and atmospheric pressure, the product data of Atkinson *et al.*[24–27] and Harris and Kerr[28] show that for the secondary alkyl peroxy radicals the rate constant ratio $k_a/(k_a + k_b)$, where k_a and k_b are the rate constants for the reaction pathways (a) and (b), respectively,

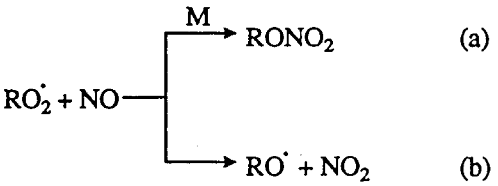


TABLE 4. Absolute room temperature rate constants for the reactions of $R\dot{O}_2$ radicals with NO

$R\dot{O}_2$	$10^{12} \times k$ (cm^3 $molecule^{-1}$ s^{-1})	T (K)	Reference
$CH_3\dot{O}_2$	7.6	298	DeMore *et al.*;[16] Atkinson *et al.*[9]
$C_2H_5\dot{O}_2$	8.9	298	DeMore *et al.*;[16] Atkinson *et al.*[9]
$CH_3CH_2CH_2\dot{O}_2$	8.9[a]	298	Atkinson *et al.*[9]
$(CH_3)_2CH\dot{O}_2$	8.9[a]	298	Atkinson *et al.*[9]
	5.0 ± 1.2	290	Peeters *et al.*[17]
$(CH_3)_3C\dot{O}_2$	> 1	298	Anastasi *et al.*[18]
	4.0 ± 1.1	290	Peeters *et al.*[17]

[a] At 760 Torr total pressure (see text).

increases monotonically with the carbon number of the $RO_2^{\cdot}$ radical. Furthermore, for a given alkyl peroxy radical the rate constant ratio $k_a/(k_a + k_b)$ is pressure- and temperature-dependent, increasing with increasing pressure and with decreasing temperature.[25,27,28]

The pressure and temperature-dependent rate constant ratios k_a/k_b for secondary alkyl peroxy radicals[24–27] are fit by the fall-off expression[29]

$$\frac{k_a}{k_b} = \left(\frac{Y_o^{300}\,[M](T/300)^{-m_o}}{1 + \dfrac{Y_o^{300}\,[M](T/300)^{-m_o}}{Y_\infty^{300}\,(T/300)^{-m_\infty}}} \right) F^z \qquad \text{(II)}$$

where

$$z = \left\{ 1 + \left[\log\left(\frac{Y_o^{300}\,[M](T/300)^{-m_o}}{Y_\infty^{300}\,(T/300)^{-m_\infty}} \right) \right]^2 \right\}^{-1}$$

and $Y_o^{300} = \alpha\, e^{\beta n}$, n is the number of carbon atoms in the alkyl peroxy radical, and α and β are constants. The most recent evaluation[29] of the experimental data of Atkinson *et al.*[24–27] leads to $Y_\infty^{300} = 0.826$, $\alpha = 1.94 \times 10^{-22}$ cm^3 $molecule^{-1}$, $\beta = 0.97$, $m_o = 0$, $m_\infty = 8.1$ and $F = 0.411$. The experimental data of Harris and Kerr[28] for the heptyl nitrates formed from the OH radical reaction with n-heptane at 730 Torr total pressure over the temperature range 253–325 K are in good agreement with predictions from this equation.

Although the rate constant ratios k_a/k_b at room temperature and atmospheric pressure for secondary $RO_2^{\cdot}$ radicals depend primarily on the number of carbon atoms in the $RO_2^{\cdot}$ molecule, the corresponding rate constant ratios for primary and tertiary $RO_2^{\cdot}$ radicals are significantly lower, by a factor of ~2.5 for primary and a factor of ~3.3 for tertiary alkyl peroxy radicals.[27,29] Accordingly,

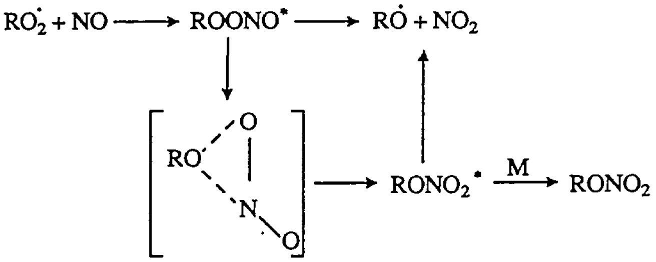
$$(k_a/k_b)_{\text{primary}} \approx 0.40\ (k_a/k_b)_{\text{secondary}}$$

and

$$(k_a/k_b)_{\text{tertiary}} \approx 0.3\ (k_a/k_b)_{\text{secondary}}.$$

It should be noted that the use of the above equations to calculate rate constant ratios k_a/k_b is solely applicable to alkyl peroxy radicals. Thus, although no definitive data exist, computer modeling data suggest[1] that the rate constant ratios for δ-hydroxyalkyl peroxy radicals (for example, the $RCH(OH)CH_2CH_2CH(O\dot{O})R_1$ radical) are much lower than those for the corresponding alkyl peroxy radicals.

These reactions of $RO_2^{\cdot}$ radicals with NO are postulated[25] to occur by



and it is therefore expected that the overall rate constant is independent of total pressure, but that the rate constant ratio k_a/k_b is pressure (and temperature) dependent, as observed.

Reaction with NO_2

The reactions of alkyl peroxy radicals with NO_2 all proceed via combination to yield the corresponding peroxynitrates[9]

$$RO_2^{\cdot} + NO_2 \overset{M}{\rightarrow} ROONO_2$$

The IUPAC recommendations[9] for the values of k_0, k_∞, F and the rate constant, k, at 298 K and 760 Torr total pressure of air for the reactions of NO_2 with $CH_3\dot{O}_2$ and $C_2H_5\dot{O}_2$ radicals are given in Table 5. The rate constant at 298 K and 760 Torr total pressure of air calculated from the IUPAC recommendation for the reaction of the $CH_3O_2^{\cdot}$ radical with NO_2 (Table 5) is in excellent agreement with that of $(4.4 \pm 0.4) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} measured by Bridier *et al.*[30] at 298 ± 1 K and 760 Torr total pressure of air. These reactions are in the fall-off

TABLE 5. Recommended[a] rate constant parameters k_0, k_∞ and F for the gas-phase reactions of $R\dot{O}_2$ radicals with NO_2, together with calculated rate constants at 298 K and 760 Torr total pressure

$R\dot{O}_2$	k_0 (cm^6 molecule^{-2} s^{-1})	k_∞ (cm^3 molecule^{-1} s^{-1})	F(298 K)	$10^{12} \times k$ (298 K, 760 Torr)
$CH_3\dot{O}_2$	$2.5 \times 10^{-30}(T/300)^{-5.5}$	7.5×10^{-12}	0.4	4.1
$C_2H_5\dot{O}_2$	$1.3 \times 10^{-29}(T/300)^{-6.2}$	8.8×10^{-12}	0.31	6.1

[a] From Atkinson *et al.*[9]

regime between second- and third-order kinetics at and below atmospheric pressure at room temperature, and this is in agreement with the thermal decomposition data for the corresponding peroxynitrates CH_3OONO_2 and $C_2H_5OONO_2$.[9]

Absolute rate constants have also been obtained at room temperature for the reactions of NO_2 with $(CH_3)_2CH\dot{O}_2$[31] and $(CH_3)_3C\dot{O}_2$[18] radicals, of $(5.65 \pm 0.17) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} and $\geq 5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, respectively. The rate constant of Adachi and Basco[31] for the $(CH_3)_2CH\dot{O}_2$ radicals is anticipated to be erroneously low, by analogy with the rate constant of Adachi and Basco[32] for reaction of the $C_2H_5\dot{O}_2$ radical with NO_2, for which they measured a rate constant of $(1.25 \pm 0.07) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at room temperature, independent of total pressure over the range 44–676 Torr.[32]

Based upon the data for the $CH_3\dot{O}_2$ and $C_2H_5O_2\cdot$ radicals, it is recommended that the limiting high-pressure rate constants for the $\geq C_2$ alkyl peroxy radicals are identical to that for the $C_2H_5\dot{O}_2$ radical,

$$k(R\dot{O}_2 + NO_2) = 9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} ,$$

approximately independent of temperature over the range ~250–350 K. This recommendation is consistent with the kinetic data of Zabel *et al.*[33] for the thermal decompositions of a series of alkyl peroxynitrates ($ROONO_2$, where R = CH_3, C_2H_5, C_4H_9, C_6H_{13} and C_8H_{17}) at 253 K and 600 Torr total pressure of N_2, which showed that the thermal decomposition rates for the C_2–C_8 alkyl peroxynitrates were reasonably similar. In particular, the thermal decomposition rates for the C_4–C_8 alkyl peroxynitrates were within ±30% of the calculated high pressure thermal decomposition rate of $C_2H_5OONO_2$.[33] The pressures at which these $R\dot{O}_2$ + NO_2 reactions will exhibit kinetic fall-off behavior from the second- to third-order regime will decrease as the size of the $RO_2\cdot$ radical increases, and it is expected that at room temperature and 760 Torr total pressure the $\geq C_3$ alkyl peroxy radical reactions are close to the limiting high-pressure region. The thermal decomposition reactions of the alkyl peroxynitrates are discussed in Sec. 2.6.

Reaction with HO_2 Radicals

Relatively few data exist for the reactions of HO_2 radicals with alkyl peroxy radicals. Absolute rate constants have been determined only for the $CH_3\dot{O}_2$, $C_2H_5\dot{O}_2$, cyclopentylperoxy and cyclohexylperoxy radicals. The Arrhenius expressions recommended by the IUPAC panel for the $CH_3\dot{O}_2$ and $C_2H_5\dot{O}_2$ reactions are[9]: $k(CH_3\dot{O}_2 + HO_2) = 3.8 \times 10^{-13} e^{780/T}$ cm^3 molecule^{-1} s^{-1} (5.2×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K); and $k(C_2H_5\dot{O}_2 + HO_2) = 6.5 \times 10^{-13} e^{650/T}$ cm^3 molecule^{-1} s^{-1} (5.8×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K). For the reactions of the cyclopentylperoxy and cyclohexylperoxy radicals with the HO_2 radical, Rowley *et al.*[34] have measured rate constants over the temperature range 249–364 K of $(2.1 \pm 1.3) \times 10^{-13} e^{(1323 \pm 185)/T}$ cm^3 molecule^{-1} s^{-1} and $(2.6 \pm 1.2) \times 10^{-13} e^{(1245 \pm 124)/T}$ cm^3 molecule^{-1} s^{-1}, respectively. At 298 K, the rate constants for these two reactions are both $(1.7-1.8) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.[34]

Based upon the recommendations[9] for the $CH_3\dot{O}_2$ and $C_2H_5\dot{O}_2$ reactions and the rate constants for the cyclopentylperoxy and cyclohexylperoxy radicals,[34] a rate constant at 298 K for the reactions of HO_2 radicals with $RO_2\cdot$ radicals of

$$k(HO_2 + R\dot{O}_2) = 1.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

is indicated, with a likely overall uncertainty of a factor of 2. The temperature dependencies of the reactions studied to date are negative. A mean value of $B = -1000$ K is chosen in the expression $k = A\,e^{-B/T}$ to yield the recommendation of

$$k(HO_2 + R\dot{O}_2) = 3.5 \times 10^{-13} e^{1000/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The IUPAC recommendations[9] should be used for the reactions of the $CH_3\dot{O}_2$ and $C_2H_5\dot{O}_2$ radicals with HO_2. The reaction of the $HOCH_2CH_2OO^{\cdot}$ radical with the HO_2 radical also has a rate constant of ~1×10^{-11} cm^3 molecule^{-1} s^{-1} at room temperature (see Sec. 2.2).

The reactions of the $CH_3\dot{O}_2$, $C_2H_5\dot{O}_2$, cyclopentylperoxy and cyclohexylperoxy radicals with the HO_2 radical have been shown to proceed by H-atom abstraction to form the hydroperoxide[34–37]

$$R\dot{O}_2 + HO_2 \rightarrow RO_2H + O_2$$

Reaction with $R\dot{O}_2$ Radicals

Numerous studies of the self-reactions of $R\dot{O}_2$ radicals have been carried out.[38,39] These reactions can proceed by the three pathways

$$2\ R_1R_2CHO_2^{\cdot} \rightarrow 2\ R_1R_2CHO^{\cdot} + O_2 \qquad \text{(a)}$$

$$2\ R_1R_2CHO_2^{\cdot} \rightarrow R_1R_2CHOH + R_1R_2CO + O_2 \qquad \text{(b)}$$

$$2\ R_1R_2CHO_2^{\cdot} \rightarrow R_1R_2CHOOCHR_1R_2 + O_2 \qquad \text{(c)}$$

with pathway (b) not being accessible for tertiary $RO_2^{\cdot}$ radicals. At around room temperature, product studies of the self-reactions of $CH_3\dot{O}_2$,[40–42] $C_2H_5O_2^{\cdot}$[43,44] and $(CH_3)_3C\dot{O}_2$ radicals[45] show no evidence for the occurrence of reaction pathway (c). In the following discussion, pathway (c) is taken to be of negligible importance and only pathways (a) and (b) are assumed to occur.

The IUPAC panel recommendations[9] for the overall rate constants ($k = k_a + k_b$) and the rate constant ratio k_a/k for the $\leqslant C_3$ $RO_2^{\cdot}$ radicals are given in Table 6, together with the literature data for the $\geqslant C_4$ $R\dot{O}_2$ radicals. For the self-reaction of the *tert*-butyl peroxy radical, the rate constants reported by Anastasi *et al.*,[18] Kirsch *et al.*[48] and Lightfoot *et al.*[46] at room temperature and above are in good agreement.[46] Because of the wider temperature range studied, the Arrhenius expression of Lightfoot *et al.*[46] is preferred. Although an Arrhenius expression is given in Table 6 for the self-reaction of neopentyl peroxy radicals,[46] the rate constants measured by Lightfoot *et al.*[46] exhibit non-Arrhenius behavior (note that the three parameter expression of $k = 3.02 \times 10^{-19}$ $(T/298)^{9.46}$ $e^{4260/T}$ cm^3 molecule^{-1} s^{-1} cited by Lightfoot *et al.*[46] does not fit their data, and the expression $k = 3.02 \times 10^{-19}$ $(T/298)^{9.46}$ $e^{4530/T}$ cm^3 molecule^{-1} s^{-1} appears to be a better fit). The overall rate constant k and branching ratio k_a/k determined by Wallington *et al.*[49] at 297 K for the self-reaction of neopentyl peroxy radicals are in excellent agreement with the more extensive measurements of Lightfoot *et al.*[46]

The Arrhenius expressions for k_a/k are only applicable over the cited temperature ranges, since over extended temperature ranges the calculated values exceed unity. The more correct temperature-dependent format uses the ratio k_a/k_b (see, for example, Carter and Atkinson[29] for alkyl nitrate formation from the $RO_2^{\cdot}$ + NO reactions), and Lightfoot *et al.*[46] have derived the rate constant ratio $k_a/k_b = 197\ e^{-(1658 \pm 98)/T}$ for the self-reaction of neopentyl peroxy radicals over the temperature range 248–373 K.

For all of the alkyl peroxy radicals for which data are available and for which both reaction pathways (a) and (b) are allowed, the reaction pathway (a) to yield the alkoxy radicals increases in importance as the temperature increases (Table 6 and Lightfoot *et al.*[46]), with this pathway accounting for 30–60% of the overall reaction at 298 K. For the self-recombination reaction of $CH_3O_2^{\cdot}$ radicals, Kan and Calvert[50] and Kurylo *et al.*[51] have shown that, in contrast to the combination reaction of HO_2 radicals,[9] H_2O vapor has no effect on the measured room temperature rate constant.

In addition to these $RO_2^{\cdot}$ self-combination reaction studies, rate constants have been obtained for the reac-

TABLE 6. Rate constants, k, at 298 K and temperature-dependent parameters, $k = A\,e^{-B/T}$, for the gas-phase combination reactions of $R\dot{O}_2$ radicals

$R\dot{O}_2 + R\dot{O}_2$	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	$10^{13} \times k$ (298 K) (cm^{-3} molecule^{-1}s^{-1})	k_a/k	Reference
$CH_3\dot{O}_2 + CH_3\dot{O}_2$	0.11	-365 ± 200	$3.7^{+1.2}_{-0.9}$	$5.4\ e^{-870/T}$	Atkinson *et al.*[9]
$C_2H_5\dot{O}_2 + C_2H_5\dot{O}_2$	0.098	110^{+300}_{-100}	$0.68^{+0.22}_{-0.17}$	0.62 ± 0.10 (298 K)	Atkinson *et al.*[9]
$CH_3CH_2CH_2\dot{O}_2 + CH_3CH_2CH_2\dot{O}_2$			3^{+9}_{-2}		Atkinson *et al.*[9]
$(CH_3)_3CCH_2\dot{O}_2 + (CH_3)_3CCH_2\dot{O}_2$	0.0016	-1961 ± 100	10.4 ± 0.9	0.40 (298 K)	Lightfoot *et al.*[46]
$(CH_3)_2CH\dot{O}_2 + (CH_3)_2CH\dot{O}_2$	1.6	2200 ± 300	$0.010^{+0.010}_{-0.005}$	$2.0\ e^{-380/T}$ (300–400 K)	Atkinson *et al.*[9]
cyclo-$C_6H_{11}\dot{O}_2$ + cyclo-$C_6H_{11}\dot{O}_2$	0.074	274	0.284 ± 0.016	0.29 ± 0.02 (298 K)	Rowley *et al.*[47]
$(CH_3)_3C\dot{O}_2 + (CH_3)_3C\dot{O}_2$	10	3894	0.00021		Lightfoot *et al.*[46]
$CH_3\dot{O}_2 + (CH_3)_3C\dot{O}_2$	0.37	1420	0.032	$5.9\ e^{-1130/T}$ (313–393 K)	Osborne and Waddington[45]
$(CH_3)_3CCH_2\dot{O}_2 + (CH_3)_3C\dot{O}_2$			0.3 ± 0.1 (373 K)		Lightfoot *et al.*[46]
$CH_3\dot{O}_2 + CH_3C\dot{O}_3$			110	0.5 (298 K)	Atkinson *et al.*[9]

tions of the $CH_3\dot{O}_2$ radical with $(CH_3)_3CO_2^{\cdot}$[45,52] and $CH_3C(O)O_2\cdot$ radicals[53,54] and for the reaction of the $(CH_3)_3CO_2\cdot$ radical with the $(CH_3)_3CCH_2O_2\cdot$ radical.[46] The rate data obtained or recommended[9] are given in Table 6, with those of Osborne and Waddington[45] being used for the temperature-dependent expressions k and k_a/k given in Table 6 for the $CH_3O_2\cdot + (CH_3)_3CO_2\cdot$ reaction. For the reaction of the $CH_3\dot{O}_2$ radical with $CH_3CO_3^{\cdot}$ radicals, the two pathways

$$CH_3\dot{O}_2 + CH_3C\dot{O}_3 \rightarrow CH_3\dot{O} + CH_3C\dot{O}_2 + O_2 \qquad (a)$$

$$CH_3\dot{O}_2 + CH_3C\dot{O}_3 \rightarrow CH_3COOH + HCHO + O_2 \qquad (b)$$

are of approximately equal importance at 298 K.[9]

In the absence of further experimental data for a wider variety of $R\dot{O}_2$ radicals, the following rate constants are recommended as being reasonably representative for primary, secondary and tertiary alkyl peroxy radicals at 298 K:

$$k(\text{primary } R\dot{O}_2 + \text{primary } R\dot{O}_2) \sim 2.5 \times 10^{-13}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

$$k(\text{secondary } R\dot{O}_2 + \text{secondary } R\dot{O}_2) \sim 5 \times 10^{-15}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

$$k(\text{tertiary } R\dot{O}_2 + \text{tertiary } R\dot{O}_2) \sim 2 \times 10^{-17}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1},$$

all with uncertainties at 298 K of at least a factor of 5. For the self-reactions of primary and secondary $R\dot{O}_2$ radicals, the rate constant ratio $k_a/k \sim 0.45 \pm 0.2$ at 298 K. For the self-reactions of tertiary $RO_2\cdot$ radicals, only reaction pathway (a) can occur.

For the reactions of non-identical alkyl peroxy radicals,

$$R_1\dot{O}_2 + R_2\dot{O}_2 \rightarrow \text{products}$$

the sparse data set indicates that the rate constants are approximately given by the geometric mean equation,[55] with $k_{12} \sim 2(k_1k_2)^{0.5}$, where k_{12} is the rate constant for the $R_1O_2\cdot + R_2O_2\cdot$ reaction and k_1 and k_2 are the rate constants for the self-reactions of $R_1O_2\cdot$ and $R_2O_2\cdot$ radicals, respectively. Clearly, a much wider data base is required concerning the reactions of the HO_2 radical with alkyl peroxy ($R\dot{O}_2$) radicals and, to a lesser extent, for cross-combination reactions of $R\dot{O}_2$ radicals.

Alkoxy ($R\dot{O}$) Radical Reactions

Under atmospheric conditions the major alkoxy radical removal processes involve reaction with O_2, unimolecular decomposition and unimolecular isomerization (see, for example, Carter and Atkinson[1] and Atkinson and Carter[56]). For the case of the 2-pentoxy radical, these reactions are shown in Reaction Scheme (1) below where the isomerization reaction proceeds by a (generally) 6-member ring transition state. In addition, reactions with NO and NO_2, though minor under most conditions, must be considered.

Reaction with O_2. Absolute rate constants for the reactions of alkoxy radicals with O_2 have been determined for $CH_3\dot{O}$,[57–60] $C_2H_5\dot{O}$ [58,61] and $(CH_3)_2CH\dot{O}$ [62] radicals, and the IUPAC recommendations[9] for the rate constants for these reactions are given in Table 7.

Based on the recommended rate constants for the reactions of $C_2H_5\dot{O}$ and $(CH_3)_2CH\dot{O}$ radicals with O_2, it is recommended that for the primary $(RCH_2\dot{O})$ and secondary $(R_1R_2CH\dot{O})$ alkoxy radicals formed from the alkanes

$$k(RCH_2\dot{O} + O_2) = 6.0 \times 10^{-14}\, e^{-550/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$
$$= 9.5 \times 10^{-15}\ \text{cm}^3\ \text{molecule s}^{-1} \text{ at 298 K,}$$

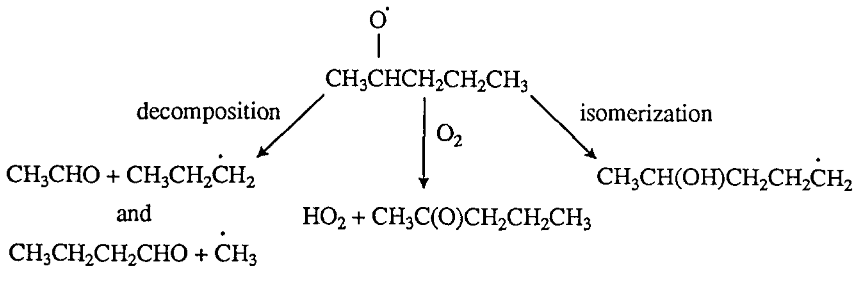
and

$$k(R_1R_2CH\dot{O} + O_2) = 1.5 \times 10^{-14}\, e^{-200/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$
$$= 8 \times 10^{-15}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \text{ at 298 K.}$$

Baldwin *et al.*[63] and Balla *et al.*[62] have derived relationships between the rate constants for the reactions of the alkoxy radicals with O_2 and the exothermicities of these reactions, and such a relationship has also been suggested by Atkinson and Carter.[56] Based on the three reactions for which recommendations are given (Table 7), a unit-weighted least-squares analysis leads to (ΔH_{O_2} in kcal mol^{-1})

$$k(R\dot{O} + O_2) = 1.3 \times 10^{-19} n\, e^{-(0.32\Delta H_{O_2})}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \qquad \text{(I)}$$

at 298 K, where n is the number of abstractable H atoms in the alkoxy radical. While this equation differs from those of Baldwin *et al.*[63] ($k(RO^{\cdot} + O_2) = 6.1 \times 10^{-22}\, n$



Reaction Scheme (1)

TABLE 7. Recommended 298 K rate constants and temperature dependent expressions, $k = Ae^{-B/T}$, for the reactions of O_2 with alkoxy ($R\dot{O}$) radicals[a]

$R\dot{O}$	A (cm^3 molecule^{-1} s^{-1})	B (K)	k(298 K) (cm^3 molecule^{-1} s^{-1})
$CH_3\dot{O}$	7.2×10^{-14}	1080	1.9×10^{-15}
$CH_3CH_2\dot{O}$	6.0×10^{-14}	550	9.5×10^{-15}
$(CH_3)_2CH\dot{O}$	1.5×10^{-14}	200	8×10^{-15}

[a] From Atkinson *et al.*[9]

$e^{-(0.49\Delta H_{O_2})}$ cm^3 molecule^{-1} s^{-1} or $3.3 \times 10^{-21} n\, e^{-(0.42\Delta H_{O_2})}$ cm^3 molecule^{-1} s^{-1} at 298 K) and Balla *et al.*[62] ($k(RO^{\bullet} + O_2) = 1.0 \times 10^{-22}\, n e^{-0.51\Delta H_{O_2}}$ cm^3 molecule^{-1} s^{-1} at 298 K), these expressions give reasonably similar rate constants for values of $\Delta H_{O_2} \sim -32$ kcal mol^{-1} (corresponding to the $C_2H_5O^{\bullet}$ radical). At 760 Torr total pressure of air and 298 K, Eq. (I) leads to

$$k_{O_2}[O_2] = 0.67\, n\, e^{-(0.32\Delta H_{O_2})}\ \mathrm{s}^{-1} \qquad \text{(II)}$$

The above recommendations for primary and secondary alkoxy radicals are slightly different than those recommended by Atkinson.[2] The rate constants for the reactions of O_2 with substituted alkoxy radicals formed from, for example, the alkenes after initial OH radical reaction (for example, the $HOCH_2CH_2\dot{O}$ radical) are discussed in the respective sections below.

Alkoxy Radical Decompositions. The gas-phase decomposition reactions of alkoxy radicals formed from the OH radical-initiated reactions of alkanes have been the subject of several previous reviews and discussions.[1,2,56,63–68] These previous articles have derived relationships between the measured Arrhenius activation energies for the alkoxy radical decompositions (E_d) and the heats of the decomposition reaction (ΔH_d), with the Arrhenius pre-exponential factors for these decomposition reactions all being of a similar magnitude. Most of these relationships have assumed, or shown, that a single relationship between E_d and ΔH_d exists, with

$$E_d = a + b\Delta H_d$$

irrespective of the structure of the alkoxy radical or the leaving alkyl group.[1,2,63,65,66] Choo and Benson,[67] however, presented data indicating that the parameter "a" in the above relationship depends on the leaving alkyl group, with this parameter decreasing monotonically along the alkyl leaving-group series $\dot{C}H_3$, $\dot{C}_2H_5$, $(CH_3)_2\dot{C}H$ and $(CH_3)_3\dot{C}$.

Many of the rate constant data for the alkoxy radical decomposition reactions have been determined relative to the alkoxy radical combination reaction with NO[65,66,68]

$$R\dot{O} + NO \xrightarrow{M} RONO$$

and changes in the $R\dot{O}$ + NO rate constants and, especially, in the heats of the alkoxy radical reactions (ΔH_d) over the past decade makes a reanalysis necessary. Using recent data for the alkyl radical heats of formation,[9,69–72] the recommended Arrhenius parameters for selected alkoxy radical decompositions [those of $CH_3\dot{O}$, $C_2H_5\dot{O}$, $(CH_3)_2CH\dot{O}$, $CH_3CH_2CH(\dot{O})CH_3$, $(CH_3)_3C\dot{O}$ and $CH_3CH_2C(CH_3)_2\dot{O}$ radicals][68,73,74] and the present recommendation for the temperature-dependent rate constants for the $R\dot{O}$ + NO reactions of $k_\infty(R\dot{O} + NO) = 2.3 \times 10^{-11}\, e^{150/T}$ cm^3 molecule^{-1} s^{-1} (see below), then

$$E_d = 11.2 + 0.79\Delta H_d,$$

with the energies in kcal mol^{-1}, and

$$A_d = (2 \times 10^{14}\ \mathrm{d})\ \mathrm{s}^{-1}$$

where d is the reaction path degeneracy for the alkoxy radical decomposition reactions.

This relationship, however, is derived from only a few alkoxy radical decomposition reactions, and the recent data of Lightfoot *et al.*[46] for the decomposition and reaction with O_2 of the 2,2-dimethyl-1-propoxy $[(CH_3)_3CCH_2\dot{O}]$ radical shows that the above relationship between E_d and ΔH_d does not hold for this particular alkoxy radical. Specifically, Lightfoot *et al.*[46] obtained a rate constant ratio of $k_d/k_{O_2} = (2.0 \pm 0.2) \times 10^{20}$ molecule cm^{-3} at 298 K, consistent with the lower limit derived by Wallington *et al.*[49] With a value of $k_{O_2} = 4.7 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} calculated from Eq. (I) with $\Delta H_{O_2} = -30.6$ kcal mol^{-1} (as obtained from group additivity calculations), this leads to $k_d = 9.4 \times 10^5$ s^{-1} at 298 K, in close agreement with the value derived by Lightfoot *et al.*[46] Since $\Delta H_d = 9.8$ kcal mol^{-1} from group additivity calculations (which can be compared with the heat of reaction of 8.2 ($\pm$2.1) kcal mol^{-1} calculated by Lightfoot *et al.*[46]), the expressions given above would predict that $k_d \sim 2$ s^{-1}, some six orders of magnitude in error.

It is therefore clear that the alkoxy radicals formed from the OH radical reactions with the alkenes and ethers[56] are not the only alkoxy radicals for which the rates of the various reaction processes cannot be accurately predicted.

The empirical method of assessing the relative importance of decomposition versus O_2 reaction for alkoxy radicals proposed by Atkinson and Carter[56] is thus extended further and an attempt is made to place it on a numerical basis. Figure 1 shows a plot of the values of ΔH_d and ΔH_{O_2}

for the alkoxy radicals dealt with by Atkinson and Carter,[56] plus the $(CH_3)_3CCH_2\dot{O}$ radical formed from neopentane, with the dominant reaction pathways at 298 K and atmospheric pressure of air being denoted by (O) for decomposition, (●) for O_2 reaction, and (Δ) for those cases where both decomposition and O_2 reaction are observed to occur at 298 K and 760 Torr total pressure of air. The line drawn separates dominant decomposition from dominant O_2 reaction, and is defined by the data for the $HOCH_2CH_2\dot{O}$ and $CH_3CH_2CH(\dot{O})CH_3$ radicals, with allowance being made for the fact that the decomposition/O_2 reaction ratios for these alkoxy radicals differ from unity at 298 K and 760 Torr total pressure of air. Within the uncertainties of the heats of reaction for the $(CH_3)_3CCH_2O^{\bullet}$ radical, the position of this radical on the plot is consistent with decomposition and O_2 reaction being competitive.

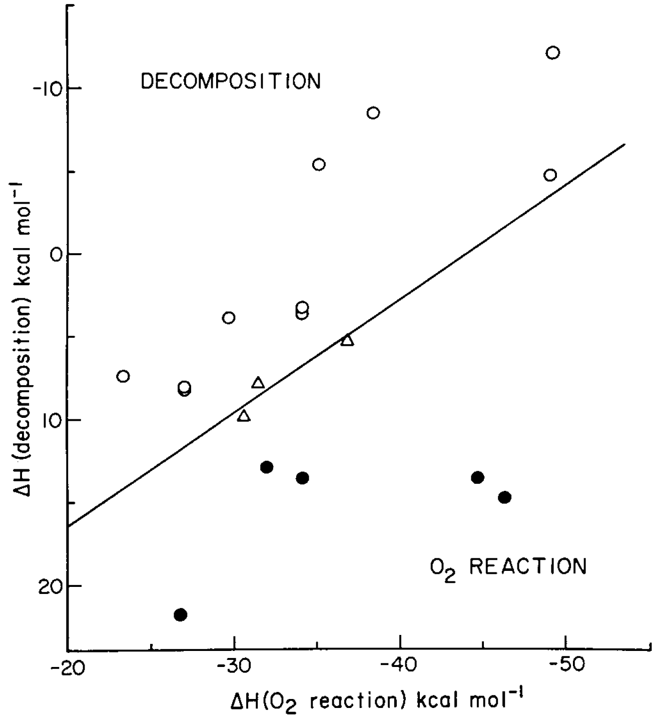


FIG. 1. Plot of the values of ΔH(decomposition) against ΔH(O_2 reaction) for a series of alkoxy radicals. (O) Alkoxy radicals reacting dominantly by decomposition at 298 K and atmospheric pressure of air; (●) alkoxy radicals reacting dominantly by reaction with O_2 at 298 K and atmospheric pressure of air; (Δ) alkoxy radicals reacting by both decomposition and O_2 reaction at 298 K and atmospheric pressure of air; (—) line separating dominant decomposition from O_2 reaction.

The boundary line is given by

$$\Delta H_d^{line} = 30.3 + 0.69\Delta H_{O_2}$$

with the energies being in kcal mol^{-1}. By definition, on this line $k_d^{line} = k_{O_2}[O_2]$. For most alkoxy radicals, the values of ΔH_d and ΔH_{O_2} are such that the alkoxy radical does not fall on this boundary line. By making the approximate (and probably incorrect) assumption that,

$$k_d/k_d^{line} = e^{-[0.79(\Delta H_d - 30.3 - 0.69\Delta H_{O_2}) \times 10^3/RT]}$$

then

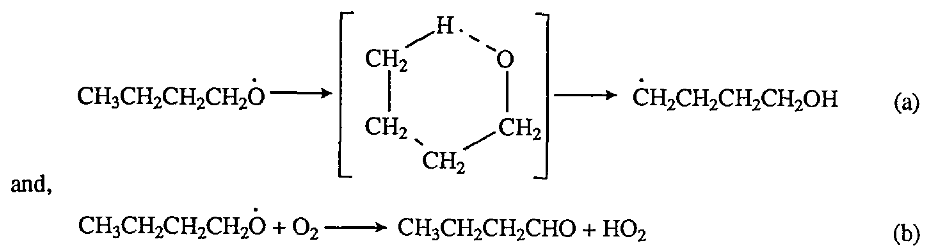
$$k_d = \{2.4 \times 10^{17}\, nd\, e^{(0.60\Delta H_{O_2} - 1.33\Delta H_d)}\}\ s^{-1} \text{ at } 298\ K, \quad (III)$$

where the energies are again in kcal mol^{-1}.

These two expressions for $k_{O_2}[O_2]$ and k_d at 298 K and atmospheric pressure of air (Eqs. (II) and (III), respectively) appear to give semi-quantitatively correct data for the alkoxy radicals, and allow the alkoxy radical decompositions and reactions with O_2 to be (semi)-quantitatively compared with the alkoxy radical isomerizations (see below). With regards to the situation at temperatures other than 298 K, as an approximation it is reasonable to use a temperature independent rate constant for the O_2 reaction (but of course the correct O_2 concentration must be taken into account) [a temperature dependence of 1000 K corresponds to a variation of the rate constant by a factor of 2.3 over the temperature range 250–300 K]. The value of k_d at 298 K can be combined with a pre-exponential factor of $A_d = (2 \times 10^{14}\ d)\ s^{-1}$ to derive approximate values of k_d at other temperatures. Clearly, this postulated, and empirical, method for assessing the relative importance of the various alkoxy radical reactions under atmospheric conditions needs to be tested against a wider data base.

The alkoxy radical decomposition reactions may be in the fall-off region between first-order and second-order kinetics at room temperature and atmospheric pressure.[63,65,74–77] For the two alkoxy radicals for which pressure dependent decomposition rate constants have been observed [2-propoxy[77] and 2-methyl-2-propoxy (*t*-butoxy)[74–76]], the rate constants at room temperature and atmospheric pressure are reasonably close to the limiting high pressure values[75–77] [see also Table II in Baldwin *et al.*,[63] which predicts that the corrections for fall-off behavior are small for C_3 and higher alkoxy radicals, being less than a factor of 2 at room temperature and atmospheric pressure].

Alkoxy Radical Isomerizations. No direct experimental data are available, but isomerization rate constants have been estimated initially by Carter *et al.*[78] and subsequently, and in more detail, by Baldwin *et al.*[63] The major relevant experimental data available concern measurements of the rate constant ratio for the reactions shown in Reaction Scheme (2), obtained from product yields determined in *n*-butane-NO_x-air,[79] HONO-*n*-butane-air[80] and *n*-butyl nitrite-air[81] photolyses. Rate constant ratios of k_a/k_b of 1.65×10^{19} molecule cm^{-3} at 303 K,[79] 1.5×10^{19} molecule cm^{-3} at 295 K[80] and 1.9×10^{19} molecule cm^{-3} at 298 ± 2 K[81] were derived from these studies. These rate constant ratios are in good agreement, with an average value of $k_a/k_b = 1.7 \times 10^{19}$ molecule cm^{-3} at ~299 K. Using the rate constant estimated as described above for reaction (b), k_{O_2}, this leads to a rate constant of



Reaction Scheme (2)

k_a = 6.7 × 10^4 s^{-1} at 299 K, a factor of ~8 lower than the estimate of Baldwin *et al.*[63] Considering the large uncertainties in the estimation technique, this estimate is probably in fairly good agreement with the experimental data. However, the data of Dóbé *et al.*[82] for the isomerization of the 2-pentoxy radical lead to an isomerization rate of ~4 × 10^3 s^{-1} at 298 K, significantly lower than the thermochemical estimates. The reasons for this discrepancy are not presently known, but may be due to the difficulties in quantitatively monitoring the end products of this isomerization reaction.[82]

Analogous to the procedure carried out by Carter and Atkinson,[1] the estimated Arrhenius parameters of Baldwin *et al.*[63] have been modified to yield values of k_a which are a factor of 8 lower at 298 K, and the resulting Arrhenius parameters are given in Table 8 for 1,5-H shift isomerizations of alkoxy radicals (the isomerizations expected to be of importance under atmospheric conditions). These estimates, however, must still be considered to be highly uncertain, and further studies of these isomerization rate constants are needed.

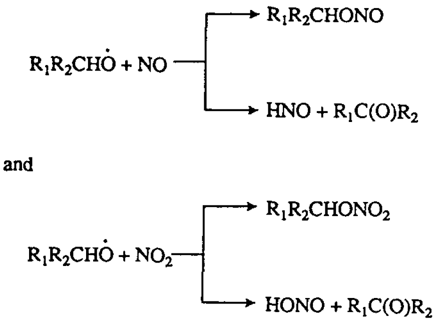
The rate constants for alkoxy radical isomerization given in Table 8 can be combined with the estimated alkoxy radical decomposition rates [Eq. (III)] and rates of reaction with O_2 [Eq. (II)] to assess the relative importances of these three reaction pathways at 298 K and 760 Torr total pressure of air. Table 9 gives calculated rates of removal due to decomposition, unimolecular isomerization and reaction with O_2 at 298 K and 760 Torr total pressure of air for a series of alkoxy radicals formed from alkanes, haloalkanes, alkenes, haloalkenes and ethers, together with the available literature data. In all cases, the most important removal pathway is correctly predicted. However, this empirical estimation method appears to grossly overestimate the decomposition rates for exothermic decompositions, and it may be more appropriate to set an upper limit to an alkoxy radical decomposition rate of ~2 × 10^7 s^{-1} at 298 K. It is obvious that more theoretical and experimental work is necessary before we have any scientifically valid and quantitative understanding of the atmospherically important reactions of alkoxy radicals.

For the cyclohexyloxy (cyclo-$C_6H_{11}\dot{O}$) radical, the reaction with O_2

$$\text{cyclo-}C_6H_{11}\dot{O} + O_2 \rightarrow \text{cyclohexanone} + HO_2$$

accounts for 42 ± 5% of the overall reaction pathways at 296 ± 2 K and atmospheric pressure of air[83] (consistent with the product data of Rowley *et al.*[47]). This relative importance of the O_2 reaction suggests that the isomerization reaction is not important for the cyclo-$C_6H_{11}\dot{O}$ radical, and that the competing pathway is the alkoxy radical decomposition reaction.[47]

Reactions of $R\dot{O}$ Radicals with NO and NO_2. Alkoxy radicals can also react with NO and NO_2 under atmospheric conditions



Absolute rate constants have been measured for the reactions of $CH_3\dot{O}$, $C_2H_5\dot{O}$ and $(CH_3)_2CH\dot{O}$ radicals with NO and NO_2, and the recommended 298 K limiting high-pressure rate constants and temperature-dependent parameters are given in Tables 10 and 11, respectively. The rate constants for the reactions of the $CH_3\dot{O}$ radical with NO and NO_2 are in the fall-off region between second- and third-order kinetics,[9] with calculated rate constants at 298 K and 760 Torr total pressure of air of 2.6 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} and 1.5 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1}, respectively.

The kinetic data obtained by Balla *et al.*[62] for the reactions of the $(CH_3)_2CH\dot{O}$ radical with NO and NO_2 were at, or close to, the high pressure limit, and show that these reactions have rate constants at room temperature of (3 – 4) × 10^{-11} cm^3 $molecule^{-1}$ s^{-1}, with small negative temperature dependencies.[62]

A large amount of relative rate data have been obtained for these NO and NO_2 reactions, as discussed by Batt.[68] These relative rate data show that for the reaction of $R\dot{O}$ radicals with NO, the addition rate constants at ~400 K are ~3 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1}, with an uncertainty of a factor of ~2–3. While H-atom abstraction from the $R\dot{O}$ + NO reactions is observed at low total pressures,[84,85] at total pressures close to the high pressure limit the H-atom abstraction process appears to be minor (<0.05).[68]

For the $R\dot{O}$ reactions with NO_2, the relative rate data cited by Batt[68] suggest that $k(R\dot{O} + NO_2)$ ~3 × 10^{-11}

TABLE 8. Estimated Arrhenius parameters, $k = Ae^{-E_a/RT}$, and room temperature rate constants for 1,5-H shift isomerizations of alkoxy radicals

Type of H Abstracted	E(Abstraction)[a] (kcal mol^{-1})	E_a(Isom)[b] (kcal mol^{-1})	A[c] (s^{-1})	k(298 K) (s^{-1})
$-CH_3$	7.8	8.3	8.2×10^{10}	6.7×10^{4}
$-CH_2-$	4.7	5.2	5.5×10^{10}	8.4×10^{6}
$>CH-$	4.7	5.2	2.7×10^{10}	4.1×10^{6}
$-CH_2OH$	6.6	7.1	5.5×10^{10}	3.4×10^{5}
$-CH(OH)-$	3.5[d]	4.0	2.7×10^{10}	3.1×10^{7}

[a] E(abstraction) = activation energy for abstraction by RȮ in bimolecular systems (i.e., no ring strain). Estimates of Baldwin *et al.*,[63] increased by 0.6 kcal mol^{-1}, have been used.

[b] E_a(Isom) = E(abstraction) + 0.5 kcal mol^{-1} ring strain.

[c] Estimates of Baldwin *et al.*,[63] decreased by a factor of 2.9 (see text), used.

[d] Baldwin *et al.*[63] did not give an estimate for this abstraction. It is assumed that replacing –H with –OH decreases E(abstraction) by 1.2 kcal mol^{-1}, based on their estimates for abstraction from $-CH_3$ and $-CH_2-$ groups.

TABLE 9. Calculated rates (s^{-1}) of competing alkoxy radical reactions at 298 K and 760 Torr total pressure of air. Dominant reaction is in italics, and literature data are given in parentheses

Radical	Decomposition	Reaction with O_2	Isomerization
$CH_3CH(\dot{O})C(O)CH_3$[a]	*2.2×10^{11}*	5.1×10^{4}	
$CHCl_2\dot{O}$[a]	*3.8×10^{12}*	1.5×10^{5}	
$CH_3OC(CH_3)_2CH_2\dot{O}$	*2.0×10^{7}*	2.4×10^{3}	$\geq 7 \times 10^{4}$
$CH_3CH(\dot{O})CH(OH)CH_3$	*2.4×10^{7}*	9.0×10^{3}	
$CH_3CH_2CH(OH)CH_2\dot{O}$	*9.3×10^{5}*	7.6×10^{3}	6.7×10^{4}
$CH_3CH(OH)CH_2\dot{O}$	*8.1×10^{5}*	7.6×10^{3}	
$HOCH_2CHCl\dot{O}$[a]	*3.3×10^{11}*	4.8×10^{6}	
$CH_3CH_2CH(\dot{O})CH_2OH$	*3.9×10^{6}*	3.7×10^{4}	
$CH_3CH(\dot{O})CH_2OH$	*2.6×10^{6}*	3.7×10^{4}	
$HOCH_2CH_2\dot{O}$	*8.6×10^{4}*	*3.1×10^{4}*	
$(CH_3)_3CCH_2\dot{O}$	*9.8×10^{3}*	*2.4×10^{4}*	
$CH_3CH(\dot{O})CH_2CH_3$	*5.4×10^{4}*	*8.7×10^{4}*	
	(4.3×10^{3})[b]		
$CH_3CH(\dot{O})CH_2CH_2CH_3$	4.9×10^{3}	*4.6×10^{4}*	*6.7×10^{4}*
	(9.0×10^{3})[c]		
$CH_3CH_2CH_2CH_2\dot{O}$	1.6×10^{2}	*2.2×10^{4}*	*6.7×10^{4}*
$CH_3CH_2OCH(\dot{O})CH_3$[a]	*2.0×10^{7}*	4.5×10^{6}	6.7×10^{4}
$(CH_3)_3COCH(\dot{O})CH_3$[a]	*2.0×10^{7}*	4.5×10^{6}	2.0×10^{5}
$CH_3CH_2\dot{O}$	7.8×10^{1}	*3.8×10^{4}*	
	(1.7×10^{-1})[b]	(4.9×10^{4})[d]	
$CH_2Cl\dot{O}$	8.7	*7.3×10^{4}*	
$CH_3\dot{O}$	5.3×10^{-2}	*1.0×10^{4}*	
		(9.8×10^{3})[d]	
$(CH_3)_3COCH_2\dot{O}$	1.1×10^{-3}	*3.8×10^{6}*	2.0×10^{5}
$CH_3OCH_2\dot{O}$	1.5×10^{-2}	*2.2×10^{6}*	

[a] Decomposition reaction is exothermic; see text.

[b] Data from Batt,[68] revised using $k(R\dot{O} + NO) = 2.3 \times 10^{-11}\, e^{150/T}$ cm^3 molecule^{-1} s^{-1} (see text).

[c] From Dóbé *et al.*,[82] revised using $k(R\dot{O} + NO) = 2.3 \times 10^{-11}\, e^{150/T}$ cm^3 molecule^{-1} s^{-1}.

[d] From present recommendations.

TABLE 10. Rate constant parameters for the gas-phase combination reactions of RȮ radicals with NO (from Atkinson *et al.*[9])

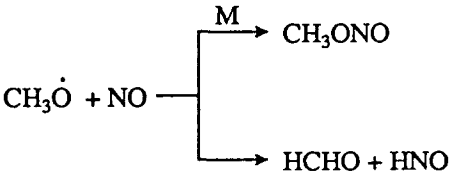
RȮ	k_0(cm^6 molecule^{-2} s^{-1})	k_∞(cm^3 molecule^{-1} s^{-1})	F	Temperature Range (K)
$CH_3\dot{O}$	$1.6 \times 10^{-29}\,(T/300)^{-3.5}$	$3.6 \times 10^{-11}\,(T/300)^{-0.6}$	0.6	200–400
$C_2H_5\dot{O}$		4.4×10^{-11}		200–300
$(CH_3)_2CH\dot{O}$		3.4×10^{-11}		200–300

TABLE 11. Recommended rate constant parameters for the combination reactions of R$\dot{O}$ radicals with NO_2 (from Atkinson *et al.*[9])

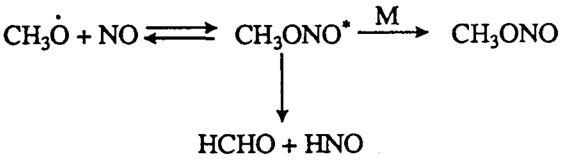
R$\dot{O}$	k_0(cm^6 molecule^{-2} s^{-1})	k_∞(cm^3 molecule^{-1} s^{-1})	F	Temperature Range (K)
$CH_3\dot{O}$	2.8×10^{-29} $(T/300)^{-4.5}$	2.0×10^{-11}	0.44	200–400
$C_2H_5\dot{O}$		2.8×10^{-11}		200–300
$(CH_3)_2CH\dot{O}$		3.5×10^{-11}		200–300

cm^3 molecule^{-1} s^{-1} at ~400 K (similar to the rate constants for the corresponding NO reactions), and that the H-atom abstraction channel is minor, with the most recent relative rate data yielding H-atom abstraction rate constants at ~400 K of ~6 × 10^{-13} cm^3 molecule^{-1} s^{-1} for $CH_3\dot{O}$, ~4 × 10^{-12} cm^3 molecule^{-1} s^{-1} for $C_2H_5\dot{O}$, and ~1 × 10^{-12} cm^3 molecule^{-1} s^{-1} for the $(CH_3)_2CH\dot{O}$ radical.[68]

As discussed by Frost and Smith[84] and Smith,[86] these reactions of R$\dot{O}$ radicals with NO and NO_2 can proceed by two parallel, and independent, pathways, for example,



or by formation of HCHO + HNO from the energy-rich RONO* intermediate:



It is likely that the second alternative, involving formation of the H-atom abstraction products from the RONO* intermediate, is the operative reaction scheme. Hence at the high-pressure limit, RONO formation is the sole process expected, and the situation would then be analogous to the R$^\cdot$ + O_2 reaction system (see above).

The relative rate data[68] are consistent with the absolute rate constants available (Tables 10 and 11), and the following recommendations for all alkoxy (R$\dot{O}$) radicals are made:

$$k_\infty(\text{RO}^\cdot + \text{NO}) = 2.3 \times 10^{-11}\, e^{150/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
$$= 3.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K},$$

with the H-atom abstraction pathway being of minor or negligible importance under tropospheric conditions, and

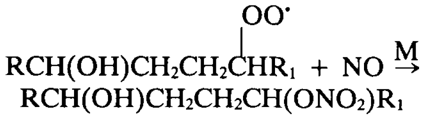
$$k_\infty(\text{R}\dot{\text{O}} + \text{NO}_2) = 2.3 \times 10^{-11}\, e^{150/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
$$= 3.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K},$$

with the H-atom abstraction process being of negligible importance under atmospheric conditions. For the $CH_3\dot{O}$ and $C_2H_5\dot{O}$ radical reactions, the recommended rate constants[9] should be used. Furthermore, the $CH_3\dot{O}$ radical reactions are in the fall-off region under atmospheric conditions.[9]

Under ambient tropospheric conditions, these alkoxy radical reactions with NO and NO_2 are generally of negligible importance, but may be important in laboratory environmental chamber experiments. These reactions are, however, of potential importance for tertiary alkoxy radicals, such as the $(CH_3)_3C\dot{O}$ radical, where O_2 reaction cannot occur and the decomposition reaction is the other competing process. For example, for the *tert*-butoxy radical, $(CH_3)_3C\dot{O}$, the thermal decomposition rate constant is[74] k_∞ = 1.1 × 10^{14} $e^{-7519/T}$ s^{-1} (k_∞ = 1.21 × 10^3 s^{-1} at 298 K). At 298 K and 760 Torr total pressure of air or N_2, the rate constant $k[(CH_3)_3C\dot{O} \rightarrow CH_3C(O)CH_3 + \dot{C}H_3]$ is in the fall-off region and is a factor of 1.26 lower[76] (~960 s^{-1}). Hence, at 298 K and 760 Torr total pressure of air the NO and NO_2 reactions with the $(CH_3)_3C\dot{O}$ radical become significant for NO_x concentrations ≳2.5 × 10^{12} molecule cm^{-3} (100 parts-per-billion mixing ratio).

The reactions of the alkyl radicals formed from the OH (and NO_3) radical reactions with the alkanes in the presence of NO are then as shown below [Reaction Scheme (3)] for the $(CH_3)_3C\dot{C}H_2$ radical formed from 2,2-dimethylpropane (the "stable" products are underlined, the alkyl nitrates ($RONO_2$) are not specifically identified, and the R$\dot{O}$ + NO and R$\dot{O}$ + NO_2 combination reactions are neglected) [where $RONO_2$ is the corresponding alkyl nitrate formed from the alkyl peroxy radicals]. In the absence of NO, the alkyl peroxy radicals react with HO_2 and R$\dot{O}_2$ radicals.

As discussed above, alkoxy radical isomerization can also occur for the longer chain (> C_3) alkanes in addition to decomposition and reaction with O_2. For example, Reaction Scheme (4) shows the reactions for the 1-butoxy radical formed from *n*-butane. It is expected by analogy with the reactions of alkyl radicals (Table 2) and β-hydroxyalkyl radicals[10,87,88] (Sec. 2.2) that the δ-hydroxyalkyl radicals will react rapidly and solely with O_2 to form the δ–hydroxyalkyl peroxy radicals. However, this reaction sequence has not been experimentally confirmed under tropospheric conditions, and the fractions of the reactions of the δ-hydroxyalkyl peroxy radicals with NO which yield the corresponding δ-hydroxyalkyl nitrates have not been experimentally determined.[1] The limited data available concerning alkyl nitrate formation from these hydroxy-substituted alkyl peroxy radicals (from computer model fits to environmental chamber data) suggest that this alkyl nitrate formation is minimal, and Carter and Atkinson[1] recommend that alkyl nitrate formation from the reaction



$$\mathrm{RCH(OH)CH_2CH_2\overset{OO^{\cdot}}{C}HR_1 + NO \xrightarrow{M} RCH(OH)CH_2CH_2CH(ONO_2)R_1}$$

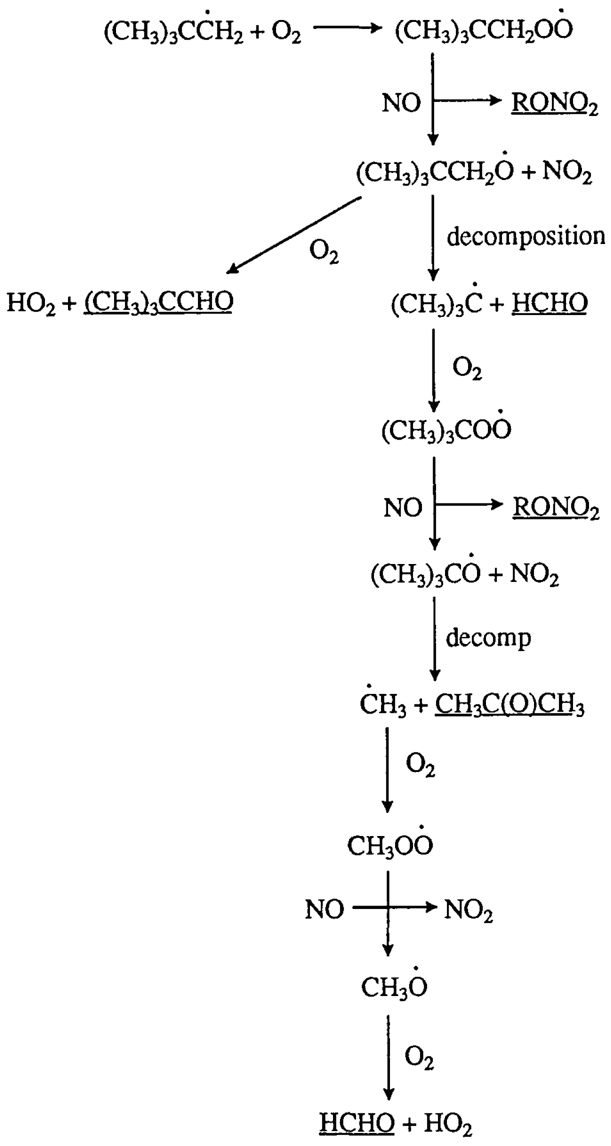
is essentially zero.

The α-hydroxy radicals expected to be formed subsequent to the initial isomerization reaction, such as the $HOCH_2CH_2CH_2\dot{C}HOH$ radical formed from the 1-butoxy radical isomerization, are expected (see Refs 1, 2 and 9 and Sec. 2.2) to react with solely O_2 under tropospheric conditions to form the HO_2 radical and the carbonyl.

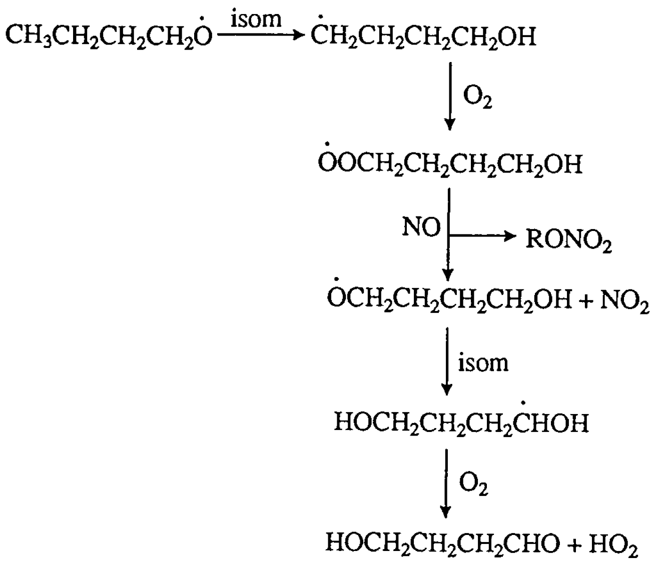
$$R_1R_2\dot{C}OH + O_2 \rightarrow R_1C(O)R_2 + HO_2$$

These α-hydroxy radical reactions are discussed in Sec. 2.2.

The further reactions of the "first-generation" products arising from the above reactions are discussed in Secs. 2.5 (carbonyls, hydroperoxides and alcohols) and 2.6 (alkyl peroxynitrates, alkyl nitrates and nitrites) below.



Reaction Scheme (3)



Reaction Scheme (4)

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2.2. Alkenes

As discussed previously,[1,2] the major tropospheric loss processes of the alkenes are by reaction with OH and NO_3 radicals and O_3. The conjugated dienes also react with NO_2, and this reaction can be important in environmental chamber experiments carried out at NO_2 concentrations significantly higher than ambient (see, for example, Refs. 3 and 4), as can the reactions of alkenes with $O(^3P)$ atoms.[4]

OH Radical Reactions

The kinetics and mechanisms of the reactions of the OH radical with the alkenes, cycloalkenes and dienes have been reviewed and evaluated by Atkinson,[5] and that review and evaluation is updated in Sec. 3.3. For ethene and the methyl-substituted ethenes (propene, 2-methylpropene, the 2-butenes, 2-methyl-2-butene and 2,3-dimethyl-2-butene), the OH radical reactions proceed essentially totally by OH radical addition to the carbon-carbon double bond at atmospheric pressure, with H-atom abstraction from the $-CH_3$ substituent groups accounting for $<5\%$ of the total reaction at room temperature.[5] For 1-butene, the product data of Hoyermann and Sievert[6] and Atkinson *et al.*[7] show that H-atom abstraction accounts for $<10\%$ of the overall reaction at room temperature. To date, only for 1,3-and 1,4-cyclohexadiene has H-atom abstraction been shown to occur to any significant extent,[8] with this process accounting for $\sim 9\%$ and $\sim 15\%$ of the overall OH radical reactions with 1,3- and 1,4-cyclohexadiene, respectively, at room temperature. However, for the alkenes with alkyl side chains a small amount of H-atom abstraction must occur with, for example, this pathway being calculated to account for 10–15% of the overall OH radical reaction for 1-heptene at 298 K.[9]

The rate constants, k, at 298 K and the temperature-dependent parameters (with $k = A e^{-B/T}$) at 760 Torr total pressure of air and for temperatures ≤ 425 K for a number of monoalkenes, dienes, cycloalkenes and monoterpenes are given in Table 12. For all but ethene and propene (and propadiene[5]), these rate constants can be considered to be the high-pressure limits which, for the $\geq C_4$ alkenes, are essentially attained at total pressures of ≥ 50 Torr of air.[5] For ethene and propene, the Troe fall-off parameters k_o, k_∞ and F derived by Atkinson[5] and in Sec. 3.3 are (M = air): ethene, $k_o = 6 \times 10^{-29}\ (T/298)^{-4}$ cm^6 molecule^{-2} s^{-1}, $k_\infty = 9.0 \times 10^{-12}\ (T/298)^{-1.1}$ cm^3 molecule^{-1} s^{-1} and $F = 0.70$ at 298 K; propene, $k_o = 3 \times 10^{-27}\ (T/298)^{-3}$ cm^6 molecule^{-2} s^{-1}, $k_\infty = 2.8 \times 10^{-11}\ (T/298)^{-1.3}$ cm^3 molecule^{-1}s^{-1} and $F = 0.5$ at 298 K.

As discussed above, OH radical addition to the $>C=C<$ bond(s) is the dominant reaction pathway. For monoalkenes, dienes or trienes with non-conjugated $>C=C<$ bonds, the OH radical can add to either end of the double bond(s), and Cvetanovic[10] reported that for propene addition to the terminal carbon occurs $\sim 65\%$ of the time, as expected on thermochemical grounds[11]

$$OH + CH_3CH=CH_2 \xrightarrow{M} 0.35\ CH_3CH(OH)\dot{C}H_2 + 0.65\ CH_3\dot{C}HCH_2OH$$

The resulting β-hydroxyalkyl radicals then react rapidly with O_2, with the measured room temperature rate constants being in the range $(3-30) \times 10^{-12}$ cm^3 molecule^{-1}s^{-1} (Table 13). Under atmospheric conditions, the sole reaction of the β-hydroxyalkyl radicals is then with O_2. For example,

$$CH_3\dot{C}HCH_2OH + O_2 \xrightarrow{M} CH_3CH(O\dot{O})CH_2OH$$

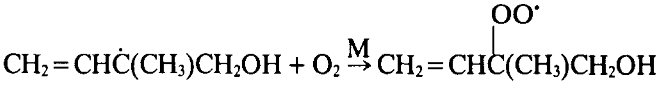
For dienes with conjugated double bonds, such as 1,3-butadiene, isoprene (2-methyl-1,3-butadiene), myrcene, ocimene, α- and β-phellandrene and α-terpinene, OH radical addition to the $>C=C-C=C<$ system is expected to occur at the 1- and/or 4-positions, leading to formation of the thermochemically favored allylic radicals.[4]

$$OH + CH_2=CHC(CH_3)=CH_2 \xrightarrow{M} HOCH_2\dot{C}HC(CH_3)=CH_2 \text{ and } CH_2=CH\dot{C}(CH_3)CH_2OH$$

These initially formed β-hydroxy allylic radicals may isomerize to δ-hydroxy allylic radicals.[4]

$$CH_2=CH\dot{C}(CH_3)CH_2OH \rightarrow \dot{C}H_2CH=C(CH_3)CH_2OH$$

By analogy with the allyl ($\dot{C}_3H_5$) radical, for which Morgan *et al.*[15] have measured a rate constant for combination with O_2 of $\sim 4 \times 10^{-13}$ cm^3 molecule^{-1}s^{-1} at 380 K and a total pressure of 50 Torr of Ar diluent, these various hydroxy-substituted allyl-type radicals are expected to react solely with O_2 under tropospheric conditions



$$CH_2=CH\dot{C}(CH_3)CH_2OH + O_2 \xrightarrow{M} CH_2=CH\overset{OO^{\cdot}}{\overset{|}{C}}(CH_3)CH_2OH$$

$$HOCH_2C(CH_3)=CH\dot{C}H_2 + O_2 \rightarrow HOCH_2C(CH_3)=CHCH_2O\dot{O}$$

TABLE 12. Rate constants k at 298 K and 760 Torr total pressure of air and Arrhenius parameters ($k = Ae^{-B/T}$; $T \leq 425$ K) for the reaction of OH radicals with alkenes at 760 Torr total pressure of air[a] [from Ref. 5 and Sec. 3.3.]

Alkene	$10^{12} \times k$(298 K) (cm^3 molecule^{-1} s^{-1})	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	B (K)
Ethene[b]	8.52	1.96	−438
Propene[c]	26.3	4.85	−504
1-Butene	31.4	6.55	−467
cis-2-Butene	56.4	11.0	−487
trans-2-Butene	64.0	10.1	−550
2-Methylpropene	51.4	9.47	−504
1-Pentene	31.4	5.86[d]	−500[d]
cis-2-Pentene	65		
trans-2-Pentene	67		
3-Methyl-1-butene	31.8	5.32	−533
2-Methyl-1-butene	61		
2-Methyl-2-butene	86.9	19.2	−450
1-Hexene	37		
2-Methyl-1-pentene	63		
2-Methyl-2-pentene	89		
trans-4-Methyl-2-pentene	61		
2,3-Dimethyl-2-butene	110		
3,3-Dimethyl-1-butene	28		
1-Heptene	40		
trans-2-Heptene	68		
2,3-Dimethyl-2-pentene	98		
trans-4,4-Dimethyl-2-pentene	55		
trans-4-Octene	69		
1,3-Butadiene	66.6	14.8	−448
2-Methyl-1,3-butadiene	101	25.4	−410
Myrcene	215		
Ocimene (*cis*- and *trans*-)	252		
Cyclopentene	67		
Cyclohexene	67.7		
Cycloheptene	74		
1-Methylcyclohexene	94		
Camphene	53		
2-Carene	80		
3-Carene	88		
Limonene	171		
α-Phellandrene	313		
β-Phellandrene	168		
α-Pinene	53.7	12.1	−444
β-Pinene	78.9	23.8	−357
Sabinene	117		
α-Terpinene	363		
γ-Terpinene	177		
Terpinolene	225		

[a] Except for ethene and propene, these are essentially the high-pressure rate constants k_∞.
[b] $k_\infty = 9.0 \times 10^{-12}(T/298)^{-1.1}$ cm^3 molecule^{-1} s^{-1}.
[c] $k_\infty = 2.8 \times 10^{-11}(T/298)^{-1.3}$ cm^3 molecule^{-1} s^{-1}.
[d] Estimated[5]

TABLE 13. Rate constants for the gas-phase reactions of β-hydroxyalkyl radicals with O_2

$R^\cdot$	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1})	at T(K)	Reference
$HOCH_2\dot{C}H_2$	3.0 ± 0.4	293 ± 3	Miyoshi *et al.*[12]
$CH_3\dot{C}HCH_2OH$	11.6 ± 2.2	296 ± 4	Miyoshi *et al.*[13]
$CH_3CH(OH)\dot{C}H_2$	3.82 ± 0.60	296 ± 4	Miyoshi *et al.*[13]
$CH_3CH(OH)\dot{C}HCH_3$	28 ± 18	300	Lenhardt *et al.*[14]

To date, few direct experimental data are available concerning the atmospherically important reactions of these β(or δ-)-hydroxyalkyl peroxy radicals. As for the alkyl peroxy radicals formed from the alkanes (Sec. 2.1.) these radicals are expected to react with NO,

$$CH_3CH(OH)CH_2O\dot{O} + NO \begin{cases} \longrightarrow CH_3CH(OH)CH_2\dot{O} + NO_2 \\ \xrightarrow{M} CH_3CH(OH)CH_2ONO_2 \end{cases}$$

NO_2 (to form thermally unstable peroxynitrates),

$$CH_3CH(OH)CH_2OO^{\cdot} + NO_2 \overset{M}{\rightleftarrows} CH_3CH(OH)CH_2OONO_2$$

HO_2 radicals,

$$CH_3CH(OH)CH_2O\dot{O} + HO_2 \rightarrow CH_3CH(OH)CH_2OOH + O_2$$

and organic peroxy radicals

$$CH_3CH(OH)CH_2O\dot{O} + R\dot{O}_2 \rightarrow \text{products}$$

In fact, to date the only kinetic data concern the self-reaction of the $HOCH_2CH_2OO^{\cdot}$ radical[16–18] and its reactions with HO_2 radicals[16–18] and NO.[19,20] Based on the data of Jenkin and Cox,[16] Anastasi *et al.*[17] and Murrells *et al.*,[18] the IUPAC panel recommended[21] for the reactions

$$2\,HOCH_2CH_2O\dot{O} \begin{cases} \longrightarrow 2\,HOCH_2CH_2\dot{O} + O_2 & \text{(a)} \\ \longrightarrow HOCH_2CHO + HOCH_2CH_2OH + O_2 & \text{(b)} \end{cases}$$

that $(k_a + k_b) = 2.3 \times 10^{-12}$ cm^3 molecule^{-1}s^{-1} and $k_a/(k_a + k_b) = 0.36 \pm 0.1$ at 298 K, and that the rate constant for the reaction of HO_2 radicals with the $HOCH_2CH_2O\dot{O}$ radical

$$HOCH_2CH_2O\dot{O} + HO_2 \rightarrow \text{products}$$

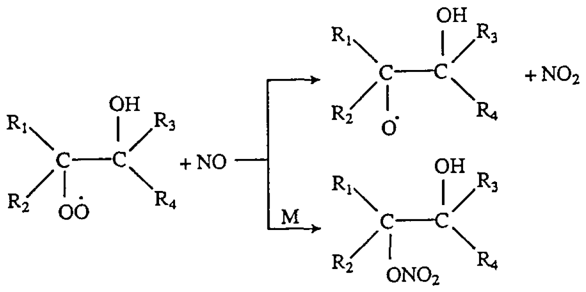
is $k(HO_2 + HOCH_2CH_2O\dot{O}) = 1.0 \times 10^{-11}$ cm^3 molecule^{-1}s^{-1} at 298 K.[21] The $HOCH_2CH_2O\dot{O}$ radical self-reaction rate constant is a factor of ~10 higher than that recommended for primary alkylperoxy radicals formed from the alkanes (Sec. 2.1. above). The rate constant for the reaction of the $HOCH_2CH_2O\dot{O}$ radical with the HO_2 radical is identical to that recommended for alkylperoxy radicals in Sec. 2.1.

No data are available for the reactions of the β-hydroxyalkylperoxy radicals with NO_2, but an indirect estimate for the rate constant for the reaction of the $HOCH_2CH_2O\dot{O}$ radical (formed after OH radical addition to ethene) with NO

$$HOCH_2CH_2O\dot{O} + NO \rightarrow HOCH_2CH_2\dot{O} + NO_2$$

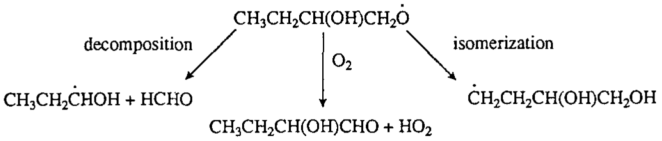
of $(9.0 \pm 4.0) \times 10^{-12}$ cm^3 molecule^{-1}s^{-1} at 298 ± 2 K has been derived by Becker *et al.*[20] (which supersedes the earlier study of Schmidt *et al.*[19]). This rate constant for reaction of NO with a β-hydroxyalkyl peroxy radical is essentially identical to the recommendation for the rate constants for the reactions of NO with the $\geq C_2$ alkyl peroxy radicals formed from the alkanes (Sec. 2.1.), implying that these alkylperoxy radical rate constants are also applicable to the β-hydroxyalkyl peroxy radicals.

In the presence of NO, the β-hydroxyalkyl peroxy radicals are therefore expected to form NO_2 plus the corresponding β-hydroxyalkoxy radical, with a small amount of β-hydroxyalkyl nitrate also being formed.[22]



At atmospheric pressure and room temperature, Shepson *et al.*[22] determined formation yields of $CH_3CH(OH)CH_2ONO_2$ and $CH_3CH(ONO_2)CH_2OH$ from propene of ~0.016 ± 0.008 for each nitrate.

The β-hydroxyalkoxy radicals can then decompose, react with O_2 or isomerize, as discussed in Sec. 2.1. above. Thus, for the alkoxy radical formed after internal addition of the OH radical to 1-butene:



The experimental data for the simple alkenes (ethene, propene, 1-butene, and the 2-butenes) show that at room temperature and atmospheric pressure, decomposition dominates over reaction with O_2.[7,23,24] Indeed, the available data show that for the β-hydroxyalkoxy radicals formed from the $\geq C_3$ alkenes, the reaction with O_2 is negligible and only the products arising from decomposition of the β-hydroxyalkoxy radicals are observed at room temperature and atmospheric pressure.[7,23] For ethene, Niki *et al.*[24] showed that both reaction with O_2 and decomposition of the $HOCH_2CH_2\dot{O}$ radical occurs

$$HOCH_2CH_2\dot{O} \rightarrow \dot{C}H_2OH + HCHO \qquad \text{(a)}$$

$$HOCH_2CH_2\dot{O} + O_2 \rightarrow HOCH_2CHO + HO_2 \qquad \text{(b)}$$

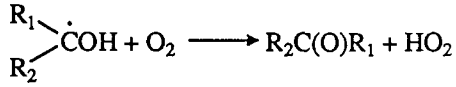
with $k_b/k_a = (5.4 \pm 1.0) \times 10^{-20}$ cm^3 molecule^{-1} at 298 K and 700 Torr total pressure of air.[24] For the $CH_3CH_2CH(OH)CH_2\dot{O}$ radical formed from 1-butene, the experimental data of Atkinson *et al.*[7] show that isomerization is not important, in accord with the estimates arising from the discussion in Sec. 2.1.

Hence, apart from ethene, for which reaction of the $HOCH_2CH_2\dot{O}$ radical with O_2 and decomposition are competitive at 298 K and atmospheric pressure, the β-hydroxyalkoxy radicals formed subsequent to OH radical reactions with the simpler monoalkenes (propene and the butenes) undergo decomposition, and the estimation method proposed in Sec. 2.1. allows the relative importance of reaction with O_2, decomposition and isomerization to be assessed.

The α-hydroxy radicals formed from the decomposition reactions of the β-hydroxyalkoxy radicals react rapidly with O_2, with rate constants at room temperature of $\sim(0.9\text{–}4) \times 10^{-11}$ cm^3 molecule^{-1}s^{-1} (Table 14). Under atmospheric conditions, these reactions with O_2 will then be the sole loss process for the α-hydroxy radicals. The simplest α-hydroxy radical, $\dot{C}H_2OH$, reacts with O_2 to form the HO_2 radical and HCHO,[25–28]

$$\dot{C}H_2OH + O_2 \rightarrow HCHO + HO_2$$

and product studies have shown that the higher (C_2–C_4) α-hydroxy radicals also react via H-atom abstraction to yield the corresponding carbonyls[29–32]



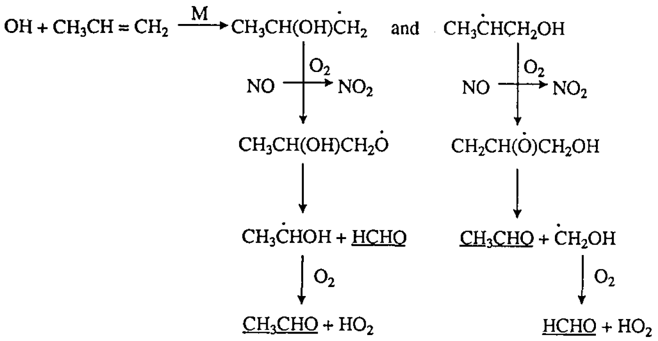
$$R_1R_2\dot{C}OH + O_2 \longrightarrow R_2C(O)R_1 + HO_2$$

Grotheer *et al.*[32,33] and Nesbitt *et al.*[34] have studied the temperature dependence of the rate constant for the reaction of the $\dot{C}H_2OH$ radical with O_2. These studies[32–34] show that the rate constant decreases below room temperature[34] and also decreases slightly above room temperature, and then increases more rapidly with increasing temperature, exhibiting a minimum at ~450 K[32,33] (see also Ref. 2). A similar slight decrease in the rate constant for the $CH_3\dot{C}HOH + O_2$ reaction with increasing temperature over the range 300–474 K was observed by Grotheer *et al.*,[32] with the rate constant then increasing at higher temperatures (474–682 K).[32] The lack of a deuterium isotope effect on the room temperature rate constant for the reactions of the $\dot{C}H_2OH$ and $\dot{C}H_2OD$ radicals with O_2[33,35] and the temperature dependence of the rate constant shows that this reaction proceeds by initial O_2 addition,

$$\dot{C}H_2OH + O_2 \rightarrow [\dot{O}OCH_2OH \rightleftarrows HOOCH_2\dot{O}]^\ddagger \rightarrow HCHO + HO_2$$

with the initially formed energy-rich $HOCH_2O\dot{O}$ radical isomerizing via a five-membered transition state to the $HOOCH_2\dot{O}$ radical with subsequent decomposition. Similar reaction mechanisms are expected to occur for the $\geq C_2$ α-hydroxy radicals.

For propene, the OH radical-initiated reaction scheme, in the presence of NO, is then ("stable" products are underlined and the minor amount of nitrate formation[22] is neglected for clarity)



and similarly for ethene and the butenes (1-butene, *cis*- and *trans*-2-butene and 2-methylpropene).

However, such reaction schemes involving dominant β-hydroxyalkoxy radical decomposition may not apply to the higher alkenes such as the $\geq C_5$ 1-alkenes. Thus, Paulson and Seinfeld[36] have obtained a yield of heptanal ($CH_3(CH_2)_5CHO$) from the OH radical reaction with 1-octene in the presence of NO_x of 15 ± 5%, much lower than the ~80–85% expected if the β-hydroxyalkoxy radicals undergo only decomposition (the remaining 15–20% of the overall reaction is predicted to proceed by initial H-atom abstraction from the $-CH_2-$ groups,[9] leading to the formation of products other than heptanal). This observation suggests that other reaction channels are operative for the more complex β-hydroxyalkoxy radicals, possibly including isomerization as predicted from the discussion in Sec. 2.1. Indeed, for the OH radical reaction with 1-pentene the estimation method proposed in Sec. 2.1. predicts that the $CH_3CH_2CH_2CH(OH)CH_2\dot{O}$ radical will undergo mainly isomerization, while the $CH_3CH_2CH_2CH(O^\cdot)CH_2OH$ radical (that formed preferentially from the initial OH radical addition) will undergo decomposition. For the $\geq C_6$ 1-alkenes, both of the β-hydroxyalkoxy radicals formed are predicted to react mainly by isomerization, reasonably consistent with the data for 1-octene.[36]

TABLE 14. Room temperature rate constants k for the reactions of α-hydroxy radicals with O_2

α-Hydroxy radical	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1})	at T(K)	Reference
$\dot{C}H_2OH$	9.4	298	Atkinson *et al.*[21]
$CH_3\dot{C}HOH$	19	298	Atkinson *et al.*[21]
$CH_3CH_2\dot{C}HOH$	26.1 ± 4.1	296 ± 4	Miyoshi *et al.*[13]
$CH_3\dot{C}(OH)CH_3$	37.1 ± 6.2	296 ± 4	Miyoshi *et al.*[13]

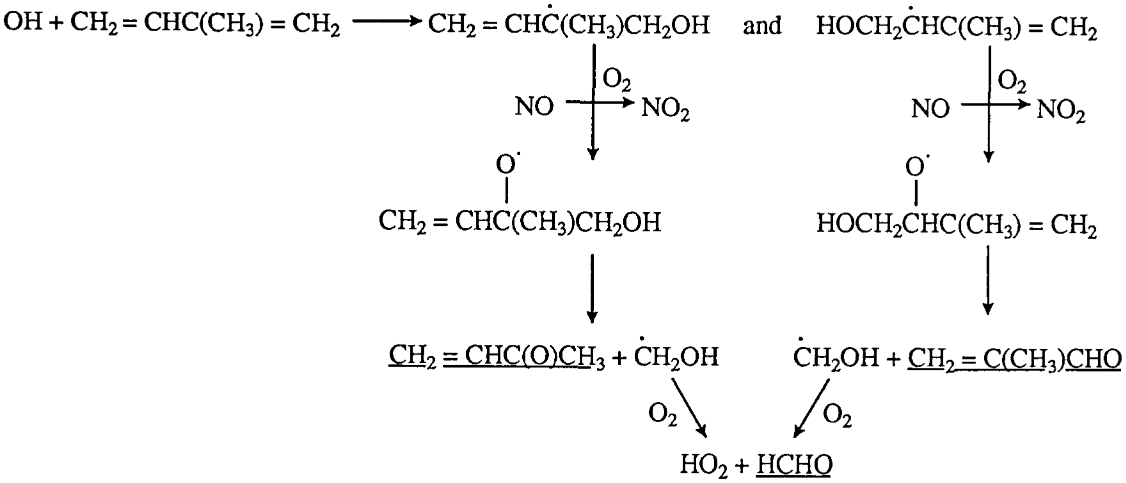
Similar reaction schemes are expected to apply to the conjugated dienes. For example, for isoprene (2-methyl-1,3-butadiene) the simple reaction sequence, with no isomerization of the initially formed β-hydroxy allylic radicals and with decomposition of the β-hydroxyperoxy radicals, is expected to lead[37] to the formation of methyl vinyl ketone plus HCHO (OH radical addition to the $CH_2=C(CH_3)-$ bond) and methacrolein plus HCHO (OH radical addition to the $CH_2=CH-$ bond). For example, Reaction Scheme (5) shows the reaction sequence for terminal OH radical addition (the "stable" first-generation products are underlined), with organic nitrate formation from the $R\dot{O}_2 + NO$ reaction being omitted for clarity. As shown above for the propene reaction, the same ultimate products are formed from internal OH radical addition with subsequent decomposition of the β-hydroxyalkoxy radicals. However, for unsymetrical dienes the expected products formed depend on which $>C=C<$ bond OH addition occurs. For conjugated dienes, the estimation technique of Ohta[38] allows the fraction of the overall OH radical addition reaction proceeding at each $>C=C<$ double bond to be calculated (this information cannot be obtained from the estimation technique of Atkinson[9,39]). Thus for isoprene, rate constants for OH radical addition to the $CH_2=CH-$ and $CH_2=C<$ bonds of isoprene are calculated[38] to be in the ratio 34/66 at room temperature.

For the OH radical-initiated reaction of 1,3-butadiene at 298 ± 2 K, Maldotti *et al.*[40] observed the formation of acrolein (the expected product, together with HCHO, based on the above reaction scheme) from irradiated NO_x-1,3-butadiene-air mixtures, with $[\text{acrolein}]_{\text{max}}/[\text{1,3-butadiene}]_{\text{initial}} = 0.59 \pm 0.07$. Based on the rate constants for the OH radical reactions with acrolein and 1,3-butadiene,[5] this ratio corresponds to a formation yield of acrolein from the OH radical-initiated reaction of 1,3-butadiene of 0.98 ± 0.12. Additionally, furan is formed in minor amount from the OH radical-initiated reaction of 1,3-butadiene, with a yield of 0.039 ± 0.011.[41]

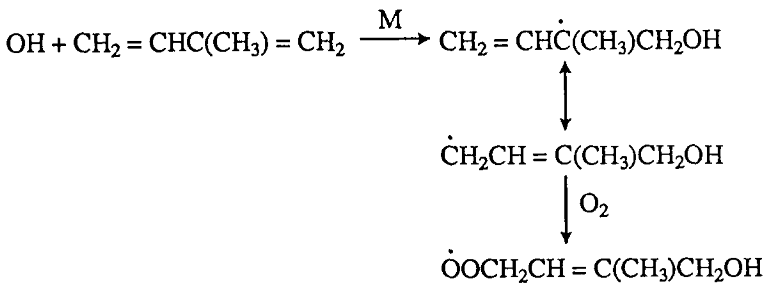
However, two recent studies of the products formed from the gas-phase reaction of the OH radical with isoprene[3,4] show that methyl vinyl ketone and methacrolein (together with their expected HCHO co-product) do not account for the entire reaction pathways. In the Fourier transform infrared absorption spectroscopy study of Tuazon and Atkinson,[3] the reaction of isoprene with the $O(^3P)$ atom formed from photolysis of NO_2 was not taken into account. This reaction is calculated to contribute ~10–15% of the overall isoprene reacted, and the product yields of Tuazon and Atkinson[3] and Atkinson *et al.*,[41] corrected to take into account this $O(^3P)$ atom reaction, are then: methyl vinyl ketone, 33%; methacrolein, 24%, 3-methylfuran, 5%; organic nitrates, ~13%; and unidentified carbonyl compounds, ~25%. The formaldehyde yield was consistent with being a co-product formed together with methyl vinyl ketone and methacrolein.[3] Paulson *et al.*[4] determined yields of methyl vinyl ketone, methacrolein and 3-methylfuran of 35.5%, 25% and 4%, respectively, from a generally similar product study, but using gas chromatography for product analysis. These two studies are in excellent agreement, and show that methyl vinyl ketone and methacrolein formation account for ~60% of the overall OH radical reaction with isoprene in the presence of NO_x. The data of Tuazon and Atkinson[3] indicate that organic nitrate formation, presumably from the reactions,

$$R\dot{O}_2 + NO \xrightarrow{M} RONO_2$$

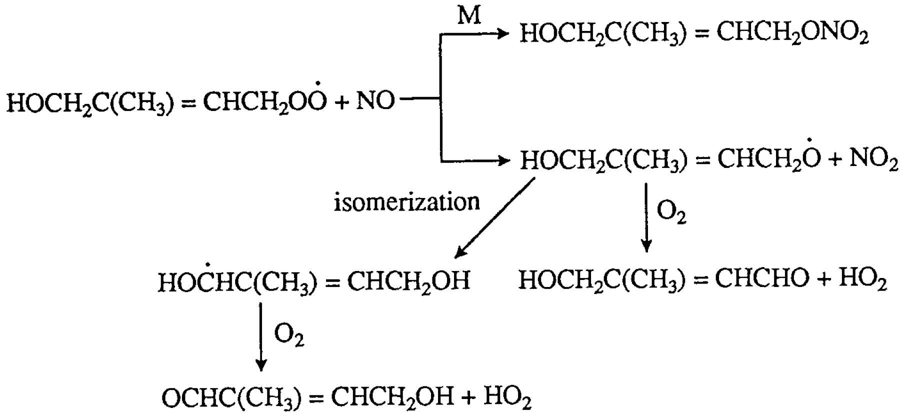
accounts for ~13% of the overall reaction, and that other carbonyl compounds, including possibly hydroxycarbonyls, account for ~25% of the reaction. These other, as yet unidentified, carbonyls and/or hydroxycarbonyls may arise from reactions of the δ-hydroxyalkoxy radicals formed through the reaction sequence:



Reaction Scheme (5)



followed by



Reaction Scheme (5)

and similarly for terminal OH radical addition to the other $>C=C<$ bond. 3-Methylfuran also arises from the OH radical-initiated reaction of isoprene, possibly in part after the formation of δ-hydroxyalkoxy radicals.[41,42] Aerosol formation from isoprene photooxidation has been shown to be of negligible importance under atmospheric conditions,[43] and the aerosol composition has been investigated by Palen *et al.*[44]

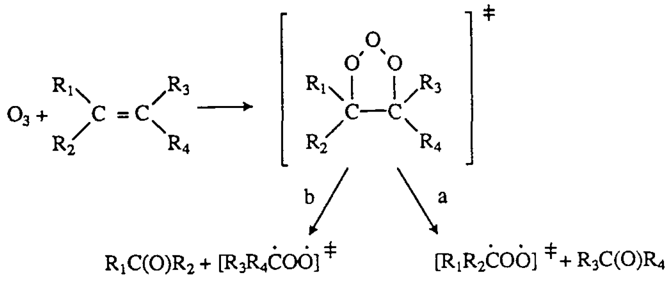
To date, few quantitative product studies have been carried out for the monoterpenes,[45–48] and the reported data are given in Table 15 (the study of Hakola *et al.*[48] supersedes that of Arey *et al.*[45]). The yields reported by Hatakeyama *et al.*[46] for specific C_9 and C_{10} carbonyls formed from α- and β-pinene may be high because of contributions to the observed infrared absorptions from other, as yet unidentified, carbonyl-containing compounds. It appears clear that only a relatively small fraction of the overall reaction products have been accounted for, and Arey *et al.*[45] and Hakola *et al.*[48] observed no significant products by gas chromatography with flame ionization detection from the OH radical reactions with myrcene[45] or camphene[48] in the presence of NO_x.

Hatakeyama *et al.*[46] observed that the pinonaldehyde yield in the absence of NO was significantly lower than in the presence of NO. Aerosol formation from the reactions of the OH radical with α- and β-pinene has been studied by Hatakeyama *et al.*[46] and Pandis *et al.*,[43] and the aerosol composition investigated.[44] These references[43,44,46] should be consulted for further details.

Clearly, further product and mechanistic data are required for the OH radical reactions with the more complex alkenes, especially for the monoterpenes (including conjugated dienes) of biogenic importance.

O_3 Reaction

The kinetics and mechanisms of the gas-phase reactions of O_3 with the alkenes, cycloalkenes and dienes were last reviewed and evaluated by Atkinson and Carter[49] and that review and evaluation is updated in Sec. 5.2. The kinetic data for alkenes of atmospheric importance (taken from Ref. 49 and Sec. 5.2.) are given in Table 16. These reactions proceed by initial O_3 addition to the $>C=C<$ bond to yield an energy-rich ozonide, which rapidly decomposes to a carbonyl and an initially energy-rich biradical.



where [ ]‡ denotes an energy-rich species. It has generally been assumed that $k_a \sim k_b$ for the alkene systems.[50] However, Horie and Moortgat[51] concluded from a product study that this is not the case for the propene reaction, for which they obtained 62% formation of ($HCHO + [CH_3\dot{C}HO\dot{O}]‡$) and 38% formation of

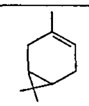
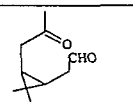
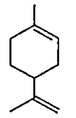
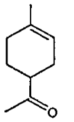
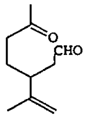
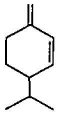
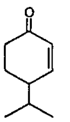
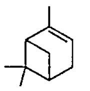
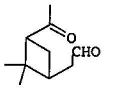
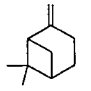
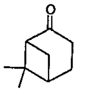
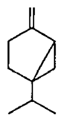
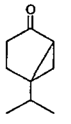
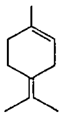
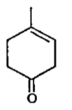
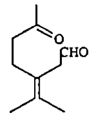
$(CH_3CHO + [\dot{C}H_2O\dot{O}]^{\ddagger})$. The energy-rich biradicals can then be collisionally stabilized or unimolecularly decompose.

$$[R_1R_2\dot{C}O\dot{O}]^{\ddagger} + M \rightarrow R_1R_2\dot{C}O\dot{O} + M$$

$$[R_1R_2\dot{C}O\dot{O}]^{\ddagger} \rightarrow \text{products.}$$

The fraction of the initially formed biradical which is collisionally stabilized is pressure dependent.[52,53] For *trans*-2-butene, the fraction of the biradical which was stabilized was observed to increase from essentially zero at zero total pressure of air to a high-pressure limit of 0.185, attained at ~600 Torr total pressure of air.[52] For ethene, however, a significant fraction of the initially-formed biradical is formed thermally "cold" at low pressures,[53,54] and Hatakeyama *et al.*[53] determined this fraction to be 0.20 ± 0.03 by extrapolation of data obtained over the total pressure range 10–1140 Torr to zero pressure. At room temperature and one atmosphere total pressure, the fractional yields of stabilized biradicals formed from the alkenes studied to date are given in Table 17. The yield of stabilized biradicals from ethene obtained by Hatakeyama *et al.*[52,53] is in excellent agreement with values of 0.38, 0.37 and 0.35 obtained by Su *et al.*,[55] Kan *et al.*[56] and Niki *et al.*,[57] respectively, and that for *trans*-2-butene of Hatakeyama *et al.*[52] agrees well with the stabilized biradical yield of 0.18 obtained by Niki *et al.*[58] from *cis*-2-butene.

TABLE 15. Products observed and their molar formation yields from the reactions of the OH radical with monoterpenes in the presence of NO_x

Monoterpene	Structure	Product	Yield	Reference
3-Carene			0.34 ± 0.08[a,b]	Hakola *et al.*[48]
Limonene			0.29 ± 0.06[a,b]	Hakola *et al.*[48]
			0.20 ± 0.03[a,b]	Hakola *et al.*[48]
β-Phellandrene			0.29 ± 0.07[a,b]	Hakola *et al.*[47]
α-Pinene			0.28 ± 0.05[a,b] 0.56 ± 0.04[c]	Hakola *et al.*[48] Hatakeyama *et al.*[46]
β-Pinene			0.27 ± 0.04[a,b] 0.79 ± 0.08[c]	Hakola *et al.*[48] Hatakeyama *et al.*[46]
		HCHO	0.54 ± 0.05[c]	Hatakeyama *et al.*[46]
Sabinene			0.17 ± 0.03[a,b]	Hakola *et al.*[48]
Terpinolene			0.26 ± 0.06[a,b]	Hakola *et al.*[48]
			0.08 ± 0.02[d]	Arey *et al.*;[45] Hakola *et al.*[48]

[a] Product identification confirmed by Hakola *et al.*[47,48]

[b] Indicated uncertainties are two least-squares standard deviations and include uncertainties in the analytical calibration factors.

[c] Indicated uncertainties are one standard deviation; the 6,6-dimethylbicyclo[3.1.1]heptan-2-one and pinonaldehyde as measured by Fourier transform infrared absorption spectroscopy may have included IR contributions from other as yet unidentified carbonyl compounds.

[d] Product identification tentative.

TABLE 16. Rate constants k at 298 K and Arrhenius parameters, $k = A\,e^{-B/T}$, for the gas-phase reactions of O_3 with alkenes, cycloalkenes and dialkenes (from Ref. 49 and Sec. 5.2.)

Alkene	$10^{18} \times k$(298 K) (cm^3 molecule^{-1} s^{-1})	$10^{15} \times A$ (cm^3 molecule^{-1} s^{-1})	B (K)
Ethene	1.59	9.14	2580
Propene	10.1	5.51	1878
1-Butene	9.64	3.36	1744
2-Methylpropene	11.3	2.70	1632
cis-2-Butene	125	3.22	968
trans-2-Butene	190	6.64	1059
1-Pentene	10.0		
2-Methyl-2-butene	403	6.51	829
1-Hexene	11.0		
cis-3-Methyl-2-pentene	450		
trans-3-Methyl-2-pentene	560		
2,3-Dimethyl-2-butene	1130	3.03	294
1,3-Butadiene	6.3	13.4	2283
2-Methyl-1,3-butadiene	12.8	7.86	1913
Myrcene	470		
cis-,trans-Ocimene	540		
Cyclopentene	630		
Cyclohexene	72		
Cycloheptene	290		
Camphene	0.90		
2-Carene	230		
3-Carene	37		
Limonene	200		
α-Phellandrene	1850		
β-Phellandrene	47		
α-Pinene	86.6	1.01	732
β-Pinene	15		
Sabinene	86		
α-Terpinene	8470		
γ-Terpinene	140		
Terpinolene	1380		

TABLE 17. Yields of stabilized biradicals from the gas-phase reactions of O_3 with alkenes at room temperature and atmospheric pressure

Alkene	Yield	Reference
Ethene	0.38	Su *et al.*[55]
	0.37 ± 0.02[a]	Kan *et al.*[56]
	0.35 ± 0.05	Niki *et al.*[57]
	0.390 ± 0.053	Hatakeyama *et al.*[52,53]
	0.47	Horie and Moortgat[51]
Propene	0.254 ± 0.023	Hatakeyama *et al.*[52]
	0.44	Horie and Moortgat[51]
2-Methylpropene	0.174 ± 0.032	Hatakeyama *et al.*[52]
cis-2-Butene	0.18	Niki *et al.*[58]
trans-2-Butene	0.185 ± 0.028	Hatakeyama *et al.*[52]
	0.42	Horie and Moortgat[51]
2,3-Dimethyl-2-butene	0.30	Niki *et al.*[59]
1-Octene	0.22	Paulson and Seinfeld[36]
Cyclopentene	0.052 ± 0.013	Hatakeyama *et al.*[52]
Cyclohexene	0.032 ± 0.024	Hatakeyama *et al.*[52]
Cycloheptene	0.029 ± 0.015	Hatakeyama *et al.*[52]
1-Methylcyclohexene	0.104 ± 0.065	Hatakeyama *et al.*[52]
Methylenecyclohexane	0.216 ± 0.026	Hatakeyama *et al.*[52]
α-Pinene	0.125 ± 0.040	Hatakeyama *et al.*[52]
β-Pinene	0.249 ± 0.024	Hatakeyama *et al.*[52]

[a] Independent of temperature over the range 283–304 K.

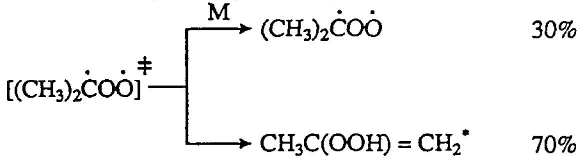
However, the biradical stabilization yields at room temperature and atmospheric pressure determined by Hatakeyama *et al.*[52,53] from the conversion of SO_2 to sulfuric acid aerosol do not agree well with the yields reported by Horie and Moortgat[51] from a product analysis/modeling study. In the absence of further data, it is recommended that the biradical stabilization yield from ethene at 298 K and atmospheric pressure is 0.37, and for the other alkenes that the data of Hatakeyama *et al.*[52] and Niki *et al.*[58,59] be used.

Thus, at ~760 Torr total pressure of air and ~298 K the fractions of $[\dot{C}H_2O\dot{O}]^{\ddagger}$ and $[CH_3\dot{C}HO\dot{O}]^{\ddagger}$ stabilized from the ethene and 2-butene systems are 0.37 and 0.18, respectively. Assuming that $k_a = k_b$ for the decomposition routes of the initially formed ozonide (but see above and Horie and Moortgat)[51] and that the $[\dot{C}H_2O\dot{O}]^{\ddagger}$ and $[CH_3\dot{C}HO\dot{O}]^{\ddagger}$ biradicals formed from propene react identically to those formed from ethene and the 2-butenes, a total stabilized biradical yield from propene ($\dot{C}H_2O\dot{O}$ plus $CH_3\dot{C}HO\dot{O}$) of 0.275 is predicted, in good agreement with the observed yield of 0.254 ± 0.023.[52] However, the data of Hatakeyama *et al.*[52] for the stabilized biradical yield from 2-methylpropene (0.174) at room temperature and atmospheric pressure are not consistent with the above data for the stabilization yield of $[\dot{C}H_2O\dot{O}]^{\ddagger}$ (0.37) and the stabilization yield of 0.30 for the $[(CH_3)_2\dot{C}O\dot{O}]^{\ddagger}$ biradical in the 2,3-dimethyl-2-butene system.[59] This suggests that the stabilization yields of these biradical species are dependent on the reaction system in which they are formed, in agreement with the differing $[\dot{C}H_2O\dot{O}]^{\ddagger}$ biradical stabilization yields observed from ethene (0.37) and vinyl chloride (0.25).[52,60]

Experimental data concerning the decomposition pathways of the energy-rich biradicals arise mainly from the low pressure (4–8 Torr) stopped flow-mass spectrometric studies of Herron and Huie,[50,61] Martinez *et al.*,[62,63] Martinez[64] and Martinez and Herron,[65,66] and the atmospheric pressure studies with Fourier infrared absorption spectroscopic or gas chromatographic detection of reactants and products of Niki *et al.*,[54,58,59] Su *et al.*,[55] Horie and Moortgat,[51,67] Paulson *et al.*,[68] Paulson and Seinfeld,[36] Atkinson *et al.*[69] and Atkinson and Aschmann.[70] Based on these studies, the energy-rich biradicals can undergo decomposition by three pathways [Reaction Scheme (6)] (see, for example, Niki *et al.*[59] and Martinez and Herron[66]). While the $O(^3P)$ atom elimination channel has been observed for the O_3 reaction with *trans*-1,2-dichloroethene,[54] to date there is no evidence for its occurrence for the simple monoalkenes at atmospheric pressure of air,[36,59,66] although Martinez and Herron[65] obtained a fit between experimental and predicted data at low pressure (~4 Torr) for 2,3-dimethyl-2-butene when a 20% $O(^3P)$-atom channel was included.

However, for the reaction of O_3 with isoprene, Paulson *et al.*[68] concluded from their product study that the $O(^3P)$ atom channel accounted for 45 ± 20% of the overall reaction (i.e., $\Delta[O(^3P)]/\text{-}\Delta[\text{isoprene}] = 0.45 \pm 0.20$) at room temperature and atmospheric pressure.[68]

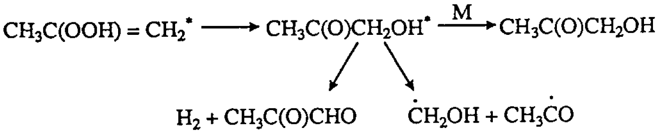
The occurrence of the hydroperoxide channel has been shown from the studies of Niki *et al.*[59] and Martinez and Herron[65] of the products and mechanism of the reaction of O_3 with 2,3-dimethyl-2-butene. Approximately 30% of the initially energy-rich biradical $[(CH_3)_2\dot{C}O\dot{O}]^{\ddagger}$ was observed to be stabilized at atmospheric pressure,[59] with the major decomposition route involving isomerization to the hydroperoxide[59,65] (the percentages are those of Niki *et al.*[59] at atmospheric pressure),



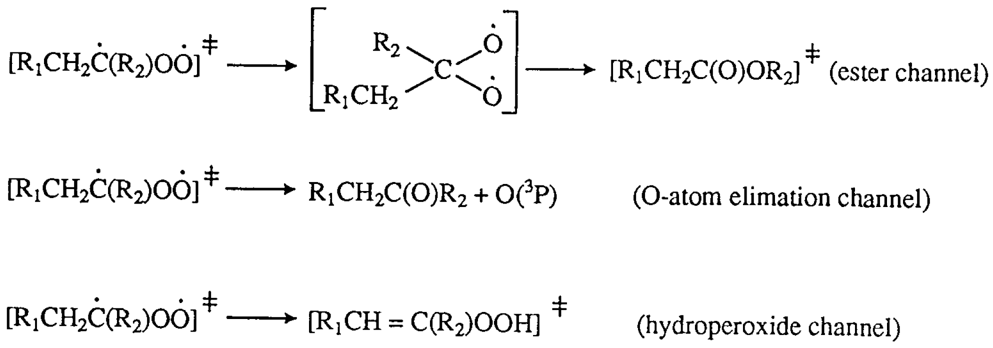
followed by dissociation of this energy-rich unsaturated hydroperoxide to an OH radical and the $CH_3CO\dot{C}H_2$ radical,[59]

$$CH_3C(OOH)=CH_2^* \rightarrow CH_3CO\dot{C}H_2 + OH$$

or, at low total pressures (~4 Torr), to an energy-rich hydroxyacetone molecule which can be collisionally stabilized or decompose.[65]



The product study of Niki *et al.*[59] concerning the products and reaction mechanism of the O_3 reaction with 2,3-dimethyl-2-butene showed that, through the isomerization and decomposition reaction of the $[(CH_3)_2\dot{C}O\dot{O}]^{\ddagger}$ biradical, this reaction is a significant source of OH radicals, with an OH radical formation yield under atmospheric conditions of ~0.70. This direct formation of OH radicals from the O_3 reaction with

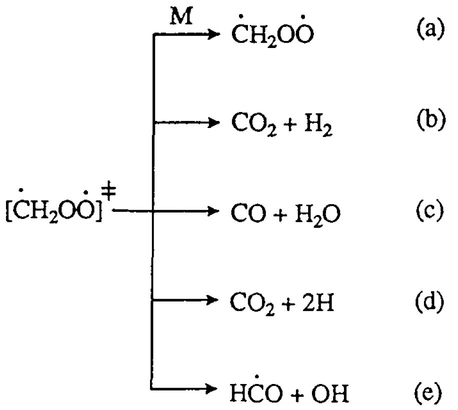


Reaction Scheme (6)

2,3-dimethyl-2-butene is consistent with other reports of OH radical (or other reactive radical) involvement in O_3-alkene reactions under atmospheric conditions.[36,68–72] Recently, Paulson *et al.*,[68] Paulson and Seinfeld,[36] Atkinson *et al.*[69] and Atkinson and Aschmann[70] have demonstrated the direct formation of OH radicals during the reactions of O_3 with a series of alkenes, dienes and monoterpenes, and the reported OH radical formation yields[36,59,68–70] are given in Table 18.

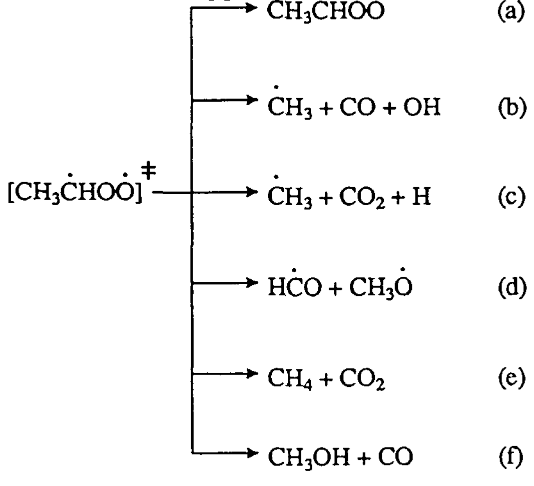
The majority of the product and reaction mechanism data for the reactions of O_3 with the simple monoalkenes concerns the reactions of ethene,[51,55,61] propene,[50,51] and *trans*-2-butene.[51] For the reaction of O_3 with ethene, the reactions are postulated to include:

$$O_3 + CH_2{=}CH_2 \rightarrow HCHO + [\dot{C}H_2O\dot{O}]^{\ddagger}$$



The studies of Herron and Huie[61] (supposedly adjusted to be applicable to atmospheric pressure[1,21,73]), Su *et al.*[55] and Horie and Moortgat[51] lead to fractions of the pathways (a)-(d) of: channel (a), 37%; channel (b), ~13%;[21,51] channel (c), 31–58%;[21,51,55] and channel (d), 6–10%.[21,51] However, Atkinson *et al.*[69] observed OH radicals to be formed with an ~12% yield, presumably via channel (e). Clearly, significant discrepancies between the various studies are apparent, even for the reactions of the simplest biradical, $[\dot{C}H_2O\dot{O}]^{\ddagger}$.

For the $[CH_3\dot{C}HO\dot{O}]^{\ddagger}$ biradical formed from the reaction of O_3 with propene, the postulated reactions are:



Recent studies and evaluations[2,21,51] have concluded that channels (a)–(f) account for: channel (a), 15–42%; channel (b) 16–30%; channel (c), 17–34%; channel (d), 0–7%; channel (e) 14–17% and channel (f), 0–7%. These various studies lead to differing product distributions from the O_3 reaction with propene. As one example, the OH radical formation yields vary from 0.10[51] to 0.15,[2] while Atkinson and Aschmann[70] obtained an OH radical formation yield of 0.33 (uncertain by a factor of ~1.5) from monitoring the formation of (cyclohexanone + cyclohexanol) formed from OH radical reaction with cyclohexane in a reacting O_3-propene-cyclohexane-air mixture. It is also of interest to note that Japar *et al.*[71] postulated an ~30% formation of a radical species which could react with propene (possibly the OH radical).

Thus, even for ethene and propene there are significant uncertainties in the details of the reaction pathways occurring, the radicals formed, and the product formation yields under atmospheric conditions.

The gas-phase reactions of O_3 with cycloalkenes have been studied by Niki *et al.*,[54] Hatakeyama *et al.*,[74,75] Izumi *et al.*[76] and Hatakeyama and Akimoto.[77] While these references should be consulted for further details, the formation of significant yields of dicarbonyls were observed,[74,75,77] and aerosol formation occurred readily.[76]

To date, there have been few quantitative product studies of the reactions of ozone with isoprene and the monoterpenes. For isoprene, Kamens *et al.*[78] and Niki *et al.*[54] observed the formation of HCHO, methacrolein, and methyl vinyl ketone. Both groups[54,78] reported HCHO, methyl vinyl ketone, and methacrolein yields of 85–96%, 13–18%, and 33–42%, respectively. The use of isotope labeling allowed Niki *et al.*[54] to conclude that the majority of the HCHO formed arose from secondary reactions. The recent study of Paulson *et al.*[68] has provided evidence that the O_3 reaction with isoprene leads to the formation of OH radicals and $O(^3P)$ atoms in large amounts, with molar yields of 68 ± 15% and 45 ± 20%, respectively, and the formation of these species leads to secondary reactions which complicate the analysis of the O_3-isoprene reaction.[68] Based on computer modeling of product data, Paulson *et al.*[68] concluded that the products formed from the O_3 reaction with isoprene are methacrolein, methyl vinyl ketone, and propene, with yields of 67 ± 9%, 26 ± 6% and 7 ± 3%, respectively.

Several studies have investigated the products of the ozone reactions with monoterpenes (see, for example, Schuetzle and Rasmussen,[79] Hull,[80] Yokouchi and Ambe,[81] Hatekayama *et al.*,[82] Jay and Stieglitz,[83] and Hakola *et al.*[47,48]). Yokouchi and Ambe[81] used high concentrations [$\sim(3\text{–}15) \times 10^{15}$ molecule cm^{-3}] of ozone and of the monoterpenes α- and β-pinene and limonene, and observed ready formation of aerosols, as may be expected. Using gas chromatography (GC) and GC/MS techniques, they identified pinonaldehyde (2,2-dimethyl-3-acetylcyclobutyl ethanol) and, to a lesser extent, pinonic acid (2,2-dimethyl-3-acetylcyclobutyl acetic acid) from α-pinene and 6,6-dimethylbicyclo[3.1.1]heptan-2-

TABLE 18. OH radical formation yields from the gas-phase reactions of O_3 with alkenes at room temperature and atmospheric pressure

Alkene	OH radical formation yield[a]	Reference
Ethene	0.12	Atkinson *et al.*[69]
Propene	0.33	Atkinson and Aschmann[70]
1-Butene	0.41	Atkinson and Aschmann[70]
cis-2-Butene	0.41	Atkinson and Aschmann[70]
trans-2-Butene	0.64	Atkinson and Aschmann[70]
2-Methylpropene	0.84	Atkinson and Aschmann[70]
2-Methyl-1-butene	0.83	Atkinson and Aschmann[70]
2-Methyl-2-butene	0.89	Atkinson and Aschmann[70]
2,3-Dimethyl-2-butene	~0.70	Niki *et al.*[59]
	1.00	Atkinson and Aschmann[70]
1-Octene	0.45 ± 0.20	Paulson and Seinfeld[36]
1,3-Butadiene	0.08	Atkinson and Aschmann[70]
Isoprene	0.68 ± 0.15	Paulson *et al.*[68]
	0.27	Atkinson *et al.*[69]
Cyclohexene	0.68	Atkinson and Aschmann[70]
Camphene	≤ 0.18	Atkinson *et al.*[69]
3-Carene	1.06	Atkinson *et al.*[69]
Limonene	0.86	Atkinson *et al.*[69]
Myrcene	1.15	Atkinson *et al.*[69]
cis- and *trans*-Ocimene	0.63	Atkinson *et al.*[69]
β-Phellandrene	0.14	Atkinson *et al.*[69]
α-Pinene	0.85	Atkinson *et al.*[69]
β-Pinene	0.35	Atkinson *et al.*[69]
Sabinene	0.26	Atkinson *et al.*[69]
Terpinolene	1.03	Atkinson *et al.*[69]

[a] The estimated uncertainties for the yields of Atkinson *et al.*[69] and Atkinson and Aschmann[70] are a factor of 1.5.

one from β-pinene. No products were identified from the limonene reaction.[81]

The product study of Hatakeyama *et al.*[82] was carried out at much lower reactant concentrations (typically ~3 × 10^{13} molecule cm^{-3}), using FT-IR absorption spectroscopy and GC/MS for analysis. From the α-pinene reaction, CO, CO_2, HCHO, pinonaldehyde and nor-pinonaldehyde were identified with molar formation yields of CO, CO_2 and HCHO of 9%, 30% and 22%, respectively, and the "total aldehydes" yield was ~51% (reported to be mainly pinonaldehyde and nor-pinonaldehyde). The products identified from the β-pinene reaction were CO_2, HCHO and 6,6-dimethylbicyclo[3.1.1] heptan-2-one, with molar yields of 27%, 76%, and 40%, respectively.[82] Aerosol formation accounted for 14–18% of the overall reaction. The product studies of Hakola *et al.*[47,48] have used GC and GC/MS to determine carbonyl product yields, and the data of Hatakeyama *et al.*,[82] Jay and Stieglitz[83] and Hakola *et al.*,[47,48] are given in Table 19. No significant formation of products was observed by Hakola *et al.*[48] by GC-FID and GC/MS from the O_3 reactions with 3-carene or limonene. The chemical composition of the aerosols formed from isoprene and β-pinene has been investigated by Palen *et al.*[44] (see also Pandis *et al.*[43] concerning the aerosol yields from these terpenes).

The stabilized biradicals are known to react with aldehydes, SO_2, CO, H_2O and NO_2, and it is expected that they will also react with NO.[1,49] Based upon the available data for the reactions of $\dot{C}H_2O\dot{O}$ radicals with these reactants, with rate constants relative to the reaction of $\dot{C}H_2O\dot{O}$ with SO_2 of: HCHO, ~0.25;[55] CO, 0.0175;[55] H_2O, (2.3 ± 1) × 10^{-4}[84] and NO_2, 0.014,[85] it appears that the reaction of stabilized biradicals with water vapor will be their dominant loss process under atmospheric conditions.

In addition to the expected formation of carboxylic acids from these reactions of the energy-rich biradicals with H_2O,[1]

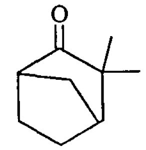
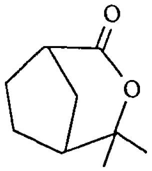
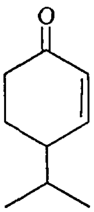
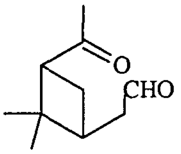
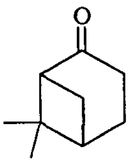
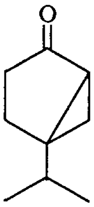
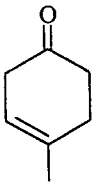
$$R\dot{C}HO\dot{O} + H_2O \rightarrow \rightarrow RC(O)OH + H_2O$$

the recent studies of Gäb *et al.*,[86] Becker *et al.*,[87] Simonaitis *et al.*[88] and Hewitt and Kok[89] have reported the formation of H_2O_2 and organic hydroperoxides from the reactions of O_3 with alkenes. There are significant discrepancies between these studies; Simonaitis *et al.*[88] using a 31000 liter chamber obtained H_2O_2 yields of 9–19% for *trans*-2-butene, isoprene and several monoterpenes,[88] much higher than the yields reported by Becker *et al.*[87] from studies conducted in a 130 liter chamber.

NO_3 Radical Reaction

The kinetics and mechanisms of the gas-phase reaction of the NO_3 radical with alkenes, cycloalkenes and dienes have recently been reviewed and evaluated by Atkinson,[90] and that review and evaluation is updated in Sec. 4.3. The

TABLE 19. Carbonyl products observed, and their formation yields, from the gas-phase reactions of O_3 with monoterpenes at room temperature and atmospheric pressure

Monoterpene	Product	Yield	Reference
Camphene		a 0.36 ± 0.06[b]	Jay and Stieglitz[83] Hakola *et al.*[48]
		a ~0.2	Jay and Stieglitz[83] Hakola *et al.*[48]
β-Phellandrene		0.29 ± 0.06[b]	Hakola *et al.*[47]
α-Pinene	HCHO	0.22 ± 0.01	Hatakeyama *et al.*[82]
		0.51 ± 0.06[c] 0.19 ± 0.04[b]	Hatakeyama *et al.*[82] Hakola *et al.*[48]
β-Pinene	HCHO	0.76 ± 0.02	Hatakeyama *et al.*[82]
		0.40 ± 0.02[c] 0.23 ± 0.05[b]	Hatakeyama *et al.*[82] Hakola *et al.*[48]
Sabinene		0.50 ± 0.09[b]	Hakola *et al.*[48]
Terpinolene		0.40 ± 0.06[b]	Hakola *et al.*[48]

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[a] No product yields reported.

[b] Indicated errors are two least-squares standard deviations combined with estimated overall uncertainties in the GC-FID calibration factors of the monoterpene and product of ±10% each. OH radicals scavenged by excess cyclohexane.

[c] The 6,6-dimethylbicyclo[3.1.1]heptan-2-one and pinonaldehyde as measured by Fourier transform infrared absorption spectroscopy may have included IR contributions from other, as yet unidentified, carbonyl compounds.

room temperature rate constants and temperature-dependent parameters for a series of atmospherically important alkenes (taken from Ref. 90 and Sec. 4.3.) are given in Table 20. These reactions proceed by NO_3 radical addition to the $>C=C<$ bond, with H-atom abstraction being insignificant.[90]

The products of the gas-phase reactions of the NO_3 radical with a series of alkenes at room temperature and atmospheric pressure have been studied by Akimoto *et al.*,[91] Hoshino *et al.*,[92] Bandow *et al.*,[93] Shepson *et al.*,[22] Kotzias *et al.*,[94] Skov *et al.*,[95] Barnes *et al.*[96] and Hjorth *et al.*,[97] and the reaction mechanisms have been discussed by Atkinson.[90] The studies of Bandow *et al.*,[93] Shepson *et al.*,[22] Barnes *et al.*[96] and Hjorth *et al.*[97] allow the general features of the reaction mechanisms under atmospheric conditions to be understood. Under atmospheric conditions, rapid addition of O_2 will occur to the initially formed nitratoalkyl radical, leading to the formation of β-nitratoalkyl peroxy radicals. Taking the NO_3 radical reaction with propene as an example:

$$\mathrm{NO_3 + CH_3CH{=}CH_2 \xrightarrow{M} CH_3\dot{C}HCH_2ONO_2}$$
$$\text{and } \mathrm{CH_3CH(ONO_2)\dot{C}H_2}$$

followed by, for example

$$\mathrm{CH_3\dot{C}HCH_2ONO_2 + O_2 \xrightarrow{M} CH_3CH(O\dot{O})CH_2ONO_2}$$

When NO_3 radicals are present, NO concentrations must be extremely low,[21] and these β-nitratoalkyl peroxy radicals will then either react with HO_2 and other $R\dot{O}_2$ radicals, or reversibly add NO_2 to yield the thermally unstable nitrato peroxynitrates[22,90,93,96,97]

$$\mathrm{CH_3CH(O\dot{O})CH_2ONO_2 + NO_2 \overset{M}{\rightleftarrows} CH_3CH(OONO_2)CH_2ONO_2}$$

Because of the expected rapid thermal decomposition of the peroxy nitrates, these species act as a temporary reservoir of the β-nitratoalkyl peroxy radicals. If NO is present at sufficiently high concentrations to react with the peroxy radicals, then the corresponding alkoxy radical will be formed together with NO_2, and dinitrates may be formed from the $R\dot{O}_2$ + NO reaction.

$$\mathrm{CH_3CH(O\dot{O})CH_2ONO_2 + NO} \begin{cases} \xrightarrow{M} \mathrm{CH_3CH(ONO_2)CH_2ONO_2} & \text{(a1)} \\ \longrightarrow \mathrm{CH_3CH(\dot{O})CH_2ONO_2 + NO_2} & \text{(a2)} \end{cases}$$

In the absence of NO, the β-nitratoalkylperoxy radicals will react with HO_2 or other organic peroxy radicals. For example, for the $CH_3CH(O\dot{O})CH_2ONO_2$ radical formed from propene

$$\mathrm{CH_3CH(O\dot{O})CH_2ONO_2 + HO_2 \longrightarrow CH_3CH(OOH)CH_2ONO_2 + O_2} \quad \text{(b)}$$

$$\mathrm{CH_3CH(O\dot{O})CH_2ONO_2 + R\dot{O}_2} \begin{cases} \longrightarrow \mathrm{CH_3CH(\dot{O})CH_2ONO_2 + R\dot{O} + O_2} & \text{(c1)} \\ \longrightarrow \mathrm{CH_3CH(OH)CH_2ONO_2} \text{ and } & \text{(c2)} \\ \quad \mathrm{CH_3C(O)CH_2ONO_2 + R\dot{O}_2} \text{ products} & \end{cases}$$

The alkoxy radicals formed from reactions (a2) and (c1) can then react with O_2, decompose or isomerize, as discussed in Sec. 2.1. above, and can also react with NO_2

$$\mathrm{CH_3CH(\dot{O})CH_2ONO_2 \longrightarrow CH_3CHO +} \begin{array}[t]{c} \mathrm{\dot{C}H_2ONO_2} \\ \downarrow \\ \mathrm{HCHO + NO_2} \end{array} \quad \text{(d)}$$

$$\mathrm{CH_3CH(\dot{O})CH_2ONO_2 + O_2 \longrightarrow CH_3C(O)CH_2ONO_2 + HO_2} \quad \text{(e)}$$

$$\mathrm{CH_3CH(\dot{O})CH_2ONO_2 + NO_2 \xrightarrow{M} CH_3CH(ONO_2)CH_2ONO_2} \quad \text{(f)}$$

Based on this reaction scheme, in the absence of NO dinitrates are expected to be formed from reaction (f), and hence their yields should decrease with decreasing NO_2 concentration. This is consistent with the studies of Shepson *et al.*[22] and Bandow *et al.*[93] for propene and with the more recent data of Barnes *et al.*[96] and Hjorth *et al.*[97] Under atmospheric conditions the formation of dinitrates from reaction (f) is expected to be of no importance. Neglecting isomerization of the alkoxy radicals (but see Hjorth *et al.*)[97] the expected major products of the NO_3 radical-initiated reactions of the simple alkenes are then carbonyl compounds [reaction (d)], nitratocarbonyls [reactions (c2) and (e)], nitratoalcohols [reaction (c2)] and nitratohydroperoxides [reaction (b)].

The products observed by Barnes *et al.*[96] and Hjorth *et al.*[97] from the gas-phase reactions of the NO_3 radical with a series of alkenes and dienes, and their measured formation yields, are given in Table 21. While the agreement is good for the carbonyls formed from propene and for $CH_3C(O)CH(ONO_2)CH_3$ from *trans*-2-butene, there are significant discrepancies for the 2-methylpropene reaction product yields and for the CH_3CHO yield from *trans*-2-butene. Interestingly, Hjorth *et al.*[97] observed the formation of $CH_3CH(OH)CH(ONO_2)CH_3$ from the 2-butenes, indicating the occurrence of reaction (c2). These differences in the product yields may be due, at least in part, to the fact that those of Barnes *et al.*[96] were obtained after addition of NO to the reaction system to promote the thermal decompositions of the peroxynitrates such as $CH_3CH(OONO_2)CH_2ONO_2$, while the yields reported by Hjorth *et al.*[97] were those after the peroxynitrates had been allowed to thermally decompose, without addition of NO. The addition of NO to the reaction systems can lead to the formation of OH radicals[22,98] and hence the formation of OH radical reaction products,

TABLE 20. Room temperature rate constants k and temperature-dependent parameters, $k = A\,e^{-B/T}$, for the gas-phase reactions of the NO_3 radical with a series of alkenes [from Ref. 90 and Sec. 4.3.]

Alkene	A (cm^3 molecule^{-1} s^{-1})	B (K)	k(cm^3 molecule^{-1} s^{-1}) at 298 K
Ethene[a]			2.05×10^{-16}
Propene	4.59×10^{-13}	1156	9.49×10^{-15}
1-Butene	2.04×10^{-13}	843	1.21×10^{-14}
2-Methylpropene			3.32×10^{-13}
cis-2-Butene			3.50×10^{-13}
trans-2-Butene[b]			3.90×10^{-13}
2-Methyl-2-butene			9.37×10^{-12}
2,3-Dimethyl-2-butene			5.72×10^{-11}
1,3-Butadiene			1.0×10^{-13}
2-Methyl-1,3-butadiene	3.03×10^{-12}	446	6.78×10^{-13}
Myrcene			1.1×10^{-11}
Ocimene			2.2×10^{-11}
Cyclopentene			4.6×10^{-13}
Cyclohexene			5.3×10^{-13}
Cycloheptene			4.8×10^{-13}
Camphene			6.6×10^{-13}
2-Carene			1.9×10^{-11}
3-Carene			9.1×10^{-12}
Limonene			1.22×10^{-11}
α-Pinene	1.19×10^{-12}	−490	6.16×10^{-12}
β-Pinene			2.51×10^{-12}
α-Phellandrene			8.5×10^{-11}
β-Phellandrene			8.0×10^{-12}
Sabinene			1.0×10^{-11}
α-Terpinene			1.8×10^{-10}
γ-Terpinene			2.9×10^{-11}
Terpinolene			9.7×10^{-11}

[a] $k = 4.88 \times 10^{-18}\,T^2\,e^{-2282/T}$ cm^3 molecule^{-1} s^{-1} over the temperature range 290–523 K recommended.

[b] $k = 1.22 \times 10^{-18}\,T^2\,e^{382/T}$ cm^3 molecule^{-1} s^{-1} over the temperature range 204–378 K recommended.

and Shepson *et al.*[22] observed enhanced formation of HCHO and CH_3CHO relative to $CH_3C(O)CH_2ONO_2$ from a reacting propene system after the addition of NO. The product data of Shepson *et al.*[22] obtained prior to the addition of NO show that similar yields of HCHO and CH_3CHO are formed from propene, with the yield of $CH_3C(O)CH_2ONO_2$ being a factor of ~2 higher.

The product studies of Barnes *et al.*[96] for α- and β-pinene, 3-carene and limonene led to the formation of aerosols, although for α- and β-pinene IR spectral features indicated the presence of $>C=O$ and $-ONO_2$ groups. Aerosol formation could be expected because of the relatively high concentrations of monoterpenes ($\sim 5 \times 10^{14}$ molecule cm^{-3}) used.[96]

It is clear that further product studies are required before the reaction mechanisms and product yields of these NO_3 radical reactions with the alkenes are reliably known.

NO_2 Reactions

NO_2 reacts with conjugated dialkenes with rate constants at room temperature of $> 10^{-20}$ cm^3 molecule^{-1} s^{-1}.[98,99] These reactions are of negligible importance as an atmospheric loss process of the alkenes and dienes, but may be of some importance in environmental chamber experiments carried out at high NO_2 concentrations, (see, for example, Refs. 3 and 4).

The only monoalkene or non-conjugated diene which has been shown to react with NO_2 at room temperature at an observable rate is 2,3-dimethyl-2-butene,[98,100] with the room temperature rate constants for the other non-conjugated alkenes being $< 10^{-20}$ cm^3 molecule^{-1} s^{-1}.[98,99] The room temperature rate constants for the gas-phase reactions of NO_2 with 2,3-dimethyl-2-butene and selected dienes are given in Table 22. As shown by Atkinson *et al.*[98] and Niki *et al.*,[100] the reaction sequences are generally as follows, taking 1,3-butadiene as an example

$$NO_2 + CH_2{=}CHCH{=}CH_2 \overset{M}{\rightleftarrows} CH_2{=}CH\dot{C}HCH_2NO_2$$

with the initial reaction being reversible, at least for 2,3-dimethyl-2-butene.[100] The initially formed radical then adds O_2 and reacts as follows

$$\begin{tikzcd} CH_2{=}CH\dot{C}HCH_2NO_2 + O_2 \arrow[r, "M"] & CH_2{=}CHCH(O\dot{O})CH_2NO_2 \arrow[d, shift left, "NO_2"] \\ & CH_2{=}CHCH(OONO_2)CH_2NO_2 \arrow[u, shift left] \end{tikzcd}$$

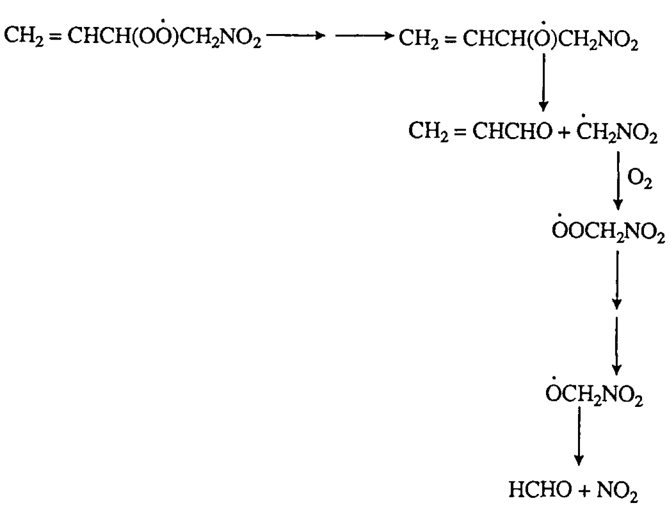
TABLE 21. Products and their yields observed from the gas-phase reactions of the NO_3 radical with a series of alkenes at room temperature and atmospheric pressure

Alkene	Product	Yield (molar) Barnes *et al.*[96]	 Hjorth *et al.*[97]
Propene	HCHO	0.08	0.10 ± 0.05
	CH_3CHO	0.12	0.10 ± 0.05
	total nitrates	~0.58[a]	
1-Butene	HCHO	0.11	
	CH_3CH_2CHO	0.12	
	total nitrates	~0.60[a]	
2-Methylpropene	HCHO	0.80	0.24 ± 0.08
	$CH_3C(O)CH_3$	0.85	0.24 ± 0.08
	total nitrates	~0.25[a]	
trans-2-Butene	CH_3CHO	0.70	0.34 ± 0.12[b]
	$CH_3C(O)CH(ONO_2)CH_3$	0.55	0.41 ± 0.13[b]
	$CH_3CH(ONO_2)CH(ONO_2)CH_3$	0.04	
	$CH_3CH(OH)CH(ONO_2)CH_3$		0.15 ± 0.05[b]
2-Methyl-2-butene	CH_3CHO		0.22 ± 0.06
	$CH_3C(O)CH_3$		0.22 ± 0.06
2,3-Dimethyl-2-butene	$CH_3C(O)CH_3$		1.04 ± 0.26
	$(CH_3)_2C(ONO_2)C(ONO_2)(CH_3)_2$		0.05 ± 0.02
1,3-Butadiene	HCHO	0.12	
	$CH_2=CHCHO$	0.12	
	CO	0.04	
	total nitrates	~0.60[a]	
2-Methyl-1,3-butadiene (isoprene)	HCHO	0.11	
	CO	0.04	
	total nitrates	~0.80[a]	

[a] Estimated from the use of IR absorption cross-sections for 14 compounds containing the $—ONO_2$ group.

[b] Yields also apply for *cis*-2-butene.

to form a thermally unstable nitro-peroxynitrate. The following reactions are expected:

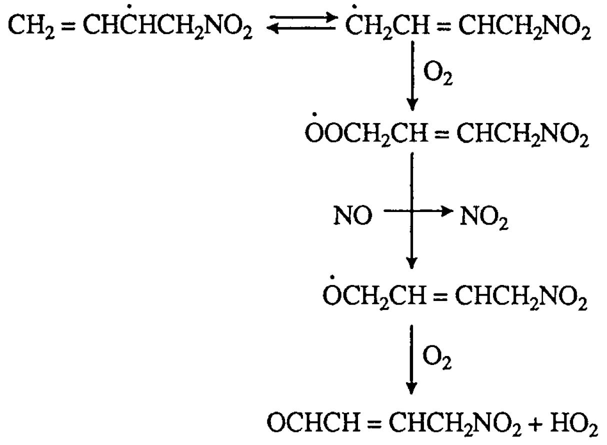


$$\begin{aligned}
&CH_2=CHCH(O\dot{O})CH_2NO_2 \longrightarrow \quad \longrightarrow CH_2=CHCH(\dot{O})CH_2NO_2\\
&\qquad\downarrow\\
&CH_2=CHCHO + \dot{C}H_2NO_2\\
&\qquad\downarrow O_2\\
&\dot{O}OCH_2NO_2\\
&\qquad\downarrow\\
&\qquad\downarrow\\
&\dot{O}CH_2NO_2\\
&\qquad\downarrow\\
&HCHO + NO_2
\end{aligned}$$

For isoprene, an analogous reaction sequence leads to the formation of methyl vinyl ketone and methacrolein, together with the HCHO co-product, and indeed this is observed.[3,4] In the presence of NO the dark NO_2 reactions with isoprene[4] and 1,3-cyclohexadiene[98] (and presumably other dienes) lead to the production of OH radicals. The presence of NO is expected to lead to the facile conversion of the peroxy radicals to the corresponding alkoxy radicals, and in effect remove the peroxynitrates as temporary sinks for the peroxy radicals:

$$CH_2=CHCH(O\dot{O})CH_2NO_2 + NO \rightarrow CH_2=CHCH(\dot{O})CH_2NO_2 + NO_2$$

However, the reaction scheme shown above does not lead to the production of OH radicals, and this probably means that reaction pathways leading to the formation of HO_2 radicals occur, by reaction of an alkoxy radical with O_2 to form a carbonyl + HO_2. One possibility involves the reactions:



followed by:

$$HO_2 + NO \rightarrow OH + NO_2$$

TABLE 22. Room temperature rate constants, k, for the gas-phase reactions of NO_2 with selected alkenes and dienes at atmospheric pressure of air

Alkene	$10^{20} \times k(\mathrm{cm^3\ molecule^{-1}\ s^{-1}})^a$
2,3-Dimethyl-2-butene	1.0
1,3-Butadiene	3.0
2-Methyl-1,3-butadiene (isoprene)	15
Myrcene	26
Ocimene (*cis*- and *trans*-)	89
α-Phellandrene	1300
β-Phellandrene	~70
α-Terpinene	650

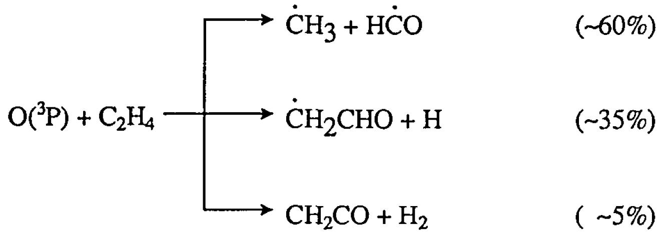
[a] From Glasson and Tuesday,[101] Atkinson *et al.*,[98,102] Gu *et al.*,[42] Ohta *et al.*,[99] Niki *et al.*,[100] Shorees *et al.*,[103] and Paulson *et al.*[4] Uncertainties are a factor of ~1.5, except for β-phellandrene, for which the uncertainty is a factor of ~2.

O(^{3}P) Atom Reactions

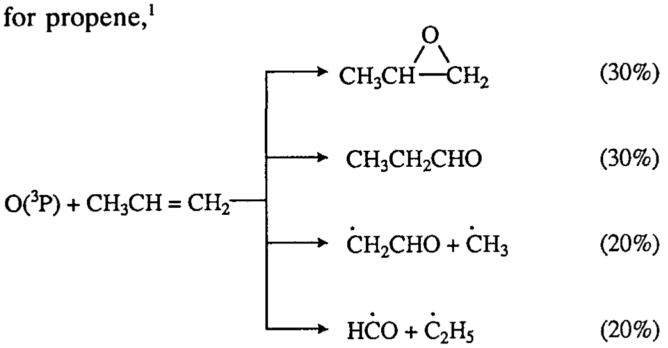
The O(^{3}P) atom reactions with the alkenes are of little importance under atmospheric conditions, but can become significant in laboratory irradiations of NO_x-alkene-air mixtures (see, for example, Paulson *et al.*[4] and Paulson and Seinfeld[36]). The kinetics, reaction mechanisms and products formed under atmospheric conditions have been previously reviewed by Cvetanovic and Singleton,[104] Atkinson and Lloyd[1] and Cvetanovic.[105] The rate constants have been reviewed and evaluated by Cvetanovic,[105] and that review should be consulted for kinetic information. It should also be noted that a good correlation between the OH radical and O(^{3}P) atom reaction rate constants exists,[39] with (rate constants in units of 10^{-12} cm^3 molecule^{-1} s^{-1})

$$\ln k^{O(^3P)} = -4.09 + 1.76 \ln k^{OH}$$

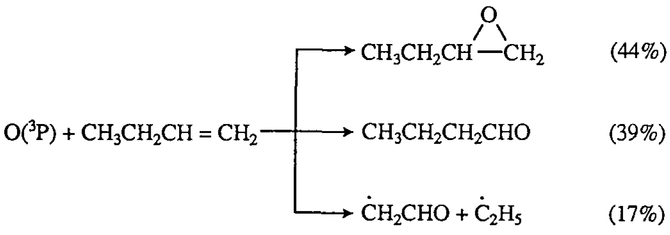
The initial reaction involves addition of the O(^{3}P) atom to the $>C=C<$ bond, followed by collisional stabilization to a carbonyl or an epoxide or decomposition. As generally recommended by Atkinson and Lloyd,[1] for ethene at atmospheric pressure and 298 K, the products are,[1,106,107]



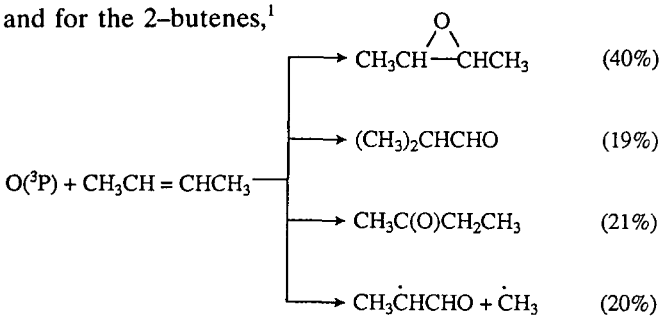
for propene,[1]



for 1-butene,[1]



and for the 2-butenes,[1]

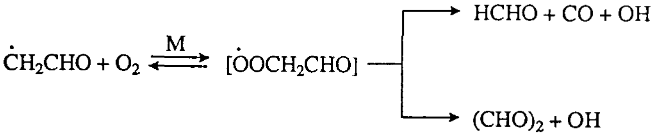


although other fragmentation pathways cannot be excluded for the 2-butenes.

The atmospheric reactions of the carbonyl compounds and epoxides are dealt with in Sec. 2.5 below. The $\dot{C}H_2CHO$ (vinoxy) radical reacts with O_2,[108,109] NO[108] and NO_2.[110] Under atmospheric conditions, the only important reaction is with O_2. The rate constant for the O_2 reaction is in the fall-off region between second- and third-order kinetics at ≤100–300 Torr of He, N_2 or SF_6 at room temperature.[108,109] The limiting high-pressure rate constant for this reaction is[108,109]

$$k_\infty(\dot{C}H_2CHO + O_2) = 2.5 \times 10^{-13}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ \text{at}\ 298\ \mathrm{K},$$

with little or no temperature dependence over the range 292–476 K[108] (see also Lorenz *et al.*[109]). The magnitude of the rate constant and the pressure dependence shows that the vinoxy radical reaction with O_2 proceeds by initial addition to form the $\dot{O}OCH_2CHO$ radical (or its isomer). While the products of this reaction have not been directly monitored, there is evidence from the OH radical-initiated reaction of acetylene[111,112] that OH radicals are one product. Hence, based on the studies of Gutman and Nelson[108] and Schmidt *et al.*,[111,112] the reaction possibly proceeds by



$$\dot{C}H_2CHO + O_2 \overset{M}{\rightleftarrows} [\dot{O}OCH_2CHO] \rightarrow \begin{cases} HCHO + CO + OH \\ (CHO)_2 + OH \end{cases}$$

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2.3. Alkynes

The potentially atmospherically important reactions of the alkynes are with OH and NO_3 radicals and O_3. At the present time, kinetic and product data are available primarily for acetylene, propyne, 1-butyne and 2-butyne.

OH Radical Reaction

The kinetic and mechanistic data for the gas-phase reactions of the OH radical with alkynes have been reviewed and evaluated by Atkinson,[1] and that review and evaluation is updated in Sec. 3.5. The limiting high-pressure second-order rate constants at 298 K and the temperature parameters recommended by Atkinson[1] (see also Sec. 3.5) are given in Table 23. For acetylene, the rate constant is in the fall-off region between second- and third-order kinetics below ~1000 Torr.[1] The recommended parameters in the Troe fall-off expression are[1]: $k_o = 5.0 \times 10^{-30} (T/298)^{-1.5}$ cm^6 molecule^{-2} s^{-1}; $k_\infty = 9.4 \times 10^{-12} e^{-700/T}$ cm^3 molecule^{-1} s^{-1}, and $F = 0.6$ at 298 K, leading to k(acetylene) $= 8.15 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K and 760 Torr total pressure of air.

For the other alkynes studied to date, the rate constants determined at 760 Torr total pressure of air are probably at or close to the high pressure limiting values.[1] These reactions proceed by initial OH radical addition to the $-C{\equiv}C-$ bond,[1] and the OH-acetylene adduct can isomerize to the vinoxy ($\dot{C}H_2CHO$) radical[2,3] with subsequent decomposition or reaction. While the formation of ketene has been observed at low pressures,[4] ketene formation is of negligible importance under atmospheric conditions [with a $\leq 0.5\%$ yield of ketene being observed from acetylene].[5] Schmidt *et al.*[2,3] observed the intermediate formation of the vinoxy radical, with glyoxal being a major product. In the presence of O_2, OH radicals were efficiently regenerated,[2,3] possibly from the reaction of the $\dot{C}H_2CHO$ radical with O_2 (see Sec. 2.2 above). Hatakeyama *et al.*[5] investigated the products of the reactions of OH and OD radicals with acetylene, propyne and 2-butyne in the presence of one atmosphere of air. Glyoxal, methylglyoxal and biacetyl were observed from acetylene, propyne and 2-butyne, respectively, in both the absence and presence of NO_x.[5] For acetylene, formic acid was also observed in appreciable yield.[5] The reaction of OH radicals with acetylene appears to proceed via (at atmospheric pressure where the initially formed adduct is collisionally stabilized),

$$OH + CH{\equiv}CH \xrightarrow{M} HOCH{=}\dot{C}H$$

$$HOCH{=}\dot{C}H \rightarrow \dot{C}H_2CHO \xrightarrow{O_2} (CHO)_2 + OH$$

$$HOCH{=}\dot{C}H + O_2 \rightarrow HOCH{=}CHO\dot{O}$$

$$HOCH{=}CHO\dot{O} \rightarrow H\dot{C}O + HCOOH$$

$$\begin{tikzcd} HOCH{=}CHO\dot{O} + NO \arrow[r] & HO\dot{C}HCHO + NO_2 \arrow[d, "O_2"] \\ & (CHO)_2 + HO_2 \end{tikzcd}$$

The fraction of reaction leading directly to OH formation, without conversion of NO to NO_2, is uncertain at the present time. The product yields obtained by Hatakeyama *et al.*[5] were as follows: from acetylene, HCOOH, 0.4 ± 0.1; $(CHO)_2$, 0.7 ± 0.3; from propyne, HCOOH, 0.12 ± 0.02; $CH_3C(O)CHO$, 0.53 ± 0.03; and from 2-butyne, CH_3COOH, 0.12 ± 0.01; and $CH_3C(O)C(O)CH_3$, 0.87 ± 0.07. Other products must thus be formed from propyne.

TABLE 23. Rate constants k_∞ at 298 K and temperature-dependent parameters, $k = Ae^{-B/T}$, for the reaction of OH radicals with alkynes at the high-pressure limit (from Ref. 1)

Alkyne	$10^{12} \times k_\infty$ (cm^3 molecule^{-1} s^{-1})	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	B (K)
Acetylene	0.90	9.4	700
Propyne	5.9		
1-Butyne	8.0	8.0	0
2-Butyne	27.4	10	−300

O_3 Reactions

Rate constants have been determined for the reactions of O_3 with acetylene, propyne, 1-butyne, 2-butyne and butadiyne.[6] There are significant discrepancies between the various studies, and no recommendations were made by Atkinson and Carter.[6] The most recent data of Atkinson and Aschmann[7] gave rate constants at 294 ± 2 K of (in cm^3 molecule^{-1} s^{-1} units): acetylene, 7.8×10^{-21}; propyne, 1.4×10^{-20}; and 1-butyne, 2.0×10^{-20}. These rate constants are sufficiently low that the O_3 reactions are of negligible importance as an alkyne loss process. No definitive product data are available, although α-dicarbonyls have been observed from the reaction of O_3 with acetylene, propyne, 1-butyne and 2-butyne.[8]

NO_3 Radical Reactions

The kinetics and mechanisms of the gas-phase reactions of the NO_3 radical with alkynes have been reviewed and evaluated by Atkinson,[9] and that review and evaluation is updated in Sec. 4.5. The room temperature rate constants and temperature-dependent parameters given in the review of Atkinson[9] (see also Sec. 4.5) are given in Table 24. These reactions are sufficiently slow that they can be neglected for atmospheric purposes.

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TABLE 24. Room temperature rate constants k and temperature-dependent parameters, $k = Ae^{-B/T}$, for the gas-phase reactions of NO_3 radicals with alkynes (from Atkinson[9]; see also Sec. 4.5)

Alkyne	A (cm^3 molecule^{-1} s^{-1})	B (K)	k (cm^3 molecule^{-1} s^{-1})	at T(K)
Acetylene			$<5 \times 10^{-17}$	298
Propyne	1.63×10^{-11}	3328	2.30×10^{-16}	298
1-Butyne	3.2×10^{-11}	3320	4.6×10^{-16}	295 ± 2
2-Butyne			6.7×10^{-14}	295 ± 2

2.4. Aromatic Compounds

The aromatic compounds of concern in polluted urban atmospheres are the aromatic hydrocarbons (benzene, alkyl-substituted benzenes and styrene) and their aromatic ring-retaining products (aromatic aldehydes and phenolic compounds). Additionally, there is interest in the atmospheric chemistry of the 2- through 4-ring polycyclic aromatic hydrocarbons (PAH) and their derivatives. In this section, only the monocyclic aromatic compounds are considered, and the articles of Atkinson and Carter,[1] Atkinson *et al.*,[2-4] Zielinska *et al.*,[5,6] Arey *et al.*,[7-9] Atkinson,[10,11] Helmig *et al.*[12] and Atkinson and Arey[13] should be consulted concerning the gas-phase atmospheric chemistry of the 2- to 4-ring PAH.

Benzene and Alkyl-Substituted Benzenes

O_3 and NO_3 Radical Reactions. The monocyclic aromatic hydrocarbons react only very slowly with O_3, with room temperature rate constants of $<10^{-20}$ cm^3 molecule^{-1} s^{-1} having been measured for benzene,[1,14] toluene,[1,14] the xylenes[1,14] and the trimethylbenzenes,[1] and the O_3 reactions of benzene and the alkyl-substituted benzenes are hence of negligible atmospheric importance.

The kinetics and mechanisms of the gas-phase reactions of the NO_3 radical with aromatic hydrocarbons have been reviewed and evaluated by Atkinson,[11] and that review and evaluation is updated in Sec. 4.9. The room temperature rate constants for the gas-phase reactions of the NO_3 radical with benzene and the alkyl-substituted benzenes are given in Table 25, and it can be seen that these rate constants are in the range $\sim10^{-16}$–10^{-15} cm^3 molecule^{-1} s^{-1}. A deuterium isotope effect has been observed for the gas-phase reactions of the NO_3 radical with toluene[11,15] and *o*- and *p*-xylene,[16] showing that the rate-determining step in these NO_3 radical reactions involves H- (or D-) atom abstraction from the C–H (or C–D) bonds of the alkyl substituent group(s). Thus, the NO_3 radical reactions with the alkyl-substituted benzenes proceed by an overall H-atom abstraction from the C–H bonds of the alkyl substituent group(s)[11,15,16]

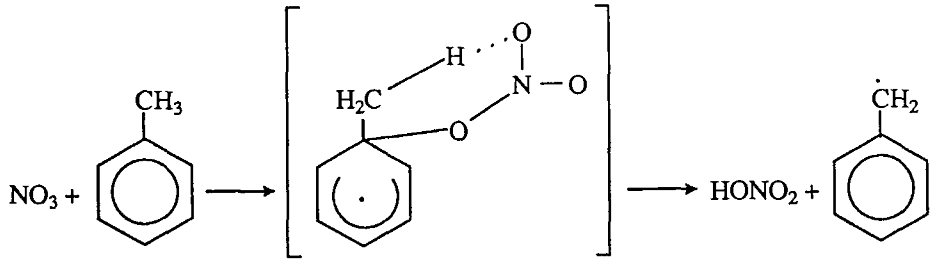
$$NO_3 + C_6H_5CH_3 \rightarrow HONO_2 + C_6H_5\dot{C}H_2$$

The magnitude of these NO_3 radical reaction rate constants indicates that the NO_3 radical reactions with benzene, toluene and the xylenes are of negligible importance as a tropospheric loss process, and that the NO_3 radical reactions for the trimethylbenzenes will also be of negligible or minor importance. However, for tetralin the NO_3 radical reaction may well be a minor ($\sim10\%$) tropospheric loss process, and similarly for other alkyl-substituted benzenes with $-CH_2-$ and/or $>CH-$ groups adjacent to the aromatic ring,[11] since it has been postulated that these reactions [see Reaction Scheme (7)] proceed by the intermediate formation of a six-membered transition state[11].

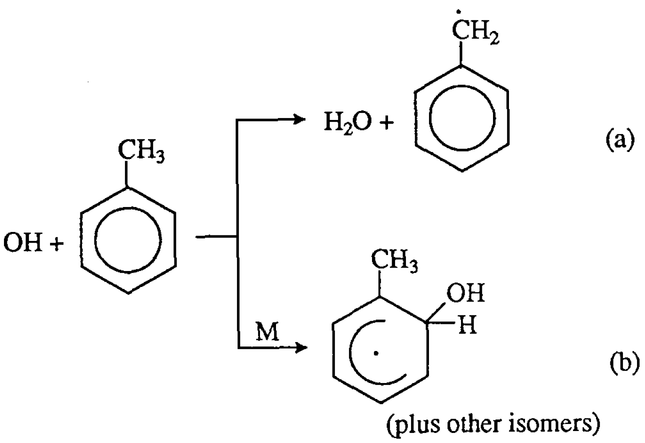
TABLE 25. Room temperature (296 ± 2 K) rate constants for the gas-phase reactions of the NO_3 radical with benzene and alkyl-substituted benzenes (from reference 11; see also Sec. 4.9)

Aromatic	$10^{16} \times k$ (cm^3 molecule^{-1} s^{-1})
Benzene	<0.3
Toluene	0.68
o-Xylene	3.8
m-Xylene	2.33
p-Xylene	4.5
Ethylbenzene	≤5.7
1,2,3-Trimethylbenzene	19
1,2,4-Trimethylbenzene	18
1,3,5-Trimethylbenzene	8.0
1-Methyl-4-isopropylbenzene (*p*-cymene)	10
1,2,3,4-Tetrahydronaphthalene (tetralin)	88

OH Radical Reactions. In the troposphere, the aromatic hydrocarbons react essentially only with the OH radical. The kinetics and mechanisms of the OH radical reactions with the aromatic hydrocarbons have been reviewed and evaluated by Atkinson,[10] and that review and evaluation is updated in Sec. 3.11. The 298 K rate constants as recommended by Atkinson[10] (see also Sec. 3.11) are given in Table 26, and the temperature dependencies at temperatures ≤ 325 K for benzene and toluene are also noted (for the xylenes and trimethylbenzenes the rate constants are essentially independent of temperature over the restricted temperature ranges around 298 K studied[10]). These OH radical reactions can proceed by two pathways: H-atom abstraction from the alkyl substituent groups (or for benzene, from the aromatic ring C–H bonds) and OH radical addition to the aromatic ring.[10,17] For example, for toluene:



Reaction Scheme (7)



In general, the H-atom abstraction pathway [reaction (a)] is of relatively minor importance, with $k_a/(k_a + k_b) \leq 0.1$ at room temperature and atmospheric pressure for toluene, the xylenes and trimethylbenzenes,[10] and these rate constant ratios $k_a/(k_a + k_b)$ as derived from kinetic or product data are also given in Table 26.

TABLE 26. Rate constants k for the gas-phase reactions of the OH radical with aromatic hydrocarbons at 298 K and atmospheric pressure and rate constant ratios $k_a/(k_a + k_b)$ obtained from kinetic data (from reference 10, except as indicated)

Aromatic	$10^{12} \times k$ (298 K) (cm^3 molecule^{-1} s^{-1})	$k_a/(k_a + k_b)$ (298 K)
Benzene	1.23[a]	0.05
Toluene	5.96[b]	0.12 (0.07[c])
Ethylbenzene	7.1	
o-Xylene	13.7	0.10 (0.05–0.06[d])
m-Xylene	23.6	0.04 (0.04[d])
p-Xylene	14.3	0.08 (0.08[d])
n-Propylbenzene	6.0	
Isopropylbenzene	6.5	
o-Ethyltoluene	12.3	
m-Ethyltoluene	19.2	
p-Ethyltoluene	12.1	
1,2,3-Trimethylbenzene	32.7	0.06
1,2,4-Trimethylbenzene	32.5	0.06
1,3,5-Trimethylbenzene	57.5	0.03
tert-Butylbenzene	4.6	
Tetralin	34.3	

[a] $k = 2.47 \times 10^{-12}\, e^{-207/T}$ cm^3 molecule^{-1} s^{-1} (234–354 K) at ~100 Torr total pressure of argon; $k_\infty \approx 3.58 \times 10^{-12}\, e^{-280/T}$ cm^3 molecule^{-1} s^{-1}.

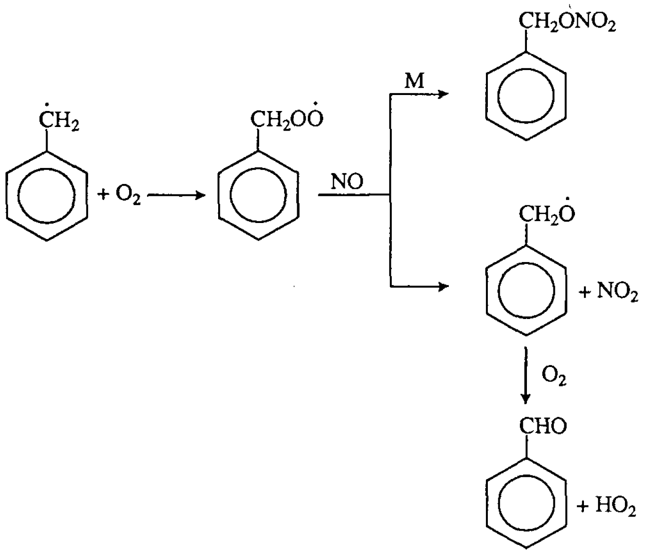
[b] $k \approx k_\infty = 1.81 \times 10^{-12}\, e^{355/T}$ cm^3 molecule^{-1} s^{-1} (213–324 K).

[c] Derived from the product data of Atkinson *et al*.[17]

[d] Derived from the product data of Bandow and Washida[18] and Atkinson *et al*.[19]

The hydroxycyclohexadienyl radical formed in pathway (b) can thermally dissociate back to reactants, with a thermal decomposition lifetime of the hydroxycyclohexadienyl radical of ~0.3 s at 298 K and atmospheric pressure.[10] For the hydroxycyclohexadienyl radical formed from benzene, rate expressions for the thermal decomposition rate constant k_{-b} of $k_{-b} = 9.4 \times 10^{12}\, e^{-8540/T}\ s^{-1}$ and $k_{-b} = 9.0 \times 10^{12}\, e^{-8570/T}\ s^{-1}$ have been derived by Atkinson[10] and Knispel *et al*.,[20] respectively, and similar thermal decomposition rates are expected for the hydroxycyclohexadienyl-type radicals formed from toluene,[10,20] the xylenes[10] and the trimethylbenzenes[10] (see also Sec. 3.11).

Under tropospheric conditions, the reactions subsequent to the H-atom abstraction reaction (a) are reasonably well understood.[21] The benzyl and alkyl-substituted benzyl radicals react rapidly with O_2,[22-25] NO[22,25] and NO_2,[24,25] and the literature rate constants for the O_2, NO and NO_2 reactions with the benzyl and substituted-benzyl radicals are given in Table 27. Under tropospheric conditions, the sole reaction of the benzyl and alkyl-substituted benzyl radicals will be with O_2, by an addition reaction, with subsequent reactions of the benzyl peroxy radicals (in the presence of NO) leading to the formation of aromatic aldehydes and benzyl or alkyl-substituted benzyl nitrates. The fraction of benzyl nitrate formation from the reaction of the benzyl peroxy radical with NO is ~0.10–0.12 at room temperature and atmospheric pressure.[17,27,28] Similar reaction pathways account for the observation of the tolualdehydes and methylbenzyl nitrates from the xylene isomers.[18,19,29]



The major OH radical reaction pathway is hence by OH radical addition to the aromatic ring to yield hydroxycyclohexadienyl or alkyl-hydroxycyclohexadienyl radicals [reaction (b)]. The hydroxycyclohexadienyl radical formed from benzene has been observed by ultraviolet absorption spectroscopy,[20,30,31] and the reactions of the hydroxycyclohexadienyl and methylhydroxycyclohexadienyl radicals with NO,[20,31,32] NO_2[20,31-36] and O_2[20,31,37] studied both directly[20,31] and indirectly.[20,32-37] The reported rate constants for these reactions of the hydroxycyclohexadienyl-type radicals are given in Table 28. The rate constants obtained from these various studies[20,31-37] are in reasonable agreement, and the most recent data[20,32,35,36]

TABLE 27. Rate constants k for the gas-phase reactions of benzyl and substituted-benzyl radicals with O_2, NO and NO_2

Radical	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1})			at	Reference
	O_2	NO	NO_2	T (K)	
Benzyl	0.99 ± 0.07	9.5 ± 1.2		a	Ebata *et al.*[22]
	1.12 ± 0.11			295	Nelson and McDonald[23]
	0.997 ± 0.08			350	
	1.03 ± 0.04			372	
o-Methylbenzyl	1.2 ± 0.07	8.7 ± 0.8		a	Ebata *et al.*[22]
	1.00 ± 0.05		50 ± 2	a	Devolder *et al.*[24]
	0.93 ± 0.16	10.5 ± 0.8	57.4 ± 10	297 ± 3	Goumri *et al.*[25]
m-Methylbenzyl	1.11 ± 0.1	12.7 ± 0.4	56 ± 11	297 ± 3	Goumri *et al.*[25]
p-Methylbenzyl	1.1 ± 0.10	8.9 ± 0.9		a	Ebata *et al.*[22]
	1.10 ± 0.08		49.7 ± 1.4	a	Devolder *et al.*[24]
m-Fluorobenzyl	0.6 ± 0.05	9.0 ± 0.4	48 ± 2	297 ± 3	Goumri *et al.*[26]
	0.51 ± 0.06	7.45 ± 1.2	41 ± 10	297 ± 3	Goumri *et al.*[25]
p-Fluorobenzyl	0.82 ± 0.04	10 ± 0.4	49 ± 2	297 ± 3	Goumri *et al.*[26]
	0.78 ± 0.05	8.9 ± 1.3	50 ± 4	297 ± 3	Goumri *et al.*[25]

[a] Room temperature, not specified.

TABLE 28. Rate constants k for the gas-phase reactions of hydroxycyclohexadienyl and alkyl-substituted hydroxycyclohexadienyl radicals with O_2, NO and NO_2

Radical	k(cm^3 molecule^{-1} s^{-1})			at	Reference
	O_2	NO	NO_2	T (K)	
Hydroxycyclohexadienyl	$\leq 2 \times 10^{-16}$ [a]	$(1.0 \pm 0.5) \times 10^{-12}$	$(8.5 \pm 2.1) \times 10^{-12}$	298	Zellner *et al.*[31]
		$< 1 \times 10^{-14}$		319	Zetzsch *et al.*;[32] Knispel *et al.*[20]
			$(2.75 \pm 0.2) \times 10^{-11}$	305	Zetzsch *et al.*;[32] Knispel *et al.*[20]
			$(2.45 \pm 0.2) \times 10^{-11}$	320	
			$(2.50 \pm 0.2) \times 10^{-11}$	333	
			$(2.50 \pm 0.2) \times 10^{-11}$	349	
	$(1.8 \pm 0.5) \times 10^{-16}$			298	Knispel *et al.*[20]
	$(1.88 \pm 0.47) \times 10^{-16}$			299	
	$(2.61 \pm 0.79) \times 10^{-16}$			314	
	$(2.94 \pm 0.11) \times 10^{-16}$			333	
	$(3.77 \pm 0.43) \times 10^{-16}$			354	
			$(4 \pm 2) \times 10^{-11}$	353	Goumri *et al.*[36]
Methylhydroxycyclohexadienyl	$< 1 \times 10^{-15}$			353	Perry *et al.*[37]
	$< 1 \times 10^{-15}$			397	
			$> 10^{-11}$	353	Bourmada *et al.*[33,34]
			$(4 \pm 2) \times 10^{-11}$	353	Goumri *et al.*[35]
		$< 3 \times 10^{-14}$		333	Zetzsch *et al.*[32]; Knispel *et al.*[20]
			$(3.6 \pm 0.4) \times 10^{-11}$	300	Zetzsch *et al.*;[32] Knispel *et al.*[20]
			$(3.6 \pm 0.3) \times 10^{-11}$	311	
			$(3.6 \pm 0.3) \times 10^{-11}$	320	
			$(4.0 \pm 0.6) \times 10^{-11}$	338	
	$(5.4 \pm 0.6) \times 10^{-16}$			300	Knispel *et al.*[20]
	$(4.3 \pm 0.6) \times 10^{-16}$			321	

[a] Derived from the observed lack of increased decay of the hydroxycyclohexadienyl radical in NO–O_2 mixtures compared to NO–N_2 mixtures.[31]

show that the hydroxycyclohexadienyl and methylhydroxycyclohexadienyl radicals both react rapidly with NO_2 with similar room temperature rate constants of $\sim 3 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}. The corresponding reactions with O_2 have much lower reported room temperature rate constants, of $\sim 1.8 \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1} for the hydroxycyclohexadienyl radical and $\sim 5 \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1} for the methylhydroxycyclohexadienyl radical.[20] No reactions with NO were observed by Zetzsch and co-workers,[20,32] with upper limits to the rate constants of $<(1-3) \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} being determined for the hydroxycyclohexadienyl and methylhydroxycyclohexadienyl radicals. The rate constant for the NO reaction with the hydroxycyclohexadienyl radical reported by Zellner *et al.*[31] may have been in error due to the presence of NO_2 impurity in the NO sample used.[20,32]

These absolute rate constant data indicate that at room temperature and atmospheric pressure of air the potentially important reactions of the hydroxycyclohexadienyl-type radicals are with O_2 and NO_2, with the NO_2 reactions being of significance for NO_2 concentrations $>3 \times 10^{12}$ molecule cm^{-3} for the OH-benzene adduct and $>9 \times 10^{12}$ molecule cm^{-3} for the OH-toluene adduct. This is the concentration regime often used in environmental chamber NO_x-air irradiations of aromatic hydrocarbons (see, for example, Refs. 17 and 19). The recent product study of Atkinson *et al.*[17] of the OH radical-initiated reactions of benzene and toluene was conducted at atmospheric pressure of air over the NO_2 concentration range $(1.5-29.5) \times 10^{13}$ molecule cm^{-3}, and the reported absolute rate constants for the O_2 and NO_2 reactions of the hydroxycyclohexadienyl-type radicals (Table 28) lead to the prediction that under these concentration conditions[17] the OH-toluene adducts should react mainly ($\sim 85\%$) with O_2 at the lowest NO_2 concentrations used, and mainly ($\sim 75\%$) with NO_2 at the highest NO_2 concentrations used. The observed yields of the cresols (which have previously been assumed to arise from reaction of the OH-toluene adducts with O_2[38–41]) were independent of the NO_2 concentration. Furthermore, the nitrotoluene yields (nitrotoluene having been assumed to be formed by reaction of the OH-toluene adduct with NO_2 in competition with the reaction of the OH-toluene adduct with O_2[38]) did not extrapolate to zero at zero NO_2 concentration,[17] and analogous data were obtained for the benzene[17] and xylene[19] systems.

The cresol formation yields from the OH radical-initiated reaction of toluene measured by Atkinson *et al.*[17] at NO_2 concentrations of $(1.5-29.5) \times 10^{13}$ molecule cm^{-3} are in agreement within the error limits with the yields derived from computer modeling of environmental chamber experiments carried out at lower NO_2 concentrations ($\leq 1.0 \times 10^{13}$ molecule cm^{-3}).[42,43] These observations suggest that, except for the possibility that the O_2 and NO_2 reactions with the OH-toluene adducts lead to cresol formation with identical isomer distributions and yields, the reported absolute rate constants for the hydroxycyclohexadienyl radical reactions are not applicable under atmospheric conditions. It is possible that the reaction with O_2 leads to a thermally unstable OH-aromatic-O_2 adduct[44] and/or that the rate constants measured by Knispel *et al.*[20] were high due to the formation of peroxy radicals in the presence of O_2 and the subsequent reactions of the OH-aromatic adducts with peroxy radicals [it should be noted that the studies of Zellner *et al.*,[31] Bourmada *et al.*,[33,34] Goumri *et al.*,[35,36] Zetzsch *et al.*[32] and Knispel *et al.*[20] all agree that the NO_2 reactions with the OH-aromatic adducts are $\gtrsim 1 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at room temperature (Table 28)]. Circumstantial evidence for the importance of the NO_2 reaction with OH-aromatic adducts under ambient tropospheric conditions arises from ambient air and laboratory measurements of nitropolycyclic aromatic hydrocarbons, which show that nitro-PAH products yields from the OH radical-initiated gas-phase reactions of the PAH measured at concentrations of NO_2 in the 10^{14} molecule cm^{-3} range appear to be applicable under ambient atmospheric conditions.[9,13]

These data suggest that it is possible that the OH-aromatic adducts formed from reaction (b) react with NO_2, and not O_2, under conditions used in "smog chamber" experiments (and possibly also under ambient atmospheric conditions), and that previous chemical mechanisms for the atmospheric photooxidations of aromatic hydrocarbons are incorrect. In addition to reactions of the hydroxycyclohexadienyl-type radicals with NO_2 and O_2, the reactions of these radicals with O_3 need to be considered, since the room temperature rate constants for the reactions of O_3 with organic radicals such as the alkyl radicals[45] and the $CH_3\dot{S}$ radical[46] are in the range $(0.2-5) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}.

Thus, at the present time the actual reactions of the hydroxycyclohexadienyl radicals formed from the OH radical reactions with the aromatic hydrocarbons are not known, and it is distinctly possible that they do not involve reaction with O_2, even under atmospheric conditions (see also Sec. 6.1, Addendum). At present, the only definitive data concerning the reactions subsequent to the addition reaction of OH radicals with the aromatic hydrocarbons are the products formed (assuming that they are applicable to tropospheric conditions). For toluene, the most studied aromatic hydrocarbon (see, for example, Refs. 17, 27, 28, 42, 43, 47–55), these include *o*-, *m*- and *p*-cresol, *o*-, *m*- and *p*-nitrotoluene, benzyl nitrate, glyoxal, methylglyoxal, peroxyacetyl nitrate [PAN] (a secondary product which can be formed from the reactions of methylglyoxal), $CH_3COCOCH = CH_2$, $CHOCOCH = CH_2$, $CH_3COCH = CH_2$, $CH_3COCH = CHCH = CH_2$, $CHOC(OH) = CHCHO$, $CH_3COCH = CHCHO$, and $CH_3COCH = CHCH = CHCHO$. The formation yields of the ring-retaining products from benzene, toluene and the xylenes are given in Table 29.

The other products whose yields have been measured with some accuracy are the α-dicarbonyls from a series of aromatic hydrocarbons, and the available data are given in Table 30. In addition, the expected co-products of the α-dicarbonyls have been observed,[57,60] but generally only in small yields.

TABLE 29. Observed ring-retaining product yields from the OH radical-initiated reactions of aromatic hydrocarbons under atmospheric conditions

Aromatic	Product	Yield	Reference
Benzene	Phenol	0.236 ± 0.044	Atkinson *et al.*[17]
	Nitrobenzene	$\{0.0336 \pm 0.0078 + (3.07 \pm 0.92) \times 10^{-16} [NO_2]\}$[a]	Atkinson *et al.*[17]
Toluene	Benzaldehyde	0.12	Atkinson *et al.*[42]
		0.073 ± 0.022	Atkinson *et al.*[47]
		0.054	Shepson *et al.*[50]
		0.071	Leone *et al.*[43]
		0.11 ± 0.01	Bandow *et al.*[52]
		0.104 ± 0.029	Gery *et al.*[28]
		0.0645 ± 0.0080	Atkinson *et al.*[17]
	Benzyl Nitrate	0.007 ± 0.004	Gery *et al.*[28]
		0.0084 ± 0.0017	Atkinson *et al.*[17]
	o-Cresol	0.21	Atkinson *et al.*[42]
		0.131 ± 0.072	Atkinson *et al.*[47]
		0.16	Leone *et al.*[43]
		0.22	Gery *et al.*[28]
		0.204 ± 0.027	Atkinson *et al.*[17]
	m- + *p*-Cresol[b]	0.05	Gery *et al.*[28]
		0.048 ± 0.009	Atkinson *et al.*[17]
	m-Nitrotoluene[c]	$\{(0.0135 \pm 0.0029) + (1.90 \pm 0.25) \times 10^{-16} [NO_2]\}$[a]	Atkinson *et al.*[17]
o-Xylene	*o*-Tolualdehyde	0.073 ± 0.036	Takagi *et al.*[56]
		0.047	Shepson *et al.*[50]
		0.05 ± 0.01	Bandow and Washida[18]
		0.172 ± 0.070	Gery *et al.*[29]
		0.0453 ± 0.0059	Atkinson *et al.*[19]
	2-Methylbenzyl nitrate	0.009 ± 0.002	Takagi *et al.*[56]
		~0.012	Gery *et al.*[29]
		$\{(0.0135 \pm 0.0051) + (5.5 \pm 4.6) \times 10^{-17} [NO_2]\}$[a]	Atkinson *et al.*[19]
	2,3-Dimethylphenol	0.097 ± 0.024	Atkinson *et al.*[19]
	3,4-Dimethylphenol	0.064 ± 0.015	Atkinson *et al.*[19]
	2,3- + 3,4-Dimethylphenol	0.012 ± 0.006	Takagi *et al.*[56]
		0.102 ± 0.039[d]	Gery *et al.*[29]
	3-Nitro-*o*-xylene	0.005 ± 0.002	Takagi *et al.*[56]
		0.0059 ± 0.0018	Atkinson *et al.*[19]
	4-Nitro-*o*-xylene	0.075 ± 0.045	Takagi *et al.*[56]
		$\{(0.0111 \pm 0.0029) + (9.9 \pm 2.2) \times 10^{-17} [NO_2]\}$[a]	Atkinson *et al.*[19]
	Nitro-*o*-xylenes[e]	0.068 ± 0.019	Gery *et al.*[29]

TABLE 29. Observed ring-retaining product yields from the OH radical-initiated reactions of aromatic hydrocarbons under atmospheric conditions – Continued

Aromatic	Product	Yield	Reference
m-Xylene	*m*-Tolualdehyde	0.04 ± 0.01	Bandow and Washida[18]
		0.122 ± 0.059	Gery *et al.*[29]
		0.0331 ± 0.0041	Atkinson *et al.*[19]
	3-Methylbenzyl nitrate	~0.010	Gery *et al.*[29]
		0.0061 ± 0.0027	Atkinson *et al.*[19]
	2,4-Dimethylphenol	0.099 ± 0.023	Atkinson *et al.*[19]
	2,6-Dimethylphenol	0.111 ± 0.033	Atkinson *et al.*[19]
	2,4- + 2,6-Dimethylphenol	0.178 ± 0.065[f]	Gery *et al.*[29]
	4-Nitro-*m*-xylene	0.0018 ± 0.0009	Atkinson *et al.*[19]
	5-Nitro-*m*-xylene	$\{(0.0032 \pm 0.0012) + (1.6 \pm 0.8) \times 10^{-17} [NO_2]\}$[a]	Atkinson *et al.*[19]
	Nitro-*m*-xylenes	0.033 ± 0.025[g]	Gery *et al.*[29]
p-Xylene	*p*-Tolualdehyde	0.08 ± 0.01	Bandow and Washida[18]
		0.10	Becker and Klein[57]
		0.0701 ± 0.0103	Atkinson *et al.*[19]
	4-Methylbenzyl-nitrate	0.0082 ± 0.0016	Atkinson *et al.*[19]
	2,5-Dimethylphenol	0.188 ± 0.038	Atkinson *et al.*[19]
	2-Nitro-*p*-xylene	$\{(0.0120 \pm 0.0035) + (2.8 \pm 2.6) \times 10^{-17} [NO_2]\}$[a]	Atkinson *et al.*[19]

[a] NO_2 concentration in molecule cm^{-3}.
[b] *m*-cresol:*p*-cresol ~1:10.[28]
[c] *o*-nitrotoluene:*m*-nitrotoluene:*p*-nitrotoluene = 7:72:21;[28] 5:70:25.[17]
[d] 2,3-dimethylphenol:3,4-dimethylphenol ~74 ± 11:26 ± 11.[29]
[e] 4-nitro-*o*-xylene accounted for 86 ± 7% of total.[29]
[f] 2,4-dimethylphenol: 2,6-dimethylphenol = 58 ± 19:42 ± 19;[29] no 3,5-dimethylphenol observed.
[g] Mainly (71 ± 49%) 4-nitro-*m*-xylene; remainder 5-nitro-*m*-xylene.

Thus, for toluene approximately 10% of the overall reaction occurs by H-atom abstraction to form, in the presence of NO, benzaldehyde and benzyl nitrate. The cresols account for a further approximately 25% of the overall OH radical reaction, and glyoxal plus methylglyoxal (together with their co-products) account for approximately 25% of the reaction, although the co-products are not known. The remaining reaction products, accounting for approximately 40% of the overall OH radical reaction, are not quantitatively known, although a variety of ring-cleavage products (other than the α-dicarbonyls) have been observed.[48-50,54] The situation is similar for benzene,[17,53] *o*-xylene,[18,19,29,47,53,56,58] *m*-xylene[18,19,29,53] and *p*-xylene[18,19,57] (see Tables 29 and 30).

Styrenes

Kinetic and product studies of the atmospherically-important gas-phase reactions of styrene,[1,10,11,15,61-63] α- and β-methylstyrene[10,61] and β-dimethylstyrene[10,64] have been carried out. The rate constants (all obtained at room temperature) for the gas-phase reactions of styrene and the methyl-substituted styrenes with OH and NO_3 radicals and O_3 are given in Table 31. The OH radical-initiated reaction of β-methylstyrene was observed to lead to the formation of benzaldehyde with a yield of 0.98 ± 0.14,[61] while β-dimethylstyrene formed benzaldehyde (with a yield of 1.05 ± 0.15) and acetone (with a yield of 0.89 ± 0.05),[64] consistent with the product data from styrene (see below).

To date, styrene is the most studied of the styrenes.

TABLE 30. α-Dicarbonyl yields from the OH radical-initiated reactions of a series of aromatic hydrocarbons under atmospheric conditions

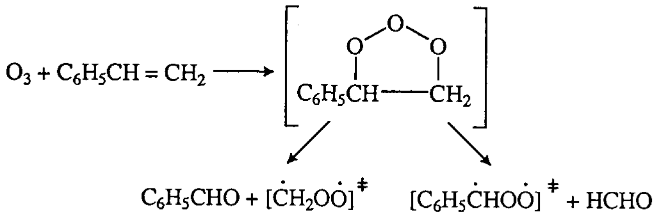
	α-Dicarbonyl Yield[a]			
Aromatic	Glyoxal	Methylglyoxal	Biacetyl	Reference
Benzene	0.207 ± 0.019			Tuazon *et al.*[53]
Toluene	0.08	0.075		Shepson *et al.*[50]
	0.111 ± 0.013	0.146 ± 0.014		Tuazon *et al.*[51]
	0.15 ± 0.04	0.14 ± 0.04		Bandow *et al.*[52]
	0.105 ± 0.019	0.146 ± 0.006		Tuazon *et al.*[53]
	0.098	0.106		Gery *et al.*[28]
o-Xylene			0.18 ± 0.04	Darnall *et al.*[58]
			0.260 ± 0.102	Takagi *et al.*[56]
			0.137 ± 0.016	Atkinson *et al.*[47]
	0.034	0.116	0.085	Shepson *et al.*[50]
	0.08 ± 0.04	0.23 ± 0.03	0.10 ± 0.02	Bandow and Washida[18]
	0.087 ± 0.012	0.246 ± 0.020		Tuazon *et al.*[53]
m-Xylene	0.104 ± 0.020	0.265 ± 0.035		Tuazon *et al.*[51]
	0.13 ± 0.03	0.42 ± 0.05		Bandow and Washida[18]
	0.086 ± 0.011	0.319 ± 0.009		Tuazon *et al.*[53]
p-Xylene	0.120 ± 0.020	0.111 ± 0.015		Tuazon *et al.*[51]
	0.24 ± 0.02	0.12 ± 0.02		Bandow and Washida[18]
	0.225 ± 0.039	0.105 ± 0.034		Tuazon *et al.*[53]
1,2,3-Trimethylbenzene	0.072 ± 0.001	0.18 ± 0.01	0.45 ± 0.02	Bandow and Washida[59]
	0.058 ± 0.008	0.152 ± 0.025	0.316 ± 0.036	Tuazon *et al.*[53]
1,2,4-Trimethylbenzene	0.078 ± 0.005	0.37 ± 0.01	0.11 ± 0.01	Bandow and Washida[59]
	0.048 ± 0.005	0.357 ± 0.017	0.048 ± 0.009	Tuazon *et al.*[53]
1,3,5-Trimethylbenzene		0.64 ± 0.03		Bandow and Washida[59]
		0.602 ± 0.033		Tuazon *et al.*[53]

[a]Indicated error limits are two standard deviations.

O_3 Reaction

The magnitude of the rate constant for reaction of styrene with O_3, when compared to the literature rate constants[1] at room temperature for the gas-phase reactions of O_3 with benzene and the methyl-substituted benzenes of $k < 10^{-20}$ cm^3 molecule^{-1} s^{-1}, shows that the reaction of O_3 with styrene proceeds by initial addition of O_3 to the $-CH=CH_2$ substituent group. Product studies using FT–IR absorption spectroscopy to monitor the reactants and products[63] showed that the major products of the gas-phase reaction of O_3 with styrene in one atmosphere of air were formaldehyde (HCHO) and benzaldehyde (C_6H_5CHO), together with a minor amount of formic acid (HCOOH). The observed product formation yields were[63]: HCHO, 0.37 ± 0.05; C_6H_5CHO, 0.41 ± 0.05; and HCOOH, ~0.01–0.02. Analyses of reaction samples from analogous experiments by gas chromatography (GC) and combined gas chromatography-mass spectrometry (GC-MS) yielded the same major products as identified from the FT–IR data.[63]

The available kinetic and product data suggest that the reaction then proceeds by



where $[\ ]^{\ddagger}$ denotes an initially energy-rich biradical species. The subsequent reactions of the $[\dot{C}H_2O\dot{O}]^{\ddagger}$ radical formed from the O_3 reaction with ethene have been discussed in Sec. 2.2 above, with the thermalized $\dot{C}H_2O\dot{O}$ biradical being expected to react with water vapor to form HCOOH under atmospheric conditions. The reactions of the $[C_6H_5\dot{C}HO\dot{O}]^{\ddagger}$ radical are not presently known. The product data obtained by Tuazon *et al.*[63] are reasonably consistent with the above reaction scheme, providing that the $[C_6H_5\dot{C}HO\dot{O}]^{\ddagger}$ biradical does not lead to the formation of C_6H_5CHO in high yield.

TABLE 31. Room temperature rate constants for the gas-phase reactions of OH and NO_3 radicals and O_3 with the styrenes

Styrene	k(cm^3 molecule^{-1} s^{-1}) for reaction with OH[a]	NO$_3$[b]	O$_3$[c]
$C_6H_5CH=CH_2$	5.8×10^{-11}	1.5×10^{-13}	1.71×10^{-17}
$C_6H_5C(CH_3)=CH_2$	5.2×10^{-11}		
$C_6H_5CH=CHCH_3$	5.9×10^{-11}		
$C_6H_5CH=C(CH_3)_2$	3.3×10^{-11}		

[a] From Ref. 10.
[b] From Ref. 11.
[c] From Ref. 63 and Sec. 5.7.

OH Radical Reaction

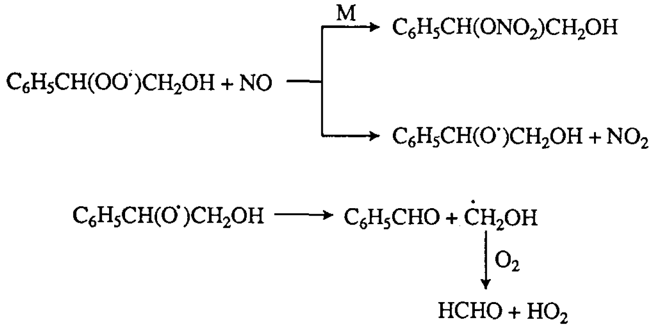
Analogous to the O_3 reaction, the magnitude of the OH radical reaction rate constant suggests that the reaction of the OH radical with styrene proceeds by initial OH radical addition to the substituent $-CH=CH_2$ group[10]

$$OH + C_6H_5CH=CH_2 \xrightarrow{M} C_6H_5\dot{C}HCH_2OH \text{ and } C_6H_5CH(OH)\dot{C}H_2$$

The products of the OH radical reaction with styrene in air have been investigated by Bignozzi *et al.*[61] and Tuazon *et al.*[63] Bignozzi *et al.*[61] observed benzaldehyde as the major product, and derived a formation yield of benzaldehyde of 1.03 ± 0.15 from the time-concentration profiles of styrene and benzaldehyde in an irradiated NO_x-styrene-air mixture. More recently, Tuazon *et al.*[63] have used FT-IR absorption spectroscopy to monitor the reactants and products in irradiated C_2H_5ONO–NO–styrene-air mixtures, and observed HCHO and C_6H_5CHO as the major products, with formation yields of 0.72 ± 0.07 and 0.63 ± 0.06, respectively. A further product was observed by Tuazon *et al.*[63] which contained a nitrate $(-ONO_2)$ group. Heuss and Glasson[65] also observed HCHO and C_6H_5CHO as the major products of the NO_x-air photooxidation of styrene.

The products observed in these studies[61,63,65] are those expected to arise from the reactions subsequent to the initial OH radical addition to the $-CH=CH_2$ substituent group. Thus, in the presence of NO

$$C_6H_5\dot{C}HCH_2OH + O_2 \xrightarrow{M} C_6H_5CH(OO^{\bullet})CH_2OH$$



$$C_6H_5CH(OO^{\bullet})CH_2OH + NO \begin{cases} \xrightarrow{M} C_6H_5CH(ONO_2)CH_2OH \\ \longrightarrow C_6H_5CH(O^{\bullet})CH_2OH + NO_2 \end{cases}$$

$$C_6H_5CH(O^{\bullet})CH_2OH \longrightarrow C_6H_5CHO + \dot{C}H_2OH \xrightarrow{O_2} HCHO + HO_2$$

and analogously for the $C_6H_5CH(OH)\dot{C}H_2$ radical.

NO_3 Radical Reaction

The products of the gas-phase reaction of styrene with the NO_3 radical have been investigated by Tuazon *et al.*[63] using FT-IR absorption spectroscopy to monitor the reactants and products. Formaldehyde (HCHO) and benzaldehyde (C_6H_5CHO) were observed as products, each with formation yields of ~0.10–0.12.

Three as yet unidentified nitrogen-containing compounds were also formed as products of these NO_3 radical reactions with styrene.[63] These products (A, B and C) had infrared absorption bands which indicated the presence of $-ONO_2$ plus $-OONO_2$; and $-ONO_2$ plus $>C=O$ groups. Product A was formed in the initial stages of the reaction, and then disappeared rapidly (as expected from the presence of the thermally unstable peroxynitrate, $-OONO_2$, group). Product B was more stable than A, but a steady decrease in its concentration with time was also observed.[63] Product C was the most stable of these three nitrogen-containing compounds.

The NO_3 radical reaction with styrene is expected to proceed by initial NO_3 radical addition to the $-CH=CH_2$ substituent group[11]:

$$NO_3 + C_6H_5CH=CH_2 \xrightarrow{M} C_6H_5CH(ONO_2)\dot{C}H_2 \text{ and } C_6H_5\dot{C}HCH_2ONO_2$$

followed by the reactions (taking the $C_6H_5\dot{C}HCH_2ONO_2$ radical as an example)

$$C_6H_5\dot{C}HCH_2ONO_2 + O_2 \xrightarrow{M} C_6H_5CH(OO^{\bullet})CH_2ONO_2$$

$$C_6H_5CH(O\dot{O})CH_2ONO_2 + NO_2 \rightleftarrows C_6H_5CH(OONO_2)CH_2ONO_2 \text{ (possibly product A)}$$

$$C_6H_5CH(OO^{\bullet})CH_2ONO_2 + \begin{Bmatrix} NO \\ RO_2^{\bullet} \end{Bmatrix} \rightarrow C_6H_5CH(O^{\bullet})CH_2ONO_2$$

(where the $RO_2^{\bullet}$ radical can include the $C_6H_5CH(OO\bullet)CH_2ONO_2$ or $C_6H_5CH(ONO_2)CH_2OO^{\bullet}$ radical)

$$C_6H_5CH(O^{\cdot})CH_2ONO_2 + O_2 \rightarrow C_6H_5C(O)CH_2ONO_2 + HO_2$$
(possibly product C)

$$C_6H_5CH(O^{\cdot})CH_2ONO_2 \rightarrow C_6H_5CHO + \dot{C}H_2ONO_2 \xrightarrow{\text{fast}} HCHO + NO_2$$

Analogous intermediate or first-generation products ($C_6H_5CH(ONO_2)CH_2OONO_2$ and $C_6H_5CH(ONO_2)$-CHO) are expected to be formed from the $C_6H_5CH(ONO_2)\dot{C}H_2$ radical.

Aromatic Aldehydes

The only aromatic aldehyde which has been studied to any extent is benzaldehyde. The potential atmospheric reactions are photolysis and chemical reaction with OH and NO_3 radicals and O_3. No data are available concerning the O_3 reaction, but it is expected to be of no significance as an atmospheric loss process.[1] The NO_3 radical reaction has a room temperature rate constant of 2.6×10^{-15} cm^3 molecule^{-1} s^{-1} [11], very similar to that for acetaldehyde. This NO_3 radical reaction is expected to proceed by H-atom abstraction from the –CHO substituent group

$$C_6H_5CHO + NO_3 \rightarrow HONO_2 + C_6H_5\dot{C}O$$

followed by reactions of the $C_6H_5\dot{C}O$ radical (see below).

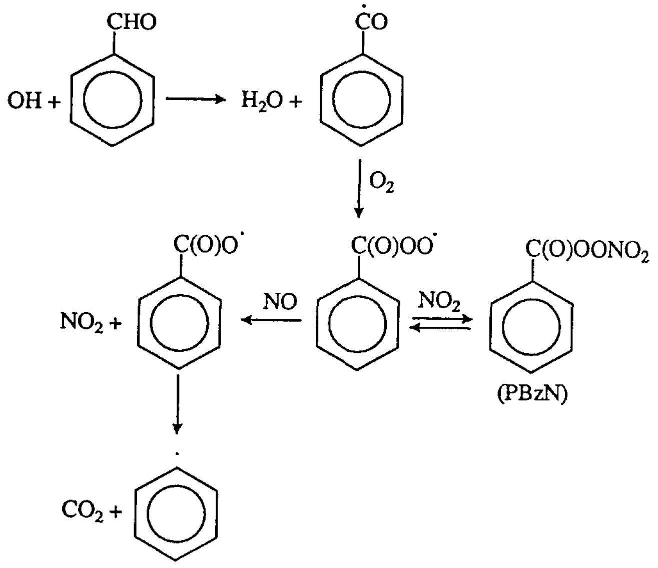
The rate constant for the OH radical reaction is 1.29×10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K[10]. In terms of their importance as atmospheric loss processes, the OH radical reaction will dominate over the NO_3 radical reaction by approximately an order of magnitude. The OH radical reaction also proceeds by H-atom abstraction from the –CHO group (OH radical addition to the aromatic ring is expected to be slower than the OH radical reaction with benzene since the –CHO group is electron withdrawing[66]). Niki *et al.*[67] conducted a product study of the Cl atom-initiated reaction of benzaldehyde, and observed the formation of *o*- and (tentatively) *p*-nitrophenol. More recently, Atkinson and Aschmann[68] have observed the formation of *o*-nitrophenol from the gas-phase OH radical-initiated reaction of benzaldehyde in the presence of NO, in 21 ± 4% yield. By analogy with the reactions of acetaldehyde (see Sec. 2.5 below), the OH radical-initiated reaction of benzaldehyde in the presence of NO is expected to proceed by Reaction Scheme (8), leading to formation of the phenyl ($C_6H_5^{\cdot}$) radical. Preidel and Zellner[69] have investigated the kinetics of the reactions of the phenyl radical with O_2, NO and NO_2 over the temperature range 297–407 K, and determined rate constants of[69]

$$k(C_6H_5^{\cdot} + NO) = 4.0 \times 10^{-12}\, e^{300/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1},$$

$$k(C_6H_5^{\cdot} + NO_2) = 1.3 \times 10^{-12}\, e^{540/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

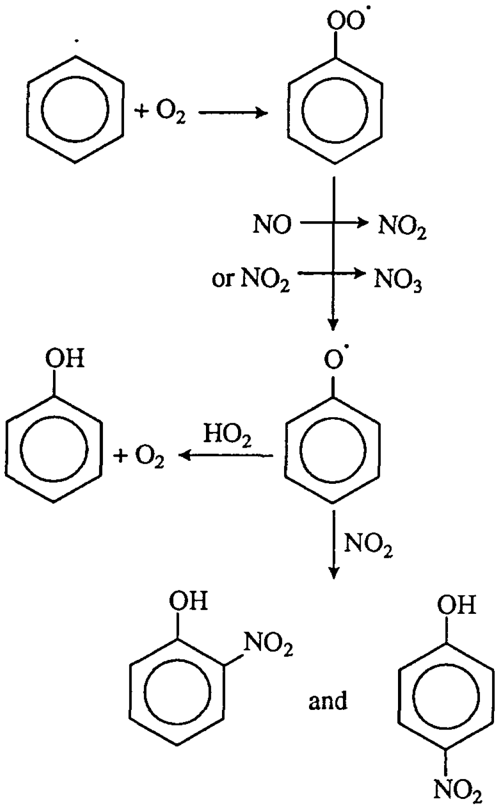
and

$$k(C_6H_5^{\cdot} + O_2) < 2 \times 10^{-17}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}.$$



Reaction Scheme (8)

These data indicate that the previously postulated reaction sequence[21,38,67] of



does not occur, and other reaction routes leading to the formation of (presumably) phenoxy radicals (at least in part) must be operative.

Peroxybenzoyl nitrate (PBzN) is analogous to PAN in that it is in thermal equilibrium with NO_2 and the $C_6H_5C(O)O\dot{O}$ radical. The thermal decomposition of PBzN has been studied by Ohta and Mizoguchi,[70] Kenley and Hendry[71] and Kirchner *et al.*[72]

$$C_6H_5C(O)OONO_2 \xrightarrow{M} C_6H_5C(O)OO^{\cdot} + NO_2$$

The rate constants of Ohta and Mizoguchi[70] and Kirchner *et al.*[72] are in good agreement. Based on the more extensive, pressure-dependent measurements of Kirchner *et al.*,[72] the following parameters in the Troe fall-off equation are recommended: $k_0 = 3.4 \times 10^{-2}\ e^{-11138/T}$ cm^6 molecule^{-2} s^{-1}; $k_\infty = 1.1 \times 10^{17}\ e^{-14073/T}$ cm^3 molecule^{-1} s^{-1}; and $F = 0.25$. The thermal decomposition rate constant at 298 K and 760 Torr total pressure of air is then 3.2×10^{-4} s^{-1} ($k_\infty = 3.4 \times 10^{-4}$ s^{-1} at 298 K).

Kirchner *et al.*[72] also measured the rate constant ratio k_a/k_b for the reactions of the benzoylperoxy radical with NO_2 and NO,

$$C_6H_5C(O)OO^{\cdot} + NO_2 \xrightarrow{M} C_6H_5C(O)OONO_2 \qquad (a)$$

$$C_6H_5C(O)OO^{\cdot} + NO \rightarrow C_6H_5C(O)O^{\cdot} + NO_2 \qquad (b)$$

with $k_a/k_b = 0.63 \pm 0.07$ at 750 Torr total pressure of N_2, independent of temperature over the range 310–322 K.

It is clear from experimental and computer modeling studies of the NO_x-air photooxidations of toluene that benzaldehyde also photolyzes.[28,42,43] The absorption cross sections in the wavelength region 220–300 nm ($S_0 \rightarrow S_3$ bands) have been given by Itoh[73] and absorption extends to 400 nm in the $S_0 \rightarrow S_1$ and $S_0 \rightarrow T_1$ bands.[74] The photodissociation quantum yields, the photodissociation products (in particular, whether the products are radical species or not) and their wavelength dependencies are, however, not known.

Phenolic Compounds

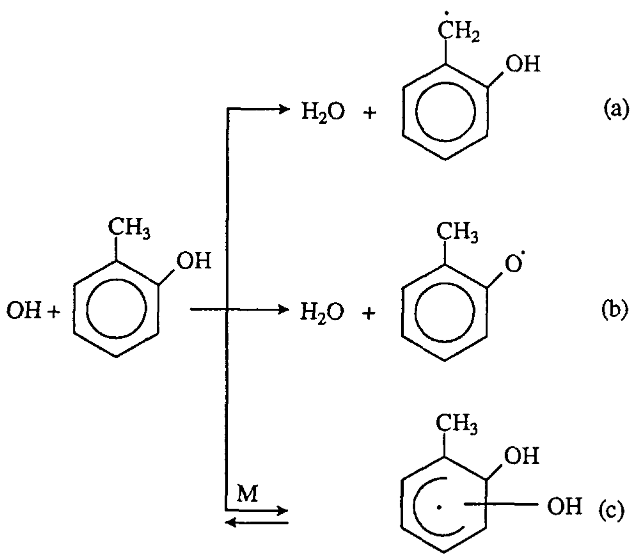
Phenol, the cresols and the dimethylphenols are formed from the atmospheric degradation of benzene, toluene and the xylenes, respectively (Table 29), and data are available concerning the atmospheric reactions of these compounds. The potential atmospheric loss processes of phenolic compounds are reaction with NO_3 and OH radicals and with O_3, together with wet and dry deposition (these compounds are readily incorporated into rain and cloud-water and fog). The room temperature rate constants for the gas-phase reactions of OH radicals, NO_3 radicals and O_3 with phenol, the cresols and the dimethylphenols are given in Table 32. The reactions with O_3 will be a minor removal process for the phenolic compounds under atmospheric conditions.

The OH radical reactions proceed by OH radical addition to the aromatic ring and by H-atom abstraction from the substituent –OH and –CH_3 groups.[10]

TABLE 32. Room temperature rate constants for the gas-phase reactions of OH and NO_3 radicals and O_3 with phenol, the cresols and the dimethylphenols, and with 2-nitrophenol

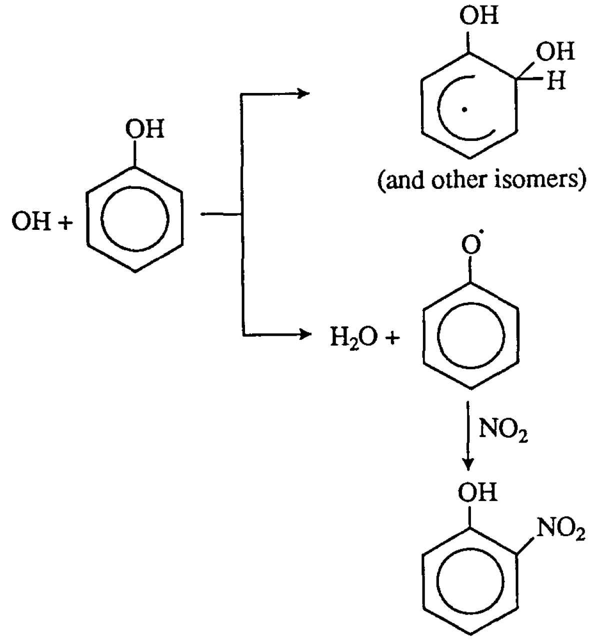
Phenol	Rate constants k (cm^3 molecule^{-1} s^{-1}) for reaction with		
	OH[a]	NO_3[b]	O_3[c]
Phenol	2.63×10^{-11}	3.78×10^{-12}	
o-Cresol	4.2×10^{-11}	1.37×10^{-11}	2.6×10^{-19}
m-Cresol	6.4×10^{-11}	9.74×10^{-12}	1.9×10^{-19}
p-Cresol	4.7×10^{-11}	1.07×10^{-11}	4.7×10^{-19}
2,3-Dimethylphenol	8.0×10^{-11}		
2,4-Dimethylphenol	7.2×10^{-11}		
2,5-Dimethylphenol	8.0×10^{-11}		
2,6-Dimethylphenol	6.6×10^{-11}		
3,4-Dimethylphenol	8.1×10^{-11}		
3,5-Dimethylphenol	1.1×10^{-10}		
2-Nitrophenol	9.0×10^{-13}	$<2 \times 10^{-14}$	

[a] From Atkinson.[10]
[b] From Atkinson[11] and Sec. 4.9.
[c] From Atkinson and Carter.[1]



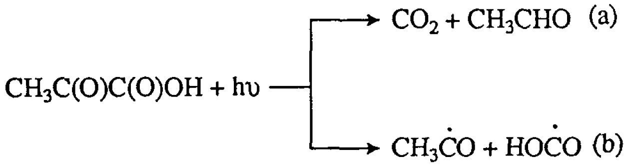
At 298 K, kinetic studies[10] indicate that the H-atom abstraction processes account for ~9% of the overall OH radical reaction for phenol [via pathway (b)] and ~7% of the overall OH radical reaction for *o*-cresol [via pathways (a) and (b)].

In the presence of NO_x, the OH radical-initiated reactions of phenol and the cresols lead to the formation, in low yield, of nitrophenols, and the yields recently measured by Atkinson *et al.*[75] are given in Table 33. The close correspondence of the nitrophenol formation yields from phenol and *o*-cresol with the fraction of the overall OH radical reaction estimated to proceed by H-atom abstraction from the –OH group[10] implies that the formation of 2-nitrophenol from phenol arises from the reaction sequence



By analogy with the OH radical-initiated reactions of benzene, toluene and the xylenes in the presence of NO_x,[17,19] nitrophenol formation subsequent to OH radical addition to the aromatic ring is expected to be of minor importance,[75] and may be expected to give rise to non-ortho nitro-substituted isomers.[17,19]

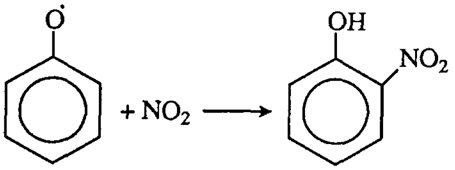
No detailed knowledge of the products and mechanism of the OH radical addition reaction pathways is known, although pyruvic acid ($CH_3C(O)C(O)OH$) has been reported as a product of the *o*-cresol reaction.[76] Pyruvic acid photolyzes rapidly,[77,78] with a photolysis rate, relative to that for photolysis of NO_2, of 0.033 under atmospheric conditions.[78] The photolysis products of pyruvic acid include CO_2 and acetaldehyde.[79,80] Berges and Warneck[80] obtained photodissociation quantum yields at λ = 350 nm for the processes



$$CH_3C(O)C(O)OH + h\nu \rightarrow CO_2 + CH_3CHO \quad (a)$$
$$CH_3C(O)C(O)OH + h\nu \rightarrow CH_3\dot{C}O + HO\dot{C}O \quad (b)$$

of $\phi_a = 0.48 \pm 0.01$ and $\phi_b = 0.39 \pm 0.10$, with an overall quantum yield for the photodissociation of pyruvic acid of 0.88.

The NO_3 radical reactions with the phenols have been postulated to proceed by an overall H-atom abstraction process after initial NO_3 radical addition to the aromatic ring, through the intermediary of a 6-membered transition state[11,81] [see Reaction Scheme (9)], followed by the reactions of the phenoxy radical with HO_2 to form phenol or with NO_2 to form nitrophenols.



The initial NO_3 radical addition to the aromatic ring is expected to be reversible because of the short lifetime of the NO_3-aromatic adduct with respect to thermal decomposition back to reactants,[11,82] and a decomposition rate for the NO_3-monocyclic aromatic adducts of $\sim 5 \times 10^8\ s^{-1}$ at 298 K has been estimated[11,82] from a study of the reactions of naphthalene in N_2O_5–NO_3–NO_2–air mixtures.[82]

However, such a reaction mechanism would be expected to lead to a unit, or near unit, yield of nitrophenols. The nitrophenol product formation yields determined by Atkinson *et al.*[75] and given in Table 33 show, however, that this is not the case for phenol and *o*- and *m*-cresol. These observations indicate that the NO_3 radical reactions with the phenols are more complex than previously thought, and that other reaction pathways, possibly involving ring cleavage, occur.

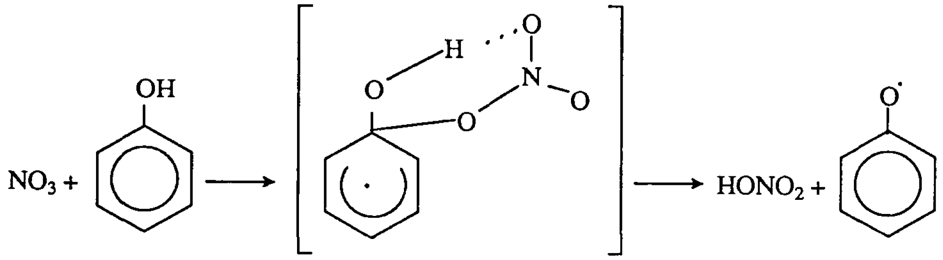
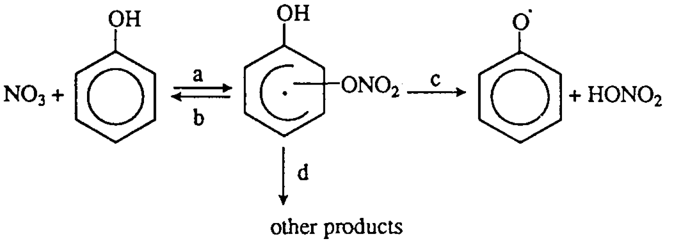


TABLE 33. Nitrophenol formation yields from the gas-phase reactions of OH and NO_3 radicals with phenol and the cresols, in the presence of NO_x (from Atkinson *et al.*[75])

Reactant	Product	Reaction with	
		OH	NO_3
Phenol	2-Nitrophenol	0.067 ± 0.015	0.251 ± 0.051
o-Cresol	6-Methyl-2-nitrophenol	0.051 ± 0.015	0.128 ± 0.028
m-Cresol	3-Methyl-2-nitrophenol	0.016 ± 0.010	0.168 ± 0.029
	5-Methyl-2-nitrophenol	~0.016	0.196 ± 0.036
p-Cresol	4-Methyl-2-nitrophenol	0.10 ± 0.04	0.74 ± 0.16



The measured rate constants k are then given by $k = k_a(k_c + k_d)/(k_b + k_c + k_d)$, where k_a, k_b, k_c and k_d are the rate constants for reactions (a) through (d). The product data given in Table 33 suggest that $k_c \sim k_d$, to within a factor of ~10. Furthermore, the observation of a dramatically lower rate constant for the reaction of the NO_3 radical with 2-nitrophenol than for phenol and the cresols (Table 32) suggests that the rate constant k_a for initial addition of the NO_3 radical to the aromatic ring is strongly dependent on the identity and position of substituent groups on the aromatic ring, as is the case for the corresponding OH radical reactions.[10] Clearly, further work is needed concerning the atmospheric products and mechanisms of the reactions of phenolic compounds.

The reactions of the α- and δ-dicarbonyls are dealt with in Sec. 2.5 below.

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2.5. Oxygen-Containing Organic Compounds

In this section, the atmospheric chemistry of those oxygen-containing organic compounds which are either emitted into the troposphere directly or are formed in the atmosphere as degradation products of other organics is dealt with. The atmospheric chemistry of benzaldehyde has been discussed in Sec. 2.4 above.

A. *Aliphatic Aldehydes, Ketones and α-Dicarbonyls*

The aliphatic aldehydes and ketones are formed as intermediate "stable" chemical products during the atmospheric degradation reactions of a wide variety of organic compounds in addition to any direct emissions. These carbonyls arise from the reactions of the alkyl peroxy and alkoxy radicals discussed in Secs. 2.1 and 2.2 above. In addition, a number of α-dicarbonyls (for example, glyoxal, methylglyoxal and biacetyl) are formed as intermediate reactive products from the aromatic hydrocarbons (Sec. 2.4). In the atmosphere, these carbonyls can photolyze and react with OH, NO_3 and HO_2 radicals.

Photolysis

The photolysis rates of carbonyls under tropospheric and environmental chamber conditions are given by

$$k_{\text{photolysis}} = \int_{\lambda_1}^{\lambda_2} J_\lambda \sigma_\lambda \phi_\lambda \, d\lambda$$

where J is the radiation flux, σ is the absorption cross section and ϕ is the photolytic quantum yield, all of which are a function of wavelength, λ, over the wavelength range λ_1 to λ_2 (for tropospheric purposes, this wavelength range is ~290–800 nm). The radiation flux, J_λ, is either experimentally measured or calculated for clear sky conditions and is not dealt with further here. The absorption cross-sections, σ_λ, and quantum yields, ϕ_λ are obtained from experimental studies, and the available data are discussed below.

Formaldehyde. The absorption cross-sections and quantum yields have been most recently evaluated by NASA[1] and IUPAC.[2] The most recent IUPAC recommendation[2] accepts the absorption cross-section data of Moortgat and Schneider[3] for wavelengths ≤ 300 nm, and those of Cantrell *et al.*,[4] determined over the temperature range 223–293 K, for $\lambda = 301$–356 nm. The recommended absorption cross-sections and quantum yields for the processes

$$HCHO + h\nu \rightarrow H + H\dot{C}O \qquad (a)$$

$$HCHO + h\nu \rightarrow H_2 + CO \qquad (b)$$

are tabulated in the IUPAC evaluation.[2]

Acetaldehyde. The quantum yields for the photolysis of acetaldehyde have been reviewed and evaluated by the IUPAC panel.[2] The recommended quantum yields for the processes (a) and (b)

$$CH_3CHO + h\nu \rightarrow CH_4 + CO \qquad (a)$$

$$CH_3CHO + h\nu \rightarrow \dot{C}H_3 + H\dot{C}O \qquad (b)$$

$$CH_3CHO + h\nu \rightarrow CH_3\dot{C}O + H \qquad (c)$$

are those tabulated in the IUPAC evaluation.[2] Pathway (c) is of negligible importance, as is the possible photodissociation to form ketene plus H_2.[5,6] Absorption cross-sections have been measured by Martinez *et al.*[7] at 300 ± 2 K and a spectral resolution of 0.5 nm over the wavelength region 200–366 nm, and the values have been tabulated as averages over 1 nm (>280 nm) or 4 nm (<280 nm) wavelength regions.[7] The absorption cross-sections from this study[7] are recommended.

Propanal. Photodissociation quantum yields for propanal have been measured by Shepson and Heicklen[8,9] and Heicklen *et al.*[10] The more recent study of Heicklen *et al.*[10] supersedes the previous work[8,9] from the same laboratory, and these later data[10] are recommended by the IUPAC evaluation.[2] For the photodissociation,

$$CH_3CH_2CHO + h\nu \rightarrow \dot{C}_2H_5 + H\dot{C}O$$

data were obtained at 294, 302, 313, 325 and 334 nm,[10] with the quantum yields in air at 760 Torr total pressure and 298 K being 0.89, 0.85, 0.50, 0.26 and 0.15 at these wavelengths, respectively. The quantum yield for the non-radical forming process

$$CH_3CH_2CHO + h\nu \rightarrow C_2H_6 + CO$$

was observed to be essentially zero at wavelengths >313 nm.[10] Absorption cross-sections have been measured by Martinez *et al.*[7] at a spectral resolution of 0.50 nm and at 300 ± 2 K over the wavelength range 200–366 nm and tabulated as averages over 1 nm (>280 nm) or 4 nm (<280 nm) wavelength regions.[7] The absorption cross-sections from this study of Martinez *et al.*[7] are recommended.

1-Butanal. The absorption cross-sections have been measured by Martinez *et al.*[7] at a spectral resolution of 0.50 nm and at 300 ± 2 K over the wavelength range 200–366 nm and tabulated as averages over 1 nm (>280 nm) or 4 nm (<280 nm) wavelength regions.[7] The absorption cross-sections from this study of Martinez *et al.*[7] are recommended. The gas-phase photolysis of butanal has been studied by Förgeteg *et al.*[11,12] at 313 nm. At high pressure of added C_4F_8, the quantum yields of the processes

$$C_3H_7CHO + h\nu \rightarrow \dot{C}_3H_7 + HCO \qquad (a)$$

$$C_3H_7CHO + h\nu \rightarrow C_2H_4 + CH_3CHO \qquad (b)$$

were reported to be $\phi_b = 0.18$ and $\phi_a \sim 0.3$. Other photolysis pathways accounted for <5% of the overall quantum yield at 313 nm.

Higher Aldehydes. Absorption cross-sections for iso-butyraldehyde, $(CH_3)_2CHCHO$, have been measured by Martinez *et al.*[7] at a spectral resolution of 0.50 nm and at 300 ± 2 K over the wavelength range 200–366 nm, and tabulated as averages over 1 nm (>280 nm) or 4 nm (<280 nm) wavelength regions.[7] The photodissociation quantum yields of iso-butyraldehyde have been measured by Desai *et al.*,[13] and at room temperature and one atmosphere of air the quantum yields for $(CH_3)_2\dot{C}H + H\dot{C}O$ production were measured to be: 0.20 at 253.7 nm; 0.45 at 280.3 nm; 0.55 at 302.2 nm; 0.88 at 312.8 nm; 0.88 at 326.1 nm and 0.69 at 334.1 nm.[13]

For the higher aldehydes, no quantum yield data are available, and further work is needed concerning the photolysis of aldehydes and ketones under atmospheric conditions.

Acetone. The photodissociation of acetone has been studied under simulated atmospheric conditions by Gardner *et al.*[14] and Meyrahn *et al.*[15] The IUPAC evaluation[2] recommends the absorption cross-sections and photodissociation quantum yields measured by Meyrahn *et al.*[15] The absorption cross-sections measured by Martinez *et al.*[7] over the wavelength region 200–356 nm are in good agreement with those of Meyrahn *et al.*[15] The data of Martinez *et al.*[7] are tabulated as average cross-sections over 1 nm (>280 nm) or 4 nm (<280 nm) wavelength intervals, and are recommended for use in tropospheric modeling.

At 750 Torr total pressure of air, the quantum yields for $CH_3\dot{C}O$ formation were determined by Meyrahn *et al.*[15] to be 0.55 at 280 nm, 0.30 at 290 nm, 0.15 at 300 nm, 0.05 at 310 nm, 0.028 at 320 nm and ~0.033 at 330 nm.[15] These data are reasonably consistent with the average photodissociation quantum yield of 0.33 ± 0.06 measured by Cox *et al.*[16] for the wavelength region 280–330 nm and with the photolysis study of $CH_3C(O)CH_3$–HCl and $CH_3C(O)CH_3$–HCl–CO_2 mixtures of Horowitz.[17]

Higher Ketones. No data are available concerning the photodissociation quantum yields for the higher ketones under atmospheric conditions. As for acetone, these quantum yields are likely to be low. However, since these compounds also react with the OH radical, it is expected that the OH radical reactions will be the dominant atmospheric loss process. Absorption cross-sections for 2-butanone and 2- and 3-pentanone have been measured and tabulated by Martinez *et al.*[7] for the wavelength region 200–356 nm.

α-Dicarbonyls. The α-dicarbonyls for which experimental data are available are glyoxal, methylglyoxal and biacetyl. The absorption cross-sections and photodissociation data available for $(CHO)_2$ and CH_3COCHO have been reviewed and evaluated by the IUPAC panel,[2] and their recommendations should be consulted.

For biacetyl, the absorption cross-sections measured and tabulated by Plum *et al.*[18] are recommended. Plum *et al.*[18] derived an average photodissociation quantum yield of 0.158 ± 0.024 for wavelengths ≥325 nm under atmospheric conditions. In the shorter wavelength absorption band, Cox *et al.*[16] reported an average photodissociation quantum yield of 0.98 ± 0.15 for the 280–330 nm wavelength region.

Hydroxyl Radical Reactions. The kinetics and mechanisms of the OH radical reactions with carbonyl compounds have been most recently reviewed and evaluated by Atkinson,[19] and that review and evaluation is updated in Sec. 3.6. The kinetic data for selected aliphatic aldehydes and ketones and α-dicarbonyls, either as the recommended values or those measured but not recommended for lack of sufficient studies, are given in Table 34. In addition, the room temperature rate constants for 6,6-dimethylbicyclo[3.1.1]heptan-2-one (nopinone) and 3,3-dimethylbicyclo[2.2.1]heptan-2-one (camphenilone), which are formed from the OH radical and O_3 reactions with β-pinene and from the O_3 reaction with camphene, respectively (see Sec. 2.2 above), are given in Table 34. All of these reactions proceed via overall H-atom abstraction, although it should be noted that for the aldehydes the initial reaction possibly involves initial OH radical addition to the >C=O bond system,[19]

$$OH + HCHO \rightarrow H_2O + H\dot{C}O$$

$$OH + RCHO \rightarrow H_2O + R\dot{C}O$$

with H-atom abstraction from the C–H bonds of the alkyl chain being of minor importance.[19] Note, however, that for glycolaldehyde ($HOCH_2CHO$) H-atom abstraction occurs from the C–H bonds of both the $-CH_2-$ and –CHO groups in a 20:80 ratio at 298 ± 2 K.[20]

The $H\dot{C}O$ radical reacts rapidly with O_2

$$H\dot{C}O + O_2 \rightarrow HO_2 + CO$$

with a rate constant of 5.5×10^{-12} cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–400 K.[2] In contrast, the $R\dot{C}O$ ($R \neq H$) radicals rapidly add O_2 to form the corresponding acyl peroxy radicals ($RC(O)O\dot{O}$), with room temperature rate constants of 5×10^{-12} cm^3 molecule^{-1} s^{-1} for the $CH_3\dot{C}O$ radical[2] and $(5.7 \pm 1.4) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} for the $C_6H_5\dot{C}O$ radical.[21]

As for the alkyl peroxy ($R\dot{O}_2$) radicals, the $CH_3C(O)O\dot{O}$ radical reacts with NO,

$$\begin{tikzcd} CH_3C(O)O\dot{O} + NO \arrow[r] & CH_3C(O)\dot{O} + NO_2 \arrow[d, "fast"] \\ & \dot{C}H_3 + CO_2 \end{tikzcd} \qquad (a)$$

NO_2, to form peroxyacetyl nitrate (PAN),

$$CH_3C(O)O\dot{O} + NO_2 \xrightarrow{M} CH_3C(O)OONO_2 \qquad (b)$$

the HO_2 radical,

$$\begin{tikzcd} & CH_3C(O)OOH + O_2 \quad (c_1) \\ CH_3C(O)O\dot{O} + HO_2 \arrow[ur] \arrow[dr] & \\ & CH_3C(O)OH + O_3 \quad (c_2) \end{tikzcd}$$

and $R\dot{O}_2$ radicals (see Sec. 2.1). The reactions (a), (b), (c1) and (c2) have been reviewed by the IUPAC data evaluation panel,[2] and the recommended rate constants for reactions (a), (c1) and (c2) are:

$$k(CH_3C(O)O\dot{O} + NO) = 2.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

independent of temperature over the range 280–325 K,

$$k(HO_2 + CH_3C(O)O\dot{O} \rightarrow CH_3C(O)OOH + O_2) = 3.0 \times 10^{-13} e^{1040/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 250–370 K (1.0×10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K), and

$$k(HO_2 + CH_3C(O)O\dot{O} \rightarrow CH_3C(O)OH + O_3) = 1.3 \times 10^{-13} e^{1040/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 250–370 K (4.2×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K).[2] [Due to a typographical error in Ref. 2, the rate constants k_{c1} and k_{c2} were incorrectly interchanged].

TABLE 34. Rate constants k at 298 K and Arrhenius parameters, $k = CT^n e^{-D/T}$, for the reaction of OH radicals with selected oxygenated compounds [taken from Atkinson[19] and Sec. 3.6]

Organic	$10^{12}\times k$ (cm^3 molecule^{-1} s^{-1})	C (cm^3 molecule^{-1}s^{-1})	n	D(K)
Aldehydes				
HCHO	9.37	1.20×10^{-14}	1	−287
CH_3CHO	15.8	5.55×10^{-12}	0	−311
CH_3CH_2CHO	19.6			
$CH_3CH_2CH_2CHO$	23.5	5.26×10^{-12}	0	−446
$(CH_3)_2CHCHO$	26.3	6.61×10^{-12}	0	−411
$CH_3(CH_2)_3CHO$	28.5	6.34×10^{-12}	0	−448
$(CH_3)_2CHCH_2CHO$	27.4			
$(CH_3)_3CCHO$	26.5	6.82×10^{-12}	0	−405
$HOCH_2CHO$	9.9			
Ketones				
$CH_3C(O)CH_3$	0.219	5.34×10^{-18}	2	230
$CH_3C(O)CH_2CH_3$	1.15	3.24×10^{-18}	2	−414
$CH_3C(O)CH_2CH_2CH_3$	4.9			
$CH_3CH_2C(O)CH_2CH_3$	2.0			
$CH_3C(O)CH_2CH_2CH_2CH_3$	9.1			
$CH_3CH_2C(O)CH_2CH_2CH_3$	6.9			
$CH_3C(O)CH_2CH(CH_3)_2$	14.1			
6,6-Dimethylbicyclo-[3.1.1]heptan-2-one	14.3			
3,3-Dimethylbicyclo-[2.2.1]heptan-2-one	5.2			
a-Dicarbonyls				
$(CHO)_2$	11.4			
CH_3COCHO	17.2			
$CH_3COCOCH_3$	0.238	1.40×10^{-18}	2	−194
Alcohols				
Methanol	0.944	6.01×10^{-18}	2	−170
Ethanol	3.27	6.18×10^{-18}	2	−532
1-Propanol	5.53			
2-Propanol	5.32	7.21×10^{-18}	2	−631
1-Butanol	8.57			
2-Methyl-2-propanol	1.12	4.29×10^{-18}	2	−322
1-Pentanol	11.1			
2-Pentanol	11.8			
3-Pentanol	12.2			
Keto-ethers				
Hydroxyacetone ($HOCH_2C(O)CH_3$)	3.0			
Ethers				
Dimethyl ether	2.98	1.04×10^{-11}	0	372
Diethyl ether	13.1	8.91×10^{-18}	2	−837
Methyl *t*-butyl ether	2.94	6.54×10^{-18}	2	−483
Ethyl *t*-butyl ether	8.84			
Carboxylic acids				
Formic acid	0.45	4.5×10^{-13}	0	0
Acetic acid	0.8			
Priopionic acid	1.16			
Hydroperoxides				
Methyl hydroperoxide	5.54	2.93×10^{-12}	0	−190
tert-Butyl hydroperoxide	3.0			

TABLE 34. Rate constants k at 298 K and Arrhenius parameters, $k = CT^n e^{-D/T}$, for the reaction of OH radicals with selected oxygenated compounds [taken from Atkinson[19] and Sec. 3.6] – Continued

Organic	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1})	C (cm^3 molecule^{-1}s^{-1})	n	D(K)
Unsaturated carbonyls				
Acrolein	19.9			
Methacrolein	33.5	1.86×10^{-11}	0	−175
Crotonaldehyde	36			
Methyl vinyl ketone	18.8	4.13×10^{-12}	0	−452
4-Acetyl-1-methyl-cyclohexene	129			
1,4-Unsaturated Dicarbonyls				
cis-3-Hexene-2,5-dione	63			
trans-3-Hexene-2,5-dione	53			

The reaction of the $CH_3C(O)O\dot{O}$ radical with NO_2 is in the fall-off region at and below atmospheric pressure of air, and the Troe fall-off parameters recommended by the IUPAC evaluation[2] are: $k_o = 2.7 \times 10^{-28} (T/300)^{-7.1}$ cm^6 molecule^{-2} s^{-1}, $k_\infty = 1.2 \times 10^{-11} (T/300)^{-0.9}$ cm^3 molecule^{-1} s^{-1} and $F = 0.3$. This leads to a rate constant for reaction (b) at 298 K and 760 Torr total pressure of air of 1.0×10^{-11} cm^3 molecule^{-1} s^{-1}.

In the absence of further experimental information these rate constants for the reactions of the acetyl peroxy radical with NO and HO_2 radicals, and the high-pressure rate constant k_∞ for reaction with NO_2, are anticipated to be applicable to the higher acyl peroxy ($R\dot{C}O_3$) radicals [the NO_2 reactions will be closer to the high pressure limit for the higher acyl peroxy radicals than for the $CH_3C(O)O\dot{O}$ radical].

For glyoxal, Niki *et al.*[22] have shown that at 298 K and 700 Torr total pressure of $O_2 + N_2$ diluent the $HCO\dot{C}O$ radical can either decompose or react with O_2

$$OH + (CHO)_2 \rightarrow H_2O + HCO\dot{C}O$$

$$HCO\dot{C}O \rightarrow H\dot{C}O + CO \qquad (a)$$

$$HCO\dot{C}O + O_2 \rightarrow HCOC(O)O\dot{O} \qquad (b)$$

$$HCO\dot{C}O + O_2 \rightarrow 2\,CO + HO_2 \qquad (c)$$

with $k_b \sim k_c$ and $k_a/k_b = 3.5 \times 10^{18}$ molecule cm^{-3}. Thus, at 298 K and 760 Torr total pressure of air, addition of O_2 occurs 40% of the time, while formation of CO and HO_2 occurs the remaining 60% of the time. For methylglyoxal, under atmospheric conditions the corresponding $CH_3CO\dot{C}O$ radical decomposes to $CH_3\dot{C}O$ and CO rather than reacting with O_2 to yield $CH_3C(O)C(O)O\dot{O}$[23]

$$CH_3CO\dot{C}O \rightarrow CH_3\dot{C}O + CO$$

For the aldehydes and ketones, the positions of OH radical H-atom abstraction and the partial OH radical reaction rate constant at that position can be calculated using the estimation technique of Atkinson.[24] As an example, the OH radical reaction with 2-butanone is calculated to proceed via the pathways

$$OH + CH_3CH_2C(O)CH_3 \rightarrow \begin{cases} H_2O + \dot{C}H_2CH_2C(O)CH_3 & (46\%) \\ H_2O + CH_3\dot{C}HC(O)CH_3 & (46\%) \\ H_2O + CH_3CH_2C(O)\dot{C}H_2 & (8\%) \end{cases}$$

The tropospheric reactions of these substituted alkyl radicals are analogous to those for the alkyl radicals discussed in Sec. 2.1 above.

Ozone Reactions. For the carbonyls dealt with in this section, which do not contain $>C=C<$ bonds, the reactions with O_3 are of negligible atmospheric importance, and indeed only upper limits to the rate constants of $<10^{-20}$ cm^3 molecule^{-1} s^{-1} have been obtained for HCHO, CH_3CHO, $(CHO)_2$ and CH_3COCHO.[25]

Nitrate Radical Reactions. For the aliphatic carbonyl compounds dealt with in this section, NO_3 radical reaction rate constants are available only for HCHO and CH_3CHO, and these have been evaluated by the NASA[1] and IUPAC[2] panels and by Atkinson.[26] Most of the literature data are relative to the equilibrium constant for the reactions $NO_2 + NO_3 \rightleftarrows N_2O_5$ and there are significant uncertainties in the value of this equilibrium constant.[26–28] The recommendations of Atkinson[26] for the reactions of the NO_3 radical with HCHO and CH_3CHO are

$$k(NO_3 + HCHO) = 5.8 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K},$$

identical to the NASA[1] and IUPAC[2] recommendations and

$$k(NO_3 + CH_3CHO) = 1.44 \times 10^{-12} e^{1862/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 264–374 K,

$$k(NO_3 + CH_3CHO) = 2.78 \times 10^{-15}\ cm^3\ molecule^{-1}\ s^{-1} \text{ at } 298\ K,$$

essentially identical to the NASA[1] and IUPAC[2] recommendations.

With rate constants of this magnitude, these reactions with the NO_3 radical are of minimal atmospheric importance as an aldehyde loss process. The NO_3 radical reaction rate constants for the ketones are expected to be lower, in the range of 10^{-17} to 10^{-16} cm^3 $molecule^{-1}$ s^{-1} at room temperature.[26] As with the corresponding OH radical reactions, these NO_3 radical reactions proceed via H-atom abstraction

$$NO_3 + RCHO \rightarrow HONO_2 + R\dot{C}O\ (R = H, \text{alkyl})$$

and the production of HO_2 and $CH_3(O)O\dot{O}$ radicals from the NO_3 radical reactions with HCHO and CH_3CHO during nighttime hours can be significant.[29–31]

HO_2 Radical Reactions. The HO_2 radical has been shown to react with HCHO,[1,2] CH_3CHO[32,33] and $(CHO)_2$.[22] For HCHO, the initial reaction involves addition of HO_2, followed by rapid isomerization of the intermediate species via a five-member transition state to the peroxy radical,

$$HO_2 + HCHO \rightarrow [HOOCH_2\dot{O}] \rightarrow \dot{O}OCH_2OH$$

which can back-decompose to the HO_2 + HCHO reactants (presumably via the intermediary of $HOOCH_2\dot{O}$). The IUPAC evaluation recommends[2] that

$$k(HO_2 + HCHO \rightarrow HOCH_2O\dot{O}) = 9.7 \times 10^{-15}\ e^{625/T}\ cm^3\ molecule^{-1}\ s^{-1}$$

over the temperature range 275–333 K (7.9×10^{-14} cm^3 $molecule^{-1}$ s^{-1} at 298 K), and

$$k(HOCH_2O\dot{O} \rightarrow HO_2 + HCHO) = 2.4 \times 10^{12}\ e^{-7000/T}\ s^{-1}$$

over the temperature range 275–333 K (150 s^{-1} at 298 K). With this rapid back-decomposition rate of the $HOCH_2O\dot{O}$ radical, the reaction of HO_2 radicals with HCHO is expected to be of minor importance for atmospheric conditions.

The corresponding rate constants for the forward and reverse reaction of HO_2 with CH_3CHO are[33] $k(HO_2 + CH_3CHO) = 1 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1} and $k(CH_3CH(O\dot{O})OH \rightarrow HO_2 + CH_3CHO) = 100\ s^{-1}$, both at 298 K. For the reaction of the HO_2 radical with glyoxal, Niki *et al*.[22] reported a rate constant for the reaction

$$HO_2 + (CHO)_2 \rightarrow [CHOCH(OOH)\dot{O}] \rightarrow CHOCH(OH)O\dot{O}$$

of $(5.1 \pm 0.4) \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K. As for the HO_2 radical reaction with HCHO, these HO_2 radical reactions with CH_3CHO and $(CHO)_2$ are unimportant under atmospheric conditions.

B. *Alcohols*

The alcohols of interest in urban atmospheres are primarily methanol, ethanol and, to a lesser extent, the C_3 and C_4 species. The gas-phase reactions with the NO_3 radical are slow,[26] with upper limits to the room temperature rate constants of $<6 \times 10^{-16}$, $<9 \times 10^{-16}$ and $<2.3 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1} for methanol, ethanol and 2-propanol, respectively. While no kinetic data are available for the gas-phase reactions of O_3 with the alcohols,[25] the O_3 reactions are expected to be of negligible importance as an atmospheric loss process. Thus, the only loss process which requires consideration is the reaction with the OH radical. The room temperature rate constants and temperature dependencies for the OH radical reactions with the alcohols are given in Table 34.

These OH radical reactions proceed by H-atom abstraction from both the C–H and O–H bonds. For methanol, the rate constant ratio $k_a/(k_a + k_b)$, where k_a and k_b are the rate constants for the reactions,

$$OH + CH_3OH \rightarrow H_2O + CH_3\dot{O} \qquad (a)$$

$$OH + CH_3OH \rightarrow H_2O + \dot{C}H_2OH \qquad (b)$$

is 0.15 ± 0.10 at 298 K.[2]

For ethanol, the reaction channels are,

$$OH + CH_3CH_2OH \left\{\begin{array}{ll} \rightarrow H_2O + CH_3CH_2\dot{O} & (c) \\ \rightarrow H_2O + CH_3\dot{C}HOH & (d) \\ \rightarrow H_2O + \dot{C}H_2CH_2OH & (e) \end{array}\right.$$

and the $\dot{C}H_2CH_2OH$ radical formed in channel (e) (the same radical as formed from OH radical addition to ethene) thermally decomposes at temperatures ≥500–600 K.[19,34] Based on the kinetic data of Hess and Tully[34] for the reactions of ^{16}OH and ^{18}OH radicals with $C_2H_5{}^{16}OH$ (decomposition of the $\dot{C}H_2CH_2{}^{16}OH$ radical does not regenerate the ^{18}OH radical) and the room temperature product study of Meier *et al*.,[35] the IUPAC evaluation recommends[2] that at 298 K $k_c/k = k_e/k = 0.05^{+0.10}_{-0.05}$, where $k = (k_c + k_d + k_e)$.

Japar *et al*.[36] observed HCHO and $CH_3C(O)CH_3$ as the only products of the OH radical- and Cl atom-initiated reactions of *tert*-butyl alcohol, $(CH_3)_3COH$, with essentially unit yields of both products for the Cl atom reaction. The expected reaction scheme is therefore[36]

$$\begin{tikzcd}[row sep=small]
\mathrm{OH + (CH_3)_3COH} \arrow[r] & \mathrm{H_2O + \dot{C}H_2C(CH_3)_2OH} \arrow[d, "O_2"] \\
 & \mathrm{\dot{O}OCH_2C(CH_3)_2OH} \arrow[d, "NO \rightarrow NO_2"] \\
 & \mathrm{\dot{O}CH_2C(CH_3)_2OH} \arrow[d] \\
 & \mathrm{HCHO + (CH_3)_2\dot{C}OH} \arrow[d, "O_2"] \\
 & \mathrm{HO_2 + CH_3C(O)CH_3}
\end{tikzcd}$$

The estimation technique of Atkinson[24] allows the distribution of initially formed radicals to be approximately determined for the higher alcohols, and the subsequent reactions of these radicals are then as discussed in Secs. 2.1 and 2.2 above.

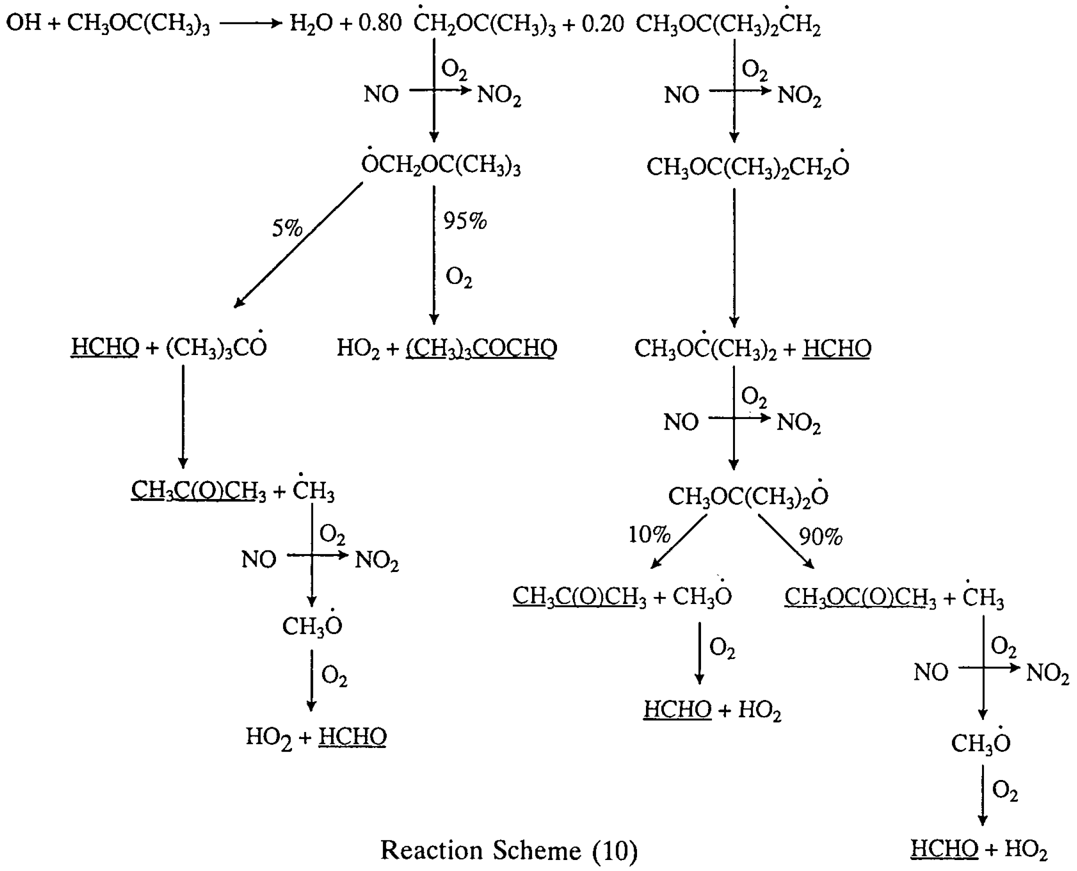
C. *Ethers*

The ethers of main atmospheric interest are dimethyl ether, diethyl ether, methyl *tert*-butyl ether and ethyl *tert*-butyl ether. The reactions of the aliphatic saturated ethers with O_3 and NO_3 radicals are expected to be of negligible importance as atmospheric loss processes, with an upper limit to the rate constant for the reaction of NO_3 radicals with CH_3OCH_3 of $<3 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K being the only available literature data.[26] Hence the major, if not sole, atmospheric loss process is by reaction with the OH radical. The kinetic data for these reactions are given in Table 34.

Japar *et al.*[36] showed that the Cl atom-initiated reaction of CH_3OCH_3 leads to the formation of methyl formate, CH_3OCHO, with a yield of 0.90 ± 0.08, and this is consistent with the unpublished data of Tuazon[37] for the OH radical-initiated reaction in the presence of NO_x. These data indicate that the reaction sequence for the OH radical-initiated reaction, in the presence of NO, is

$$\begin{tikzcd}[row sep=small]
\mathrm{OH + CH_3OCH_3} \arrow[r] & \mathrm{H_2O + CH_3O\dot{C}H_2} \arrow[d, "O_2"] \\
 & \mathrm{CH_3OCH_2O\dot{O}} \arrow[d, "NO \rightarrow NO_2"] \\
 & \mathrm{CH_3OCH_2\dot{O}} \arrow[d, "O_2"] \\
 & \mathrm{CH_3OCHO + HO_2}
\end{tikzcd}$$

The OH radical-initiated reaction of methyl *tert*-butyl ether, $CH_3OC(CH_3)_3$, in the presence of NO_x has been investigated by Japar *et al.*,[36] Smith *et al.*[38] and Tuazon *et al.*[39] The products observed, and their molar percentage yields, were: *tert*-butyl formate, 59 ± 5,[36] 68 ± 5,[38] 76 ± 7;[39] HCHO, 48 ± 5,[38] 37^{+6}_{-1};[39] methyl acetate ($CH_3C(O)OCH_3$), 14 ± 2,[38] 17 ± 2;[39] and acetone ($CH_3C(O)CH_3$), 2.6 ± 0.3[38] and 2.1 ± 0.9.[39] The HCHO yield in the study of Tuazon *et al.*[39] was observed to increase with the extent of reaction and the cited value is that extrapolated to zero reaction. These product data[36,38,39] are in reasonably good agreement, and indicate the following reaction mechanism [Reaction Scheme (10)] in the presence of NO[39] (the "first-generation" products are underlined)



Reaction Scheme (10)

The precursor alkoxy radical to $CH_3C(O)CH_3$ could then be $CH_3OC(CH_3)_2O^{\cdot}$ and/or $(CH_3)_3CO^{\cdot}$. The estimated distribution given in the reaction scheme above leads to predicted yields of $(CH_3)_3COCHO$, 76%; HCHO, 48%; $CH_3OC(O)CH_3$, 18%; and $CH_3C(O)CH_3$, 6%, reasonably consistent with the experimental data of Smith *et al.*[38] and Tuazon *et al.*[39] when consideration is taken of combination of the $(CH_3)_3CO^{\cdot}$ radical with NO to form *tert*-butyl nitrite[38] (observed as an ~6% product[38,40]). A small amount ($\leq$10%) of organic nitrate production from the $RO_2^{\cdot}$ + NO reactions cannot be ruled out.[39]

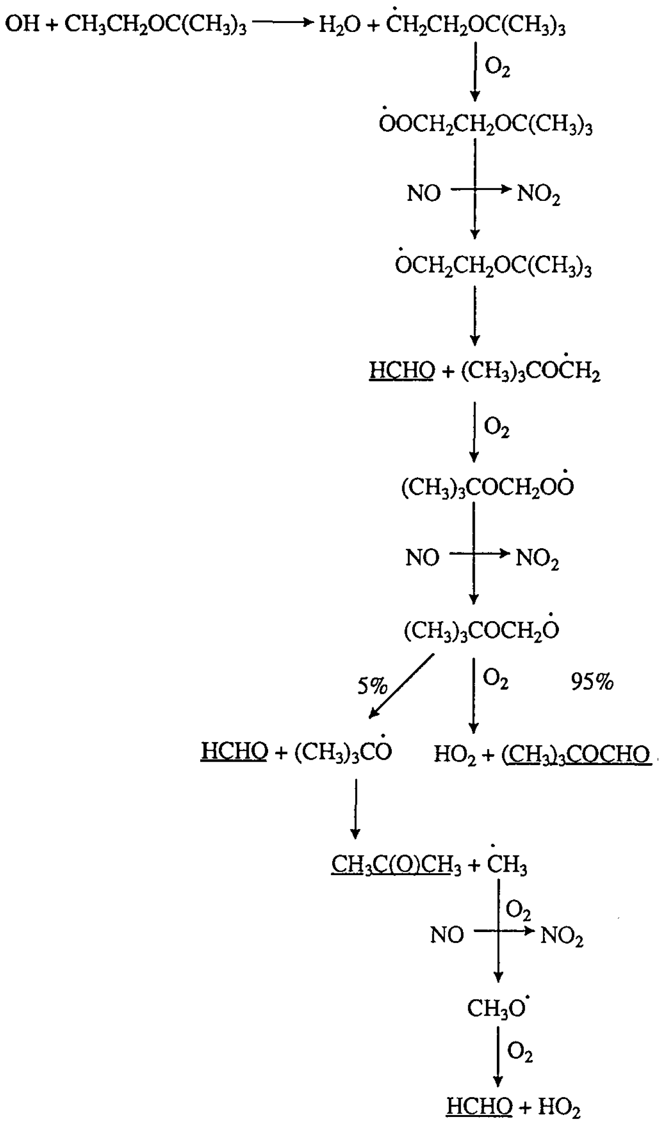
Wallington and Japar[41] observed the formation of ethyl formate (CH_3CH_2OCHO) from the reaction of the OH radical with diethyl ether in the presence of NO_x, with a yield of 0.92 ± 0.06. Since the major initial OH radical reaction pathway is expected to involve H-atom abstraction from the $-CH_2-$ groups in diethyl ether,[24] this finding[41] indicates that under atmospheric conditions the major reaction process of the dominant alkoxy radical formed, $CH_3CH_2OCH(\dot{O})CH_3$, is through decomposition,

$$CH_3CH_2OCH(\dot{O})CH_3 \rightarrow CH_3CH_2OCHO + \dot{C}H_3$$

followed by reactions of the $\dot{C}H_3$ radical to form HCHO.[41]

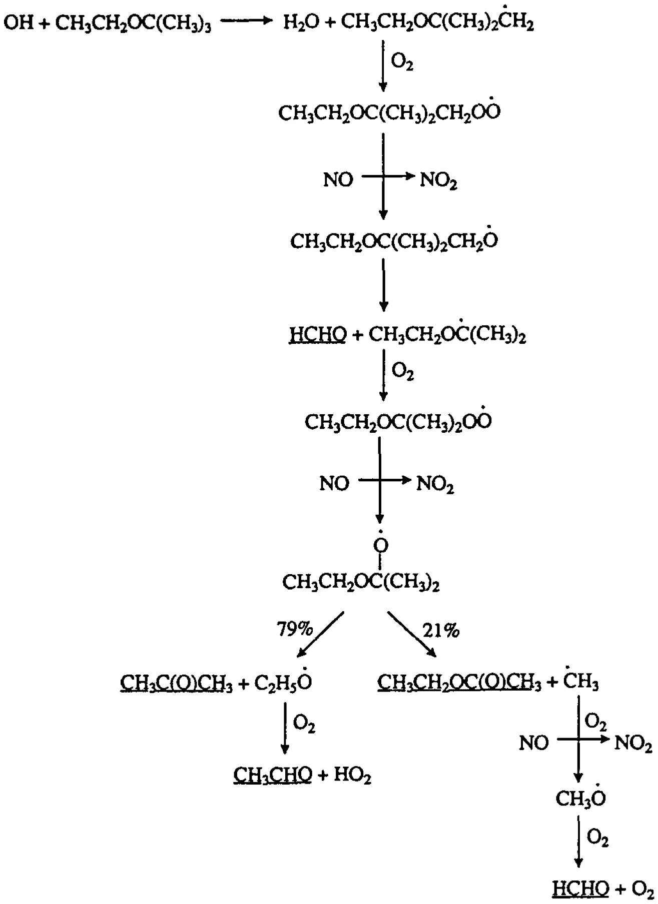
The OH radical-initiated reaction of ethyl *tert*-butyl ether, $C_2H_5OC(CH_3)_3$, has been investigated by Wallington and Japar[41] and Smith *et al.*[40] The products observed, and their molar percentage yields, were as follows: $(CH_3)_3COCHO$, 76 ± 6%,[41] 64 ± 3%;[40] $(CH_3)_3COC(O)CH_3$, 13 ± 1%;[40] $CH_3CH_2OC(O)CH_3$, 4.3 ± 0.3%;[40] CH_3CHO, 16 ± 1%;[40] $CH_3C(O)CH_3$, 1.9 ± 0.2%;[40] and HCHO, 53 ± 4%.[40] In the study of Smith *et al.*,[40] a significant fraction of the $(CH_3)_3CO^{\cdot}$ radicals formed were scavenged by NO to form *tert*-butyl nitrite. The above information suggests the following Reaction Scheme (11) at 298 K and ~760 Torr total pressure of air:

H-atom abstraction from the $-CH_3$ group of the C_2H_5 group (~3%)

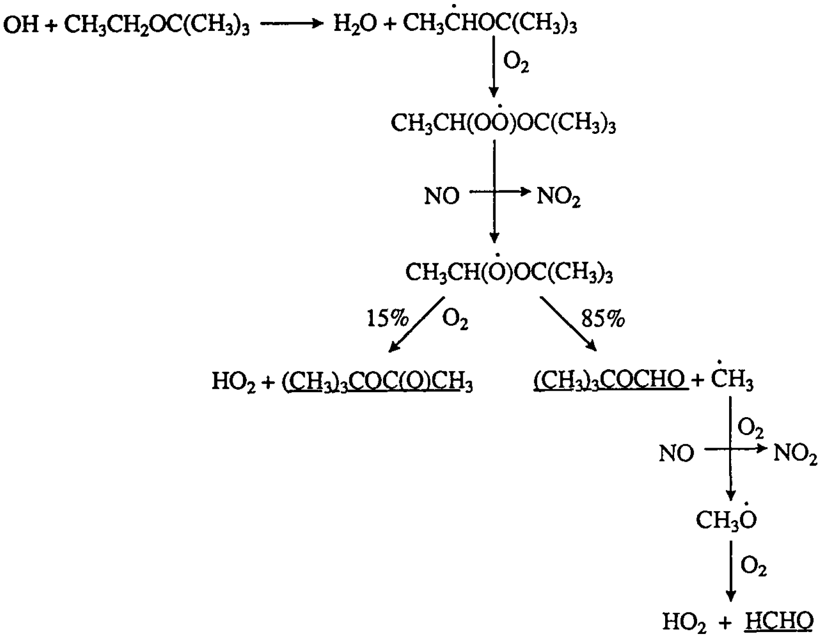


Reaction Scheme (11)

H-atom abstraction from the –C(CH$_3$)$_3$ group (19%)



H-atom abstraction from the –CH$_2$– group of the C$_2$H$_5$ group (78%)



Reaction Scheme (11) — Continued

This reaction sequence leads to product formation yields of: $(CH_3)_3COCHO$, 69%; $(CH_3)_3COC(O)CH_3$, 12%; $CH_3CH_2OC(O)CH_3$, 4%; $CH_3C(O)CH_3$, 15%; CH_3CHO, 15%; and HCHO, 93%, in reasonable agreement with the experimental data[40,41] when the interception of $(CH_3)_3C\dot{O}$ radicals by NO[40] (which otherwise would have led to $CH_3C(O)CH_3$ + HCHO formation) is taken into account.

D. *Carboxylic Acids*

The carboxylic acids of primary interest present in the gas-phase in polluted urban atmospheres are formic and acetic acid. Again, although no data have been reported for the NO_3 radical or O_3 reactions, the only important gas-phase atmospheric removal process is expected to be by OH radical reaction, and the OH radical rate constants are given in Table 34. For HCOOH, the OH radical reaction proceeds to form mainly CO_2 and an H-atom, with an H atom yield of 0.75 ± 0.25.[42] From this H-atom formation yield[42] and kinetic data for the reactions of OH radicals with HCOOH and DCOOH[42,43] and of OD radicals with HCOOD and DCOOD,[43] the OH radical reaction with formic acid appears to proceed by

$$\begin{array}{l} OH + HC(O)OH \rightarrow H_2O + HCO_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\qquad\qquad\qquad H + CO_2 \end{array}$$

with the major reaction pathway being the abstraction of the H (or D) atom from the –OH (or –OD) group.

While no product study of the OH radical reaction with $CH_3C(O)OH$ has been carried out, the rate constants of Singleton *et al.*[44] for the OH radical reactions with CH_3COOH, CD_3COOH and CD_3COOD indicate that at room temperature the major reaction pathway also involves H atom abstraction from the –OH group

$$\begin{array}{l} OH + CH_3C(O)OH \rightarrow H_2O + CH_3CO_2^{\bullet} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \dot{C}H_3 + CO_2 \end{array}$$

Since these OH radical reactions are slow, with calculated atmospheric lifetimes due to OH radical reaction of ~30–50 days, the major process(es) removing these compounds from the gas phase are likely to be wet or dry deposition, with incorporation into raindrops or cloud and fog water being of importance from the viewpoint of acid deposition.

E. *Hydroperoxides*

To date, data concerning the atmospheric chemistry of the hydroperoxides are only available for methyl hydroperoxide (CH_3OOH) and *tert*-butyl hydroperoxide [$(CH_3)_3COOH$]. The expected gas-phase atmospheric loss processes for this class of organic compounds involve photolysis and OH radical reaction. The absorption cross-sections of CH_3OOH have been evaluated by the IUPAC panel,[2] and a photodissociation quantum yield of unity is recommended.[2]

$$CH_3OOH + h\nu \rightarrow CH_3\dot{O} + OH$$

The room temperature rate constants for the OH radical reactions of CH_3OOH and $(CH_3)_3COOH$, and the temperature-dependent parameters for CH_3OOH, are given in Table 34. For CH_3OOH, the studies of Niki *et al.*[45] and Vaghjiani and Ravishankara[46] show that the OH radical reaction proceeds by two pathways,

$$OH + CH_3OOH \rightarrow H_2O + CH_3OO^{\bullet} \quad (a)$$

$$OH + CH_3OOH \rightarrow H_2O + \dot{C}H_2OOH \quad (b)$$

with $k_a = 1.79 \times 10^{-12}\ e^{219/T}$ cm^3 molecule^{-1} s^{-1} over the temperature range 203–348 K and $(k_a + k_b) = 2.93 \times 10^{-12}\ e^{190/T}$ cm^3 molecule^{-1} s^{-1} over the temperature range 223–423 K.[19,46] Thus, $k_a/(k_a + k_b) = 0.67$ at 298 K. The $\dot{C}H_2OOH$ radical rapidly decomposes

$$\dot{C}H_2OOH \rightarrow HCHO + OH$$

to regenerate the OH radical.[46]

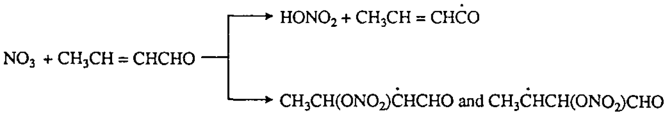
F. *Unsaturated Carbonyls*

The unsaturated carbonyl compounds of atmospheric interest include the α,β-unsaturated carbonyls formed from the atmospheric reactions of conjugated dienes and the unsaturated carbonyls formed from the atmospheric reactions of the monoterpenes limonene and terpinolene (and presumably also myrcene, ocimene and linalool) [see Sec. 2.2]. The α,β-unsaturated carbonyls of major atmospheric interest are acrolein, methacrolein and methyl vinyl ketone. As discussed in Sec. 2.2, acrolein is formed from the atmospheric degradation reactions of 1,3-butadiene, and methacrolein and methyl vinyl ketone are formed from 2-methyl-1,3-butadiene (isoprene). The major atmospheric removal processes for these organic compounds are expected to be reaction with O_3 and with OH and NO_3 radicals. As shown by the data of Gardner *et al.*[47] for acrolein, photolysis appears to be of minor importance as a loss process (with a photolysis lifetime of acrolein of ~10 days at 40° zenith angle).[47]

The kinetics of the gas-phase reactions of the NO_3 radical with acrolein and crotonaldehyde have been determined,[26] and the rate constants at 298 ± 2 K are 1.1×10^{-15} cm^3 molecule^{-1} s^{-1} and 5.1×10^{-15} cm^3 molecule^{-1} s^{-1}, respectively.[26] These reactions are expected to be analogous to the OH radical reactions (see below) in that the NO_3 radical reaction with acrolein is expected to proceed mainly by H-atom abstraction from the –CHO group,

$$NO_3 + CH_2{=}CHCHO \rightarrow HONO_2 + CH_2{=}CH\dot{C}O$$

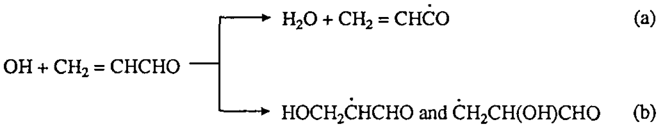
while the reaction with crotonaldehyde will proceed by both H-atom abstraction from the –CHO group and NO_3 radical addition to the $>C=C<$ bond.



These NO_3 radical reactions will be of generally minor significance as atmospheric loss processes for the α,β-unsaturated carbonyls.

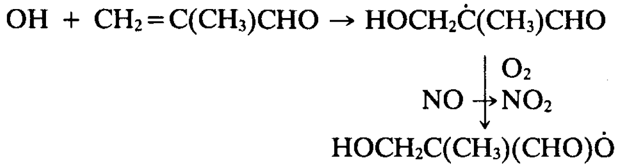
The room temperature rate constants for the gas-phase reactions of O_3 with acrolein, methacrolein, crotonaldehyde and methyl vinyl ketone have been measured (see Ref. 25 and Sec. 5.4), with recommended rate constants (Ref. 25 and Sec. 5.4) of: acrolein, 2.9×10^{-19} cm^3 $molecule^{-1}$ s^{-1} at 298 K, methacrolein, 1.36×10^{-15} $e^{-2112/T}$ cm^3 $molecule^{-1}$ s^{-1} (1.14×10^{-18} cm^3 $molecule^{-1}$ s^{-1} at 298 K); crotonaldehyde, 9.0×10^{-19} cm^3 $molecule^{-1}$ s^{-1} at 298 K; and methyl vinyl ketone, 7.51×10^{-16} $e^{-1521/T}$ cm^3 $molecule^{-1}$ s^{-1} (4.56×10^{-18} cm^3 $molecule^{-1}$ s^{-1} at 298 K). As for the alkenes, these O_3 reactions proceed by initial addition to the $>C=C<$ bonds.[25] Again, these O_3 reactions are of minor importance as atmospheric loss processes.

The major atmospheric loss process of the α,β-unsaturated carbonyls is by reaction of the OH radical, and the room temperature rate constants and temperature-dependent parameters for the OH radical reactions with acrolein, methacrolein, crotonaldehyde and methyl vinyl ketone are given in Table 34. For the aldehydes, these OH radical reactions occur by both H-atom abstraction from the –CHO group and OH radical addition to the $>C=C<$ bond.[19]

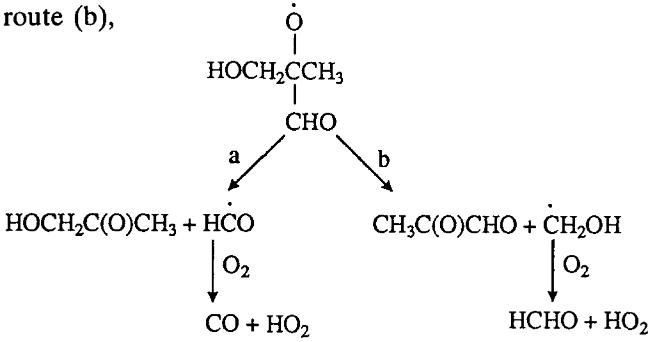


For acrolein the major reaction pathway appears to be H-atom abstraction from the –CHO group,[19] while for crotonaldehyde and methacrolein both reaction pathways occur, with the abstraction and addition pathways being of comparable importance at 298 K.[19,24,48] The subsequent reactions of the initially formed radicals are generally as discussed in Secs. 2.1 and 2.2 above.

For the OH radical-initiated reaction with methacrolein, the product study of Tuazon and Atkinson[48] shows that the $HOCH_2C(CH_3)(CHO)\dot{O}$ radical formed after OH radical addition to the terminal carbon atom of the $>C=C<$ bond

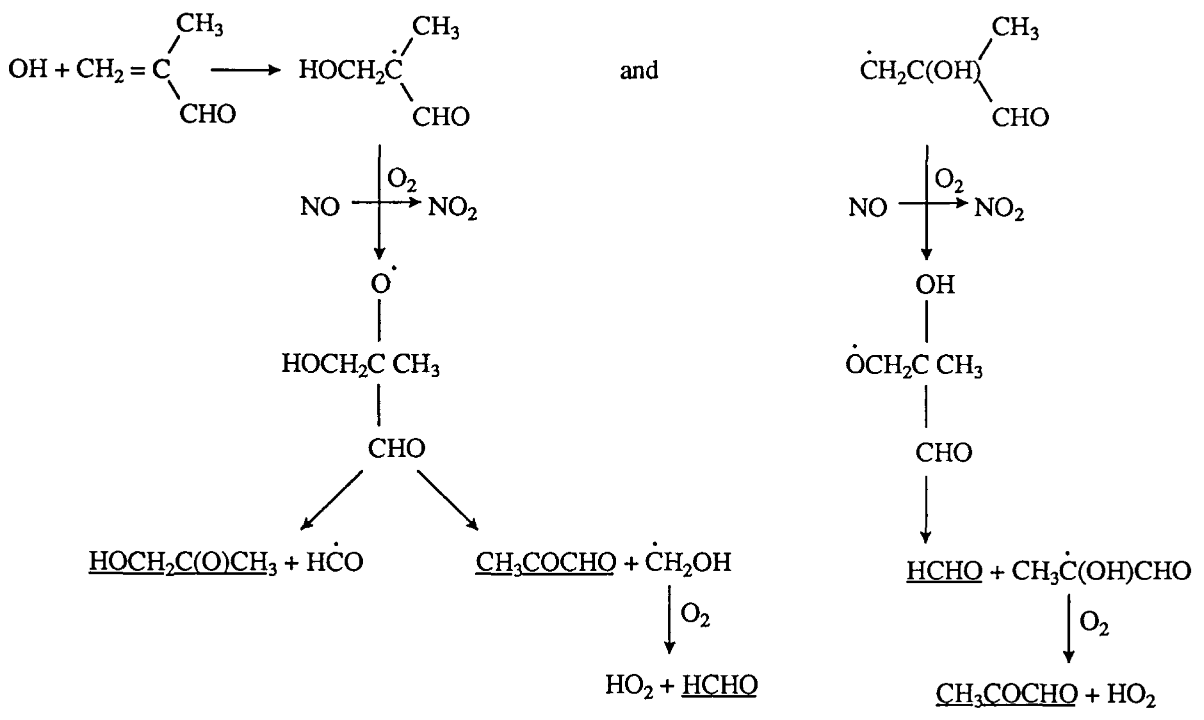


must decompose predominantly by route (a) rather than route (b),

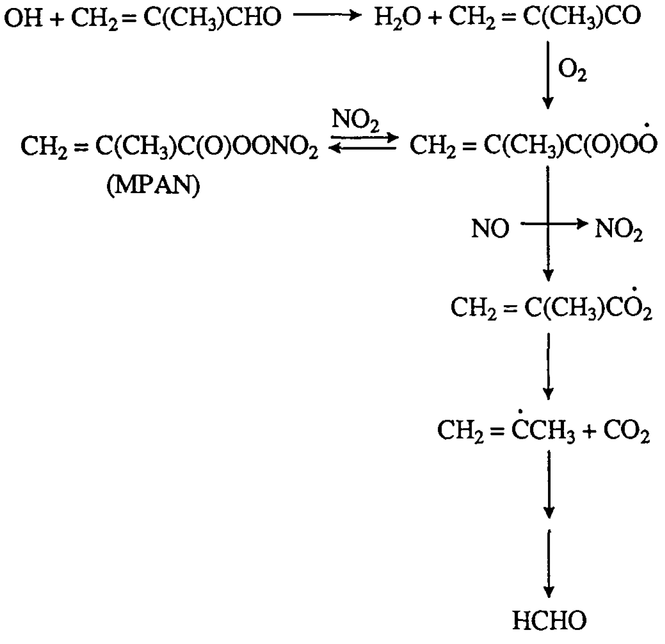


since hydroxyacetone ($HOCH_2C(O)CH_3$) was the major product observed from the OH radical addition pathway.[48]

Furthermore, it appears that terminal versus nonterminal OH radical addition to the $>C=C<$ bond in methacrolein occurs with a ratio of ~83:17 at 298 K,[48] since the $HOCH_2COCH_3$ and CH_3COCHO formation yields were 0.41 ± 0.03 and 0.084 ± 0.016, respectively, with the $HOCH_2C(O)CH_3$ arising from decomposition of the $HOCH_2C(CH_3)(CHO)\dot{O}$ radical and CH_3COCHO from the $\dot{O}CH_2C(OH)(CH_3)CHO$ radical (and possibly from the $HOCH_2C(CH_3)(CHO)\dot{O}$ radical)[48] [see Reaction Scheme (12)]. This OH radical addition process accounts for 50% of the overall OH radical reaction with methacrolein at room temperature.[48] The H-atom abstraction pathway proceeds by,[48]

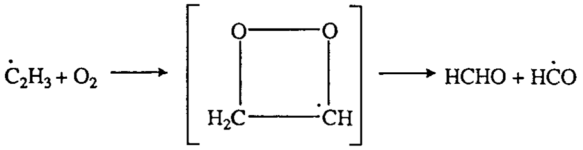


Reaction Scheme (12)

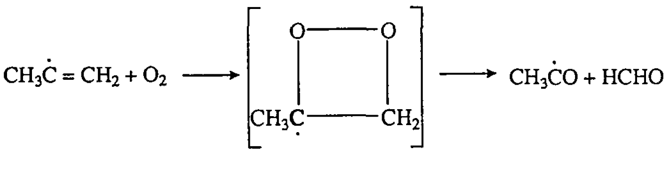


with this pathway accounting for 50 ± 16% of the overall reaction at room temperature.[48] Peroxymethacrylic nitric anhydride (MPAN, $CH_2=C(CH_3)C(O)OONO_2$), observed as a temporary reservoir product of this reaction pathway,[48] has also been prepared and studied by Bertman and Roberts[49] and Roberts and Bertman[50] (see also Sec. 2.6).

While the data of Tuazon and Atkinson[48] suggested the formation of HCHO in close to unit yield from the subsequent reactions of the $CH_2=\dot{C}CH_3$ radical, the other product(s) of this radical under atmospheric conditions were not accounted for. The reaction of the homologous vinyl ($\dot{C}_2H_3$) radical with O_2 has a room temperature rate constant of 9×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at room temperature,[51-53] with a small negative temperature dependence ($B = -126 \pm 51$ K[51]), and HCHO and $H\dot{C}O$ were observed as products.[51]



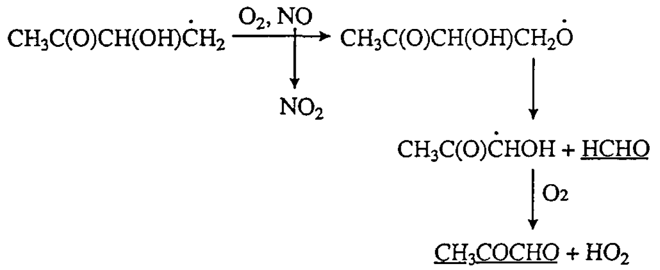
This reaction of the vinyl radical with O_2 suggests that the $CH_3\dot{C}=CH_2$ radical reaction proceeds by



For the α,β-unsaturated ketones such as methyl vinyl ketone, the only significant reaction pathway (since H-atom abstraction from the substituent alkyl group(s) will be slow[24]) involves OH radical addition to the $>C=C<$ bond.[19,54]

$$OH + CH_2=CHC(O)CH_3 \rightarrow 0.7\ HOCH_2\dot{C}HC(O)CH_3 + 0.3\ \dot{C}H_2CH(OH)C(O)CH_3$$

The subsequent reactions of these radicals are as dealt with in Secs. 2.1 and 2.2. Thus, in the presence of NO[54] Reaction Scheme (13) will occur. Formation of $HOCH_2CHO + CH_3\dot{C}O$ [route (a)] is calculated[55] to be ~10 kcal mol^{-1} more exothermic than the formation of $CH_3COCHO + \dot{C}H_2OH$ [route (b)], and glycolaldehyde is indeed observed as a major (~70%) product from the OH radical reaction with methyl vinyl ketone in the presence of NO.[54] The reactions subsequent to OH radical addition to the internal carbon atom are:[54]



The observed $HOCH_2CHO$ and CH_3COCHO formation yields from the OH radical reaction with methyl vinyl ketone of 0.64 ± 0.13 and 0.25 ± 0.06, respectively,[54] indicate that OH radical addition to the terminal and non-terminal carbon atoms of the $>C=C<$ bond occurs in the ratio 72:28 at room temperature.[54]

G. *1,4-Unsaturated Dicarbonyls*

1,4-Unsaturated dicarbonyl compounds have been postulated to be formed in the atmospheric degradation of the aromatic hydrocarbons (see, for example, Atkinson and Lloyd)[56] and 3-hexene-2,5-dione ($CH_3C(O)CH = CHC(O)CH_3$) has been observed in small yield from the photooxidation of 1,2,4-trimethylbenzene[57] and, in larger yield, from *p*-xylene.[58] Experimental data concerning the atmospherically important reactions are only available for *cis*- and *trans*-3-hexene-2,5-dione.[58,59] These isomers were observed to react with O_3, with rate constants at 298 ± 2 K of 1.8×10^{-18} and 8.3×10^{-18} cm^3 molecule^{-1} s^{-1} for *cis*- and *trans*-3-hexene-2,5-dione, respectively.[25,59] The measured OH radical reaction rate constants are given in Table 34. Photolysis of both isomers has also been observed, with the major pathway in the >320 nm spectral region being photoisomerization to the other geometric isomer.[58,59] Based upon these data, it appears that photolysis (other than photoisomerization) and/or reaction with the OH radical will be the dominant atmospheric removal processes.

Unfortunately, no definitive product data have been obtained for the OH radical reactions with these 1,4-unsaturated dicarbonyls.[59]

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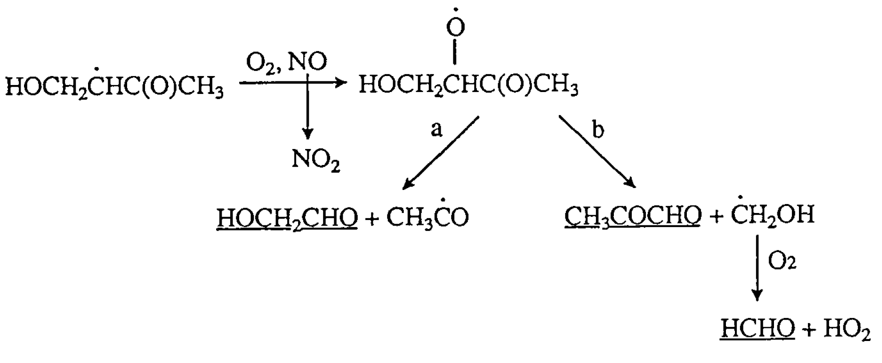

Reaction Scheme (13)

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2.6. Nitrogen-Containing Organic Compounds

The nitrogen-containing organic compounds considered in this section are the alkyl nitrates expected to be formed in the atmosphere from the alkanes and alkenes (see Secs. 2.1 and 2.2), alkyl nitrites, and peroxyacyl and peroxyalkyl nitrates. The reactions of acetyl peroxy ($RC(O)OO^{\bullet}$) radicals under atmospheric conditions are also discussed in the portion of this section dealing with the chemistry of peroxyacyl nitrates.

Alkyl Nitrates

Based upon laboratory studies concerning the formation of alkyl nitrates from the NO_x-air photooxidations of the alkanes (Sec. 2.1 and references 1–3), the major alkyl nitrates expected to be formed in the atmosphere are 2-propyl nitrate, 2-butyl nitrate, 2- and 3-pentyl nitrate, and 2- and 3-hexyl nitrate. Although no experimental data are available concerning the kinetics of the NO_3 radical or O_3 reactions, these are expected to be slow and of no significance as atmospheric loss processes. The major loss processes are then reaction with the OH radical and photolysis. The room temperature OH radical reaction rate constants are given in Table 35 (no temperature dependent data are available).

These reactions proceed by H-atom abstraction from the C–H bonds, and in the absence of product data the estimation technique of Atkinson[6] (as revised by Atkinson and Aschmann[7] to yield the substituent factors at 298 K of $F(\text{-CH}_2\text{ONO}_2) = F(>\text{CHONO}_2) = F(>\text{CONO}_2) = 0.30$ and $F(-\text{ONO}_2) = 0.18$) can be used to calculate the distribution of the nitratoalkyl radicals formed from the OH radical reactions of the $\geq C_4$ alkyl nitrates (see Reaction Scheme (14), for example, at room temperature). The expected subsequent reactions of these radicals are as discussed in Sec. 2.1. For example, in the presence of NO, the reactions expected to occur are as shown in Reaction Scheme (15). At the present time, product data are not available for these reactions,

TABLE 35. Room temperature rate constants k for the gas-phase reactions of the OH radical with alkyl nitrates and peroxyacetyl nitrate at atmospheric pressure [from Ref. 4 and Sec. 3.8]

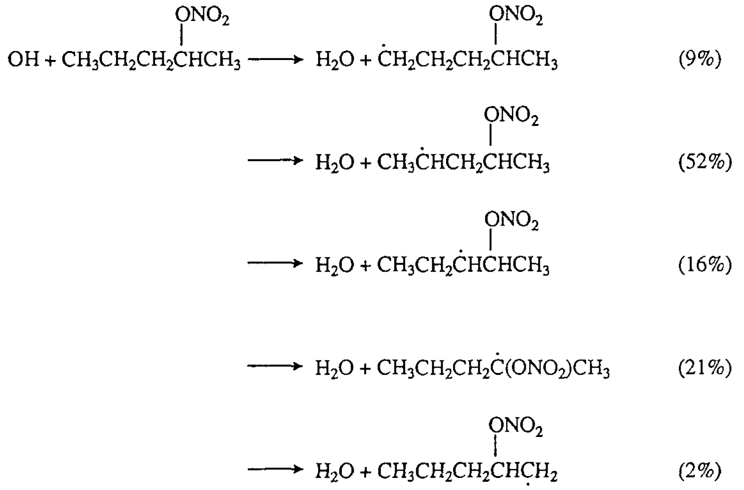
Organic	$10^{12} \times k$ (cm^3 $molecule^{-1}$ s^{-1})
Methyl nitrate	0.35
Ethyl nitrate	0.49
1-Propyl nitrate	0.73
2-Propyl nitrate	0.49
1-Butyl nitrate	1.71
2-Butyl nitrate	0.92
2-Pentyl nitrate	1.85
3-Pentyl nitrate	1.12
2-Methyl-3-butyl nitrate	1.82
2,2-Dimethyl-1-propyl nitrate	0.85
2-Hexyl nitrate	3.17
3-Hexyl nitrate	2.70
Cyclohexyl nitrate	3.30
2-Methyl-2-pentyl nitrate	1.72
3-Methyl-2-pentyl nitrate	3.02
3-Heptyl nitrate	3.69
3-Octyl nitrate	3.88
Peroxyacetyl nitrate	0.11[a]

[a] $k = 9.5 \times 10^{-13} e^{-650/T}$ cm^3 $molecule^{-1}$ s^{-1} recommended over the temperature range 270–300 K.[5]

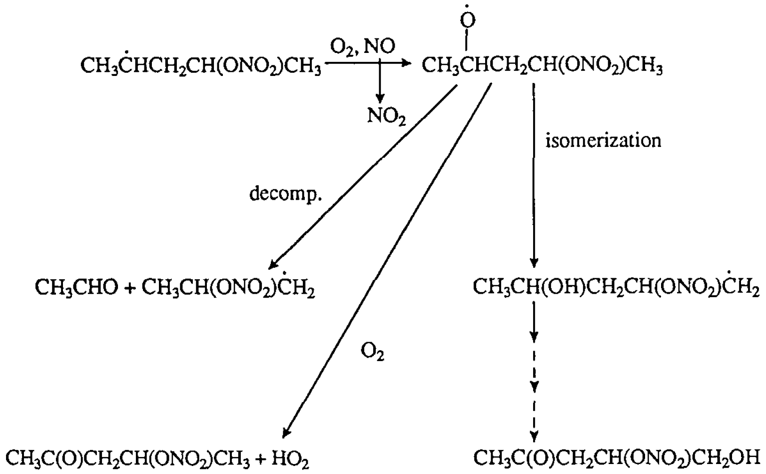
and the estimation method proposed in Sec. 2.1 for the assessment of the relative importance of the various alkoxy radical reaction pathways should be used.

The absorption cross-sections of methyl nitrate, ethyl nitrate and 1-and 2-propyl nitrate have been reviewed and evaluated by the IUPAC panel,[5] and the IUPAC recommended values[5] are based on the measurements of Roberts and Fajer[8] and Turberg *et al.*[9] The IUPAC evaluation[5] should be consulted for the absorption cross-sections for these alkyl nitrates. In addition, Roberts and Fajer[8] measured absorption cross-sections for 1- and 2-butyl nitrate, 2-methyl-2-propyl nitrate (*tert*-butyl nitrate), 2- and 3-pentyl nitrate, cyclopentyl nitrate, $CH_3C(O)CH_2ONO_2$ and $HOCH_2CH_2ONO_2$, while Turberg *et al.*[9] also measured the absorption cross-sections for 1-butyl nitrate and 3-methyl-1-butyl nitrate.

Based on the direct measurements of the photolysis rates under ambient atmospheric conditions conducted by Luke and Dickerson[10] and Luke *et al.*[11] for ethyl nitrate,[10,11] 1-propyl nitrate[11] and 1- and 2-butyl nitrate,[11] the lifetimes of these alkyl nitrates in the lower troposphere due to photolysis are in the range ~15–30 days. Moreover, these measured photolysis rates under ambient atmospheric conditions are in agreement, within the experimental errors, with those calculated assuming a



Reaction Scheme (14)



Reaction Scheme (15)

photodissociation quantum yield of unity[10,11] (see also Becker and Wirtz[12]). Photolysis leads to cleavage of the O–NO$_2$ bond,

$$RONO_2 + h\nu \rightarrow R\dot{O} + NO_2$$

followed by the reactions of the alkoxy radical (Sec. 2.1). For example, Becker and Wirtz[12] have observed the formation of acetone from the photolysis of 2-propyl nitrate:

$$\begin{array}{l} CH_3CH(ONO_2)CH_3 + h\nu \rightarrow CH_3CH(\dot{O})CH_3 + NO_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow O_2 \\ \qquad\qquad\qquad\qquad\qquad CH_3C(O)CH_3 + HO_2 \end{array}$$

Alkyl Nitrites

Under atmospheric conditions, the simple alkyl nitrites rapidly photolyze,[13] with lifetimes measured in minutes.

$$RONO + h\nu \rightarrow R\dot{O} + NO$$

Their reactions with the OH radical (reference 4 and Sec. 3.8) are of negligible importance as an atmospheric loss process.[14] Because of their rapid photolysis, the formation of alkyl nitrites from the R$\dot{O}$ + NO combination reactions can be essentially neglected under atmospheric conditions. However, the formation of alkyl nitrites from the R$\dot{O}$ + NO reactions can be important in the photooxidations, under laboratory conditions, of RONO–NO–organic–air mixtures.

Peroxyacyl Nitrates and Peroxy Nitrates

Peroxyacetyl nitrate (PAN; CH$_3$C(O)OONO$_2$) and the higher members of this class of compounds are formed from the atmospheric degradations of many organics (see Sec. 2.5) by the combination reaction of acyl peroxy radicals with NO$_2$.

$$RC(O)OO^{\cdot} + NO_2 \xrightarrow{M} RC(O)OONO_2$$

The reaction of OH radicals with PAN (the only peroxyacyl nitrate studied to date) is slow at tropospheric temperatures (Table 35) and this OH radical reaction is expected to be a significant atmospheric loss process for PAN only at the low temperatures encountered in the upper troposphere. The absorption cross-sections for PAN are given in the IUPAC evaluation.[5] The major, and usually totally dominant, loss process for PAN in the lower troposphere is by its thermal decomposition

$$CH_3C(O)OONO_2 \xrightarrow{M} CH_3C(O)O\dot{O} + NO_2$$

Thus, PAN is in equilibrium with NO$_2$ and the CH$_3$C(O)O$\dot{O}$ radical. In the presence of NO, the reaction

$$\begin{array}{l} CH_3C(O)OO^{\cdot} + NO \rightarrow CH_3C(O)\dot{O} + NO_2 \\ \qquad\qquad\qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\qquad\quad \dot{C}H_3 + CO_2 \end{array}$$

leads to removal of PAN.

The thermal decomposition rate constant for PAN is temperature and pressure dependent,[5] being in the fall-off region at room temperature at and below atmospheric pressure. Using the Troe fall-of expression, the IUPAC evaluation panel recommended for the temperature range 280–330 K that:[5] $k_o = 4.9 \times 10^{-3}\ e^{-12100/T}$ cm^3 molecule^{-1} s^{-1}, $k_\infty = 4.0 \times 10^{16}\ e^{-13600/T}$ s^{-1} and $F = 0.3$ at 298 K. Thus, k_∞(PAN) = 6.1×10^{-4} s^{-1} at 298 K, and at 298 K and 760 Torr total pressure of air k(PAN) = 5.2×10^{-4} s^{-1}, in good agreement with the atmospheric pressure data of Schurath and Wipprecht[15] ($k = 3.2 \times 10^{16}\ e^{-13592/T}$ s^{-1} = 5.0×10^{-4} s^{-1} at 298 K), Roberts and Bertman[16] ($k = 2.5 \times 10^{17}\ e^{-14343/T}$ s^{-1} = 3.1×10^{-4} s^{-1} at 298 K) and Roumelis and Glavas[17] ($k = 3.1 \times 10^{-4}$ s^{-1} at 296.7 K).

The decomposition rates of the higher peroxyacyl nitrates are expected to be similar to that for PAN, with the decomposition rate constants being closer to the high pressure limit at a given pressure than for PAN.

For the formation and decomposition of peroxypropionyl nitrate (PPN),

$$CH_3CH_2C(O)OO^{\cdot} + NO_2 \overset{M}{\rightleftarrows} CH_3CH_2C(O)OONO_2 \quad (a, -a)$$

$$\begin{array}{l} CH_3CH_2C(O)OO^{\cdot} + NO \rightarrow CH_3CH_2C(O)O^{\cdot} + NO_2 \quad (b) \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad\qquad\qquad\quad C_2H_5^{\cdot} + CO_2 \end{array}$$

Kerr and Stocker[18] obtained a rate constant ratio of k_b/k_a = 1.9 at ~730 Torr total pressure of air and 302 ± 3 K, essentially identical to the rate constant ratio for the analogous reactions of the CH$_3$C(O)OO$^{\cdot}$ radical.[5] At atmospheric pressure, Schurath and Wipprecht[15] and Mineshos and Glavas[19] determined thermal decomposition rate constants for peroxypropionyl nitrate (PPN; C$_2$H$_5$C(O)OONO$_2$) of k(PPN) = $1.6 \times 10^{17}\ e^{-14073/T}$ s^{-1} [15] and $2 \times 10^{15}\ e^{-12800/T}$ s^{-1} [19] (5.0×10^{-4} s^{-1} [15] and 4.4×10^{-4} s^{-1} [19] at 298 K and atmospheric pressure).

Roberts and Bertman[16] have studied the thermal decomposition of CH$_2$=C(CH$_3$)C(O)OONO$_2$ (MPAN) [formed from the OH radical-initiated reaction of methacrolein (Sec. 2.5)] and determined a thermal decomposition rate constant at atmospheric pressure of k(MPAN) = $1.6 \times 10^{16}\ e^{-13488/T}$ s^{-1} (3.5×10^{-4} s^{-1} at 298 K).

These data indicate that for the thermal decompositions of the peroxyacyl nitrates,

$$k(RC(O)OONO_2) = 4 \times 10^{16}\ e^{-13600/T}\ s^{-1}$$

to within a factor of ~1.5 at 298 K.

For the peroxyalkyl nitrates, ROONO$_2$, the only significant lower troposphere loss process is again thermal decomposition,

$$ROONO_2 \xrightarrow{M} RO_2^{\cdot} + NO_2$$

with the thermal decomposition rate constants for CH$_3$OONO$_2$ and C$_2$H$_5$OONO$_2$ being in the fall-off regime at pressures of one atmosphere and below.[5,20] Using the Troe fall-off expression, the IUPAC evaluation panel recommended[5] for the temperature range 250–300 K that: for CH_3OONO_2, $k_o = 9 \times 10^{-5}\ e^{-9690/T}$ cm^3 molecule^{-1} s^{-1}, $k_\infty = 1.1 \times 10^{16}\ e^{-10560/T}$ s^{-1}, and $F = 0.4$ at 298 K; and for $C_2H_5OONO_2$, $k_o = 4.8 \times 10^{-4}\ e^{-9285/T}$ cm^3 molecule^{-1} s^{-1}, $k_\infty = 8.8 \times 10^{15}\ e^{-10440/T}$ s^{-1}, and $F = 0.31$. At 760 Torr total pressure of air and 298 K, $k(CH_3OONO_2) = 1.8$ s^{-1} and $k(C_2H_5OONO_2) = 4.0$ s^{-1}, which can be compared to the limiting high-pressure values of $k_\infty(CH_3OONO_2) = 4.5$ s^{-1} and $k_\infty(C_2H_5OONO_2) = 5.4$ s^{-1} at 298 K. The decomposition rates for the higher $ROONO_2$ species are expected to be similar to that for CH_3OONO_2, except that they will be closer to the high pressure first-order limit.

Indeed, Zabel *et al.*[20] have shown that the thermal decomposition rate constants for the $C_4H_9OONO_2$, $C_6H_{13}OONO_2$ and $C_8H_{17}OONO_2$ species at 600 Torr total pressure and 253 K are within 30% of the high-pressure limiting value for $C_2H_5OONO_2$.[20] Hence it is recommended that:

$$k_\infty(ROONO_2) = 9 \times 10^{15}\ e^{-10450/T}\ s^{-1}.$$

Bridier *et al.*[21] have experimentally measured the equilibrium constant $K = k_a/k_{-a}$ for the reactions

$$CH_3O_2^{\cdot} + NO_2 \overset{M}{\rightleftarrows} CH_3OONO_2 \qquad (a, -a)$$

over the temperature range 333–373 K, with $K = 2.73 \times 10^{-28}\ e^{10910/T}$ cm^3 molecule^{-1}, in good agreement with the equilibrium constant calculated from the forward and reverse rate constants k_∞ recommended by the IUPAC evaluation[5] of $6.8 \times 10^{-28}\ e^{10560/T}$ cm^3 molecule^{-1} over the temperature range 333–373 K. Absorption cross-sections have been measured for CH_3OONO_2[21–24] and those of Cox and Tyndall,[22] Sander and Watson[23] and Morel *et al.*[24] were considered in the IUPAC evaluation.[5] The absorption cross-sections reported by Bridier *et al.*[21] for the wavelength range 200–280 nm are in general agreement with the IUPAC recommendation,[5] except for wavelengths 220–230 nm and 280 nm.

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3. Kinetics and Mechanisms of the Gas-Phase Reactions of the OH Radical with Organic Compounds

Recent kinetic and mechanistic data for the gas-phase reactions of the OH radical with organic compounds are presented and discussed in this section. Recommended rate constant expressions are given using either the Arrhenius expression, $k = A\ e^{-B/T}$, or, if curvature in the Arrhenius plot is evident, the three parameter equation $k = C\ T^n\ e^{-D/T}$, where at a given temperature T the three parameter equation can be transformed into the Arrhenius expression with $A = Ce^nT^n$ and $B = D + nT$.

3.1. Alkanes

The rate constants reported since the previous review of Atkinson[1] are given in Table 36. In addition to these rate constants, Cantrell *et al.*[17] have determined the rate constant for the OH radical reactions with methane-^{12}C relative to that for methane-^{13}C over the temperature range 273–353 K, and obtained $k(^{12}CH_4)/k(^{13}CH_4) = 1.0054 \pm 0.0009$ independent of temperature over this range.

Methane and Methane-^{13}C. Absolute rate constants for the reactions of the OH radical with methane have been determined by Bott and Cohen[2] at 1234 ± 15 K, and by Vaghjiani and Ravishankara[3] and Finlayson-Pitts *et al.*[4] over the temperature ranges 223–420 K and 278–378 K, respectively (Table 36). While the high-temperature rate constant of Bott and Cohen[2] is in good agreement (within 15%) with the recommendation of Atkinson[1] of

$$k(\text{methane}) = 6.95 \times 10^{-18}\ T^2\ e^{-1282/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1},$$

the absolute rate constants determined by Vaghjiani and Ravishankara[3] and Finlayson-Pitts *et al.*[4] over the temperature ranges 223–420 K and 278–378 K, respectively, are ~20% lower than most of the previously reported absolute rate constants. In particular, the rate constants of Vaghjiani and Ravishankara[3] and Finlayson-

Pitts *et al.*[4] at and below room temperature are significantly lower than those of Greiner,[18] Davis *et al.*[19] and Jeong and Kaufman,[20,21] possibly because of the occurrence of secondary reactions of the OH radical with the methyl radical product in the earlier studies.[3]

Thus, the CH_4/OH concentration ratios used in the studies of Greiner,[18] Davis *et al.*[19] and Jeong and Kaufman[20] were significantly lower than those used by Vaghjiani and Ravishankara,[3] and all of these earlier studies conducted with low CH_4/OH concentration ratios were possibly subject to secondary reactions[3] leading to erroneously high measured rate constants, especially at the lowest temperatures studied. Indeed, inspection of the 298 K rate data of Davis *et al.*[19] does indicate a dependence of the measured rate constant on the OH radical concentration[3] [as derived from (flash energy) × (water vapor concentration)], and a similar dependence may be present in the 373 K rate data. This observation[3] suggests that the rate constant data of Greiner,[18] Davis *et al.*,[19] Overend *et al.*[22] and Jeong and Kaufman[20,21] were subject to the occurrence of secondary reactions, and hence these studies are not used in the evaluation of the rate constant for this reaction. It should, however, be noted that while Finlayson-Pitts *et al.*[4] used a CH_4/OH concentration ratio significantly lower than employed in the study of Vaghjiani and Ravishankara,[3] these two studies[3,4] are in good agreement.

At around room temperature, the absolute rate constants of Margitan *et al.*,[23] Howard and Evenson,[24] Zellner and Steinert,[25] Tully and Ravishankara,[26] Husain *et al.*,[27] Jonah *et al.*,[28] Madronich and Felder,[29] Vaghjiani and Ravishankara[3] and Finlayson-Pitts *et al.*[4] are in reasonable agreement, ranging from 5.6×10^{-15} cm^3 $molecule^{-1}$ s^{-1} to 9.5×10^{-15} cm^3 $molecule^{-1}$ s^{-1} at ~298 K. As noted previously,[1] at higher temperatures there are discrepancies between the rate constants measured by Zellner and Steinert[25] (above ~625 K) and Jonah *et al.*[28] (400–600 K) and those of Margitan *et al.*,[23] Tully and Ravishankara,[26] Madronich and Felder[29] and Vaghjiani and Ravishankara.[3] It should be noted that the rate constants of Vaghjiani and Ravishankara[3] and Finlayson-Pitts *et al.*[4] are as low as, or lower than, the other absolute rate constants over the temperature range ~295–420 K.

The absolute rate constants of Dixon-Lewis and Williams,[30] Margitan *et al.*,[23] Howard and Evenson,[24] Ernst *et al.*,[31] Tully and Ravishankara,[26] Madronich and Felder,[29] Smith *et al.*,[32] Bott and Cohen,[2] Vaghjiani and Ravishankara[3] and Finlayson-Pitts *et al.*[4] and the relative rate constant of Cox *et al.*[33] are plotted in Arrhenius form in Fig. 2 (the studies of Smith *et al.*[32] and Bott and Cohen[2] supersede the earlier preliminary data reported by Fairchild *et al.*[34] and Cohen and Bott,[35] respectively). These rate constant data are in generally good agree-

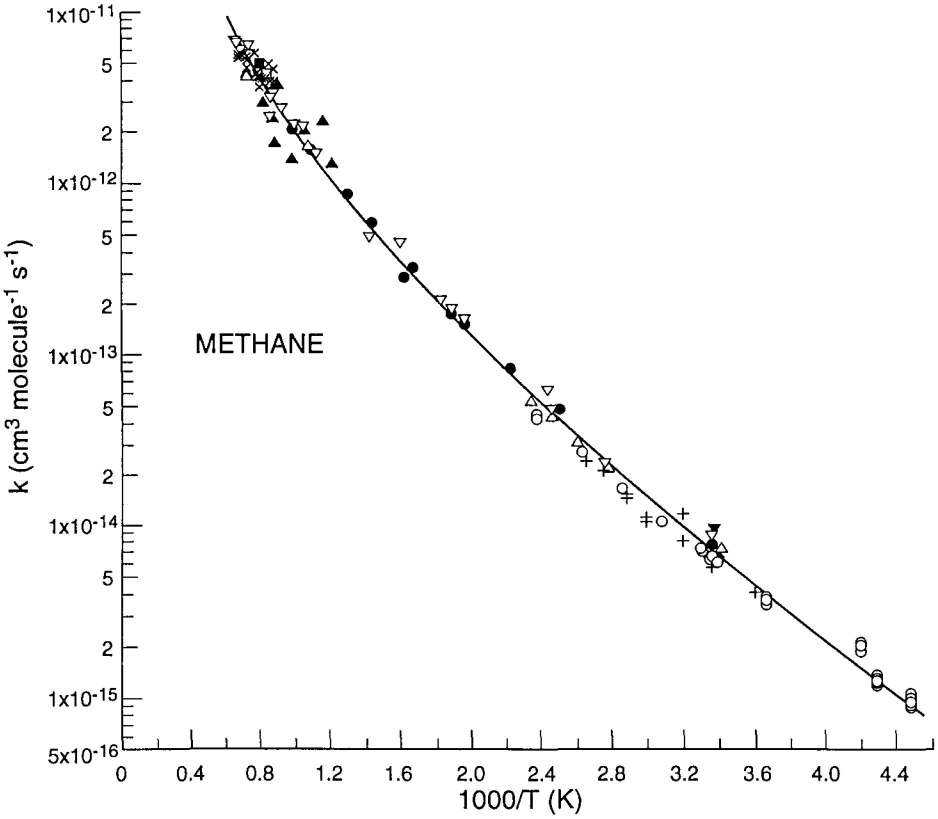

FIG. 2. Arrhenius plot of selected rate constants for the reaction of the OH radical with methane. (■) Dixon-Lewis and Williams;[30] (△) Margitan *et al.*;[23] (▼) Howard and Evenson;[24] (◆) Cox *et al.*;[33] (X) Ernst *et al.*;[31] (●) Tully and Ravishankara;[26] (▽) Madronich and Felder;[29] (▲) Smith *et al.*;[32] (□) Bott and Cohen;[2] (○) Vaghjiani and Ravishankara;[3] (+) Finlayson-Pitts *et al.*;[4] (—) recommendation (see text).

ment, and the Arrhenius plot is obviously curved. The absolute rate constants of Dixon-Lewis and Williams,[30] Margitan *et al.*,[23] Howard and Evenson,[24] Ernst *et al.*,[31] Tully and Ravishankara,[26] Madronich and Felder,[29] Smith *et al.*,[32] Bott and Cohen,[2] Vaghjiani and Ravishankara[3] and Finlayson-Pitts *et al.*[4] have been used to evaluate the rate constant for the reaction of OH radicals with methane. A unit-weighted least-squares analysis of these data,[2–4,23,24,26,29–32] using the expression $k = CT^2 e^{-D/T}$, yields the recommendation of

$$k(\text{methane}) = (7.44^{+0.41}_{-0.39}) \times 10^{-18}\ T^2\ e^{-(1361 \pm 21)/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 223–1512 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{methane}) = 6.86 \times 10^{-15}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \text{ at } 298\ \text{K},$$

with an estimated overall uncertainty at 298 K of ±20%. At temperatures ≤400 K, this recommendation is significantly different to that of

$$k(\text{methane}) = 6.95 \times 10^{-18}\ T^2\ e^{-1282/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

recommended by Atkinson[1] over the temperature range 240–1512 K, with the presently recommended 298 K rate constant being 18% lower than the previous recommendation.[1]

For the reaction of the OH radical with methane-^{13}C, Cantrell *et al.*[17] have determined a rate constant ratio of

$$k(\text{methane-}^{12}\text{C})/k(\text{methane-}^{13}\text{C}) = 1.0054 \pm 0.0009,$$

independent of temperature over the range 273–353 K. This rate constant ratio, which supersedes the earlier study of Davidson *et al.*,[36] is recommended, and agrees well with the rate constant ratio of k(methane-^{12}C)/k(methane-^{13}C) = 1.007 obtained from the *ab initio* calculations of Lasaga and Gibbs.[37]

Ethane. The absolute rate constants determined by Lafage *et al.*[5] (inadvertently omitted from the Atkinson[1] review), Abbatt *et al.*,[6] Schiffman *et al.*,[7] Dóbé *et al.*[8,9] and Bott and Cohen[10] are given in Table 36. The rate constants of Abbatt *et al.*[6] at 297 ± 2 K and Schiffman *et al.*[7] at an unspecified room temperature are ~9% lower than the recommendation of Atkinson,[1] while the rate constants of Lafage *et al.*,[5] Dóbé *et al.*[8,9] and Bott and Cohen[10] are in reasonable[5] or good[8–10] agreement with the Atkinson[1] recommendation (the rate constant of Lafage *et al.*[5] at 413 K being 40% higher than the recommended value[1]).

The rate constant data of Greiner,[18] Howard and Evenson,[38] Leu,[39] Margitan and Watson,[40] Tully *et al.*,[41,42] Jeong *et al.*,[21] Smith *et al.*,[43] Devolder *et al.*,[44] Baulch *et al.*,[45] Stachnik *et al.*,[46] Bourmada *et al.*,[47] Wallington *et al.*,[48] Zabarnick *et al.*[49] and Abbatt *et al.*[6] are plotted in Arrhenius form in Fig. 3. Analogous to the situation for the OH radical reaction with methane (see above), the rate constants of Greiner,[18] Overend *et al.*[22] and Jeong *et al.*[21] were not used in the evaluation of the rate constant for this reaction since the C_2H_6/OH radical concentration ratios were quite low, leading to the possibility of secondary reactions and erroneously high measured rate constants (in this regard see also the comment by Atkinson[1] for the OH radical reaction with ethane).

Accordingly, the rate constant data of Howard and Evenson,[38] Leu,[39] Margitan and Watson,[40] Tully *et al.*,[41,42] Smith *et al.*,[43] Devolder *et al.*,[44] Baulch *et al.*,[45] Stachnik *et al.*,[46] Bourmada *et al.*,[47] Wallington *et al.*,[48] Zabarnick *et al.*[49] and Abbatt *et al.*[6] have been used to evaluate the rate constant for the reaction of the OH radical with ethane. A unit-weighted least-squares analysis of these data,[6,38–49] using the expression $k = CT^2 e^{-D/T}$, yields the recommendation of

$$k(\text{ethane}) = (1.51^{+0.16}_{-0.15}) \times 10^{-17}\ T^2\ e^{-(492 \pm 31)/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 226–800 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{ethane}) = 2.57 \times 10^{-13}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \text{ at } 298\ \text{K},$$

with an estimated overall uncertainty at 298 K of ±20%.

The room temperature rate constants of Schiffman *et al.*[7] (the actual temperature not being specified) and Dóbé *et al.*[8,9] are in good agreement with this recommendation. Moreover, the rate constant at 1225 K of 1.52 × 10^{-11} cm^3 molecule^{-1} s^{-1} calculated from the present recommendation is in excellent agreement with that of (1.54 ± 0.24) × 10^{-11} cm^3 molecule^{-1} s^{-1} determined by Bott and Cohen[10] at 1225 K from an apparently limited study, indicating that the recommendation is applicable up to 1225 K.

This recommendation is slightly different from that recommended previously by Atkinson[1] of

$$k(\text{ethane}) = 1.42 \times 10^{-17}\ T^2\ e^{-462/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the same temperature range, with a 298 K rate constant of 2.68 × 10^{-13} cm^3 molecule^{-1} s^{-1}.

Propane. The absolute rate constants of Abbatt *et al.*,[6] Mac Leod *et al.*,[11] Schiffman *et al.*[7] and Dóbé *et al.*[8] and the relative rate constant of Nielsen *et al.*,[12] all obtained at room temperature, are given in Table 36, and are in agreement with each other and also agree with the recommendation of Atkinson.[1] The N_2H_4–O_3 reaction was used as a source of OH radicals in the relative rate study of Nielsen *et al.*,[12] and the good agreement of the rate constant for propane with the literature data[1] was used to validate the technique for the determination of

TABLE 36. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with alkanes

Alkane	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	n	B (K)	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
Methane				4.3 ± 0.9	1234 ± 15	SH-RA	Bott and Cohen[2]	
				0.00086 ± 0.00002	223	FP/LP-LIF	Vaghjiani and Ravishankara[3]	223–420
				0.00103 ± 0.00002	223			
				0.00088 ± 0.00004	223			
				0.00089 ± 0.00004	223			
				0.00086 ± 0.00004	223			
				0.00089 ± 0.00003	223			
				0.00086 ± 0.00002	223			
				0.00097 ± 0.00003	223			
				0.00104 ± 0.00002	223			
				0.00102 ± 0.00002	223			
				0.00093 ± 0.00003	223			
				0.00121 ± 0.00002	233			
				0.00119 ± 0.00001	233			
				0.00118 ± 0.00003	233			
				0.00118 ± 0.00002	233			
				0.00125 ± 0.00003	233			
				0.00133 ± 0.00002	233			
				0.00125 ± 0.00002	233			
				0.00198 ± 0.00003	250			
				0.00204 ± 0.00005	250			
				0.00182 ± 0.00002	250			
				0.00364 ± 0.00005	273			
				0.00367 ± 0.00004	273			
				0.00375 ± 0.00005	273			
				0.00371 ± 0.00016	273			
				0.00338 ± 0.00007	273			
				0.00352 ± 0.00007	273			
				0.00350 ± 0.00005	273			
				0.00592 ± 0.00018	295			
				0.00636 ± 0.00022	297			
				0.00647 ± 0.00006	297			
				0.00620 ± 0.00018	298			
				0.00630 ± 0.00007	298			
				0.00712 ± 0.00038	303			
				0.00715 ± 0.00011	303			
				0.00674 ± 0.00008	303			
				0.00674 ± 0.00013	303			
				0.00713 ± 0.00018	303			
				0.00684 ± 0.00025	303			
				0.01026 ± 0.00015	325			
				0.01598 ± 0.00011	350			
				0.02617 ± 0.00042	380			

TABLE 36. Rate constants *k* and temperature-dependent parameters for the gas-phase reactions of the OH radical with alkanes — Continued

Alkane	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	n	*B* (K)	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1})	at *T* (K)	Technique	Reference	Temperature range covered (K)
				0.04304 ± 0.00047	420			
				0.04184 ± 0.00061	420			
				0.04366 ± 0.00056	420			
				0.04336 ± 0.00063	420			
				0.04244 ± 0.00057	420			
				0.04253 ± 0.00052	420			
	1.59×10^{-8}	2.84	978	0.04287 ± 0.00052	420			
	2.94 ± 0.34		1815 ± 30					
				0.00409 ± 0.00026	278	DF-RF	Finlayson-Pitts *et al.*[4]	278–378
				0.00560 ± 0.00063	298			
				0.00575 ± 0.00098	298			
				0.0106 ± 0.0017	313			
				0.00792 ± 0.00007	313			
				0.0105 ± 0.0028	333			
				0.0109 ± 0.0006	333			
				0.0150 ± 0.0025	348			
				0.0143 ± 0.0036	348			
				0.0205 ± 0.0019	363			
	$4.0^{+1.6}_{-1.3}$		1944 ± 114	0.0236 ± 0.0008	378			
Ethane				0.287	294	DF-RF	Lafage *et al.*[5]	294–413
				1.12	413			
				0.253	294	DF-LIF	Lafage *et al.*[5]	
				0.238 ± 0.016	297 ± 2	DF-LIF	Abbatt *et al.*[6]	
				0.243 ± 0.012	a	LP-LIR	Schiffman *et al.*[7]	
				0.274 ± 0.040	298	LP-RF	Dóbé *et al.*[8,9]	
				15.4 ± 2.4	1225	SH-RA	Bott and Cohen[10]	
Propane				1.21 ± 0.10	297 ± 2	DF-LIF	Abbatt *et al.*[6]	
				1.22 ± 0.08	298	LP-LIF	Mac Leod *et al.*[11]	
				1.02 ± 0.05	a	LP-LIR	Schiffman *et al.*[7]	
				1.40 ± 0.30	298	LP-RF	Dóbé *et al.*[8]	
				1.10 ± 0.05	298 ± 2	RR [relative to *k*(2-methylpropane) = 2.33×10^{-12}][b]	Nielsen *et al.*[12]	

TABLE 36. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with alkanes – Continued

Alkane	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	n	B (K)	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
n-Butane				2.25 ± 0.10	297 ± 2	DF-LIF	Abbatt *et al.*[6]	
				2.32 ± 0.08	a	LP-LIR	Schiffman *et al.*[7]	
2-Methylpropane				20.9 ± 4.2	1146 ± 15	SH-RA	Bott and Cohen[2]	
				2.11 ± 0.09	a	LP-LIR	Schiffman *et al.*[7]	
n-Pentane				4.21 ± 0.18	297 ± 2	DF-LIF	Abbatt *et al.*[6]	
2,2-Dimethylpropane				0.79 ± 0.10	298 ± 2	PR-RA	Nielsen *et al.*[13]	
				0.84 ± 0.10	298 ± 2	RR [relative to k(n-butane) = 2.54×10^{-12}]^b	Nielsen *et al.*[13]	
2,3-Dimethylbutane				34.5 ± 5.2	1220 ± 16	SH-RA	Bott and Cohen[14]	
2,2,4-Trimethylpentane				37.2 ± 5.6	1186 ± 16	SH-RA	Bott and Cohen[14]	
2,2,3,3-Tetramethylbutane				29.9 ± 4.5	1180 ± 16	SH-RA	Bott and Cohen[14]	
3,3-Diethylpentane [$(C_2H_5)_4C$]				5.1 ± 0.8	298 ± 2	PR-RA	Nielsen *et al.*[13]	
				4.79 ± 0.30	298 ± 2	RR [relative to k(cyclohexane) = 7.49×10^{-12}]^b	Nielsen *et al.*[13]	
Cyclopropane	3.9 ± 0.6		1107 ± 51	0.110 ± 0.014	298	LP-RF	Dóbé *et al.*[8]	298–492
				0.111 ± 0.024	298 ± 3	LP-RF	Dóbé *et al.*[9]	298–492
				0.133 ± 0.008	325 ± 1			
				0.152 ± 0.022	337 ± 1			
				0.191 ± 0.042	362 ± 1			
				0.236 ± 0.016	388 ± 1			
				0.365 ± 0.058	467 ± 2			
				0.412 ± 0.034	476 ± 3			
	1.17×10^{-4}	1.5	522 ± 44	0.462 ± 0.062	492 ± 3			

TABLE 36. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with alkanes – Continued

Alkane	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	n	B (K)	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
Cyclobutane				1.75 ± 0.15	298	LP-RF	Dóbé *et al.*[8]	
				1.75 ± 0.12	298 ± 3	LP-RF	Dóbé *et al.*[9]	298–469
				2.22 ± 0.20	327 ± 1			
				2.36 ± 0.14	360 ± 2			
				2.89 ± 0.30	392 ± 2			
				3.49 ± 0.28	429 ± 2			
	5.06×10^{-4}	1.5	115 ± 40	3.98 ± 0.40	469 ± 3			
Cyclopentane				46.5 ± 9.3	1194 ± 15	SH-RA	Bott and Cohen[2]	
Cyclohexane				7.07 ± 0.35	298[c]	RR [relative to k(ethene) = 8.52×10^{-12}][b]	Japar *et al.*[15]	
				7.20 ± 0.43	296 ± 2	RR [relative to k(n-butane) = 2.51×10^{-12}][b]	Atkinson and Aschmann[16]	
trans-Pinane [(1R,2R)-2,6,6-Trimethylbicyclo[3.1.1]heptane]				13.4 ± 1.1	296 ± 2	RR [relative to k(n-butane) = 2.51×10^{-12}][b]	Atkinson and Aschmann[16]	
Tricyclene [1,7,7-Trimethyltricyclo-[2.2.1.0^{2,6}]heptane]				2.86 ± 0.23	296 ± 2	RR [relative to k(n-butane) = 2.51×10^{-12}][b]	Atkinson and Aschmann[16]	
Quadricyclane [Quadricyclo[2.2.1.0.^{2,6}0^{3,5}]-heptane]				1.83 ± 0.17	296 ± 2	RR [relative to k(n-butane) = 2.51×10^{-12}][b]	Atkinson and Aschmann[16]	

[a] Room temperature, not specified.
[b] From present and previous[1] recommendations.
[c] Room temperature, not specified; 298 K assumed.

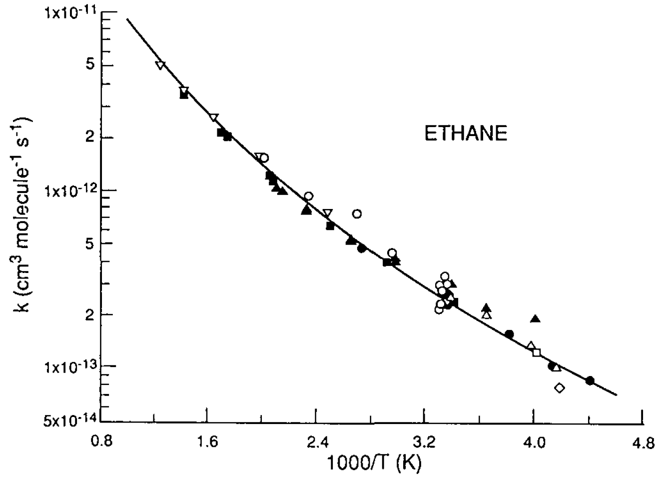

FIG. 3. Arrhenius plot of selected rate constants for the reaction of the OH radical with ethane. (○) Greiner;[18] (+) Howard and Evenson;[38] (▼) Leu;[39] (◇) Margitan and Watson;[40] (▽) Tully *et al.*;[41] (▲) Jeong *et al.*;[21] (△) Smith *et al.*;[43] (◆) Devolder *et al.*,[44] Baulch *et al.*,[45] Bourmada *et al.*,[47] Zabarnick *et al.*;[49] (■) Tully *et al.*;[42] (□) Stachnik *et al.*;[46] (●) Wallington *et al.*;[48] (X) Abbatt *et al.*;[6] (—) recommendation (see text).

rate constants for the reactions of the OH radical with a series of alkyl nitrites.[12] Based upon the discussion of Atkinson,[1] the absolute rate constants measured by Greiner,[18] Bott and Cohen,[50] Smith *et al.*,[32] Baulch *et al.*,[45] Droege and Tully,[51] Abbatt *et al.*[6] and Mac Leod *et al.*[11] and the relative rate constants of Baker *et al.*[52,53] and Atkinson *et al.*[54] are plotted in Arrhenius form in Fig. 4. These rate constant data[6,11,18,32,45,50,51,53,54] have been used to evaluate the rate constant for the reaction of the OH radical with propane. Using the expression $k = CT^2e^{-D/T}$, a unit-weighted least squares analysis of these data yields

$$k(\text{propane}) = (1.48^{+0.17}_{-0.14}) \times 10^{-17}\ T^2\ e^{-(39 \pm 39)/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 293–1220 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{propane}) = 1.15 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

with an estimated overall uncertainty at 298 K of ±20%. The room temperature (which was not specified) rate constant of Schiffman *et al.*[7] is in good agreement with this expression, as is the relative rate constant of Nielsen *et al.*[12]

This rate expression is virtually identical (to within 1% over the temperature range ~210–1500 K) to the previous recommendation[1] of

$$k(\text{propane}) = 1.50 \times 10^{-17}\ T^2\ e^{-44/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the same temperature range, and yields an identical 298 K rate constant. It is hence recommended that the previously recommended rate constant expression of

$$k(\text{propane}) = 1.50 \times 10^{-17}\ T^2\ e^{-44/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 293–1220 K continue to be used, with

$$k(\text{propane}) = 1.15 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K}.$$

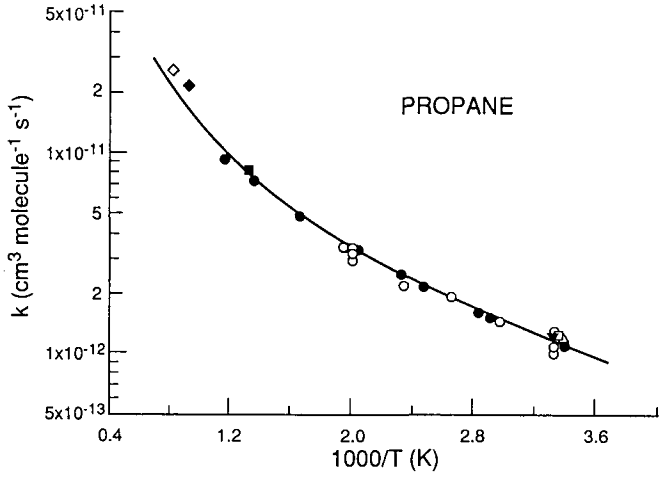

FIG. 4. Arrhenius plot of selected rate constants for the reaction of the OH radical with propane. (■) Baker *et al.*;[53] (○) Greiner;[18] (▼) Atkinson *et al.*;[54] (◇) Bott and Cohen;[50] (◆) Smith *et al.*;[32] (△) Baulch *et al.*;[45] (●) Droege and Tully;[51] (□) Abbatt *et al.*,[6] Mac Leod *et al.*;[11] (—) recommendation (see text).

However, the most recent absolute rate constant determinations of Abbatt *et al.*,[6] Mac Leod *et al.*[11] and Schiffman *et al.*[7] lead to a significantly increased confidence in the recommended rate expression, and the estimated overall uncertainty in the 298 K rate constant has been reduced to ±20%.

n-Butane. Absolute rate constants have been determined at room temperature by Abbatt *et al.*[6] and Schiffman *et al.*,[7] and these rate constants are given in Table 36. The rate constant of Schiffman *et al.*[7] cannot be used in the evaluation of this rate constant, since the temperature was not specified. Based on the discussion of Atkinson[1] for this reaction, the absolute rate constants of Greiner,[18] Stuhl,[55] Perry *et al.*,[56] Paraskevopoulos and Nip,[57] Droege and Tully[58] and Abbatt *et al.*[6] and the relative rate constant of Baker *et al.*[52,53] are plotted in Arrhenius form in Fig. 5 and are used to evaluate the rate constant for the reaction of the OH radical with *n*-butane. A unit-weighted least-squares analysis of these data,[18,53,55–58] using the expression $k = CT^2e^{-D/T}$, yields

$$k(n\text{-butane}) = (1.55^{+0.31}_{-0.26}) \times 10^{-17}\ T^2\ e^{(180 \pm 64)/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 294–753 K, where the indicated errors are two least-squares standard deviations, and

$$k(n\text{-butane}) = 2.52 \times 10^{-12}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ \text{at 298 K},$$

with an estimated overall uncertainty at 298 K of ±20%. The rate constant of Schiffman *et al.*[7] at an unspecified room temperature is in good agreement with this rate expression.

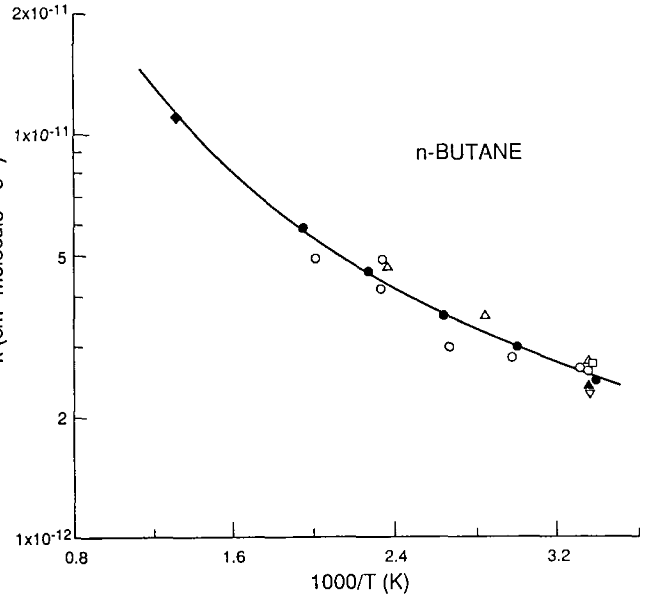

FIG. 5. Arrhenius plot of selected rate constants for the reaction of the OH radical with *n*-butane. (◆) Baker *et al.*;[53] (○) Greiner;[18] (▲) Stuhl;[55] (△) Perry *et al.*;[56] (□) Paraskevopoulos and Nip;[57] (●) Droege and Tully;[58] (▽) Abbatt *et al.*;[6] (—) recommendation (see text).

This rate expression is virtually identical (to within 1% over the temperature range ~280–620 K) to the previous recommendation[1] of

$$k(n\text{-butane}) = 1.51 \times 10^{-17}\ T^2\ e^{190/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the same temperature range, with a 298 K rate constant of 2.54 × 10^{-12} cm^3 molecule^{-1} s^{-1}. It is hence recommended that the previous recommendation[1] of

$$k(n\text{-butane}) = 1.51 \times 10^{-17}\ T^2\ e^{190/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the temperature range 294–753 K continue to be used, with

$$k(n\text{-butane}) = 2.54 \times 10^{-12}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ \text{at 298 K},$$

and with an estimated overall uncertainty in the 298 K rate constant of ±20%.

2-Methylpropane. The absolute rate constants obtained by Bott and Cohen[2] at 1146 ± 15 K and by Schiffman *et al.*[7] at room temperature (the actual temperature being unspecified) are given in Table 36. Based on the discussion of Atkinson[1] for this reaction, the absolute rate constants of Greiner,[18] Tully *et al.*[59] and Bott and Cohen[2] and the relative rate constants of Baker *et al.*[52,53] and Atkinson *et al.*[60] are plotted in Arrhenius form in Fig. 6. The rate constant of Bott and Cohen[2] significantly extends the temperature range over which reliable data are available, and a unit-weighted least-squares analysis of these rate constant data,[2,18,53,59,60] using the expression $k = CT^2e^{-D/T}$, leads to the recommendation of

$$k(\text{2-methylpropane}) = (1.11^{+0.14}_{-0.13}) \times 10^{-17}\ T^2\ e^{(256 \pm 47)/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the temperature range 293–1146 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{2-methylpropane}) = 2.33 \times 10^{-12}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ \text{at 298 K},$$

with an estimated overall uncertainty at 298 K of ±25%. The room temperature rate constant of Schiffman *et al.*[7] is in good agreement with this recommendation. This recommended expression is slightly different to the previous recommendation of Atkinson[1] of

$$k(\text{2-methylpropane}) = 1.04 \times 10^{-17}\ T^2\ e^{277/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the temperature range 293–864 K, although the 298 K rate constant is essentially identical to the previously recommended value[1] of 2.34 × 10^{-12} cm^3 molecule^{-1} s^{-1}. Because of the wider temperature range covered and the slight differences at combustion temperatures, the present recommendation is preferred.

n-Pentane. The absolute room temperature rate constant measured by Abbatt *et al.*[6] is given in Table 36. This is the first absolute rate constant reported for *n*-pentane, and is plotted together with the relative rate constants of Baldwin and Walker,[53] Atkinson *et al.*,[54] Behnke *et al.*,[61,62] Nolting *et al.*[63] and Harris and Kerr[64] in Arrhenius form in Fig. 7 (the rate constants of Harris and Kerr[64] relative to 2-methylpropane have not been reevaluated[1] since the change is ≤2% at all of the temperatures studied).

The room temperature rate constants[6,54,61–64] are in reasonable agreement, and a unit-weighted least-squares analysis of the rate constant data of Baldwin and Walker,[53] Atkinson *et al.*,[54] Behnke *et al.*,[61,62] Nolting *et al.*,[63] Harris and Kerr[64] and Abbatt *et al.*,[6] using the expression $k = CT^2e^{-D/T}$, leads to

$$k(n\text{-pentane}) = (2.11^{+0.39}_{-0.33}) \times 10^{-17}\ T^2\ e^{(223 \pm 49)/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

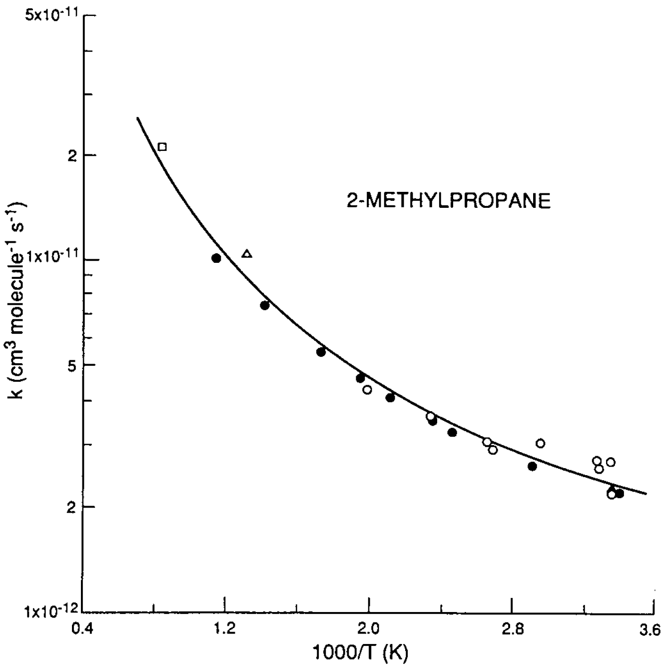

FIG. 6. Arrhenius plot of selected rate constants for the reaction of the OH radical with 2-methylpropane. (△) Baker *et al.*;[53] (○) Greiner;[18] (▲) Atkinson *et al.*;[60] (●) Tully *et al.*;[59] (□) Bott and Cohen;[2] (—) recommendation (see text).

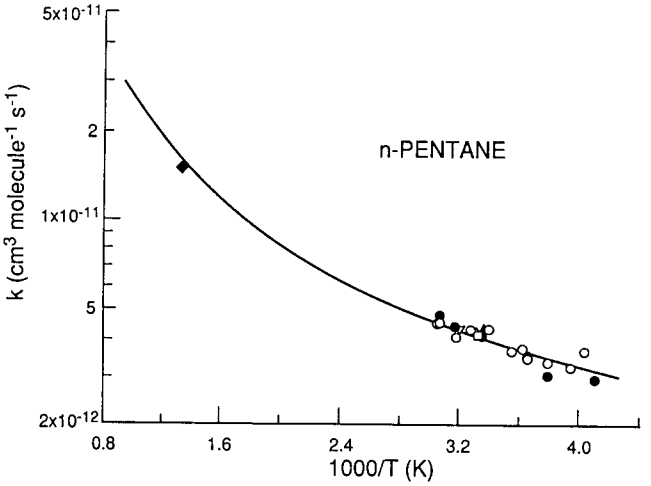

FIG. 7. Arrhenius plot of selected rate constants for the reaction of the OH radical with *n*-pentane. (◆) Baldwin and Walker;[53] (□) Atkinson *et al.*;[54] (△) Behnke *et al.*;[61,62] (▽) Nolting *et al.*;[63] (○) Harris and Kerr[64] (relative to *n*-butane); (●) Harris and Kerr[64] (relative to 2-methylpropane); (▲) Abbatt *et al.*[6]; (—) recommendation (see text).

over the temperature range 243–753 K, where the indicated errors are two least-squares standard deviations, and

$$k(n\text{-pentane}) = 3.96 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K}.$$

This expression is virtually identical (to within <1%, independent of temperature) to the previous recommendation of Atkinson[1] over the same temperature range. Thus it is recommended that the previous recommendation of Atkinson[1] continue to be used, with

$$k(n\text{-pentane}) = 2.10 \times 10^{-17}\ T^2\ e^{223/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 243–753 K, and

$$k(n\text{-pentane}) = 3.94 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

with an estimated overall uncertainty at 298 K of ±25%.

2,2-Dimethylpropane. The absolute and relative rate constants determined by Nielsen *et al.*[13] at 298 ± 2 K are given in Table 36. These rate constants are in good agreement with the previous recommendation of Atkinson[1] of

$$k(2,2\text{-dimethylpropane}) = 8.49 \times 10^{-13}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

and hence the previous recommendation[1] of

$$k(2,2\text{-dimethylpropane}) = 1.79 \times 10^{-17}\ T^2\ e^{-187/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 287–901 K is unchanged.

2,3-Dimethylbutane. The absolute rate constant measured by Bott and Cohen[14] at 1220 ± 16 K is given in Table 36, and is plotted together with the rate constants of Greiner,[18] Atkinson *et al.*[65] and Harris and Kerr[64] in Arrhenius form in Fig. 8. The rate constant measurement of Bott and Cohen[14] significantly extends the temperature range over which reliable data are available. A unit-weighted least-squares analysis of the rate constants of Greiner,[18] Atkinson *et al.*,[65] Harris and Kerr[64] and Bott and Cohen,[14] using the expression $k = CT^2e^{-D/T}$, leads to the recommendation of

$$k(2,3\text{-dimethylbutane}) = (1.21^{+0.39}_{-0.30}) \times 10^{-17}\ T^2\ e^{(512 \pm 87)/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 247–1220 K, where the indicated errors are two least-squares standard deviations, and

$$k(2,3\text{-dimethylbutane}) = 5.99 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

with an estimated overall uncertainty at 298 K of ±25%.

This recommendation supersedes the previous recommendation of Atkinson[1] of

$$k(2,3\text{-dimethylbutane}) = 6.2 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1},$$

independent of temperature over the more restricted range of 247–498 K.

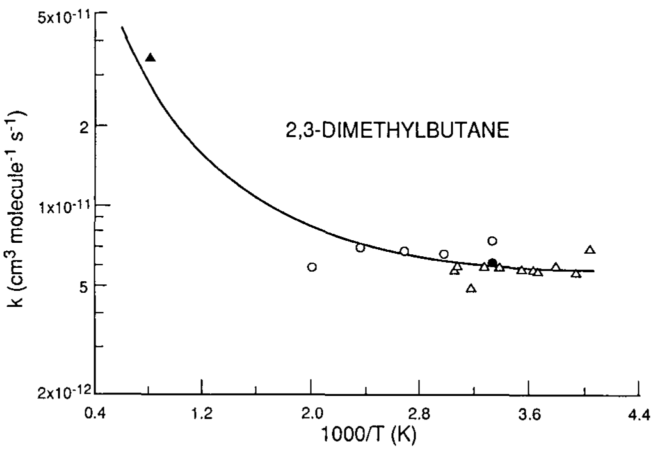

FIG. 8. Arrhenius plot of selected rate constants for the reaction of the OH radical with 2,3-dimethylbutane. (○) Greiner;[18] (●) Atkinson *et al.*;[65] (△) Harris and Kerr;[64] (▲) Bott and Cohen;[14] (—) recommendation (see text).

2,2,4-Trimethylpentane. The absolute rate constant determined by Bott and Cohen[14] at 1186 ± 16 K is given in Table 36 and is plotted together with the rate constants of Greiner[18] and Atkinson *et al.*[60] in Arrhenius form in Fig. 9. The rate constant measurement of Bott and Cohen[14] greatly extends the temperature range over which data are available. A unit-weighted least-squares analysis of the absolute rate constants of Greiner[18] and Bott and Cohen[14] and the relative rate constant of Atkinson *et al.*,[60] using the expression $k = CT^2 e^{-D/T}$, leads to the recommendation of

$$k(\text{2,2,4-trimethylpentane}) = (2.06^{+0.47}_{-0.39}) \times 10^{-17}\, T^2\, e^{(201 \pm 76)/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 297–1186 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{2,2,4-trimethylpentane}) = 3.59 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \text{ at 298 K},$$

with an estimated overall uncertainty at 298 K of ±20%.

This recommendation supersedes the previous recommendation of Atkinson[1] of

$$k(\text{2,2,4-trimethylpentane}) = 1.61 \times 10^{-11}\, e^{-440/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the more restricted temperature range of 297–493 K, with a 298 K rate constant of 3.68 × 10^{-12} cm^3 molecule^{-1} s^{-1}.

2,2,3,3-Tetramethylbutane. The absolute rate constant measured by Bott and Cohen[14] at 1180 ± 16 K is given in Table 36, and is plotted together with the absolute rate constants of Greiner[18] and Tully *et al.*[66] and the relative rate constants of Baldwin *et al.*[53,67] and Atkinson *et al.*[60] in Arrhenius form in Fig. 10. The agreement between these studies is seen to be reasonably good. A unit-weighted least-squares analysis of these rate constants of Greiner,[18] Baldwin *et al.*,[53,67] Atkinson *et al.*,[60] Tully *et al.*[66] and Bott and Cohen,[14] using the expression $k = CT^2 e^{-D/T}$, leads to the recommendation of

$$k(\text{2,2,3,3-tetramethylbutane}) = (1.90^{+0.42}_{-0.35}) \times 10^{-17}\, T^2\, e^{-(139 \pm 79)/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 290–1180 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{2,2,3,3-tetramethylbutane}) = 1.06 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \text{ at 298 K},$$

with an estimated overall uncertainty at 298 K of ±20%.

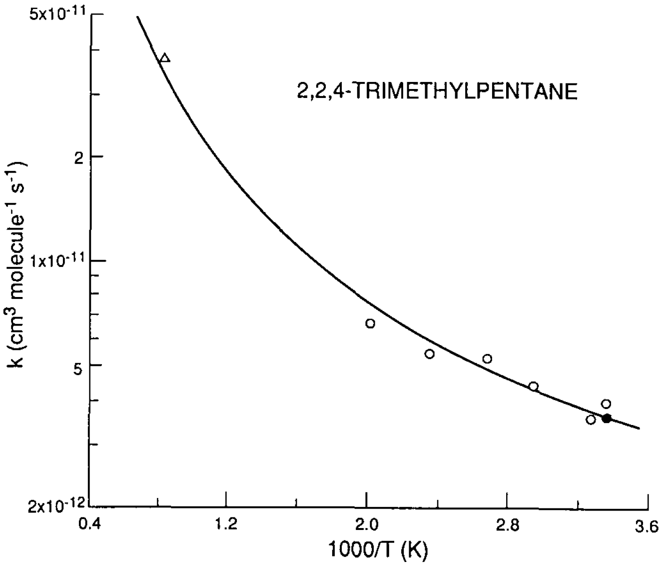

FIG. 9. Arrhenius plot of selected rate constants for the reaction of the OH radical with 2,2,4-trimethylpentane. (○) Greiner;[18] (●) Atkinson *et al.*;[60] (△) Bott and Cohen;[14] (—) recommendation (see text).

This recommendation is similar (to within 9% over the temperature range 290–753 K) to the previous recommendation of Atkinson[1] of

$$k(\text{2,2,3,3-tetramethylbutane}) = 1.63 \times 10^{-17}\, T^2\, e^{-86/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 290–753 K, with a 298 K rate constant of 1.08 × 10^{-12} cm^3 molecule^{-1} s^{-1}. However, the expanded temperature range over which the present recommendation is applicable makes its use preferable, especially for combustion modeling purposes.

Cyclopropane. The absolute rate constants determined by Dóbé *et al.*[8,9] over the temperature range 298–492 K are given in Table 36. The 298 K rate constant of Dóbé *et al.*[8,9] is a factor of ~1.4–1.8 higher than those reported

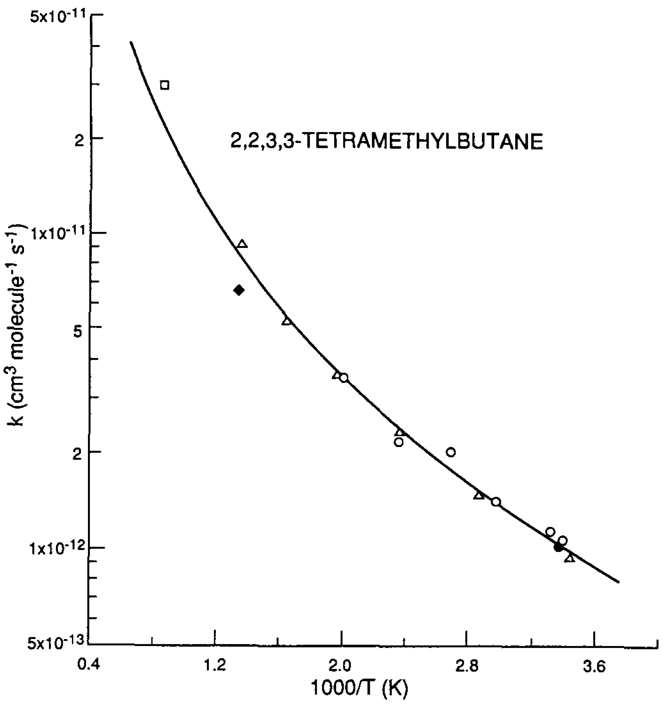

FIG. 10. Arrhenius plot of selected rate constants for the reaction of the OH radical with 2,2,3,3-tetramethylbutane. (○) Greiner;[18] (◆) Baldwin *et al.*;[53,67] (●) Atkinson *et al.*;[60] (△) Tully *et al.*;[66] (□) Bott and Cohen;[14] (—) recommendation (see text).

by Zetzsch[68] and Jolly *et al.*[69] A unit-weighted average of the room temperature rate constants of Zetzsch,[68] Jolly *et al.*[69] and Dóbé *et al.*[9] leads to the recommendation of

$$k(\text{cyclopropane}) = 8.4 \times 10^{-14}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at } 298\ \text{K},$$

with an estimated overall uncertainty of a factor of 1.5. Because of the discrepancies in the room temperature rate constants,[8,9,68,69] no recommendation is made concerning the temperature dependence.

Cyclobutane. The absolute rate constants determined by Dóbé *et al.*[8,9] over the temperature range 298–469 K are given in Table 36. These are the first absolute rate constants reported for cyclobutane, and the 298 K rate constant of Dóbé *et al.*[8,9] is a factor of ~1.5 higher than the relative rate constant of Gorse and Volman.[70] A unit-weighted average of the room temperature rate constants of Gorse and Volman[70] and Dóbé *et al.*[9] leads to the recommendation of

$$k(\text{cyclobutane}) = 1.5 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at } 298\ \text{K},$$

with an estimated overall uncertainty of a factor of 1.5. No recommendation is made for the temperature dependence of this reaction.

Cyclopentane. The absolute rate constant determined by Bott and Cohen[2] at 1194 ± 15 K is given in Table 36, and is plotted together with the rate constants of Atkinson *et al.*,[65] Jolly *et al.*[69] and Droege and Tully[71] in Arrhenius form in Fig. 11. The rate constant measurement of Bott and Cohen[2] significantly expands the temperature range over which reliable data are available. A unit-weighted least-squares analysis of the absolute rate constants of Jolly *et al.*,[69] Droege and Tully[71] and Bott and Cohen[2] and the relative rate constant of Atkinson *et al.*,[65] using the expression $k = CT^2e^{-D/T}$, leads to the recommendation of

$$k(\text{cyclopentane}) = (2.55^{+0.27}_{-0.24}) \times 10^{-17}\ T^2\ e^{(241 \pm 36)/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 295–1194 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{cyclopentane}) = 5.08 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at } 298\ \text{K}$$

with an estimated overall uncertainty at 298 K of ±20%. This recommendation is similar to that of Atkinson[1] of

$$k(\text{cyclopentane}) = 2.13 \times 10^{-17}\ T^2\ e^{299/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 295–491 K, with a 298 K rate constant of 5.16×10^{-12} cm^3 molecule^{-1} s^{-1}. However, the significantly expanded temperature range over which the present recommendation is applicable makes its use preferable, especially for combustion modeling purposes.

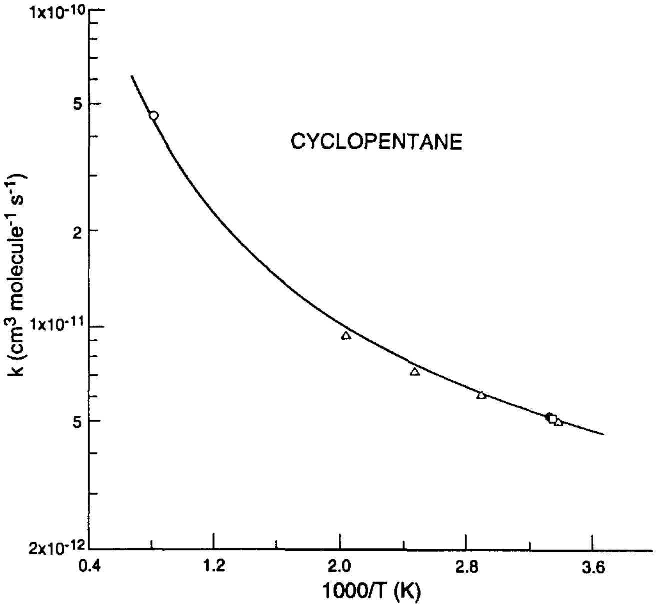

FIG. 11. Arrhenius plot of selected rate constants for the reaction of the OH radical with cyclopentane. (●) Atkinson *et al.*;[65] (□) Jolly *et al.*;[69] (△) Droege and Tully;[71] (○) Bott and Cohen;[2] (—) recommendation (see text).

Cyclohexane. The room temperature rate constants of Japar *et al.*[15] (the actual temperature being unspecified) and Atkinson and Aschmann[16] are given in Table 36. These rate constants are in good agreement with the previous recommendation[1] of

$$k(\text{cyclohexane}) = 7.49 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

and no revision of the previous recommendation[1] is necessary.

Other Alkanes. The rate constants of Nielsen *et al.*[13] for 3,3-diethylpentane and Atkinson and Aschmann[16] for *trans*-pinane, tricyclene and quadricyclane are the first reported for these alkanes, and hence no recommendations are made. For other alkanes for which data have been previously determined,[1] no new data are available, and hence the previous recommendations[1] are applicable. It is of interest to note that the present recommendations for 2,3-dimethylbutane and 2,2,4-trimethylpentane utilizing the three-parameter expression $k = CT^2e^{-D/T}$ are much more consistent with the empirical estimation method of Atkinson[72] than were the previous[1] Arrhenius expressions. This observation further indicates the usefulness of this estimation method[72] for the calculation of rate constants over extended temperature ranges (~250–1200 K) for alkanes for which either no data are available or are only available over a limited temperature range. The study of Atkinson and Aschmann[16] for strained polycycloalkanes indicates, however, that the effects of ring strain in polycyclic alkane systems was not correctly taken into account,[72] and Atkinson and Aschmann[16] propose a revised method of accounting for this ring strain in the estimation of OH radical reaction rate constants for cycloalkanes.

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3.2. Haloalkanes

The rate constants reported since the previous review of Atkinson[1] are given in Table 37. The agreement of these recent rate constant data with previous literature data[1] and any revisions of the recommended rate constants for the reactions of the OH radical with the haloalkanes are discussed below. As in previous evaluations,[1,26–28] the rate constant data of Clyne and Holt[29,30] have not been used in the evaluations of these reactions.

CH_3Cl. The rate constant determined by Brown *et al.*[2] at 298 K is given in Table 37. This rate constant of Brown *et al.*[2] is ~20% higher than the recommended 298 K rate constant of Atkinson.[1] The previous recommendation of Atkinson[1] of

$$k(\mathrm{CH_3Cl}) = 3.50 \times 10^{-18}\, T^2\, \mathrm{e}^{-585/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the temperature range 250–483 K, and

$$k(\mathrm{CH_3Cl}) = 4.36 \times 10^{-14}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

at 298 K, with an estimated overall uncertainty at 298 K of ±20%, is unchanged. It should also be noted, as discussed below, that the measured rate constants of Wayne and co-workers[2,4,12,23] for a series of haloalkanes are generally significantly higher than the rate constants determined by other research groups.

CH_2F_2. Rate constants have been determined over the temperature range 222–381 K by Talukdar *et al.*,[3] and are given in Table 37. These rate constants[3] and those of Howard and Evenson,[31] Nip *et al.*,[32] Jeong and Kaufman[33] and Bera and Hanrahan[34] are plotted in Arrhenius form in Fig. 12. The rate constants of Talukdar *et al.*[3] are in good agreement with those of Nip *et al.*[32] and Jeong and Kaufman,[33] especially over the temperature range ~240–340 K. Since the rate constant measured by Bera and Hanrahan[34] was expected[34] to have been subject to the occurrence of secondary reactions, the rate constants of Howard and Evenson,[31] Nip *et al.*,[32] Jeong and Kaufman[33] and Talukdar *et al.*[3] have been used in the evaluation of the rate constant for this reaction. A unit-weighted least-squares analysis of these data,[3,31–33] using the expression $k = CT^2\mathrm{e}^{-D/T}$, yields the recommendation of

$$k(\mathrm{CH_2F_2}) = (3.84^{+1.14}_{-0.87}) \times 10^{-18}\, T^2\, \mathrm{e}^{-(1016 \pm 78)/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the temperature range 222–492 K, where the indicated errors are two least-squares standard deviations, and

$$k(\mathrm{CH_2F_2}) = 1.13 \times 10^{-14}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ \text{at 298 K},$$

with an estimated overall uncertainty at 298 K of ±20%. This recommendation supersedes that of Atkinson[1] of

$$k(\mathrm{CH_2F_2}) = 5.06 \times 10^{-18}\, T^2\, \mathrm{e}^{-1107/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the temperature range 250–492 K, with a 298 K rate constant of 1.09×10^{-14} cm^3 molecule^{-1} s^{-1}.

CHF_2Br. The rate constants reported by Brown *et al.*[4] and Talukdar *et al.*[5] are given in Table 37 and are plotted in Arrhenius form in Fig. 13. These are the first reported measurements of the rate constants for this reaction. The rate constants of Brown *et al.*[4] are significantly higher than those of Talukdar *et al.*,[5] especially at the lowest temperatures (275 K and 298 K) studied by Brown *et al.*[4] Furthermore, at 275 K the uncertainty in the rate constant cited by Brown *et al.*[4] is high, being ±70%. Accordingly, a unit-weighted least-squares analysis of the rate constants of Talukdar *et al.*,[5] using the expression $k = CT^2\mathrm{e}^{-D/T}$, yields the recommendation of

$$k(\mathrm{CHF_2Br}) = (1.48^{+0.34}_{-0.27}) \times 10^{-18}\, T^2\, \mathrm{e}^{-(779 \pm 63)/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the temperature range 233–432 K, where the indicated errors are two least-squares standard deviations, and

$$k(\mathrm{CHF_2Br}) = 9.63 \times 10^{-15}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ \text{at 298 K},$$

with an estimated overall uncertainty at 298 K of ±40%.

CF_3Br, CF_2ClBr, CF_2Br_2, and CF_2BrCF_2Br. The upper limits to the rate constants reported by Burkholder *et al.*[6] are given in Table 37. These upper limits to the rate constants of Burkholder *et al.*[6] are consistent with the upper limits to the rate constants for CF_3Br and CF_2ClBr previously reported by Le Bras and Combourieu[35] and Clyne and Holt,[29] respectively. Based on the upper limits to the rate constants determined by Burkholder *et al.*,[6] the following recommendations are made for 298 K:

$$k(\mathrm{CF_3Br}) < 1 \times 10^{-16}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}},$$

$$k(\mathrm{CF_2ClBr}) < 1 \times 10^{-16}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}},$$

$$k(\mathrm{CF_2Br_2}) < 5 \times 10^{-16}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}},\ \text{and}$$

$$k(\mathrm{CF_2BrCF_2Br}) < 1.5 \times 10^{-16}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}.$$

CF_3I. The room temperature rate constant measured by Brown *et al.*[2] is a factor of 4 lower than that of (1.2 ± 0.2) × 10^{-13} cm^3 molecule^{-1} s^{-1} determined by Garraway and Donovan,[36] possibly due to the occurrence of secondary reactions of the OH radical with photolysis products in the study of Garraway and Donovan.[36] Since it is possible that secondary reactions were still present in the study of Brown *et al.*,[2] no recommendation for the rate constant for this reaction is made.

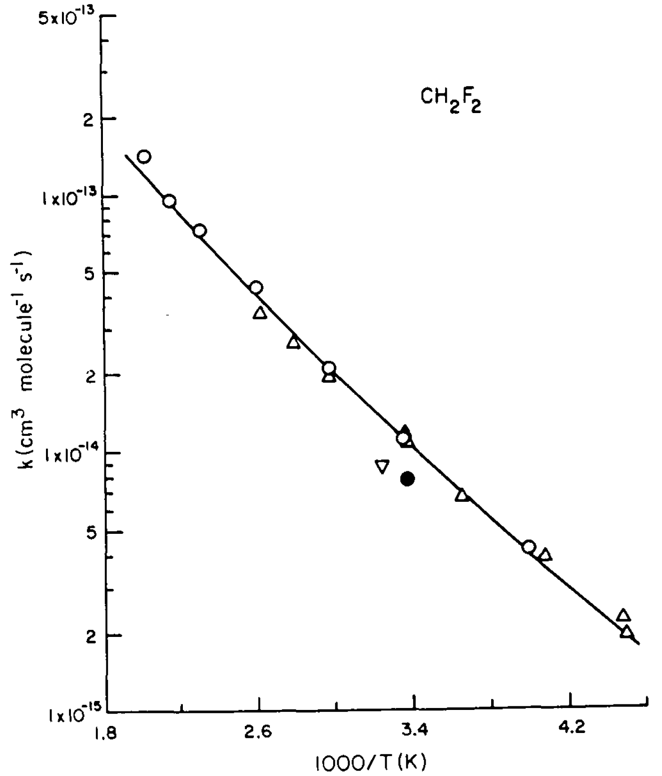

FIG. 12. Arrhenius plot of selected rate constants for the reaction of the OH radical with CH_2F_2. (●) Howard and Evenson;[31] (▲) Nip *et al.*;[32] (○) Jeong and Kaufman;[33] (▽) Bera and Hanrahan;[34] (△) Talukdar *et al.*;[3] (—) recommendation (see text).

CH_3CH_2Cl. The rate constants determined by Kasner *et al.*[7] and Markert and Nielsen[8] are given in Table 37 and are plotted together with the room temperature rate constants of Howard and Evenson[37] and Paraskevopoulos *et al.*[38] in Arrhenius form in Fig. 14. The room temperature rate constants from these four studies[7,8,37,38] are in good agreement, and a unit-weighted least-squares analysis of these data,[7,8,37,38] using the expression $k = CT^2e^{-D/T}$, yields the recommendation of

$$k(\mathrm{CH_3CH_2Cl}) = (7.71^{+0.69}_{-0.63}) \times 10^{-18}\ T^2\ \mathrm{e}^{-(152 \pm 38)/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the temperature range 294–789 K, where the indicated errors are two least-squares standard deviations, and

$$k(\mathrm{CH_3CH_2Cl}) = 4.11 \times 10^{-13}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}\ at\ 298\ K},$$

with an estimated overall uncertainty at 298 K of ±20%.

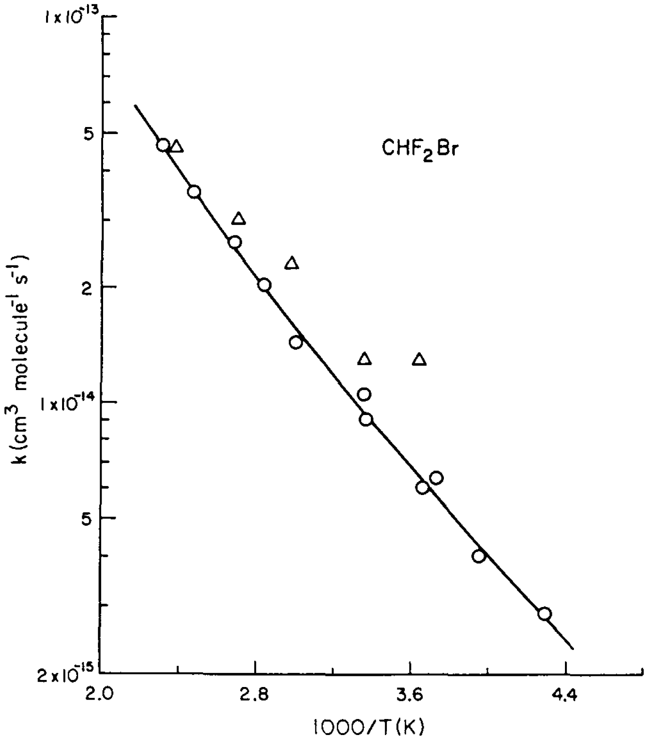

FIG. 13. Arrhenius plot of rate constants for the reactions of the OH radical with CHF_2Br. (△) Brown *et al.*;[4] (○) Talukdar *et al.*;[5] (—) recommendation (see text).

CH_3CHF_2. The absolute rate constants determined by Liu *et al.*,[11] Brown *et al.*,[12] Gierczak *et al.*[13] and Nielsen[14] as a function of temperature are given in Table 37, and are plotted together with the room temperature rate constants of Howard and Evenson,[37] Handwerk and Zellner[39] and Nip *et al.*[32] in Arrhenius form in Fig. 15. The rate constants reported by Brown *et al.*[12] at 220 K and 303 K are subject to significant uncertainties (±100% at 220 K), and the rate constant of Brown *et al.*[12] at 303 K and those of Nielsen[14] are higher than the rate constants from the remaining studies.[11,13,32,37,39] Accordingly, the rate constants of Brown *et al.*[12] and Nielsen[14] have not been used in the evaluation of the rate constant for this reaction. A unit-weighted least-squares analysis of the rate constants of Howard and Evenson,[37] Handwerk and Zellner,[39] Nip *et al.*,[32] Liu *et al.*[11] and Gierczak *et al.*,[13] using the expression $k = CT^2e^{-D/T}$, yields the recommendation of

$$k(CH_3CHF_2) = (1.98^{+0.40}_{-0.34}) \times 10^{-18}\, T^2\, e^{-(460 \pm 56)/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 212–423 K, where the indicated errors are two least-squares standard deviations, and

$$k(CH_3CHF_2) = 3.76 \times 10^{-14}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

with an estimated overall uncertainty at 298 K of ±20%.

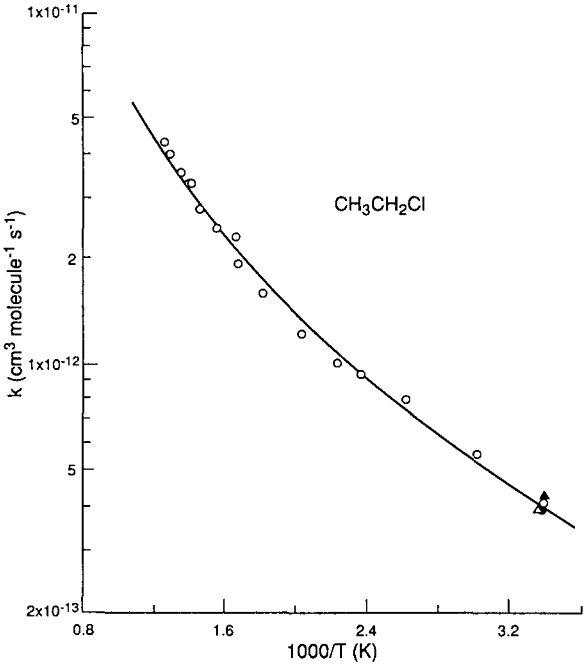

FIG. 14. Arrhenius plot of rate constants for the reaction of the OH radical with CH_3CH_2Cl. (●) Howard and Evenson;[37] (△) Paraskevopoulos *et al.*;[38] (○) Kasner *et al.*;[7] (▲) Markert and Nielsen;[8] (—) recommendation (see text).

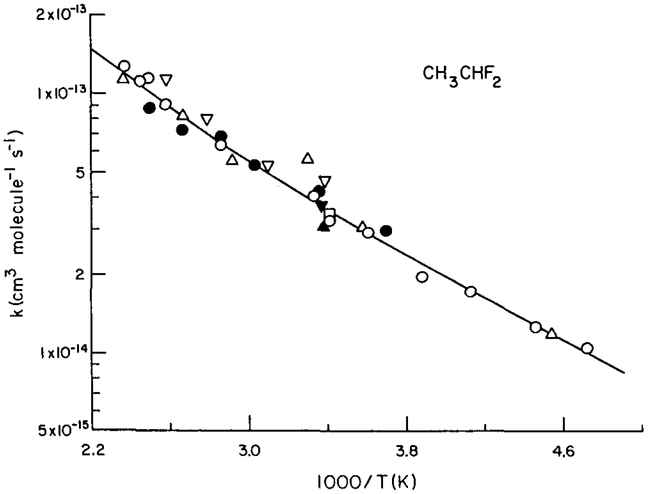

FIG. 15. Arrhenius plot of selected rate constants for the reaction of the OH radical with CH_3CHF_2. (▲) Howard and Evenson;[37] (□) Handwerk and Zellner;[39] (▼) Nip *et al.*;[32] (●) Liu *et al.*;[11] (△) Brown *et al.*;[12] (○) Gierczak *et al.*;[13] (▽) Nielsen;[14] (—) recommendation (see text).

In the previous review of Atkinson,[1] only a room temperature rate constant of

$$k(CH_3CHF_2) = 3.4 \times 10^{-14}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

at ~295 K was recommended, based on the rate constants of Howard and Evenson,[37] Handwerk and Zellner[39] and Nip *et al.*[32]

CH_2ClCH_2Cl. The room temperature relative rate constant of Arnts *et al.*[15] and the absolute rate constants determined by Taylor *et al.*[16] and Xing *et al.*[9] and Qiu *et al.*[10] are given in Table 37 and are plotted, together with the room temperature rate constant of Howard and Evenson,[37] in Arrhenius form in Fig. 16. The agreement between the room temperature rate constants is good. A unit-weighted least-squares analysis of the absolute rate constants of Howard and Evenson,[37] Taylor *et al.*[16] and Qiu *et al.*,[10] using the expression $k = CT^2e^{-D/T}$, yields the recommendation of

$$k(CH_2ClCH_2Cl) = (1.10^{+0.17}_{-0.15}) \times 10^{-17}\, T^2\, e^{-(409 \pm 55)/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 292–775 K, where the indicated errors are two least-squares standard deviations, and

$$k(CH_2ClCH_2Cl) = 2.48 \times 10^{-13}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

with an estimated overall uncertainty at 298 K of ±30%.

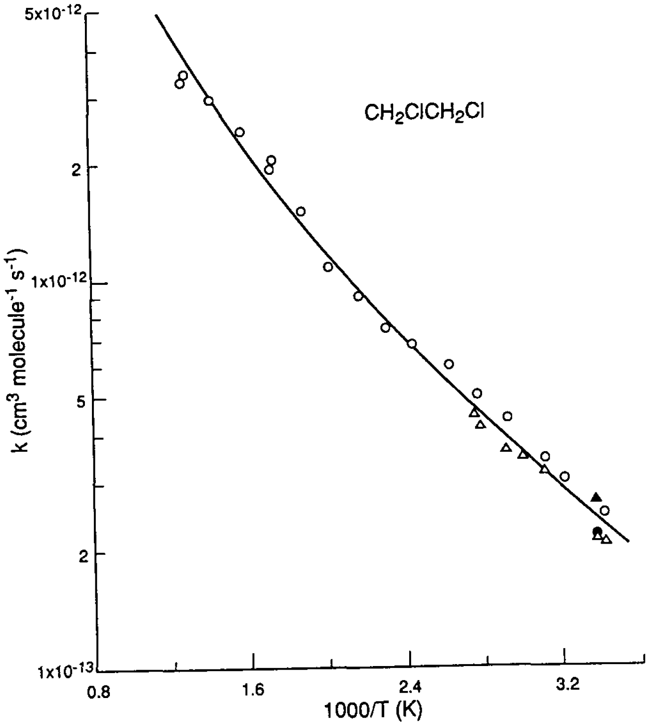

FIG. 16. Arrhenius plot of rate constants for the reaction of the OH radical with CH_2ClCH_2Cl. (●) Howard and Evenson;[37] (▲) Arnts *et al.*;[15] (○) Taylor *et al.*;[16] (△) Xing *et al.*[9] and Qiu *et al.*,[10] (—) recommendation (see text).

TABLE 37. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with haloalkanes

Haloalkane	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	n	B (K)	$10^{14} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
CH_3Cl				5.3 ± 0.8	298	DF-RF	Brown *et al.*[2]	
CH_3I				5.0 ± 2.6	271	DF-RF	Brown *et al.*[2]	271–423
				7.2 ± 0.7	298			
				10.2 ± 4.4	330			
				13.7 ± 4.8	373			
	3.1		1119 ± 204	23.0 ± 7.2	423			
CH_2F_2				0.196 ± 0.022	222	FP-LIF	Talukdar *et al.*[3]	222–381
				0.227 ± 0.013	223			
				0.398 ± 0.034	245			
				0.672 ± 0.020	273			
				1.09 ± 0.03	296			
				1.92 ± 0.04	336			
				2.66 ± 0.16	358			
	1.57 ± 0.21		1470 ± 100	3.43 ± 0.18	381			
CHF_2Br				1.3 ± 0.9	275	DF-RF	Brown *et al.*[4]	275–420
				1.3 ± 0.3	298			
				2.3 ± 0.3	336			
				3.0 ± 0.3	370			
	0.44		1050 ± 400	4.6 ± 0.9	420			
				0.29 ± 0.01	233	DF-LMR/LP-LIF	Talukdar *et al.*[5]	233–432
				0.41 ± 0.01	253			
				0.64 ± 0.05	268			
				0.61 ± 0.01	273			
				0.91 ± 0.01	297			
				1.06 ± 0.08	298			
				1.45 ± 0.04	333			
				2.03 ± 0.12	352			
				2.62 ± 0.08	373			
				3.52 ± 0.23	405			
	0.74 ± 0.16		1300 ± 100 (233–352 K)	4.65 ± 0.17	432			
CF_3Br				<0.01	294	LP-LIF/DF-LMR	Burkholder *et al.*[6]	294–424
				<0.017	297			
				<0.01	373			
				<0.02	424			
CF_3I				3.1 ± 0.5	300	DF-RF	Brown *et al.*[2]	

TABLE 37. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with haloalkanes – Continued

Haloalkane	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	n	B (K)	$10^{14} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
CF_2ClBr				<0.02	293	LP-LIF/DF-LMR	Burkholder *et al.*[6]	293–424
				<0.009	297			
				<0.007	373			
				<0.02	424			
CF_2Br_2				<0.045	293	LP-LIF/DF-LMR	Burkholder *et al.*[6]	293–424
				<0.059	297			
				<0.072	325			
				<0.092	373			
				<0.037	384			
				<0.042	424			
CH_3CH_2Cl				40.8 ± 3.1	294.8	LP-LIF	Kasner *et al.*[7]	295–789
				56.2 ± 5.1	330.5			
				79.8 ± 7.0	381.9			
				94.6 ± 4.3	421.3			
				101 ± 6.9	447.4			
				124 ± 16.1	490.0			
				160 ± 39.3	548.0			
				193 ± 25.1	595.0			
				231 ± 11.0	600.0			
				243 ± 28.8	641.0			
				275 ± 39.5	687.0			
				327 ± 32.7	710.0			
				324 ± 22.2	714.0			
				351 ± 68.1	733.0			
				397 ± 40.5	769.2			
	1.14×10^{-7}	2.59	−115 ± 314	429 ± 59.6	788.7			
				43 ± 5	295 ± 2	PR-RA	Markert and Nielsen[8]	
CH_3CH_2Br				27.6 ± 5.6	292	DF-RF	Xing *et al.*[9]; Qiu *et al.*[10]	292–418
				30.5 ± 6.1	298			
				45.3 ± 9.1	325			
				52.2 ± 10.5	340			
				69.9 ± 14.0	366			
	27.7 ± 3.4		1344 ± 86 (292–366 K)[10]	140.1 ± 28.1	418			
CH_3CHF_2				2.99 ± 0.27	270	FP-RF	Liu *et al.*[11]	270–400
				4.22 ± 0.45	298			
				5.32 ± 0.67	330			

TABLE 37. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with haloalkanes — Continued

Haloalkane	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	n	B (K)	$10^{14} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
				6.81 ± 0.83	350			
				7.30 ± 0.66	375			
	0.96 ± 0.20		940 ± 130	8.84 ± 0.74	400			
				1.20 ± 1.67	220	DF-RF	Brown *et al.*[12]	220–423
				3.10 ± 0.31	279			
				5.6 ± 2.3	303			
				5.56 ± 0.81	343			
				8.30 ± 1.14	375			
	1.42		1050 ± 250	11.18 ± 1.54	423			
				1.05 ± 0.09	212	FP-LIF/DF-LMR	Gierczak *et al.*[13]	212–423
				1.27 ± 0.11	224			
				1.73 ± 0.17	242			
				1.98 ± 0.16	258			
				2.95 ± 0.24	277			
				3.27 ± 0.26	293			
				4.02 ± 0.33	300			
				6.40 ± 0.52	349			
				9.12 ± 0.77	388			
				11.4 ± 1.0	402			
				11.1 ± 1.0	409			
	$1^{+0.18}_{-0.15}$		980 ± 50 (212–349 K)	12.7 ± 1.1	422.5			
				4.7 ± 1.1	295	PR-RA	Nielsen[14]	295–388
				5.3 ± 0.4	323			
				8.0 ± 1.0	358			
	3.9		1370 ± 260	11.3 ± 0.3	388			
CH_2ClCH_2Cl				26.4 ± 1.8	297 ± 2	RR [relative to k(ethane) = 2.54×10^{-13}]^a	Arnts *et al.*[15]	
				24.8 ± 3.8	292	LP-LIF	Taylor *et al.*[16]	292–775
				30.2 ± 4.0	311			
				34.1 ± 3.2	321			
				43.5 ± 3.0	340			
				50.1 ± 3.0	359			
				60.1 ± 5.7	377			
				68.3 ± 3.9	407			
				75.2 ± 6.3	431			
				90.8 ± 7.4	458			
				109 ± 10.8	493			
				151 ± 5.6	529			

TABLE 37. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with haloalkanes – Continued

Haloalkane	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	n	B (K)	$10^{14} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
				206 ± 7.1	570			
				195 ± 14.8	574			
				244 ± 21.2	627			
				293 ± 36.4	696			
				347 ± 35.0	771			
	0.0136	1.0	825 ± 88	325 ± 22.3	775			
				20.9 ± 4.2	292	DF-RF	Xing *et al.*[9]; Qiu *et al.*[10]	292–363
				21.4 ± 4.3	295			
				32.0 ± 6.4	321			
				34.5 ± 6.9	333			
				35.9 ± 7.2	343			
				41.4 ± 8.3	358			
	10.5 ± 1.6		1137 ± 106	44.4 ± 8.9	363			
CH_2BrCH_2Br				22.5 ± 1.5	297 ± 2	RR [relative to k(ethane) = 2.54×10^{-13}]^a	Arnts *et al.*[15]	
				18.6 ± 3.8	294	DF-RF	Xing *et al.*[9]; Qiu *et al.*[10]	294–365
				27.1 ± 5.5	319			
				32.4 ± 6.5	337			
				37.0 ± 7.4	343			
	14.6 ± 2.6		1283 ± 136	42.6 ± 8.6	365			
CH_3CF_3				0.0157 ± 0.0012	223	FP-LIF/DF-LMR	Talukdar *et al.*[3]	223–374
				0.0229 ± 0.0016	236			
				0.0333 ± 0.0029	248			
				0.0451 ± 0.0029	261			
				0.0659 ± 0.0086	266			
				0.0612 ± 0.0029	273			
				0.108 ± 0.004	294			
				0.112 ± 0.004	296			
				0.129 ± 0.008	296			
				0.137 ± 0.004	297			
				0.145 ± 0.012	298			
				0.170 ± 0.032	301			
				0.240 ± 0.008	334			
				0.382 ± 0.010	346			
				0.436 ± 0.030	357			
	2.12 ± 0.65		2200 ± 200 (261–374 K)	0.567 ± 0.036	374			

TABLE 37. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with haloalkanes — Continued

Haloalkane	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	n	B (K)	$10^{14} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
CH_3CF_2Cl				0.214 ± 0.07	270	FP-RF	Liu *et al.*[11]	270–400
				0.402 ± 0.10	298			
				0.660 ± 0.08	330			
				0.797 ± 0.11	350			
				1.15 ± 0.14	375			
	0.98 ± 0.28		1660 ± 200	1.70 ± 0.27	400			
				0.15 ± 0.09	231	DF-RF	Brown *et al.*[12]	231–423
				0.26 ± 0.05	266			
				0.37 ± 0.14	303			
				0.69 ± 0.20	339			
				1.03 ± 0.40	373			
	0.26		1230 ± 250	1.58 ± 0.71	423			
				0.0455 ± 0.0047	223	FP-LIF/DF-LMR	Gierczak *et al.*[13]	223–427
				0.0845 ± 0.0071	243			
				0.171 ± 0.014	273			
				0.299 ± 0.024	297			
				0.296 ± 0.030	299			
				1.09 ± 0.09	374			
	$1.14^{+0.35}_{-0.26}$		1750 ± 75 (223–374 K)	2.07 ± 0.18	427			
				0.245 ± 0.031	270	FP-RF	Zhang *et al.*[17]	
CH_3CFCl_2				0.420 ± 0.12	243	FP-RF	Liu *et al.*[11]	243–400
				0.524 ± 0.08	270			
				0.701 ± 0.12	298			
				0.962 ± 0.13	330			
				1.38 ± 0.02	350			
	0.36 ± 0.11		1140 ± 210	1.94 ± 0.27	400			
				0.71 ± 0.47	238	DF-RF	Brown *et al.*[12]	238–426
				0.94 ± 0.44	256			
				1.61 ± 0.55	297			
				1.36 ± 0.27	303			
				1.92 ± 0.50	336			
				2.60 ± 0.78	376			
	0.58		1100 ± 250	4.82 ± 0.60	426			
				0.200 ± 0.006	233	LP-LIF/DF-LMR	Talukdar *et al.*[3]	233–393
				0.159 ± 0.010	233			
				0.157 ± 0.007	233			
				0.266 ± 0.023	249			

TABLE 37. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with haloalkanes – Continued

Haloalkane	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	n	B (K)	$10^{14} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
				0.231 ± 0.030	253			
				0.239 ± 0.006	253			
				0.366 ± 0.085	268			
				0.345 ± 0.032	273			
				0.361 ± 0.012	273			
				0.568 ± 0.013	295			
				0.591 ± 0.015	297			
				0.581 ± 0.044	297			
				0.545 ± 0.014	297			
				0.558 ± 0.022	298			
				0.515 ± 0.024	298			
				0.609 ± 0.012	298			
				0.887 ± 0.043	324			
				1.000 ± 0.064	332			
				1.070 ± 0.024	332			
				1.36 ± 0.020	347			
				1.179 ± 0.024	347			
				1.660 ± 0.022	363			
				1.647 ± 0.072	374			
				2.02 ± 0.030	375			
	1.47 ± 0.32		1640 ± 100 (253–393 K)	2.22 ± 0.086	393			
				0.182 ± 0.065	250	FP-RF[b]	Zhang *et al.*[17]	250–297
				0.201 ± 0.090	250			
				0.339 ± 0.082	270			
				0.480 ± 0.146	297			
CH_3CCl_3				1.09 ± 0.35	298 ± 3	RR [relative to k(CH_3Cl) = 4.36×10^{-14}][a]	Nelson *et al.*[18]	
				3.36 ± 0.3	359	PR-RA	Nelson *et al.*[18]	359–402
				4.85 ± 0.5	376			
	5.4 ± 3		1801 ± 448	5.83 ± 0.2	402			
				0.779 ± 0.047	277	RR [relative to k(methane) $= 7.44 \times 10^{-18}$ T^2 $e^{-1361/T}$][a]	DeMore[19]	277–356
				0.899 ± 0.059	283			
				0.963 ± 0.072	288			
				1.13 ± 0.05	298			
				1.83 ± 0.11	326			
				2.90 ± 0.07	356			
				0.789 ± 0.074	278	DF-RF	Finlayson-Pitts *et al.*[20]	278–378
				1.12 ± 0.16	298			
				0.911 ± 0.098	298			

TABLE 37. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with haloalkanes — Continued

Haloalkane	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	n	B (K)	$10^{14} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
				1.38 ± 0.42	318			
				1.28 ± 0.09	318			
				1.61 ± 0.16	333			
				1.99 ± 0.24	338			
				1.87 ± 0.25	348			
				2.17 ± 0.11	358			
	$0.91^{+0.46}_{-0.37}$		1337 ± 150	2.68 ± 0.28	378			
				0.304 ± 0.019	233	LP-LIF	Talukdar *et al.*[21]	233–379
				0.267 ± 0.018	233			
				0.270 ± 0.019	243			
				0.349 ± 0.016	243			
				0.355 ± 0.026	252			
				0.346 ± 0.030	252			
				0.410 ± 0.013	252			
				0.405 ± 0.017	253			
				0.377 ± 0.018	253			
				0.522 ± 0.030	263			
				0.520 ± 0.022	263			
				0.579 ± 0.022	273			
				0.530 ± 0.026	273			
				0.609 ± 0.030	274			
				0.898 ± 0.064	293			
				0.899 ± 0.100	295			
				0.910 ± 0.030	296			
				0.859 ± 0.027	296			
				0.851 ± 0.023	297			
				1.49 ± 0.05	326			
				1.44 ± 0.10	326			
				1.65 ± 0.05	332			
				2.07 ± 0.06	352			
				2.24 ± 0.11	355			
				2.08 ± 0.08	356			
				2.67 ± 0.05	370			
				2.71 ± 0.05	378			
	1.75 ± 0.34		1550 ± 60 (243–379 K)	3.05 ± 0.11	379			
$CH_2ClCHCl_2$				18.4 ± 0.7	295	LP-LIF	Taylor *et al.*[22]	295–850
				19.6 ± 0.6	299			
				27.0 ± 1.5	325			
				32.0 ± 0.9	339			
				31.2 ± 2.1	360			
				42.8 ± 2.3	400			

TABLE 37. Rate constants *k* and temperature-dependent parameters for the gas-phase reactions of the OH radical with haloalkanes — Continued

Haloalkane	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	n	B (K)	$10^{14} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
				43.0 ± 2.5	404			
				46.7 ± 3.5	447			
				63.0 ± 5.0	480			
				86.0 ± 7.0	540			
				108.0 ± 4.4	600			
				129.0 ± 4.7	651			
				142.0 ± 5.5	670			
				197.0 ± 4.2	722			
				221.0 ± 16.2	775			
	4.71×10^{-8}	2.64	−70 ± 55	258.0 ± 31.2	850			
CH_2FCF_3				0.263 ± 0.08	270	FP-RF	Liu *et al.*[11]	270–400
				0.518 ± 0.07	298			
				0.808 ± 0.06	330			
				1.31 ± 0.14	350			
				1.81 ± 0.23	375			
	3.7 ± 1.5		1990 ± 280	2.72 ± 0.32	400			
				0.17 ± 0.01	231	DF-RF	Brown *et al.*[12]	231–423
				0.32 ± 0.10	253			
				0.46 ± 0.02	280			
				0.69 ± 0.15	301			
				0.85 ± 0.14	338			
				1.9 ± 0.3	373			
	0.58		1350 ± 100	2.9 ± 1.8	423			
				0.0990 ± 0.0085	223	FP-LIF/DF-LMR	Gierczak *et al.*[13]	223–450
				0.155 ± 0.013	243			
				0.276 ± 0.027	273			
				0.457 ± 0.033	294			
				0.426 ± 0.029	296			
				0.435 ± 0.038	297			
				0.450 ± 0.037	298			
				0.770 ± 0.069	324			
				1.41 ± 0.11	376			
				2.07 ± 0.18	404			
				2.50 ± 0.20	425			
	$0.57^{+0.14}_{-0.11}$		1430 ± 60 (223–324 K)	3.18 ± 0.26	450			
				0.238 ± 0.022	270	FP-RF	Zhang *et al.*[17]	
$CHCl_2CHCl_2$				23.7 ± 4.8	292	DF-RF	Xing *et al.*[9]; Qiu *et al.*[10]	292–365
				22.6 ± 4.6	298			
				26.6 ± 5.4	312			

TABLE 37. Rate constants *k* and temperature-dependent parameters for the gas-phase reactions of the OH radical with haloalkanes – Continued

Haloalkane	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	n	*B* (K)	$10^{14} \times k$ (cm^3 molecule^{-1} s^{-1})	at *T* (K)	Technique	Reference	Temperature range covered (K)
				33.8 ± 6.8	343			
	3.70 ± 0.46		815 ± 91	40.3 ± 8.1	365			
CHF_2CF_3				0.16 ± 0.22	226	DF-RF	Brown *et al.*[12]	226–423
				0.16 ± 0.14	257			
				0.29 ± 0.10	303			
				0.52 ± 0.08	341			
				0.82 ± 0.48	373			
	0.28		1350 ± 100	0.99 ± 1.45	423			
				0.0272 ± 0.0028	220	FP-LIF/DF-LMR	Talukdar *et al.*[3]	220–364
				0.0360 ± 0.0022	228			
				0.0376 ± 0.0014	229			
				0.0532 ± 0.0038	245			
				0.0751 ± 0.0025	255			
				0.103 ± 0.003	273			
				0.170 ± 0.010	297			
				0.206 ± 0.026	299			
				0.289 ± 0.016	325			
				0.442 ± 0.003	343			
				0.451 ± 0.020	355			
	0.541 ± 0.083		1700 ± 100	0.587 ± 0.020	364			
$CHFClCF_3$				0.193 ± 0.016	210	FP-LIF/DF-LMR	Gierczak *et al.*[13]	210–425
				0.25 ± 0.02	223			
				0.260 ± 0.022	233			
				0.346 ± 0.028	238			
				0.382 ± 0.038	243			
				0.399 ± 0.041	243			
				0.414 ± 0.034	244			
				0.510 ± 0.042	258			
				0.640 ± 0.052	270			
				0.661 ± 0.072	272			
				0.880 ± 0.074	293.5			
				0.975 ± 0.08	297			
				0.900 ± 0.075	298			
				1.87 ± 0.15	349			
				3.16 ± 0.26	400			
	$0.445^{+0.110}_{-0.088}$		1150 ± 60 (210–349 K)	3.91 ± 0.31	425			
$CHCl_2CF_3$				2.50 ± 0.26	270	FP-RF	Liu *et al.*[11]	270–400
				3.52 ± 0.28	298			
				4.70 ± 0.66	330			

TABLE 37. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with haloalkanes – Continued

Haloalkane	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	n	B (K)	$10^{14} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
				4.99 ± 0.62	350			
				7.36 ± 0.92	375			
	1.1 ± 0.2		1040 ± 140	8.84 ± 0.74	400			
				4.5 ± 0.9	232	DF-RF	Brown *et al.*[12]	232–426
				7.0 ± 3.0	269			
				5.9 ± 0.6	303			
				8.6 ± 4.0	339			
				10.5 ± 1.1	376			
	1.18		900 ± 150	14.5 ± 1.7	426			
				1.13 ± 0.11	213	FP-LIF/DF-LMR	Gierczak *et al.*[13]	213–380
				1.58 ± 0.29	223			
				1.48 ± 0.13	223			
				1.89 ± 0.16	229			
				2.20 ± 0.24	243			
				2.20 ± 0.18	251			
				3.05 ± 0.25	273			
				4.18 ± 0.36	294.5			
				3.66 ± 0.30	296			
				3.72 ± 0.34	297			
				3.64 ± 0.34	298			
				4.80 ± 0.39	322			
	$0.65^{+0.11}_{-0.10}$		840 ± 40 (213–322 K)	7.20 ± 0.58	380			
				4.3 ± 1.0	295	PR-RA	Nielsen[14]	295–385
				6.3 ± 1.0	323			
				6.5 ± 1.3	358			
	1.1		940 ± 200	9.7 ± 1.3	385			
$CHFBrCF_3$				1.3 ± 0.4	279	DF-RF	Brown *et al.*[4]	279–423
				1.7 ± 0.3	298			
				2.4 ± 0.5	344			
				3.9 ± 0.5	377			
	1.13		1250 ± 350	6.1 ± 1.3	423			
$CHClBrCF_3$				6.0 ± 0.4	303	DF-RF	Brown *et al.*[12,23]	
$CHCl_2CCl_3$				23.3 ± 4.7	292	DF-RF	Qiu *et al.*[10]	
CF_2BrCF_2Br				<0.19	295	LP-LIF/DF-LMR	Burkholder *et al.*[6]	295–424
				<0.013	296			
				<0.014	374			
				<0.04	424			

TABLE 37. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with haloalkanes – Continued

Haloalkane	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	n	B (K)	$10^{14} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
$CH_3CH_2CH_2Cl$				82 ± 14	295 ± 2	PR-RA	Markert and Nielsen[8]	
$CHCl_2CF_2CF_3$				2.8 ± 1.3	251	DF-RF	Brown *et al.*[4]	251–393
				3.7 ± 0.8	300			
	0.23		550 ± 750	6.1 ± 1.1	393			
				1.54 ± 0.29	270	FP-RF	Zhang *et al.*[24]	270–400
				2.60 ± 0.29	298			
				3.78 ± 0.31	330			
				5.36 ± 0.65	365			
	1.92 ± 0.52		1290 ± 90	7.76 ± 0.90	400			
				2.41 ± 0.24	295	DF-LIF	Nelson *et al.*[25]	295–364
				3.07 ± 0.33	317			
				3.67 ± 0.37	337			
	0.65 ± 0.13		970 ± 115	4.45 ± 0.46	364			
$CHFClCF_2CF_2Cl$				0.86 ± 0.11	298	FP-RF	Zhang *et al.*[24]	298–400
				1.10 ± 0.14	312			
				1.27 ± 0.10	331			
				1.53 ± 0.22	350			
				2.20 ± 0.25	375			
	0.675 ± 0.370		1300 ± 180	2.69 ± 0.40	400			
				0.90 ± 0.11	295	DF-LIF	Nelson *et al.*[25]	295–374
				1.13 ± 0.12	316			
				1.40 ± 0.14	336			
				1.82 ± 0.19	364			
	0.39 ± 0.07		1120 ± 125	1.96 ± 0.20	374			
$CH_3CF_2CFCl_2$				0.21 ± 0.02	295	DF-LIF	Nelson *et al.*[25]	295–367
				0.31 ± 0.03	308			
				0.41 ± 0.04	328			
				0.56 ± 0.07	348			
	0.71 ± 0.28		1690 ± 230	0.68 ± 0.07	367			
$CH_3CH_2CH_2CH_2Cl$				150 ± 40	295 ± 2	PR-RA	Markert and Nielsen[8]	
$CH_3CH_2CH_2CH_2CH_2Cl$				310 ± 30	295 ± 2	PR-RA	Markert and Nielsen[8]	
$CH_3CH_2CH_2CH_2CH_2CH_2Cl$				380 ± 20	295 ± 2	PR-RA	Markert and Nielsen[8]	

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[a] From present and previous[1] recommendations.

[b] Conducted at low flash intensities or low H_2O precursor concentrations. Use of higher flash intensities or higher H_2O concentrations gave higher measured rate constants.

CH_2BrCH_2Br. The room temperature relative rate constant of Arnts *et al.*[15] and the absolute rate constants of Xing *et al.*[9] and Qiu *et al.*[10] are given in Table 37 and are plotted in Arrhenius form in Fig. 17 together with the absolute room temperature rate constant of Howard and Evenson.[37] The room temperature rate constants[9,10,15,37] are in good agreement. A unit-weighted least-squares analysis of the absolute rate constants of Howard and Evenson[37] and Qiu *et al.*,[10] using the expression $k = CT^2e^{-D/T}$, yields the recommendation of

$$k(\mathrm{CH_2BrCH_2Br}) = (1.03^{+1.94}_{-0.68}) \times 10^{-17}\, T^2\, \mathrm{e}^{-(422 \pm 343)/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the temperature range 294–365 K, where the indicated errors are two least-squares standard deviations, and

$$k(\mathrm{CH_2BrCH_2Br}) = 2.22 \times 10^{-13}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}\ at\ 298\ K},$$

with an estimated overall uncertainty at 298 K of a factor of 1.5.

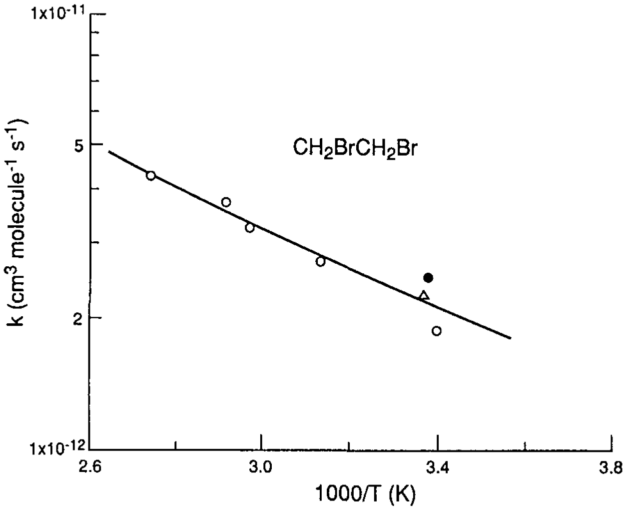

FIG. 17. Arrhenius plot of rate constants for the reaction of the OH radical with CH_2BrCH_2Br. (●) Howard and Evenson;[37] (△) Arnts *et al.*;[15] (○) Xing *et al.*[9] and Qiu *et al.*[10] (—) recommendation (see text).

CH_3CF_3. The absolute rate constants determined by Talukdar *et al.*[3] over the temperature range 223–374 K are given in Table 37, and are plotted together with the room temperature rate constant of Martin and Paraskevopoulos[40] in Arrhenius form in Fig. 18. The agreement is good, and a unit-weighted least-squares analysis of these data,[3,40] using the expression $k = CT^2e^{-D/T}$, yields the recommendation of

$$k(\mathrm{CH_3CF_3}) = (2.02^{+1.11}_{-0.71}) \times 10^{-18}\, T^2\, \mathrm{e}^{-(1459 \pm 125)/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the temperature range 223–374 K, where the indicated errors are two least-squares standard deviations, and

$$k(\mathrm{CH_3CF_3}) = 1.34 \times 10^{-15}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}\ at\ 298\ K},$$

with an estimated overall uncertainty at 298 K of a factor of 1.5.

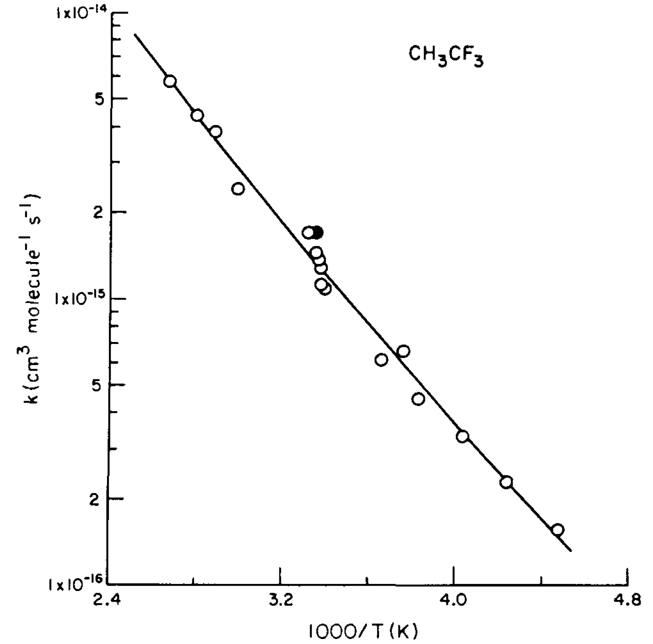

FIG. 18. Arrhenius plot of selected rate constants for the reaction of the OH radical with CH_3CF_3. (●) Martin and Paraskevopoulos;[40] (○) Talukdar *et al.*;[3] (—) recommendation (see text).

CH_3CF_2Cl. The absolute rate constants of Liu *et al.*,[11] Brown *et al.*,[12] Gierczak *et al.*[13] and Zhang *et al.*[17] are given in Table 37. The rate constants of Liu *et al.*,[11] Brown *et al.*[12] and Gierczak *et al.*,[13] together with those of Howard and Evenson,[37] Watson *et al.*,[41] Handwerk and Zellner[39] and Paraskevopoulos *et al.*,[38] are plotted in Arrhenius form in Fig. 19. A significant amount of scatter in the data is evident, with the rate constants of Brown *et al.*,[12] and, to a somewhat lesser extent, of Handwerk and Zellner,[39] Liu *et al.*[11] and Zhang *et al.*[17] being appreciably higher than the rate constants of Howard and Evenson,[37] Watson *et al.*[41] and Gierczak *et al.*[13] These discrepancies appear to be due, at least in part, to the presence of reactive haloalkene impurities in the CH_3CF_2Cl samples used and/or the occurrence of secondary reactions of OH radicals with the reaction products or CH_3CF_2Cl photolysis products.

Accordingly, a unit-weighted least-squares analysis of the rate constants of Howard and Evenson,[37] Watson *et al.*[41] and Gierczak *et al.*,[13] using the expression $k = CT^2e^{-D/T}$, yields the recommendation of

$$k(\mathrm{CH_3CF_2Cl}) = (1.77^{+0.26}_{-0.23}) \times 10^{-18}\, T^2\, \mathrm{e}^{-(1174 \pm 40)/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the temperature range 223–427 K, where the indicated errors are two least-squares standard deviations, and

$$k(\mathrm{CH_3CF_2Cl}) = 3.06 \times 10^{-15}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ \text{at } 298\ \mathrm{K},$$

with an estimated overall uncertainty at 298 K of a factor of 1.5.

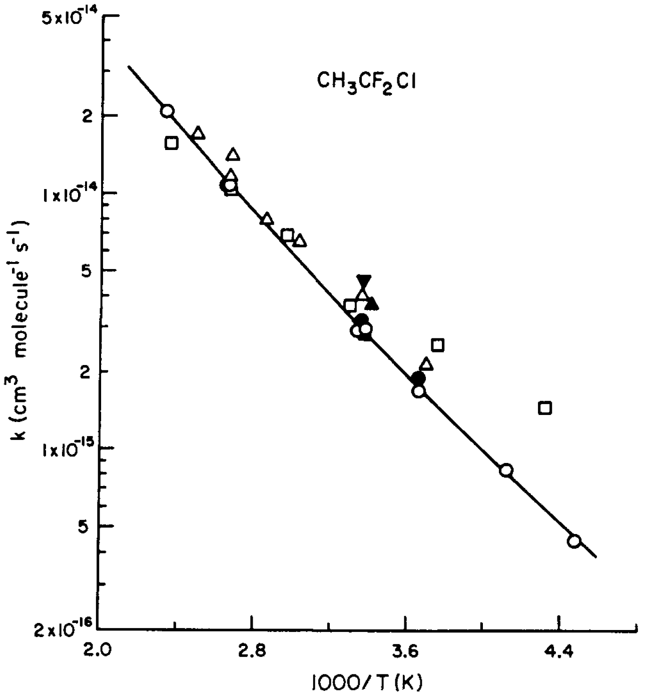

FIG. 19. Arrhenius plot of selected rate constants for the reaction of the OH radical with CH_3CF_2Cl. (■) Howard and Evenson;[37] (●) Watson *et al.*;[41] (▲) Handwerk and Zellner;[39] (▼) Paraskevopoulos *et al.*;[38] (△) Liu *et al.*;[11] (□) Brown *et al.*;[12] (○) Gierczak *et al.*;[13] (—) recommendation (see text).

This recommendation is 16–17% lower at all temperatures than the previous recommendation of Atkinson[1] of

$$k(\mathrm{CH_3CF_2Cl}) = 2.05 \times 10^{-18}\ T^2\ e^{-1171/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the temperature range 273–375 K, with a 298 K rate constant of 3.58×10^{-15} cm^3 molecule^{-1} s^{-1}.

CH_3CFCl_2. The absolute rate constants reported by Liu *et al.*,[11] Brown *et al.*,[12] Talukdar *et al.*[3] and Zhang *et al.*[17] are given in Table 37, and are plotted in Arrhenius form in Fig. 20. No previous rate constant measurements have been reported for this reaction. The measured rate constants exhibit a significant degree of scatter, more so at the lower temperatures. The rate constants of Brown *et al.*[12] are higher than those from the other studies[3,11,17] at all temperatures studied,[12] and the rate constants measured by Liu *et al.*[11] at temperatures ≤ 298 K are significantly higher than those of Talukdar *et al.*[3] and Zhang *et al.*[17] Among the proposed reasons for these discrepancies are the presence of reactive haloalkenes in the CH_3CFCl_2 samples used[3] and the occurrence of secondary reactions of OH radicals with the reaction products.[17] The most recent measurements of Zhang *et al.*[17] indicate that the earlier lower temperature data (≤ 298 K) of Liu *et al.*[11] were in error due to the occurrence of secondary reactions of OH radicals with reaction products. Talukdar *et al.*[3] also reported that preliminary experiments utilizing the flash photolysis of H_2O as the OH radical source indicated problems due to the reactions of OH radicals with photolysis products of CH_3CFCl_2 (or possibly with reaction products), and the data given in Table 37 were obtained with a discharge flow system with laser magnetic resonance detection of OH radicals or with a laser photolysis (of HONO) system with laser induced fluorescence detection of OH radicals.

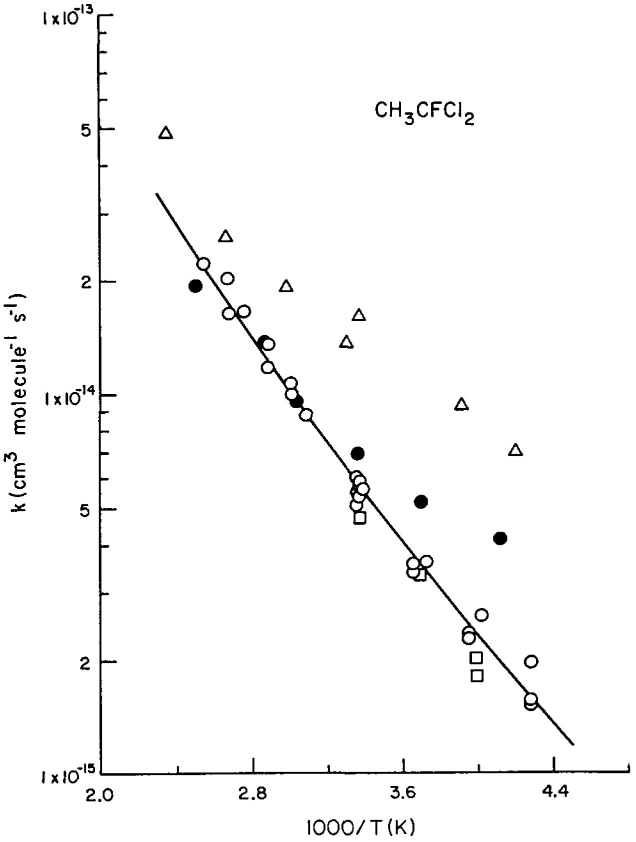

FIG. 20. Arrhenius plot of rate constants for the reaction of the OH radical with CH_3CFCl_2. (●) Liu *et al.*;[11] (△) Brown *et al*;[12] (○) Talukdar *et al.*;[3] (□) Zhang *et al.*;[17] (—) recommendation (see text).

The rate constants of Talukdar *et al.*[3] and Zhang *et al.*[17] (obtained at low flash energies and/or low water vapor concentrations and with high associated uncertainties) are in good agreement, as are those of Talukdar *et al.*[3] and Liu *et al.*[11] at temperatures ≥330 K. A unit-weighted least-squares analysis of the rate constants of Talukdar *et al.*,[3] using the expression $k = CT^2e^{-D/T}$, yields the recommendation of

$$k(\mathrm{CH_3CFCl_2}) = (1.35^{+0.37}_{-0.28}) \times 10^{-18}\ T^2\ e^{-(893 \pm 69)/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the temperature range 233–393 K, where the indicated errors are two least-squares standard deviations, and

$$k(CH_3CFCl_2) = 5.99 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K},$$

with an estimated overall uncertainty at 298 K of a factor of 1.5. As noted above, while not used in the evaluation of the rate constant for this reaction, the rate constants of Liu *et al.*[11] at temperatures ≥330 K and of Zhang *et al.*[17] over the temperature range 250–297 K are in agreement, within the experimental errors, with this recommendation.

CH_3CCl_3. The absolute rate constants of Nelson *et al.*,[18] Finlayson-Pitts *et al.*[20] and Talukdar *et al.*[21] and the relative rate constants of Nelson *et al.*[18] and DeMore[19] are given in Table 37 and are plotted, together with the absolute rate constants of Jeong and Kaufman[42,43] and Kurylo *et al.*,[44] in Arrhenius form in Fig. 21. The absolute and relative rate constants of Nelson *et al.*[18] are in good agreement with the previous rate constants of Jeong and Kaufman[42,43] and Kurylo *et al.*[44]

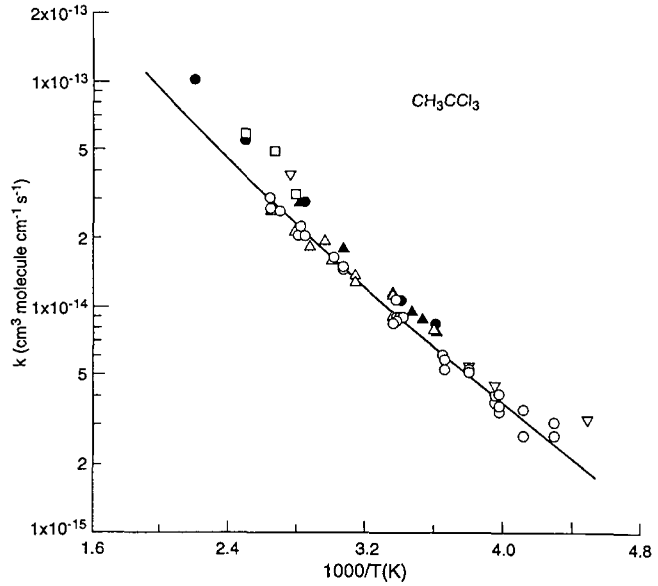

FIG. 21. Arrhenius plot of selected rate constants for the reaction of the OH radical with CH_3CCl_3. (●) Jeong and Kaufman;[42,43] (▽) Kurylo *et al.*;[44] (▲) DeMore;[19] (△) Finlayson-Pitts *et al.*;[20] (○) Talukdar *et al.*;[21] (□) Nelson *et al.*[18] (absolute rate constants); (—) recommendation (see text).

However, these rate constants of Jeong and Kaufman,[42,43] Kurylo *et al.*[44] and Nelson *et al.*[18] are significantly higher than the recent absolute rate constants of Finlayson-Pitts *et al.*[20] and Talukdar *et al.*,[21] especially at temperatures ≥270 K. The presence of undetected reactive impurities such as $CH_2=CCl_2$ in the CH_3CCl_3 samples used would lead to erroneously high measured rate constants at lower temperatures, with the effect becoming more pronounced as the temperature decreased, since the rate constant for the reaction of the OH radical with $CH_2=CCl_2$ increases with decreasing temperature (Sec. 3.4). It is, however, possible that the higher measured absolute rate constants of Jeong and Kaufman,[42,43] Kurylo *et al.*[44] and Nelson *et al.*[18] at the higher temperatures were due to thermal decomposition of CH_3CCl_3 to reactive $CH_2=CCl_2$ on surfaces.[20,21] This possible reason for the discrepancies between the measured rate constants at the higher temperatures is supported by the good agreement between the studies of Kurylo *et al.*,[44] and Talukdar *et al.*[21] at 250–270 K (Fig. 21).

The rate constants of DeMore,[19] determined relative to the rate constant for the reaction of the OH radical with CH_4, are uniformly ~20% higher than the absolute rate constants of Finlayson-Pitts *et al.*[20] and Talukdar *et al.*,[21] and this difference may be due in part to uncertainties in the recommended rate constant for the methane reference reaction.

Accordingly, a unit-weighted least-squares analysis of the absolute rate constants of Finlayson-Pitts *et al.*[20] and the 243–379 K rate constants of Talukdar *et al.*,[21] using the expression $k = CT^2 e^{-D/T}$, yields the recommendation of

$$k(CH_3CCl_3) = (2.25^{+0.46}_{-0.39}) \times 10^{-18}\, T^2\, e^{-(910 \pm 56)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 243–379 K, where the indicated errors are two least-squares standard deviations, and

$$k(CH_3CCl_3) = 9.43 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K},$$

with an estimated overall uncertainty at 298 K of ±30%. Inclusion of the 233 K rate constants of Talukdar *et al.*[21] leads to a temperature-dependent expression of $k(CH_3CCl_3) = 2.05 \times 10^{-18}\, T^2\, e^{-881/T}$ cm^3 molecule^{-1} s^{-1} over the temperature range 233–379 K, with rate constants within 3% of those calculated from the above recommendation for temperatures in the range 235–460 K.

The present recommendation is significantly different to the previous recommendation of Atkinson[1] of

$$k(CH_3CCl_3) = 5.92 \times 10^{-18}\, T^2\, e^{-1129/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 253–457 K, with $k(CH_3CCl_3) = 1.19 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K. However, because of the significantly different temperature-dependencies of the present and previous[1] recommendations, the difference in the calculated rate constants from the two recommendations decreases with decreasing temperature, and at 270 K and 250 K the present recommendation leads to rate constants which are lower than those from the previous recommendation of Atkinson[1] by 15% and 9%, respectively.

The present recommendations for the rate constants for the reactions of the OH radical with methane (Sec. 3.1) and CH_3CCl_3 lead to a rate constant ratio of $k(CH_3CCl_3)/k(CH_4) = 0.30\, e^{451/T}$ [1.59 at 270 K and 1.36 at 298 K].

$CH_2ClCHCl_2$. The absolute rate constants of Taylor *et al.*[22] are given in Table 37 and are plotted, together with the rate constants of Jeong and Kaufman[42] and Jeong *et al.*,[43] in Arrhenius form in Fig. 22. There are significant discrepancies between these two studies[22,42,43] at temperatures ≤400 K, with the rate constants of Jeong and Kaufman[42] and Jeong *et al.*[43] being increasing higher than those of Taylor *et al.*[22] as the temperature decreases. The rate constants of Taylor *et al.*[22] are in reasonable accord with empirical[45,46] and theoretical[47] expectations,[22] and it is possible that the rate constants measured by Jeong and Kaufman[42] and Jeong *et al.*[43] are erroneously high because of the presence of reactive impurities in the $CH_2ClCHCl_2$ samples used.[22] Accordingly, a unit-weighted least-squares analysis of the rate constants of Taylor *et al.*[22] has been carried out, using the expression $k = CT^2 e^{-D/T}$, to recommend that

$$k(CH_2ClCHCl_2) = (4.44^{+0.63}_{-0.55}) \times 10^{-18}\, T^2\, e^{-(208 \pm 57)/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 295–850 K, where the indicated errors are two least-squares standard deviations, and

$$k(CH_2ClCHCl_2) = 1.96\times10^{-13}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \text{ at } 298\ \text{K},$$

with an estimated overall uncertainty at 298 K of a factor of 1.5.

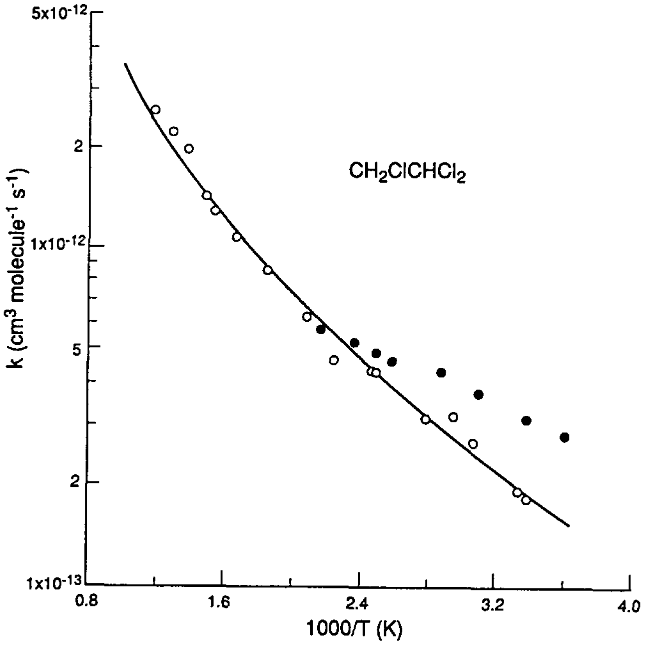

FIG. 22. Arrhenius plot of rate constants for the reaction of the OH radical with $CH_2ClCHCl_2$. (●) Jeong and Kaufman;[42,43] (○) Taylor *et al.*;[22] (—) recommendation (see text).

CH_2FCF_3. The rate constants of Liu *et al.*,[11] Brown *et al.*,[12] Gierczak *et al.*[13] and Zhang *et al.*[17] are given in Table 37 and those of Liu *et al.*,[11] Brown *et al.*[12] and Gierczak *et al.*,[13] together with the rate constants of Martin and Paraskevopoulos[40] and Jeong *et al.*,[43] are plotted in Arrhenius form in Fig. 23. The rate constants of Martin and Paraskevopoulos,[40] Liu *et al.*[11] and Gierczak *et al.*[13] are in reasonably good agreement (especially at temperatures ≤ 330 K), but are significantly lower than those of Jeong *et al.*[43] over the entire temperature range common to these studies (249–450 K) and of Brown *et al.*[12] at temperatures ≤ 301 K. The reasons for these discrepancies are not fully understood at present, but may be due in part to the presence of reactive impurities in the CH_2FCF_3 samples used by Jeong *et al.*[43] and Brown *et al.*[12]

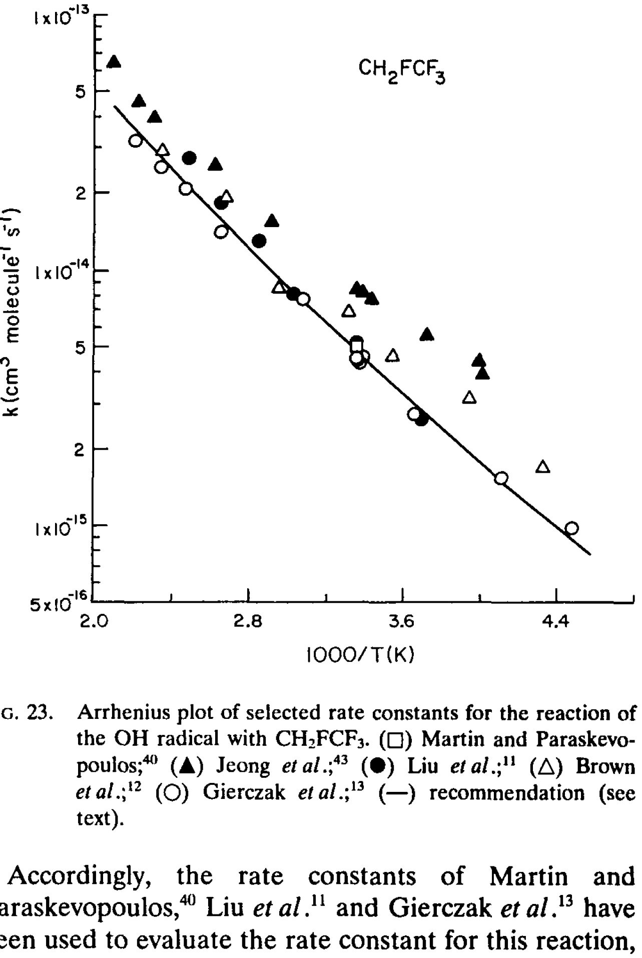

FIG. 23. Arrhenius plot of selected rate constants for the reaction of the OH radical with CH_2FCF_3. (□) Martin and Paraskevopoulos;[40] (▲) Jeong *et al.*;[43] (●) Liu *et al.*;[11] (△) Brown *et al.*;[12] (○) Gierczak *et al.*;[13] (—) recommendation (see text).

Accordingly, the rate constants of Martin and Paraskevopoulos,[40] Liu *et al.*[11] and Gierczak *et al.*[13] have been used to evaluate the rate constant for this reaction, and a unit-weighted least-squares analysis of these data,[11,13,40] using the expression $k = CT^2e^{-D/T}$, yields the recommendation of

$$k(CH_2FCF_3) = (1.61^{+0.43}_{-0.40}) \times 10^{-18}\, T^2\, e^{-(1005 \pm 88)/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 223–450 K, where the indicated errors are two least-squares standard deviations, and

$$k(CH_2FCF_3) = 4.90 \times 10^{-15}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \text{ at } 298\ \text{K},$$

with an estimated overall uncertainty at 298 K of ±40%.

This recommendation supersedes, and is significantly different to, that of Atkinson[1] of

$$k(\mathrm{CH_2FCF_3}) = 1.27 \times 10^{-18}\, T^2\, \mathrm{e}^{-769/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the temperature range 249–473 K, with a 298 K rate constant of 8.54 × 10^{-15} cm^3 molecule^{-1} s^{-1}, based on the rate constants of Martin and Paraskevopoulos[40] and Jeong *et al.*[43]

CH_2ClCF_2Cl. No new rate constants have been reported for this reaction. The previous recommendation of Atkinson[1] was based on the measured rate constants of Watson *et al.*[48] and Jeong *et al.*,[43] which are not in good agreement. Furthermore, Watson *et al.*[48] corrected their measured rate constants to account for the presence of ~0.045% of chloroethenes in the CH_2ClCF_2Cl sample used. Because of the apparently high accuracy of the rate constants measured by Watson *et al.*[41,48] (see this section and Atkinson[1]), it is recommended that the rate constant for the reaction of the OH radical with CH_2ClCF_2Cl be based on the corrected rate constants of Watson *et al.*,[48] with

$$k(\mathrm{CH_2ClCF_2Cl}) = 3.2 \times 10^{-12}\, \mathrm{e}^{-1580/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the temperature range 250–350 K, and

$$k(\mathrm{CH_2ClCF_2Cl}) = 1.6 \times 10^{-14}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}\ at\ 298\ K},$$

with an estimated overall uncertainty at 298 K of a factor of 1.6. This recommendation supersedes that of Atkinson[1] of

$$k(\mathrm{CH_2ClCF_2Cl}) = 2.80 \times 10^{-18}\, T^2\, \mathrm{e}^{-672/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the temperature range 249–473 K, with a 298 K rate constant of 2.61 × 10^{-14} cm^3 molecule^{-1} s^{-1}.

CHF_2CF_3. The rate constants of Brown *et al.*[12] and Talukdar *et al.*,[3] both determined as a function of temperature, are given in Table 37. These rate constants[3,12] and the room temperature rate constant of Martin and Paraskevopoulos[40] are plotted in Arrhenius form in Fig. 24. As seen from Table 37 and Fig. 24, the rate constants of Brown *et al.*[12] are subject to significant uncertainties (exceeding ±100% in two cases), and these rate constants[12] are not used in the evaluation of the rate constant for this reaction. A unit-weighted least-squares analysis of the rate constants of Martin and Paraskevopoulos[40] and Talukdar *et al.*,[3] using the expression $k = CT^2\mathrm{e}^{-D/T}$, yields the recommendation of

$$k(\mathrm{CHF_2CF_3}) = (9.46^{+3.96}_{-2.79}) \times 10^{-19}\, T^2\, \mathrm{e}^{-(1126 \pm 97)/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the temperature range 220–364 K, where the indicated errors are two least-squares standard deviations, and

$$k(\mathrm{CHF_2CF_3}) = 1.92 \times 10^{-15}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}\ at\ 298\ K},$$

with an estimated overall uncertainty at 298 K of a factor of 1.5.

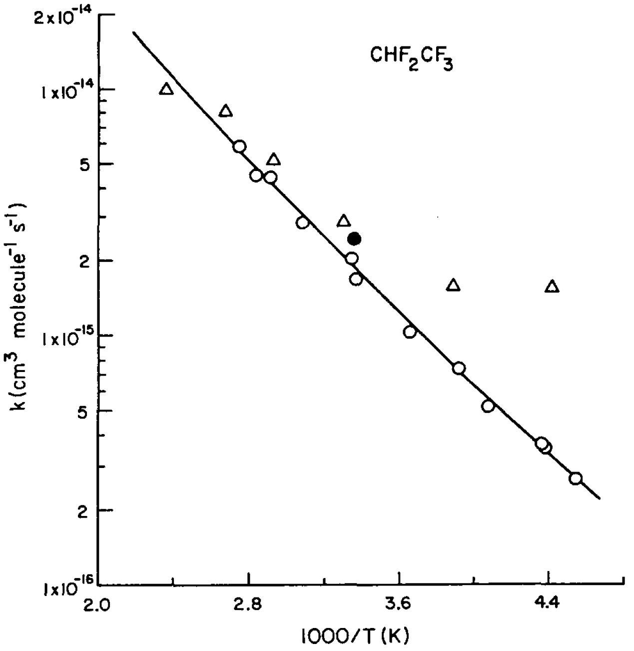

FIG. 24. Arrhenius plot of selected rate constants for the reaction of the OH radical with CHF_2CF_3. (●) Martin and Paraskevopoulos;[40] (△) Brown *et al.*;[12] (○) Talukdar *et al.*;[3] (—) recommendation (see text).

$CHFClCF_3$. The rate constants of Gierczak *et al.*[13] are given in Table 37 and are plotted, together with the rate constants of Howard and Evenson[37] and Watson *et al.*,[48] in Arrhenius form in Fig. 25. The agreement between the rate constants of Watson *et al.*[48] and Gierczak *et al.*[13] is excellent, with the room temperature rate constant of Howard and Evenson[37] being ~40% higher. A unit-weighted least-squares analysis of the rate constants of Watson *et al.*[48] and Gierczak *et al.*,[13] using the expression $k = CT^2\mathrm{e}^{-D/T}$, yields the recommendation of

$$k(\mathrm{CHFClCF_3}) = (1.03^{+0.17}_{-0.14}) \times 10^{-18}\, T^2\, \mathrm{e}^{-(675 \pm 40)/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the temperature range 210–425 K, where the indicated errors are two least-squares standard deviations, and

$$k(\mathrm{CHFClCF_3}) = 9.50 \times 10^{-15}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}\ at\ 298\ K},$$

with an estimated overall uncertainty at 298 K of ±40%.

This recommendation supersedes that of Atkinson[1] of

$$k(\mathrm{CHFClCF_3}) = 6.38 \times 10^{-13}\, \mathrm{e}^{-1233/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the temperature range 250–375 K, with a 298 K rate constant of 1.02 × 10^{-14} cm^3 molecule^{-1} s^{-1}, based on the rate constants of Howard and Evenson[37] and Watson *et al.*[48]

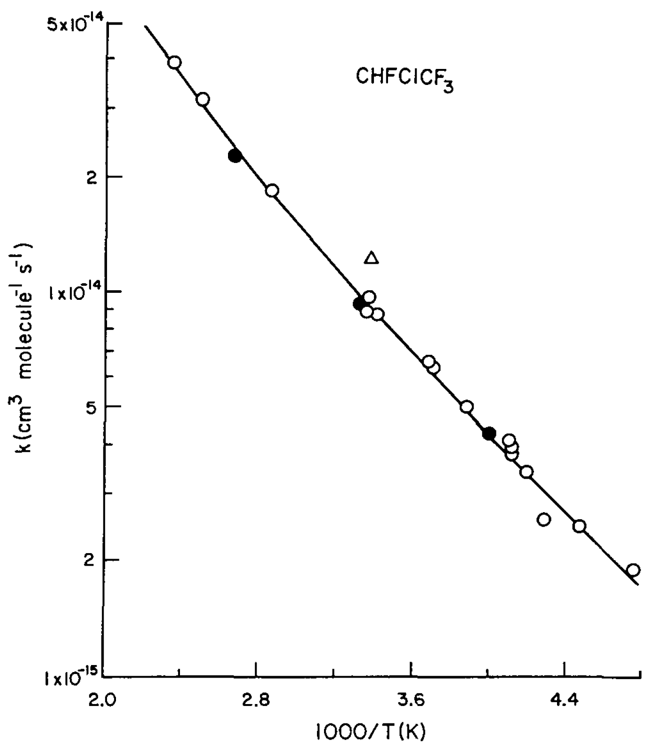

FIG. 25. Arrhenius plot of rate constants for the reaction of the OH radical with $CHFClCF_2$. (△) Howard and Evenson;[37] (●) Watson *et al.*;[48] (○) Gierczak *et al.*;[13] (—) recommendation (see text).

$CHCl_2CF_3$. The rate constants of Liu *et al.*,[11] Brown *et al.*[12], Gierczak *et al.*[13] and Nielsen[14] are given in Table 37, and are plotted, together with the room temperature rate constant of Howard and Evenson[37] and the measured rate constants of Watson *et al.*,[48] in Arrhenius form in Fig. 26. The rate constants of Brown *et al.*[12] and Nielsen[14] are significantly higher, by factors of ~1.5–2.5 and ≤1.4, respectively, than the rate constants of Howard and Evenson,[37] Watson *et al.*,[48] Liu *et al.*[11] and Gierczak *et al.*,[13] and are not used in the evaluation of the rate constant for this reaction. It should be noted that Watson *et al.*[48] corrected their measured rate constants for the presence of reactive impurities in the sample of $CHCl_2CF_3$, with this correction ranging from <1% at 375 K to ~7% at 245 K. Because of the smallness of this correction, the measured rate constants have been used in the evaluation of the rate constant for this reaction. A unit-weighted least-squares analysis of the rate constants of Howard and Evenson,[37] Watson *et al.*,[48] Liu *et al.*[11] and Gierczak *et al.*,[13] using the expression $k = CT^2e^{-D/T}$, yields the recommendation of

$$k(CHCl_2CF_3) = (1.06^{+0.30}_{-0.24}) \times 10^{-18}\, T^2\, e^{-(283 \pm 70)/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 213–400 K, where the indicated errors are two least-squares standard deviations, and

$$k(CHCl_2CF_3) = 3.64 \times 10^{-14}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

with an estimated overall uncertainty at 298 K of ±30%. This recommendation supersedes that of Atkinson[1] of

$$k(CH_2ClCF_3) = 1.16 \times 10^{-12}\, e^{-1056/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 245–375 K, with a 298 K rate constant of 3.35×10^{-14} cm^3 molecule^{-1} s^{-1}, based on the measured rate constants of Howard and Evenson[37] and Watson *et al.*[48]

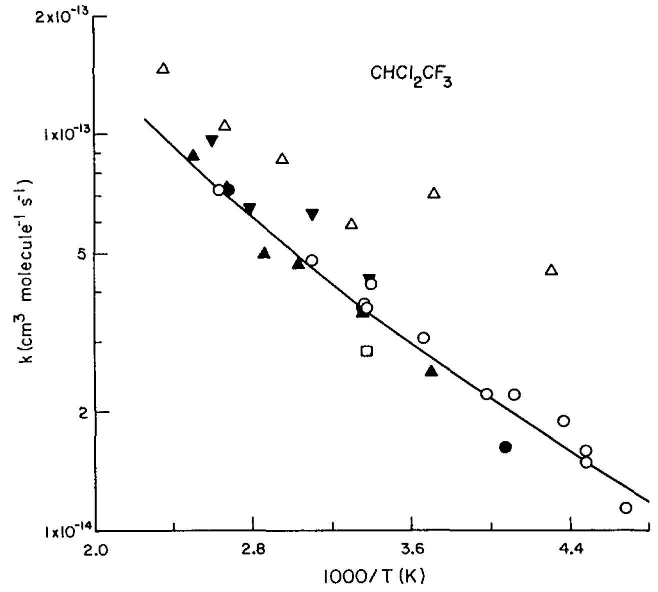

FIG. 26. Arrhenius plot of selected rate constants for the reaction of the OH radical with $CHCl_2CF_3$. (□) Howard and Evenson;[37] (●) Watson *et al.*;[48] (▲) Liu *et al*;[11] (△) Brown *et al.*;[12] (○) Gierczak *et al.*;[13] (▼) Nielsen;[14] (—) recommendation (see text).

$CHCl_2CF_2CF_3$. The rate constants of Brown *et al.*,[4] Zhang *et al.*[24] and Nelson *et al.*[25] are given in Table 37 and are plotted in Arrhenius form in Fig. 27. Over the temperature range common to both studies (295–365 K), the rate constants of Zhang *et al.*[24] and Nelson *et al.*[25] are in good agreement, but exhibit significant disagreement with the rate constant data of Brown *et al.*[4] Accordingly, the rate constants of Zhang *et al.*[24] and Nelson *et al.*[25] are used in the evaluation of the rate constant for this reaction. Since a least-squares analysis of these data[24,25] would unduly weight the 270 K and 400 K rate constants of Zhang *et al.*,[24] the room temperature rate constants and Arrhenius temperature-dependent factors *B* have been averaged to yield the recommended Arrhenius expression of

$$k(CHCl_2CF_2CF_3) = 1.13 \times 10^{-12}\, e^{-1130/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 270–400 K, and

$$k(CHCl_2CF_2CF_3) = 2.50 \times 10^{-14}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

at 298 K, with an estimated overall uncertainty at 298 K of ±35%.

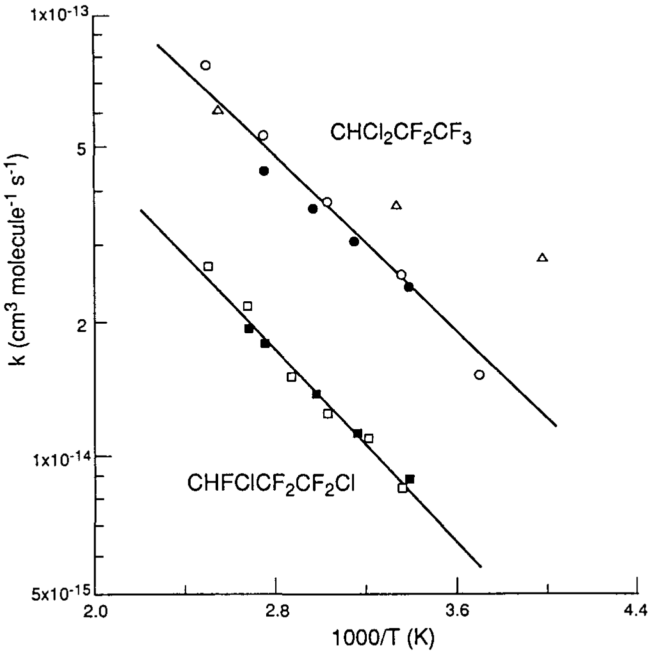

FIG. 27. Arrhenius plots of rate constants for the reactions of the OH radical with $CHCl_2CF_2CF_3$ and $CHFClCF_2CF_2Cl$. $CHCl_2CF_2CF_3$: (△) Brown *et al.*;[4] (○) Zhang *et al.*;[24] (●) Nelson *et al.*[25] $CHFClCF_2CF_2Cl$: (□) Zhang *et al.*;[24] (■) Nelson *et al.*;[25] (—) recommendations (see text).

$CHFClCF_2CF_2Cl$. The rate constants of Zhang *et al.*[24] and Nelson *et al.*[25] are given in Table 37 and are plotted in Arrhenius form in Fig. 27. These rate constants[24,25] are in good agreement, and a unit-weighted least-squares analysis yields the recommended Arrhenius expression of

$$k(CHFClCF_2CF_2Cl) = (5.49^{+2.02}_{-1.48}) \times 10^{-13}\, e^{-(1230 \pm 106)/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the temperature range 295–400 K, where the indicated errors are two least-squares standard deviations, and

$$k(CHFClCF_2CF_2Cl) = 8.85 \times 10^{-15}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ \text{at 298 K},$$

with an estimated overall uncertainty at 298 K of ±40%.

Other Haloalkanes. For $CHCl_2CHCl_2$, $CHFBrCF_3$, $CHClBrCF_3$, $CHCl_2CCl_3$, $CH_3CF_2CFCl_2$, 1-chloropropane, 1-chlorobutane, 1-chloropentane, and 1-chlorohexane, only single studies have been conducted (Table 37), and hence no recommendations are made.

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3.3. Alkenes

The rate constants reported since the previous review of Atkinson[1] are given in Table 38. In addition, rate constants have been determined by Liu *et al.*[11,12] for propene and 1-butene at 760 Torr total pressure (1 atmosphere) of argon over the temperature ranges 323–973 K and 478–873 K, respectively, and rate constants for the reaction of the OH radical with ethene have been measured by Kuo and Lee[13] at low total pressures as a function of temperature. The reaction of OH radicals with ethene has also been studied by Diau and Lee[14] over the temperature range 544–673 K under conditions where the decomposition reaction of the $HO\dot{C}_2H_4$ radical is important.

Ethene. The rate constants determined by Nielsen *et al.*[2] and Becker *et al.*[4] at 298 ± 2 K and one atmosphere total pressure, of (9.4 ± 1.6) × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} and (7.7 ± 1.0) × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}, respectively, are in agreement within the cited uncertainties with the recommended value of Atkinson[1] of 8.52 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 298 K and one atmosphere total pressure of air. The absolute rate constant measured by Bott and Cohen[3] at 1197 ± 16 K and 790 Torr total pressure, of (4.38 ± 0.66) × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}, is plotted in Arrhenius form in Fig. 28, together with the absolute rate constants of Smith,[15] Tully[16] and the > 625 K absolute rate constants of Liu *et al.*[17,18] The recommended rate expression of Atkinson[1] for H-atom abstraction of

$$k^{abs} = 4.87 \times 10^{-18}\, T^2\, e^{-1125/T}\ cm^3\ molecule^{-1}\ s^{-1},$$

based on the rate constant data of Smith[15] and Tully,[16] is also shown in Fig. 28.

Figure 28 shows that while the rate constant of Bott and Cohen[3] agrees with those of Liu *et al.*,[17,18] these studies[3,17,18] measured rate constants which are a factor of ~1.5–2 higher than those of Smith[15] and Tully.[16]

Kuo and Lee[13] have determined rate constants for this reaction with He, N_2 and O_2 diluents at total pressures in the range 1–5 Torr of He, 0.8–3.2 Torr of N_2 and 0.3–1.5 Torr of O_2 at 300 K, and in He diluent over the temperature range 251–430 K, using a discharge flow system with resonance fluorescence detection of the OH radical. At 300 K, the limiting low pressure rate constants, k_o, obtained were (in cm^6 $molecule^{-2}$ s^{-1} units): He, (2.7 ± 0.5) × 10^{-29}; N_2, (6.1 ± 1.2) × 10^{-29}; and O_2, (5.3 ± 1.1) × 10^{-29}. This limiting low pressure rate constant for He[13] is similar to that used in the previous evaluation of Atkinson[1] of 3.0 × 10^{-29} cm^6 $molecule^{-2}$ s^{-1}, while those for N_2 and O_2[13] are factors of 1.6–1.9 lower than the value of $k_o(N_2, O_2)$ = 1.0 × 10^{-28} cm^6 $molecule^{-2}$ s^{-1} at 298 K used by Atkinson.[1] A temperature dependence of the limiting low pressure rate constant k_o for M = He of $T^{-4.8}$ was determined by Kuo and Lee[13] (using a temperature dependence of the limiting high pressure rate constant similar to that recommended by Atkinson[1]). This $T^{-4.8}$ temperature dependence of k_o is significantly higher than that of T^{-3} used by Atkinson[1] and based on the data of Tully.[19]

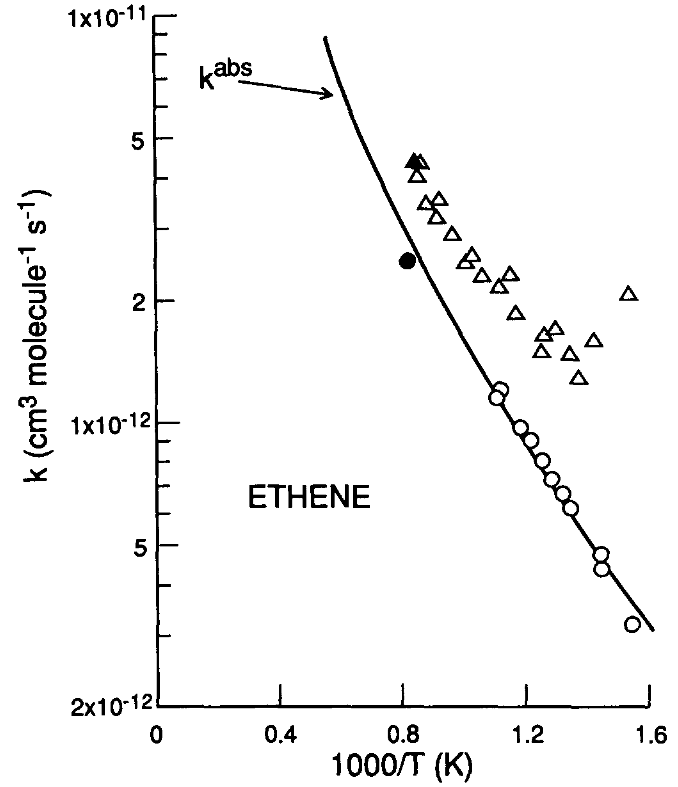

FIG. 28. Arrhenius plot of selected absolute rate constants for the reaction of the OH radical with ethene at temperatures > 625 K. (●) Smith;[15] (○) Tully;[16] (△) Liu *et al.*;[17,18] (▲) Bott and Cohen;[3] (—) recommendation of Atkinson[1] for the H-atom abstraction reaction.

It appears that a temperature dependence of T^{-4} is appropriate for k_o, and that the limiting low pressure rate constants at 298 K are

$$k_o(M = He) = 3.0 \times 10^{-29}\ cm^6\ molecule^{-2}\ s^{-1},$$

and

$$k_o(M = N_2, O_2) = 6 \times 10^{-29}\ cm^6\ molecule^{-2}\ s^{-1}.$$

The previous recommendations[1] for the limiting high pressure rate constant for OH radical addition and for the elevated temperature H-atom abstraction pathway are unchanged.

Diau and Lee[14] investigated the reaction of the OH radical with ethene at 544–673 K and at total pressures of 278–616 Torr of He. At these temperatures, the $HOCH_2\dot{C}H_2$ adduct radical rapidly thermally decomposes back to reactants,[1] and Diau and Lee[14] observed the expected biexponential OH radical decays. The data obtained[14] allowed a value of $\Delta H°$ = −30.7 ± 0.9 kcal mol^{-1} to be derived, reasonably close to the value of

-32.1 kcal mol^{-1} calculated from group additivity.[20] While both the forward and reverse rate constants are expected,[1] and were observed,[14] to be in the fall-off regime at the total pressures employed, the OH radical addition reaction (a) was observed to be more dependent on pressure than was the $HOCH_2\dot{C}H_2$ decomposition reaction (b),

$$OH + C_2H_4 \underset{b}{\overset{a}{\rightleftarrows}} HOCH_2\dot{C}H_2$$

in apparent violation of detailed balancing. Under the temperature and pressure conditions employed, a $HOCH_2\dot{C}H_2$ radical decomposition rate constant of $k(HOCH_2\dot{C}H_2 \rightarrow OH + C_2H_4) = 6.2 \times 10^{11}\ e^{-(11900 \pm 400)/T}$ s^{-1} was derived.[14] It should be noted, however, that this rate constant is in the fall-off regime.

Propene. The rate constant determined by Nielsen *et al.*[2] at 298 ± 2 K and one atmosphere total pressure of argon diluent of $(3.01 \pm 0.42) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} is in reasonable agreement with that of 2.63×10^{-11} cm^3 molecule^{-1} s^{-1} recommended by Atkinson[1] for 298 K and one atmosphere total pressure of air. The absolute rate constants measured by Liu *et al.*[11,12] at 760 Torr total pressure of argon (shown graphically and not tabulated[11,12]) are in good agreement with the recommendation of Atkinson[1] over the temperature range 323–500 K, where the reaction proceeds predominantly by OH radical addition at atmospheric pressure.

The rate constants determined by Liu *et al.*[11,12] at temperatures >625 K and by Bott and Cohen[3] at 1204 ± 16 K are plotted in Arrhenius form in Fig. 29, together with the absolute rate constants of Smith *et al.*[21] and Tully and Goldsmith.[22] Also shown is the recommendation of Atkinson[1] for the H-atom abstraction rate constant (which was based on the data of Tully and Goldsmith[22]). It can be seen that the rate constant of Bott and Cohen[3] is in good agreement with the rate constants of Liu *et al.*[11,12] (which were presented graphically and not tabulated), but that the rate constants from these studies[3,11,12] are significantly higher than those determined by Smith *et al.*[21] and Tully and Goldsmith,[22] although the discrepancies between these studies[3,11,12,21,22] decrease as the temperature increases. The previous recommendations of Atkinson[1] are unchanged.

1-Butene. Rate constants have been determined over the temperature range 478–873 K at 760 Torr total pressure of argon diluent by Liu *et al.*[11,12] (these data are shown graphically, and not tabulated). The rate constant of Liu *et al.*[11,12] at 478 K of 1.6×10^{-11} cm^3 molecule^{-1} s^{-1} is in good agreement with that of 1.74×10^{-11} cm^3 molecule^{-1} s^{-1} calculated from the recommended limiting high-pressure rate constant expression of Atkinson.[1] The rate constants decrease with increasing temperature over the range 478–673 K,[11,12] as expected[1] for a predominantly OH radical addition reaction with some fall-off behavior at the higher temperatures. Above 650 K the rate constants increase with increasing temperature,[11,12] but are significantly higher (by a factor of ~1.3–1.5) than those of Tully[16] measured over the temperature range 650–833 K (although they do appear to extrapolate to the rate constant determined by Smith[15] at 1225 K).

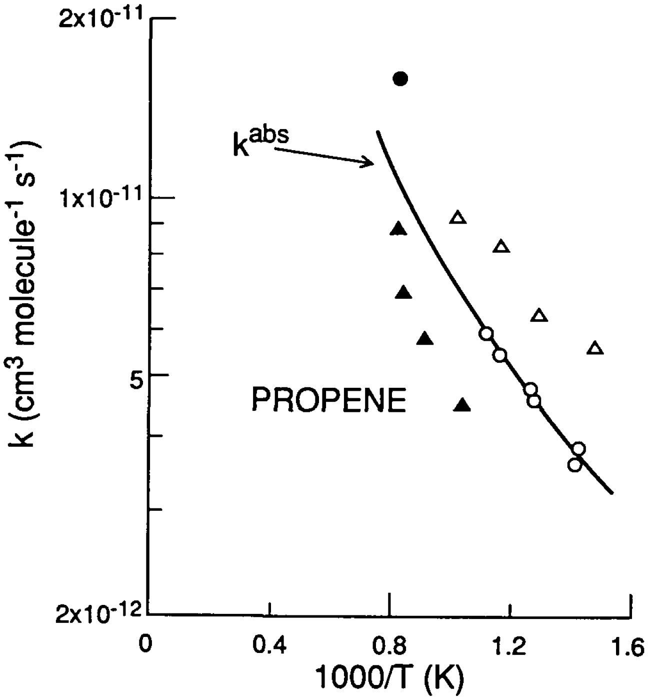

FIG. 29. Arrhenius plot of absolute rate constants for the reaction of the OH radical with propene at temperatures >625 K. (▲) Smith *et al.*;[21] (○) Tully and Goldsmith;[22] (△) Liu *et al.*[11,12] (taken from data presented graphically); (●) Bott and Cohen;[3] (—) recommendation of Atkinson[1] for the H-atom abstraction reaction.

2,3-Dimethyl-2-butene. The rate constants measured at room temperature by Atkinson *et al.*,[5,6] Corchnoy and Atkinson[7] and Atkinson and Aschmann,[8] relative to the rate constant for the reaction of the OH radical with isoprene (2-methyl-1,3-butadiene), are in excellent agreement with the recommended rate constant of Atkinson[1] of 1.10×10^{-10} cm^3 molecule^{-1} s^{-1} at 298 K.

Cyclohexene. The rate constant determined by Nielsen *et al.*[2] at 298 ± 2 K and one atmosphere total pressure of $(6.18 \pm 0.81) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} is in agreement with that of 6.77×10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K recommended by Atkinson.[1]

Other Alkenes. The rate constant measurements for *trans*-2-heptene,[9] *trans*-4-octene[9] and the monoterpenes camphene,[6] 2-carene,[7] β-phellandrene,[10] sabinene[6] and terpinolene[7] are the first reported, and hence no recommendations are made. The room temperature rate constants for *trans*-2-heptene and *trans*-4-octene determined relative to the OH radical reaction rate constants for propene and *trans*-2-butene[9] lead to a rate constant ratio of k(*trans*-2-butene)/k(propene) in excellent agreement (within 2%) with the previous recommendations.[1]

TABLE 38. Rate constants k at, or close to, the high pressure limit for the gas-phase reactions of the OH radical with alkenes

Alkene	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference
Ethene	9.4 ± 1.6	298 ± 2	PR-RA	Nielsen *et al.*[2]
	4.38 ± 0.66	1197 ± 16	SH-RA	Bott and Cohen[3]
	7.7 ± 1.0	298 ± 2	LP-LIF	Becker *et al.*[4]
Propene	30.1 ± 4.2	298 ± 2	PR-RA	Nielsen *et al.*[2]
	15.9 ± 2.4	1204 ± 16	SH-RA	Bott and Cohen[3]
2,3-Dimethyl-2-butene	107 ± 3	296 ± 2	RR [relative to k(2-methyl-1,3-butadiene) = 1.01×10^{-10}][a]	Atkinson *et al.*[5]
	111 ± 3	296 ± 2	RR [relative to k(2-methyl-1,3-butadiene) = 1.01×10^{-10}][a]	Atkinson *et al.*[6]
	111 ± 5	295 ± 2	RR [relative to k(2-methyl-1,3-butadiene) = 1.02×10^{-10}][a]	Corchnoy and Atkinson[7]
	106 ± 4	296 ± 2	RR [relative to k(2-methyl-1,3-butadiene) = 1.01×10^{-10}][a]	Atkinson and Aschmann[8]
trans-2-Heptene	67.4 ± 2.4	297 ± 2	RR [relative to k(propene) = 2.65×10^{-11}][a]	O'Rji and Stone[9]
	69.1 ± 5.3	297 ± 2	RR [relative to k(*trans*-2-butene) = 6.44×10^{-11}][a]	O'Rji and Stone[9]
trans-4-Octene	68.2 ± 5.1	297 ± 2	RR [relative to k(propene) = 2.65×10^{-11}][a]	O'Rji and Stone[9]
	69.7 ± 3.0	297 ± 2	RR [relative to k(*trans*-2-butene) = 6.44×10^{-11}][a]	O'Rji and Stone[9]
Cyclohexene	61.8 ± 8.1	298 ± 2	PR-RA	Nielsen *et al.*[2]
Camphene	53.3 ± 2.0	296 ± 2	RR [relative to k(2-methyl-1,3-butadiene) = 1.01×10^{-10}][a]	Atkinson *et al.*[6]
2-Carene	79.5 ± 2.4	295 ± 2	RR [relative to k(2-methyl-1,3-butadiene) = 1.02×10^{-10}][a]	Corchnoy and Atkinson[7]
β-Phellandrene	168 ± 23	297 ± 2	RR [relative to k(2,3-dimethyl-2-butene) = 1.11×10^{-10}][a]	Shorees *et al.*[10]
Sabinene	117 ± 5	296 ± 2	RR [relative to k(2-methyl-1,3-butadiene) = 1.01×10^{-10}][a]	Atkinson *et al.*[6]
Terpinolene	225 ± 10	295 ± 2	RR [relative to k(2-methyl-1,3-butadiene) = 1.02×10^{-10}][a]	Corchnoy and Atkinson[7]

[a] From previous evaluation.[1]

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3.4. Haloalkenes

The rate constants reported for the reactions of the OH radical with haloalkenes since the review of Atkinson[1] are given in Table 39.

Vinyl Chloride. The absolute rate constants determined by Liu *et al*.[2,6,7] at 760 Torr total pressure of argon diluent are given in Table 39, and are plotted, together with the rate constants of Perry *et al*.,[8] in Arrhenius form in Fig. 30. The temperature dependence of the rate constant is similar to that for ethene and other simple alkenes,[1] with the measured rate constant decreasing with increasing temperature over the range ~298–590 K, decreasing rapidly (by a factor of ~2) over the narrow temperature range ~590–720 K, and then increasing with increasing temperature above ~720 K. By analogy with the alkenes,[1] and as expected,[1] this behavior indicates that at temperatures ≤500 K the OH radical reaction with $CH_2=CHCl$ involves initial OH radical addition

$$OH + CH_2=CHCl \rightleftarrows HOCH_2CHCl^*$$

$$HOCH_2CHCl^* + M \rightarrow HOCH_2CHCl + M$$

with the addition adduct decomposing back to reactants or being collisionally stabilized. At temperatures ≳500–600 K, the addition adduct undergoes thermal decomposition, and above ~650 K the reaction observed is that for H-atom abstraction

$$OH + CH_2=CHCl \rightarrow H_2O + \dot{C}_2H_2Cl$$

Over the temperature range 299–423 K the rate constants measured by Perry *et al*.[8] and Liu *et al*.[2,6,7] are in good agreement, indicating that the rate constant is at, or close to, the high-pressure second-order limit at total pressures of argon ≥50 Torr.[1,8] By analogy with the rate constants for the reactions of the OH radical with alkenes,[1] rate constants at temperatures ≤ 500 K have been used in the evaluation of the low-temperature OH radical addition rate constant for this reaction. A unit-weighted least-squares analysis of the rate constants of Perry *et al*.[8] and Liu *et al*.[2] yields the recommended Arrhenius expression of

$$k(CH_2=CHCl) = (1.69^{+1.12}_{-0.67}) \times 10^{-12}\, e^{(422 \pm 188)/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 299–473 K, where the indicated errors are two least-squares standard deviations, and

$$k(CH_2=CHCl) = 6.96 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

with an estimated overall uncertainty at 298 K of ±30%.

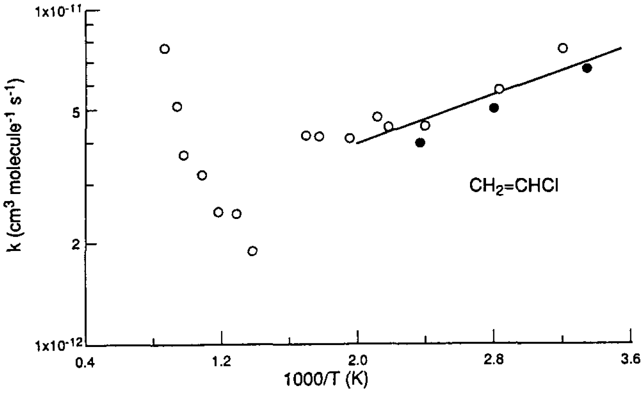

FIG. 30. Arrhenius plot of rate constants for the reaction of the OH radical with $CH_2=CHCl$ at, or close to, the high-pressure limit. (●) Perry *et al*.;[8] (○) Liu *et al*.;[2] (—) recommendation (see text).

At temperatures ≥723 K, the measured rate constant increases with increasing temperature,[2,6,7], and at 1173 K the measured rate constant is of a similar magnitude as that at 313 K.[2] Since only a single study has been carried out at temperatures >700 K, where the measured rate constants appear to be those for H-atom abstraction, no recommendation is made for this temperature region.

1,1-Dichloroethene. The absolute rate constants, or temperature-dependent rate expressions, reported by Kirchner *et al*.,[3] Zhang *et al*.[4] and Abbatt and Anderson[5] are given in Table 39. These rate constants are plotted, together with the relative rate constants of Edney *et al*.[9] and Tuazon *et al*.,[10] in Arrhenius form in Fig. 31 (for the study of Kirchner *et al*.[3] only the reported 300 K rate constant and the reported Arrhenius expression can be plot-

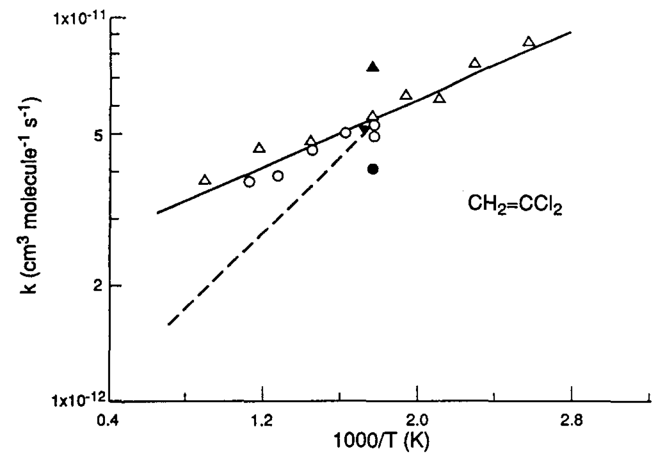

FIG. 31. Arrhenius plot of rate constants for the reaction of the OH radical with $CH_2=CCl_2$. (▲) Edney *et al.*;[9] (●) Tuazon *et al.*;[10] (△) Zhang *et al.*;[4] (○) Abbatt and Anderson;[5] (– – and ▼) Kirchner *et al.*;[3] (—) recommendation (see text).

ted, since the individual rate constants at the temperatures studied were not tabulated[3]). It can be seen from Fig. 31 that the absolute rate constants of Zhang *et al.*[4] and Abbatt and Anderson[5] are in good agreement, and that at 300 K the rate constants from these two studies[4,5] are in agreement with that reported by Kirchner *et al.*[3] However, at elevated temperatures the rate constants of Kirchner *et al.*,[3] measured at a total pressure of ~1–3 Torr, are significantly lower than those of Zhang *et al.*[4] and Abbatt and Anderson[5] measured at total pressures of 35 Torr and 26–85 Torr, respectively, and it is possible that this indicates that the rate constant for this reaction at ~1–3 Torr total pressure moves increasing into the fall-off regime as the temperature increases. The relative room temperature rate constants reported by Edney *et al.*[9] and Tuazon *et al.*[10] are ~30% higher and lower, respectively, than the absolute rate constants of Kirchner *et al.*,[3] Zhang *et al.*[4] and Abbatt and Anderson.[5] These discrepancies may be caused, in part, through the involvement of secondary reactions of Cl atoms produced in the primary reactions, although efforts were made[9,10] to eliminate or take into account these secondary reactions of Cl atoms.

A unit-weighted least-squares analysis of the absolute rate constants of Zhang *et al.*[4] and Abbatt and Anderson[5] yields the recommended Arrhenius expression of

$$k(CH_2=CCl_2) = (2.00^{+0.63}_{-0.47}) \times 10^{-12}\, e^{(506 \pm 82)/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 240–400 K, where the indicated errors are two least-squares standard deviations, and

$$k(CH_2=CCl_2) = 1.09 \times 10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

with an estimated overall uncertainty at 298 K of ±40%. This reaction proceeds by initial OH radical addition.[1]

cis-CHCl=CHCl. The absolute rate constants measured by Zhang *et al.*[4] and Abbatt and Anderson[5] are given in Table 39, and are plotted together with the relative rate constant of Tuazon *et al.*[10] in Fig. 32. The agreement is good, and a unit-weighted least-squares analysis of the absolute rate constants of Zhang *et al.*[4] and Abbatt and Anderson[5] yields the recommended Arrhenius expression of

$$k(cis\text{-}CHCl=CHCl) = (1.94^{+0.81}_{-0.57}) \times 10^{-12}\, e^{(90 \pm 108)/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 240–400 K, where the indicated errors are two least-squares standard deviations, and

$$k(cis\text{-}CHCl=CHCl) = 2.62 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

with an estimated overall uncertainty at 298 K of ±40%. The room temperature relative rate constant of Tuazon *et al.*[10] is in good agreement with this recommendation.

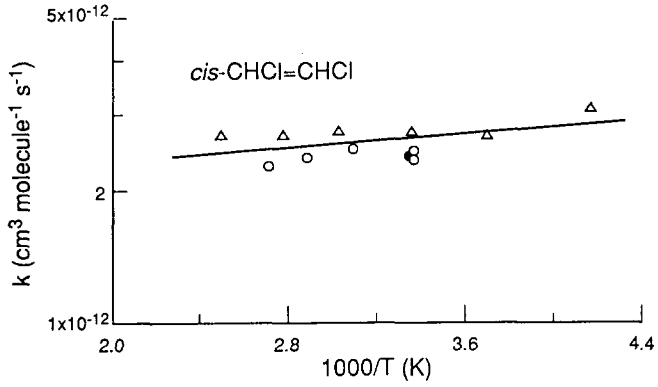

FIG. 32. Arrhenius plot of rate constants for the reaction of the OH radical with *cis*-$CHCl=CHCl$. (●) Tuazon *et al.*;[10] (△) Zhang *et al.*;[4] (○) Abbatt and Anderson;[5] (—) recommendation (see text).

trans-CHCl=CHCl. The absolute rate constants of Zhang *et al.*[4] and Abbatt and Anderson[5] are given in Table 39 and are plotted, together with the relative rate constant of Tuazon *et al.*,[10] in Arrhenius form in Fig. 33. The agreement is reasonable, and a unit-weighted least-squares analysis of the rate constants of Zhang *et al.*[4] and Abbatt and Anderson[5] yields the recommended Arrhenius expression of

$$k(trans\text{-}CHCl=CHCl) = (1.01^{+0.39}_{-0.28}) \times 10^{-12}\, e^{(250 \pm 100)/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 240–400 K, where the indicated errors are two least-squares standard deviations, and

TABLE 39. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with haloalkenes

Haloalkene	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	n	B (K)	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
$CH_2=CHCl$				7.55 ± 0.76	313	PR-RA	Liu *et al.*[2]	313–1173
				5.70 ± 0.57	353			
				4.46 ± 0.45	418			
				4.40 ± 0.40	458			
				4.74 ± 0.48	473			
				4.10 ± 0.41	513			
				4.16 ± 0.42	563			
	2.14		−352 ± 61 (313–588 K)	4.18 ± 0.42	588			
				1.90 ± 0.19	723			
				2.43 ± 0.25	773			
				2.48 ± 0.25	873			
				3.20 ± 0.32	923			
				3.67 ± 0.37	1033			
				5.10 ± 0.51	1073			
	1.4×10^{-5}	2	1200 (723–1173 K)	7.62 ± 0.77	1173			
$CH_2=CCl_2$	0.226 ± 0.027		−1143 ± 49	10.2 ± 1.2	300	DF-MS	Kirchner *et al.*[3]	298–432
				17.2 ± 0.9	240	FP-RF	Zhang *et al.*[4]	240–400
				15.1 ± 1.1	258			
				12.3 ± 0.5	270			
				12.6 ± 0.7	283			
				11.2 ± 0.6	298			
				9.60 ± 0.92	330			
				9.19 ± 0.87	360			
	2.30 ± 0.44		−472 ± 105	7.60 ± 1.43	400			
				9.86 ± 0.45	297 ± 2	DF-LIF	Abbatt and Anderson[5]	297–368
				10.6 ± 0.8	297 ± 2			
				10.0 ± 0.7	310			
				9.11 ± 0.62	328			
				7.81 ± 0.62	348			
	1.6 ± 0.6		−560 ± 110	7.57 ± 0.65	368			
cis-$CHCl=CHCl$				3.09 ± 0.22	240	FP-RF	Zhang *et al.*[4]	240–400
				2.67 ± 0.14	270			
				2.71 ± 0.28	298			
				2.75 ± 0.18	330			
				2.68 ± 0.31	360			
	2.21 ± 0.34		−65 ± 89	2.69 ± 0.36	400			

TABLE 39. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with haloalkenes – Continued

Haloalkene	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	n	B (K)	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
				2.35 ± 0.10	297 ± 2	DF-LIF	Abbatt and Anderson[5]	297–367
				2.45 ± 0.08	297 ± 2			
				2.49 ± 0.10	322			
				2.38 ± 0.13	346			
	2.0 ± 0.5		−70 ± 120	2.28 ± 0.20	367			
trans-CHCl = CHCl				2.87 ± 0.11	240	FP-RF	Zhang *et al.*[4]	240–400
				2.80 ± 0.12	263			
				2.50 ± 0.30	298			
				2.11 ± 0.24	330			
				2.09 ± 0.28	350			
	0.937 ± 0.147		−283 ± 85	1.79 ± 0.48	400			
				1.99 ± 0.22	297 ± 2	DF-LIF	Abbatt and Anderson[5]	297–367
				2.20 ± 0.08	297 ± 2			
				2.27 ± 0.10	322			
				2.21 ± 0.14	346			
	2.1 ± 0.8		−20 ± 120	2.13 ± 0.15	367			
$CHCl = CCl_2$	0.780 ± 0.085		−241 ± 61	1.76 ± 0.17	300	DF-MS	Kirchner *et al.*[3]	300–459
$CCl_2 = CCl_2$	5.53 ± 0.32		1034 ± 13	0.173 ± 0.017	301	DF-MS	Kirchner *et al.*[3]	301–433
$CFCl = CCl_2$				7.57 ± 0.40	297 ± 2	DF-LIF	Abbatt and Anderson[5]	297–364
				6.44 ± 0.38	315			
				6.08 ± 0.44	338			
	1.0 ± 0.5		−590 ± 150	5.17 ± 0.37	364			
$CF_2 = CCl_2$				7.63 ± 0.37	297 ± 2	DF-LIF	Abbatt and Anderson[5]	297-365
				7.35 ± 0.23	297 ± 2			
				6.93 ± 0.35	310			
				6.54 ± 0.34	318			
				6.50 ± 0.33	328			
				5.91 ± 0.35	336			
				6.11 ± 0.40	349			
	1.5 ± 0.5		−480 ± 100	5.25 ± 0.34	365			

$$k(trans\text{-CHCl}=\text{CHCl}) = 2.34 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \text{ at } 298\ \text{K},$$

with an estimated overall uncertainty at 298 K of a factor of 1.5.

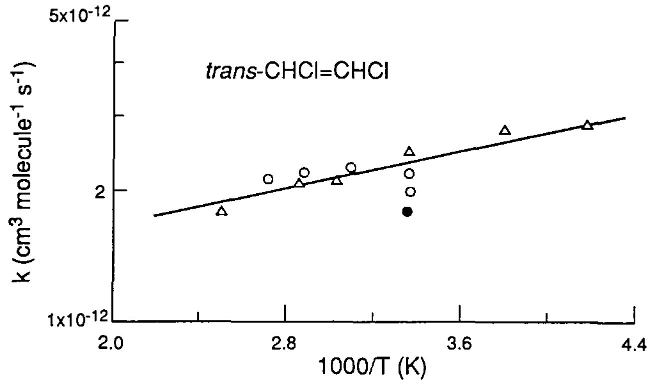

FIG. 33. Arrhenius plot of rate constants for the reaction of the OH radical with *trans*-CHCl=CHCl. (●) Tuazon et al;[10] (△) Zhang *et al.*;[4] (○) Abbatt and Anderson;[5] (—) recommendation (see text).

CHCl=CCl₂. The room temperature rate constant and Arrhenius expression of Kirchner *et al.*[3] are given in Table 39. This temperature dependent expression is significantly different to that recommended by Atkinson[1] of

$$k(\text{CHCl}=\text{CCl}_2) = 5.63 \times 10^{-13}\ e^{427/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 234–420 K, with

$$k(\text{CHCl}=\text{CCl}_2) = 2.36 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \text{ at } 298\ \text{K},$$

although the room temperature rate constant is in reasonable agreement with the recommendation of Atkinson.[1] This discrepancy is not due to the rate constants measured by Kirchner *et al.*[3] being in the fall-off regime, since the temperature dependence of Kirchner *et al.*[3] is less negative than the higher pressure data.[1] The previous recommendation[1] is unchanged.

$CCl_2=CCl_2$. The room temperature rate constant and Arrhenius expression reported by Kirchner *et al.*[3] are given in Table 39. In this case, the data of Kirchner *et al.*[3] are in good agreement (within 16% over the temperature range of 301–433 K studied[3]) with the recommendation of Atkinson[1] of

$$k(\text{CCl}_2=\text{CCl}_2) = 9.64 \times 10^{-12}\ e^{-1209/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 296–420 K, with

$$k(\text{CCl}_2=\text{CCl}_2) = 1.67 \times 10^{-13}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \text{ at } 298\ \text{K}.$$

This previous recommendation[1] is hence unchanged.

$CFCl=CCl_2$. The rate constants determined by Abbatt and Anderson[5] at total pressures of 10–85 Torr of N_2 are given in Table 39. These are the limiting high-pressure rate constants,[5] and the 297 K rate constant of $(7.57 \pm 0.40) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} is consistent with that of 7×10^{-12} cm^3 molecule^{-1} s^{-1} measured by Howard[11] at 296 K and 7 Torr total pressure of helium (and which was in the fall-off region between second- and third-order kinetics[11]).

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3.5. Alkynes

The kinetic data reported since the review and evaluation of Atkinson[1] are given in Table 40.

Acetylene. The room temperature rate constant of Arnts *et al.*,[2] obtained from a relative rate study, is in reasonable agreement with the recommended rate constant of Atkinson[1] of 8.15×10^{-13} cm^3 molecule^{-1} s^{-1} at 298 K and atmospheric pressure. The rate constants determined by Kaiser[3] from the time-concentration profiles of OH radicals and C_2H_2 in fuel-rich propane- and methane-air flames (Table 40) are within 10% of the previous recommendation of Atkinson[1] for the H-atom abstraction reaction, of

$$k^{\text{abs}} = 4.9 \times 10^{-18}\ T^2\ e^{-3600/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1},$$

while that measured by Bott and Cohen[4] at 1205 ± 16 K is 30% higher than calculated from the recommended H-atom abstraction expression of Atkinson[1] (see Fig. 34). Kaiser[3] concluded that the reaction proceeds by the formation of H + CH_2CO, although the H-atom abstraction pathway was not ruled out.

1,3-Butadiyne (Diacetylene). The rate constant of $(1.5 \pm 0.75) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} measured by Bartels *et al.*[5] at 295 K and ~1.5 Torr total pressure is in good agreement with the previous recommendation of Atkinson[1] of 1.89×10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K, based on the relative and absolute rate constants of Atkinson and Aschmann[8] and Perry.[9] This similarity between the low pressure (~1.5 Torr) data of Bartels *et al.*[5] and the higher pressure (50–735 Torr) data of Atkinson and Aschmann[8] and Perry[9] indicates that at room temperature the OH radical addition to 1,3-butadiyne is within a factor of 2 of the high-pressure limit at total pressures ≥1 Torr.

References

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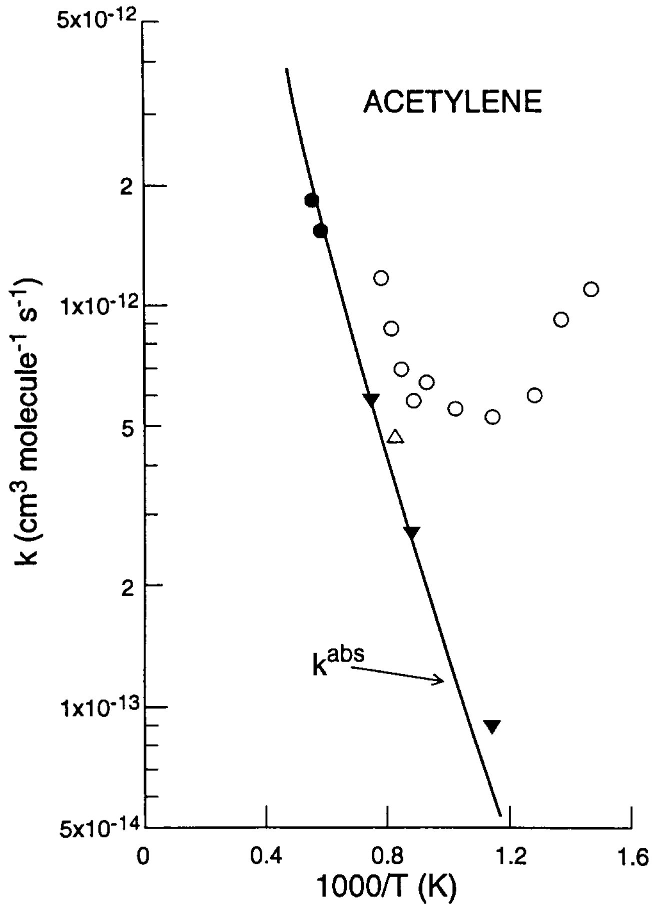


FIG. 34. Arrhenius plot of selected absolute rate constants for the reaction of the OH radical with acetylene at temperatures >625 K. (▼) Smith *et al.*[6] (the rate constant at 830 K was observed to be pressure dependent; the extrapolated zero pressure rate constant is plotted); (○) Liu *et al.*;[7] (●) Kaiser;[3] (△) Bott and Cohen;[4] (—) recommendation of Atkinson[1] for the H-atom abstraction process.

TABLE 40. Rate constants k for the gas-phase reactions of the OH radical with alkynes

Alkyne	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
Acetylene	0.721 ± 0.069	297 ± 2	RR [relative to k(ethane) = 2.54×10^{-13}][a]	Arnts *et al.*[2]	
	1.53 ± 0.25 1.83 ± 0.25 (H + CH_2CO)	1700 1770	Flame-RA	Kaiser[3]	1700-1770
	0.465 ± 0.070	1205 ± 16	SH-RA	Bott and Cohen[4]	
1,3-Butadiyne [CH≡CC≡CH]	15 ± 7.5	295	RR [relative to k(n-butane) = 2.50×10^{-12}][a]	Bartels *et al.*[5]	

[a] From present and previous[1] recommendations.

3.6. Oxygen-Containing Organics

The rate constants reported for the reactions of the OH radical with oxygen-containing organic compounds since the review and evaluation of Atkinson[1] are given in Table 41.

3.6.1. Aldehydes

Formaldehyde. The absolute rate constants determined by Yetter *et al.*[2] and Bott and Cohen[3] are given in Table 41 and are plotted in Arrhenius form in Fig. 35, together with the rate constants of Atkinson and Pitts,[33] Stief *et al.*,[34] Temps and Wagner,[35] Niki *et al.*[36] (for $^{13}CH_2O$) and Zabarnick *et al.*[37] The absolute rate constant of Bott and Cohen[3] at 1205 ± 16 K greatly entends the temperature range for which apparently reliable kinetic data are available for this reaction. The rate constants of Zabarnick *et al.*[37] exhibit a high degree of scatter and are uniformly higher than those of Atkinson and Pitts,[33] Stief *et al.*,[34] Temps and Wagner,[35] Niki *et al.*[36] and Yetter *et al.*[2] Accordingly, the absolute rate constants of Atkinson and Pitts,[33] Stief *et al.*,[34] Temps and Wagner,[35] Yetter *et al.*[2] and Bott and Cohen[3] and the relative rate constant of Niki *et al.*[36] are used in the evaluation of the rate constant for this reaction. Unit-weighted least-squares analyses of these data[2,3,33-36] have been carried out, using the three parameter expression $k = CT^n e^{-D/T}$ with $n = 1$ and $n = 2$, to obtain

$$k(\text{formaldehyde}) = (8.24^{+2.59}_{-1.98}) \times 10^{-18} T^2 e^{(753 \pm 86)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

with $n = 2$, and

$$k(\text{formaldehyde}) = (1.20^{+0.33}_{-0.26}) \times 10^{-14} T e^{(287 \pm 74)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

with $n = 1$, both over the temperature range 228–1205 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{formaldehyde}) = 9.16 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K } (n = 2), \text{ and}$$

$$k(\text{formaldehyde}) = 9.37 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K } (n = 1),$$

with an estimated overall uncertainty at 298 K of ±25%. While previous recommendations for OH radical reactions over extended temperature ranges[1] have generally used the expression $k = CT^2 e^{-D/T}$, inspection of Fig. 35 indicates that this expression predicts excessive curvature in the Arrhenius plot compared to the experimental data, and that the expression $k = CT e^{-D/T}$ provides a much better match between the predicted and experimental rate constants. It is therefore recommended for the OH radical reaction with formaldehyde that

$$k(\text{formaldehyde}) = 1.20 \times 10^{-14} T e^{287/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 228–1205 K, and

$$k(\text{formaldehyde}) = 9.37 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K},$$

with an estimated overall uncertainty at 298 K of ±25%. This recommendation supersedes that of Atkinson[1] of

$$k(\text{formaldehyde}) = 1.25 \times 10^{-17} T^2 e^{648/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the more restricted temperature range 228–426 K, with a 298 K rate constant of 9.77×10^{-12} cm^3 molecule^{-1} s^{-1}.

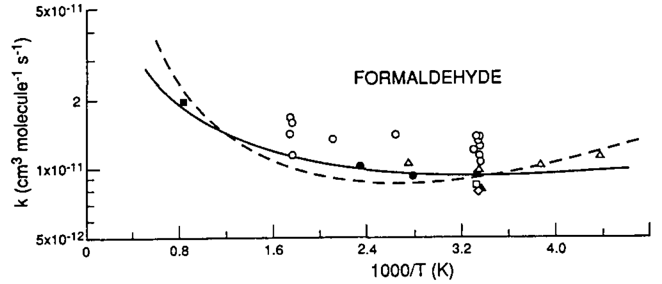


FIG. 35. Arrhenius plot of selected rate constants for the reaction of the OH radical with formaldehyde. (●) Atkinson and Pitts;[33] (△) Stief *et al.*;[34] (▲) Temps and Wagner;[35] (□) Niki *et al.*[36] (for formaldehyde-^{13}C); (○) Zabarnick *et al.*;[37] (◇) Yetter *et al.*;[2] (■) Bott and Cohen;[3] (—) recommendation using expression $k = CT e^{-D/T}$ (see text); (- - -) fit to same data set using the expression $k = CT^2 e^{-D/T}$ (see text).

Yetter *et al.*[2] showed that the OH radical reaction with HCHO proceeds essentially totally (97^{+3}_{-10}%) by the H-atom abstraction channel,

$$OH + HCHO \rightarrow H_2O + H\dot{C}O$$

in agreement with previous product data.[1]

Acetaldehyde. The rate constants measured by Dóbé *et al.*,[4] Balestra-Garcia *et al.*[5] and Scollard *et al.*[6] are given in Table 41. These rate constants[4-6] are in excellent agreement with the previous recommendation of Atkinson.[1] While the rate constants of Dóbé *et al.*[4] for acetaldehyde agree with the previous literature data,[1] this is not the case for the data of Dóbé *et al.*[4] for 2-methyl-1-propanal or 2,2-dimethyl-1-propanal, which are both a factor of ~1.8 higher than the previous data of Kerr and Sheppard[38] and Semmes *et al.*[39] The previous recommendation of Atkinson[1] for the reaction of the OH radical with acetaldehyde of

$$k(\text{acetaldehyde}) = 5.55 \times 10^{-12} e^{311/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 244–528 K, with a 298 K rate constant of 1.58×10^{-11} cm^3 molecule^{-1} s^{-1}, is hence unchanged.

2-Methyl-1-propanal and 2,2-Dimethyl-1-propanal. As noted above, the rate constants of Dóbé *et al.*[4] for these two aldehydes, given in Table 41, are a factor of ~1.8

higher than the previous literature data.[1,38,39] The previous[1] recommendations are unchanged.

Trifluoroacetaldehyde. The room temperature rate constants of Dóbé *et al.*[4] and Scollard *et al.*[6] are given in Table 41. These rate constants disagree by a factor of 2. It is tentatively recommended that the rate constant of Scollard *et al.*[6] be used, with

$$k(\mathrm{CF_3CHO}) = 5.3 \times 10^{-13}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}\ at\ 298\ K},$$

and with an estimated overall uncertainty of a factor of 2. This reaction will proceed by H-atom abstraction from the -CHO group

$$\mathrm{OH + CF_3CHO \rightarrow H_2O + CF_3\dot{C}O}$$

Chloroacetaldehyde (CH_2ClCHO) and Dichloroacetaldehyde ($CHCl_2CHO$). The rate constants of Starcke *et al.*,[9] Balestra-Garcia *et al.*[5] and Scollard *et al.*,[6] all obtained at room temperature, are given in Table 41. The agreement between these three studies[5,6,9] is good, and unit-weighted averages of these data[5,6,9] lead to the recommended 298 K rate constants of

$$k(\mathrm{CH_2ClCHO}) = 3.1 \times 10^{-12}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}},\ \text{and}$$

$$k(\mathrm{CHCl_2CHO}) = 2.5 \times 10^{-12}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}},$$

both with an estimated overall uncertainty of ±40%. At room temperature, these OH radical reactions proceed almost entirely by H-atom abstraction from the -CHO group, for example

$$\mathrm{OH + CHCl_2CHO \rightarrow H_2O + CHCl_2\dot{C}O}$$

Trichloroacetaldehyde (CCl_3CHO). The rate constants of Dóbé *et al.*,[4] Starcke *et al.*,[9] Nelson *et al.*,[8] Balestra-Garcia *et al.*[5] and Scollard *et al.*[6] are given in Table 41. The absolute rate constant of Balestra-Garcia *et al.*[5] is a factor of ~1.9 lower than most of the other room temperature rate constants (Table 41). A unit-weighted average of the room temperature rate constants of Starcke *et al.*,[9] Nelson *et al.*,[8] Balestra-Garcia *et al.*[5] and Scollard *et al.*[6] yields the recommendation of

$$k(\mathrm{CCl_3CHO}) = 1.3 \times 10^{-12}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}\ at\ 298\ K},$$

with an estimated overall uncertainty of a factor of 2. This reaction proceeds by H-atom abstraction from the -CHO group

$$\mathrm{OH + CCl_3CHO \rightarrow H_2O + CCl_3\dot{C}O}\ .$$

3.6.2. Ketones

Acetone. The absolute rate constant determined by Bott and Cohen[10] at 1217 K is given in Table 41. This measurement[10] significantly expands the temperature range over which rate constant data are available. The absolute rate constants of Wallington and Kurylo[40] and Bott and Cohen[10] and the relative rate constant of Kerr and Stocker[41] are plotted in Arrhenius form in Fig. 36. A unit-weighted least-squares analysis of these data,[10,40,41] using the expression $k = CT^2\,e^{-D/T}$, leads to the recommendation of

$$k(\mathrm{acetone}) = (5.34^{+4.15}_{-2.33}) \times 10^{-18}\ T^2\ e^{-(230 \pm 196)/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the temperature range 240–1217 K, where the indicated errors are two least-squares standard deviations, and

$$k(\mathrm{acetone}) = 2.19 \times 10^{-13}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}\ at\ 298\ K},$$

with an estimated overall uncertainty at 298 K of ±35%.

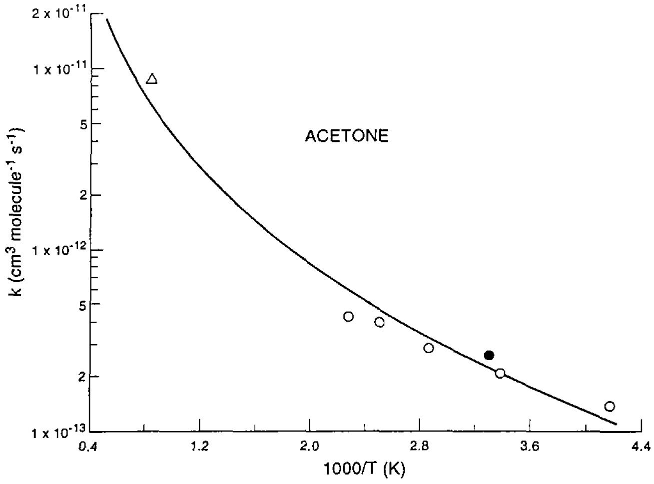


FIG. 36. Arrhenius plot of selected rate constants for the reaction of the OH radical with acetone. (●) Kerr and Stocker;[41] (○) Wallington and Kurylo;[40] (△) Bott and Cohen;[10] (—) recommendation (see text).

This recommendation supersedes, and is significantly different at temperatures other than ~298 K, than the previous recommendation of Atkinson[1] of

$$k(\mathrm{acetone}) = 2.13 \times 10^{-18}\ T^2\ e^{53/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the much more restricted temperature range 240–440 K, with a 298 K rate constant of 2.26 × 10^{-13} cm^3 $molecule^{-1}$ s^{-1}.

4-Methyl-2-pentanone. The rate constants obtained by O'Rji and Stone[12] from a relative rate study are given in Table 41. These rate constants agree with the previous recommendation of Atkinson[1] of

$$k(\text{4-methyl-2-pentanone}) = 1.41 \times 10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}\ at\ 298\ K},$$

which is therefore unchanged.

TABLE 41. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with oxygen-containing organics

Oxygenate	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
Aldehydes							
Formaldehyde			$7.95^{+2.04}_{-1.44}$	298	DF-RF	Yetter *et al.*[2]	
			19.4 ± 3.0	1205 ± 16	SH-RA	Bott and Cohen[3]	
Acetaldehyde			15.6	297	DF-RF/LIF	Dóbé *et al.*[4]	297–517
			16.9 ± 3.4	298 ± 2			
			13.8	303			
			15.1 ± 3.2	390 ± 6			
			13.8 ± 2.7	423 ± 3			
			13.5 ± 2.7	467 ± 8			
			11.8	508			
	8.6 ± 1.9	−200 ± 60	12.8	517			
			17 ± 3	298	LP-RF	Balestra-Garcia *et al.*[5]	
			16.2 ± 1	298 ± 2	RR [relative to k(ethene) $= 8.52 \times 10^{-12}$][a]	Scollard *et al.*[6]	
2-Methyl-1-propanal			46.3 ± 7.4	298 ± 2	DF-RF	Dóbé *et al.*[4]	298–519
			44.2	300			
			39.7 ± 6.4	349 ± 2			
			36.0	355			
			32.7 ± 8.0	420 ± 3			
			33.5	447			
			32.5 ± 6.2	452 ± 4			
			40.5 ± 6.2	471 ± 3			
	15.8 ± 5.0	−320 ± 130 (298–420 K)	43.8 ± 6.0	519 ± 3			
2,2-Dimethyl-1-propanal			51.6 ± 13.7	300 ± 2	DF-RF	Dóbé *et al.*[4]	300–405
			40.2 ± 15.2	386 ± 4			
	13.3 ± 6.7	−410 ± 205	33.2	405			
Formyl chloride [HC(O)Cl]			≤0.32	299.2	RR [relative to k(n-butane) $= 2.55 \times 10^{-12}$][a]	Libuda *et al.*[7]	
Phosgene [$COCl_2$]			<0.001	298 ± 3	RR[b]	Nelson *et al.*[8]	
Trifluoro-acetaldehyde [CF_3CHO]			1.11 ± 0.54	299 ± 3	DF-RF	Dóbé *et al.*[4]	
			0.53 ± 0.05	298 ± 2	RR [relative to k(acetone) $= 2.19 \times 10^{-13}$][a]	Scollard *et al.*[6]	

TABLE 41. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with oxygen-containing organics — Continued

Oxygenate	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
CF_2ClCHO			0.70 ± 0.05	298 ± 2	RR [relative to k(ethanol) = 3.27×10^{-12}]^a	Scollard *et al.*[6]	
$CFCl_2CHO$			1.1 ± 0.1	298 ± 2	RR [relative to k(ethanol) = 3.27×10^{-12}]^a	Scollard *et al.*[6]	
Chloroacetaldehyde [CH_2ClCHO]			3.2	300	RR [relative to k(n-butane) = 2.56×10^{-12}]^a	Starcke *et al.*[9]	
			3.0 ± 0.6	298	LP-RF	Balestra-Garcia *et al.*[5]	
			3.1 ± 0.2	298 ± 2	RR [relative to k(2-butanone) = 1.15×10^{-12}]^a	Scollard *et al.*[6]	
Dichloroacetaldehyde [$CHCl_2CHO$]			~2.8	300	RR [relative to k(n-butane) = 2.56×10^{-12}]^a	Starcke *et al.*[9]	
			2.4 ± 0.5	298	LP-RF	Balestra-Garcia *et al.*[5]	
			2.3 ± 0.1	298 ± 2	RR [relative to k(2-butanone) = 1.15×10^{-12}]^a	Scollard *et al.*[6]	
Trichloroacetaldehyde [CCl_3CHO]			1.61	298	DF-RF/LIF	Dóbé *et al.*[4]	298–520
			1.56 ± 0.25	300 ± 3			
			1.69 ± 0.52	304 ± 4			
			2.13 ± 0.22	339 ± 4			
			2.47 ± 0.47	391 ± 3			
			2.91 ± 0.37	449 ± 3			
			3.29	483			
	11.8 ± 2.5	600 ± 90	3.94 ± 1.10	520 ± 5			
			~1.2	300	RR [relative to k(n-butane) = 2.56×10^{-12}]^a	Starcke *et al.*[9]	
			1.63 ± 0.29	298 ± 3	RR [relative to k(ethyl acetate) = 1.6×10^{-12}]^a	Nelson *et al.*[8]	
			0.86 ± 0.17	298	LP-RF	Balestra-Garcia *et al.*[5]	
			1.6 ± 0.2	298 ± 2	RR [relative to k(toluene) = 5.96×10^{-12}]^a	Scollard *et al.*[6]	

TABLE 41. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with oxygen-containing organics – Continued

Oxygenate	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
Acetyl chloride [$CH_3C(O)Cl$]			0.0091 ± 0.0032[c]	298 ± 3	RR [relative to k(trichloromethane) = 1.03×10^{-13}][a]	Nelson *et al.*[8]	
Ketones							
Acetone			8.80 ± 1.32	1217	SH-RA	Bott and Cohen[10]	
Acetone-d_6			0.0358 ± 0.0029	298	FP-RF	Wallington *et al.*[11]	
1,1,1-Trifluoroacetone			0.0151 ± 0.0013	298	FP-RF	Wallington *et al.*[11]	
4-Methyl-2-pentanone			14.1 ± 0.8	297 ± 2	RR [relative to k(propene) = 2.65×10^{-11}][a]	O'Rji and Stone[12]	
			14.1 ± 0.7	297 ± 2	RR [relative to k(*trans*-2-butene) = 6.44×10^{-11}][a]	O'Rji and Stone[12]	
6,6-Dimethylbicyclo-[3.1.1]heptan-2-one (nopinone)			15	d	RR[b]	Hatakeyama[13]	
			14.3 ± 0.8	296 ± 2	RR [relative to k(cyclohexane) = 7.45×10^{-12}][a]	Atkinson and Aschmann[14]	
3,3-Dimethylbicyclo-[2.2.1]heptan-2-one (camphenilone)			5.15 ± 0.63	296 ± 2	RR [relative to k(cyclohexane) = 7.45×10^{-12}][a]	Atkinson and Aschmann[14]	
4-Acetyl-1-methylcyclohexene			129 ± 6	296 ± 2	RR [relative to k(2-methyl-1,3-butadiene) = 1.01×10^{-10}][a]	Atkinson and Aschmann[14]	
Ketenes							
Ketene [CH_2CO]			106 ± 20	193	DF-RF	Brown *et al.*[15]	193–423
			89 ± 27	204			
			46 ± 16	234			
			55 ± 10	269			
			33 ± 6	298			
			22 ± 5	373			
	6.2^{+10}_{-4}	−510 ± 420	21 ± 2	423			
			12.0 ± 3.4	296	DF-LMR	Oehlers *et al.*[16]	

TABLE 41. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with oxygen-containing organics – Continued

Oxygenate	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
Alcohols							
Methanol			0.88 ± 0.18	298	PR-RA	Pagsberg *et al.*[17]	
			0.90 ± 0.09	298 ± 2	PR-RA	Nelson *et al.*[18]	
			1.00 ± 0.23	298 ± 2	RR [relative to k(cyclohexane) = 7.49×10^{-12}][a]	Nelson *et al.*[18]	
			8.64 ± 1.30	1205 ± 16	SH-RA	Bott and Cohen[3]	
Methanol-d_4 [CD_3OD]			0.323 ± 0.002	298	FP-RF	Wallington *et al.*[11]	
Ethanol			3.04 ± 0.25	298 ± 2	PR-RA	Nelson *et al.*[18]	
			3.46 ± 0.52	298 ± 2	RR [relative to k(cyclohexane) = 7.49×10^{-12}][a]	Nelson *et al.*[18]	
			8.80 ± 1.32	1204 ± 16	SH-RA	Bott and Cohen[3]	
Ethanol-d_6 [CD_3CD_2OD]			1.15 ± 0.09	298	FP-RF	Wallington *et al.*[11]	
2-Chloroethanol [$ClCH_2CH_2OH$]			1.28 ± 0.09	298	FP-RF	Wallington *et al.*[11]	
2,2,2-Trifluoroethanol [CF_3CH_2OH]			0.0955 ± 0.0071	298	FP-RF	Wallington *et al.*[11]	
2,2,2-Trichloroethanol [CCl_3CH_2OH]			0.245 ± 0.024	298	FP-RF	Wallington *et al.*[11]	
1-Propanol			5.64 ± 0.48	298 ± 2	PR-RA	Nelson *et al.*[18]	
			5.50 ± 0.44	298 ± 2	RR [relative to k(cyclohexane) = 7.49×10^{-12}][a]	Nelson *et al.*[18]	
			5.84 ± 0.24	293	LP-LIF	Tully[19]	

TABLE 41. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with oxygen-containing organics – Continued

Oxygenate	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
2-Propanol			5.69 ± 1.09	298 ± 2	PR-RA	Nelson *et al.*[18]	
			5.78 ± 0.75	298 ± 2	RR [relative to k(cyclohexane) = 7.49 × 10^{-12}][a]	Nelson *et al.*[18]	
			5.10 ± 0.21	293	LP-LIF	Tully[19]	
1-Butanol			7.80 ± 0.20	298 ± 2	PR-RA	Nelson *et al.*[18]	
			8.56 ± 0.70	298 ± 2	RR [relative to k(cyclohexane) = 7.49 × 10^{-12}][a]	Nelson *et al.*[18]	
			9.60 ± 0.41	293	LP-LIF	Tully[19]	
1-Pentanol			12.0 ± 1.6	298 ± 2	PR-RA	Nelson *et al.*[18]	
			10.5 ± 1.3	298 ± 2	RR [relative to k(cyclohexane) = 7.49 × 10^{-12}][a]	Nelson *et al.*[18]	
1-Hexanol			12.2 ± 2.4	298 ± 2	PR-RA	Nelson *et al.*[18]	
			12.9 ± 1.2	298 ± 2	RR [relative to k(cyclohexane) = 7.49 × 10^{-12}][a]	Nelson *et al.*[18]	
1-Heptanol			13.7 ± 1.5	298 ± 2	RR [relative to k(cyclohexane) = 7.49 × 10^{-12}][a]	Nelson *et al.*[18]	
1-Octanol			14.4 ± 1.5	298 ± 2	RR [relative to k(cyclohexane) = 7.49 × 10^{-12}][a]	Nelson *et al.*[18]	
Hydroxyketones and Ketoethers							
Hydroxyacetone [CH_3COCH_2OH]			3.0 ± 0.3	298	FP-RF	Dagaut *et al.*[20]	
Methoxyacetone [$CH_3OCH_2COCH_3$]			6.8 ± 0.6	298	FP-RF	Dagaut *et al.*[20]	
Ethers							
Dimethyl ether			2.30 ± 0.23	295 ± 3	RR [relative to k(n-butane) = 2.50 × 10^{-12}][a]	Wallington *et al.*[21]	
			2.35 ± 0.24	298 ± 2	PR-RA	Nelson *et al.*[18]	

TABLE 41. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with oxygen-containing organics – Continued

Oxygenate	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
			3.19 ± 0.70	298 ± 2	RR [relative to k(cyclohexane) = 7.49×10^{-12}]^a	Nelson *et al.*[18]	
Diethyl ether			13.1 ± 0.3	242	RR [relative to k(2,3-dimethylbutane) = $1.21 \times 10^{-17}\ T^2\ e^{512/T}$]^a	Bennett and Kerr[22]	242–325
			11.8 ± 0.8	263			
			11.7 ± 0.8	273			
			10.3 ± 0.6	289			
			10.3 ± 1.0	304			
			10.1 ± 0.6	317			
			9.70 ± 0.13	325			
			11.3 ± 0.1	298 ± 2	PR-RA	Nelson *et al.*[18]	
			12.8 ± 0.6	298 ± 2	RR [relative to k(cyclohexane) = 7.49×10^{-12}]^a	Nelson *et al.*[18]	
			13.2 ± 1.7	250	RR [relative to k(2,3-dimethylbutane) = $1.21 \times 10^{-17}\ T^2\ e^{512/T}$]^a	Semadeni *et al.*[23]	250–373
			13.5 ± 1.3	263			
			12.8 ± 1.9	273			
			13.2 ± 0.4	283			
			12.6 ± 1.1	298			
			11.9 ± 0.8	308			
			10.9 ± 1.3	323			
			11.3 ± 0.7	338			
			11.6 ± 0.8	353			
			10.9 ± 1.2	373			
Di-*n*-propyl ether			19.3 ± 0.8	295 ± 3	RR [relative to k(diethyl ether) = 1.32×10^{-11}]^a	Wallington *et al.*[21]	
			24.4 ± 0.7	242	RR [relative to k(diethyl ether) = $8.91 \times 10^{-18}\ T^2\ e^{837/T}$]^a	Bennett and Kerr[22]	242–323
			22.2 ± 1.4	264			
			22.2 ± 0.9	273			
			22.6 ± 1.1	283			
			22.1 ± 2.8	300			
			22.1 ± 1.8	323			
			19.9 ± 1.7	298 ± 2	PR-RA	Nelson *et al.*[18]	
			20.3 ± 1.8	298 ± 2	RR [relative to k(cyclohexane) = 7.49×10^{-12}]^a	Nelson *et al.*[18]	

TABLE 41. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with oxygen-containing organics – Continued

Oxygenate	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
Di-isopropyl ether [$(CH_3)_2CHOCH(CH_3)_2$]			10.7 ± 2.0	298 ± 2	PR-RA	Nelson *et al.*[18]	
			11.3 ± 0.7	298 ± 2	RR [relative to k(cyclohexane) = 7.49×10^{-12}]^a	Nelson *et al.*[18]	
Methyl n-butyl ether			12.6 ± 0.3	295 ± 3	RR [relative to k(diethyl ether) = 1.32×10^{-11}]^a	Wallington *et al.*[21]	
			17.7 ± 3.6	247	RR [relative to k(2,3-dimethylbutane) = $1.21 \times 10^{-17}\ T^2\ e^{512/T}$]^a	Semadeni *et al.*[23]	247–353
			16.1 ± 5.2	263			
			15.5 ± 1.8	298			
			14.1 ± 1.3	313			
			13.1 ± 1.0	353			
Methyl *tert*-butyl ether			3.20 ± 0.08	295 ± 3	RR [relative to k(n-butane) = 2.50×10^{-12}]^a	Wallington *et al.*[21]	
			2.68 ± 0.47	295 ± 3	RR [relative to k(diethyl ether) = 1.32×10^{-11}]^a	Wallington *et al.*[21]	
			3.09 ± 0.20	246	RR [relative to k(diethyl ether) = $8.91 \times 10^{-18}\ T^2\ e^{837/T}$]^a	Bennett and Kerr[22]	246–314
			3.13 ± 0.29	251			
			3.16 ± 0.27	275			
			3.41 ± 0.11	284			
			3.37 ± 0.08	306			
			3.63 ± 0.38	314			
			2.99 ± 0.12	298	RR [relative to k(n-butane) = 2.54×10^{-12}]^a	Smith *et al.*[24]	
Ethyl n-butyl ether			22.2 ± 1.0	295 ± 3	RR [relative to k(diethyl ether) = 1.32×10^{-11}]^a	Wallington *et al.*[21]	
			19.0 ± 0.7	253	RR [relative to k(diethyl ether) = $8.91 \times 10^{-18}\ T^2\ e^{837/T}$]^a	Bennett and Kerr[22]	253–315
			18.9 ± 0.7	263			
			18.1 ± 0.6	278			
			17.8 ± 0.7	294			
			17.9 ± 0.2	300			
			17.8 ± 0.9	315			
			18.7 ± 0.7	298 ± 2	PR-RA	Nelson *et al.*[18]	

TABLE 41. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with oxygen-containing organics – Continued

Oxygenate	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
			25.2 ± 3.4	248	RR [relative to k(2,3-dimethylbutane) $= 1.21 \times 10^{-17} T^2 e^{512/T}$]^a	Semadeni *et al.*[23]	248–353
			26.4 ± 9.7	251			
			26.8 ± 4.1	261			
			24.0 ± 4.4	273			
			21.3 ± 1.7	298			
			19.7 ± 2.2	323			
			20.1 ± 1.1	353			
Ethyl *tert*-butyl ether			8.63 ± 0.26	295 ± 3	RR [relative to k(diethyl ether) $= 1.32 \times 10^{-11}$]^a	Wallington *et al.*[21]	
			6.32 ± 1.88	253	RR [relative to k(diethyl ether) = $8.91 \times 10^{-18} T^2 e^{837/T}$]^a	Bennett and Kerr[22]	253–325
			5.96 ± 0.29	273			
			5.77 ± 0.80	293			
			5.85 ± 1.17	302			
			5.95 ± 1.00	325			
			9.78 ± 0.34	298	RR [relative to k(n-hexane) $= 5.61 \times 10^{-12}$]^a	Smith *et al.*[25]	
Di-n-butyl ether			26.8 ± 3.2	295 ± 3	RR [relative to k(diethyl ether) $= 1.32 \times 10^{-11}$]^a	Wallington *et al.*[21]	
			27.2 ± 0.2	298 ± 2	PR-RA	Nelson *et al.*[18]	
			28.8 ± 1.2	298 ± 2	RR [relative to k(cyclohexane) $= 7.49 \times 10^{-12}$]^a	Nelson *et al.*[18]	
			41.0 ± 2.0	251	RR [relative to k(2,3-dimethylbutane) = $1.21 \times 10^{-17} T^2 e^{512/T}$]^a	Semadeni *et al.*[23]	251–353
			38.0 ± 0.6	258			
			36.5 ± 3.9	265			
			32.6 ± 2.5	273			
			30.2 ± 1.5	298			
			26.2 ± 0.5	323			
			26.2 ± 1.4	353			
			47.2 ± 4.2	248	RR [relative to k(diethyl ether) $= 8.91 \times 10^{-18} T^2 e^{837/T}$]^a	Semadeni *et al.*[23]	248–343
			46.8 ± 3.8	251			
			44.8 ± 2.4	254			
			39.9 ± 1.4	260			
			41.9 ± 5.3	263			
			40.0 ± 4.2	266			
			41.0 ± 3.5	268			
			38.3 ± 2.7	273			

TABLE 41. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with oxygen-containing organics – Continued

Oxygenate	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
			38.3 ± 2.5	273			
			39.1 ± 3.4	275			
			31.6 ± 4.4	286			
			27.9 ± 1.1	297			
			32.2 ± 1.0	298			
			28.9 ± 1.2	301			
			26.0 ± 2.4	317			
			27.6 ± 0.7	328			
			24.1 ± 2.6	343			
Di-*n*-pentyl ether			30.2 ± 2.6	295 ± 3	RR [relative to k(diethyl ether) = 1.32×10^{-11}][a]	Wallington *et al.*[21]	
			34.0 ± 2.6	298 ± 2	PR-RA	Nelson *et al.*[18]	
			34.0 ± 0.9	298	RR [relative to k(di-*n*-butyl ether) = 2.88×10^{-11}][a]	Semadeni *et al.*[23]	263–373
1,1-Dimethoxyethane [$(CH_3O)_2CHCH_3$]			8.9 ± 1.0	298	FP-RF	Dagaut *et al.*[26]	
2,2-Dimethoxypropane [$CH_3OC(CH_3)_2OCH_3$]			4.09 ± 0.89	240	FP-RF	Dagaut *et al.*[26]	240–440
			3.93 ± 0.17	298			
			3.75 ± 0.18	350			
			3.80 ± 0.51	400			
	3.55 ± 0.39	−30 ± 35	3.93 ± 0.35	440			
2,2-Diethoxypropane [$CH_3CH_2OC(CH_3)_2OCH_2CH_3$]			11.1 ± 1.7	240	FP-RF	Dagaut *et al.*[26]	240–440
			11.7 ± 1.3	298			
			10.5 ± 1.0	350			
			11.7 ± 1.0	400			
	10.6 ± 2.5	−15 ± 75	10.6 ± 0.7	440			
1,1,3-Trimethoxypropane [$(CH_3O)_2CHCH_2CH_2OCH_3$]			16.7 ± 1.0	298	FP-RF	Dagaut *et al.*[26]	
$CHF_2OCHClCF_3$			0.021 ± 0.007	298	DF-RF	Brown *et al.*[27,28]	
CHF_2OCF_2CHFCl			0.017 ± 0.005	302	DF-RF	Brown *et al.*[27,28]	302–422
	0.61	1080 ± 500	0.047 ± 0.007	422			
$CH_2FOCH(CF_3)_2$			0.073 ± 0.022	299	DF-RF	Brown *et al.*[27,28]	299–422
	1.53	900 ± 500	0.177 ± 0.014	422			

TABLE 41. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with oxygen-containing organics – Continued

Oxygenate	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
1,8-Cineole			11.1 ± 1.2	295 ± 2	RR [relative to k(cyclohexane) = 7.43×10^{-12}]^a	Corchnoy and Atkinson[29]	
Furan			41.9 ± 2.1	300 ± 2	RR [relative to k(propene) = 2.60×10^{-11}]^a	Bierbach *et al.*[30]	
2-Methylfuran			61.9 ± 3.2	300 ± 2	RR [relative to k(propene) = 2.60×10^{-11}]^a	Bierbach *et al.*[30]	
2-Ethylfuran			108 ± 22	300 ± 2	RR [relative to k(propene) = 2.60×10^{-11}]^a	Bierbach *et al.*[30]	
2,5-Dimethylfuran			132 ± 10	300 ± 2	RR [relative to k(*trans*-2-butene) = 6.32×10^{-11}]^a	Bierbach *et al.*[30]	
tert-Butyl formate [$(CH_3)_3COCHO$]			0.737 ± 0.06	298	RR [relative to k(n-butane) = 2.54×10^{-12}]^a	Smith *et al.*[24]	
tert-Butyl acetate [$(CH_3)_3COC(O)CH_3$]			0.439 ± 0.036	298	RR [relative to k(n-butane) = 2.54×10^{-12}]^a	Smith *et al.*[25]	
			0.413 ± 0.052	298	RR [relative to k(propane) = 1.15×10^{-12}]^a	Smith *et al.*[25]	
			0.501 ± 0.045	298	RR [relative to k(*tert*-butyl formate) = 7.37×10^{-13}]^e	Smith *et al.*[25]	
Acetic acid [CH_3COOH]			0.867 ± 0.065	296.8	LP-RA	Singleton *et al.*[31]	297–446
			0.563 ± 0.044	326.2			
			0.488 ± 0.017	356.4			
			0.409 ± 0.014	396.8			
			0.395 ± 0.007	446.2			
Acetic acid dimer [$(CH_3COOH)_2$]			0.0093 ± 0.0266	296.8	LP-RA	Singleton *et al.*[31]	297–326
			0.114 ± 0.075	326.2			
Acetic acid-d_3 [CD_3COOH]			0.810 ± 0.037	297.8	LP-RA	Singleton *et al.*[31]	298–445
			0.648 ± 0.027	326.9			
			0.483 ± 0.015	356.7			
			0.447 ± 0.007	374.2			
			0.413 ± 0.014	396.8			
			0.354 ± 0.009	444.6			

Table 41. Rate constants *k* and temperature-dependent parameters for the gas-phase reactions of the OH radical with oxygen-containing organics – Continued

Oxygenate	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
Acetic acid-d_3 dimer [$(CD_3COOH)_2$]			−0.0229 ± 0.369	297.8	LP-RA	Singleton *et al.*[31]	
Acetic acid-d_4 [CD_3COOD]			0.236 ± 0.017	297.8	LP-RA	Singleton *et al.*[31]	298–444
			0.139 ± 0.008	326.5			
			0.113 ± 0.009	357.0			
			0.107 ± 0.006	397.0			
			0.114 ± 0.007	444.0			
Acetic acid-d_4 dimer [$(CD_3COOD)_2$]			−0.0141 ± 0.0199	297.8	LP-RA	Singleton *et al.*[31]	
Propionic acid [CH_3CH_2COOH]			1.02 ± 0.55	298.2	LP-RA	Singleton *et al.*[31]	298–445
			0.880 ± 0.193	327.1			
			1.14 ± 0.15	356.6			
			1.20 ± 0.06	374.9			
			1.09 ± 0.04	397.1			
	1.07 ± 0.05	0	1.04 ± 0.03	444.7			
Propionic acid dimer [$(CH_3CH_2COOH)_2$]			1.11 ± 0.45	298.2	LP-RA	Singleton *et al.*[31]	298–357
			1.65 ± 0.62	327.1			
			1.88 ± 25.0	356.6			
1,2-Epoxybutane			1.91 ± 0.08	298	FP-RF	Wallington *et al.*[11]	

[a] From present and previous[1] recommendations.

[b] No details concerning reference organic given.

[c] Cited data do not appear consistent with graphical presentation[8] or with prior work.[1,32]

[d] Room temperature, not stated.

[e] From Smith *et al.*[24]

3.6.3. Ketenes

Ketene (CH_2CO). The absolute rate constants of Brown *et al.*[15] and Oehlers *et al.*[16] are given in Table 41. The room temperature rate constant measured by Brown *et al.*[15] of 3.3×10^{-11} cm^3 molecule^{-1} s^{-1} (Table 41) is a factor of ~2.8 higher than the absolute rate constant of Oehlers *et al.*[16] and a factor of 1.9 higher than the relative rate constant of Hatakeyama *et al.*[42] Based on a unit-weighted average of the rate constants of Hatakeyama *et al.*[42] and Oehlers *et al.*,[16] it is recommended that

$$k(\text{ketene}) = 1.5 \times 10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \text{ at 298 K},$$

with an estimated overall uncertainty of a factor of 1.5.

3.6.4. Alcohols

Methanol. The absolute rate constants of Pagsberg *et al.*,[17] Nelson *et al.*[18] and Bott and Cohen[3] and the relative rate constant of Nelson *et al.*[18] are given in Table 41 and are plotted, together with the rate constants of Overend and Paraskevopoulos,[43] Ravishankara and Davis,[44] Tuazon *et al.*,[45] Wallington and Kurylo,[46] Hess and Tully[47] and McCaulley *et al.*,[48] in Fig. 37. A unit-weighted least-squares analysis of the absolute rate constants of Overend and Paraskevopoulos,[43] Ravishankara and Davis,[44] Wallington and Kurylo,[46] Hess and Tully,[47] McCaulley *et al.*,[48] Nelson *et al.*[18] (which is taken to supersede that of Pagsberg *et al.*[17]) and Bott and Cohen[3] and the relative rate constant of Tuazon *et al.*,[45] using the expression $k = CT^2 e^{-D/T}$, leads to the recommendation of

$$k(\text{methanol}) = (6.01^{+0.58}_{-0.53}) \times 10^{-18}\ T^2\ e^{(170 \pm 34)/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 240–1205 K, where the indicated errors are two least-squares standard deviations, and

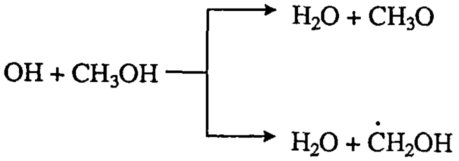
$$k(\text{methanol}) = 9.44 \times 10^{-13}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \text{ at 298 K},$$

with an estimated overall uncertainty at 298 K of ±25%. Over the temperature range 200–2200 K, this recommendation agrees to within 5% with the previous recommendation of Atkinson[1] of

$$k(\text{methanol}) = 6.39 \times 10^{-18}\ T^2\ e^{148/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 240–866 K, with a 298 K rate constant of 9.32×10^{-13} cm^3 molecule^{-1} s^{-1}.

At 298 K, formation of the $CH_3\dot{O}$ radical



$$OH + CH_3OH \rightarrow H_2O + CH_3\dot{O}$$
$$OH + CH_3OH \rightarrow H_2O + \dot{C}H_2OH$$

accounts for 15± 8% of the overall reaction.[48]

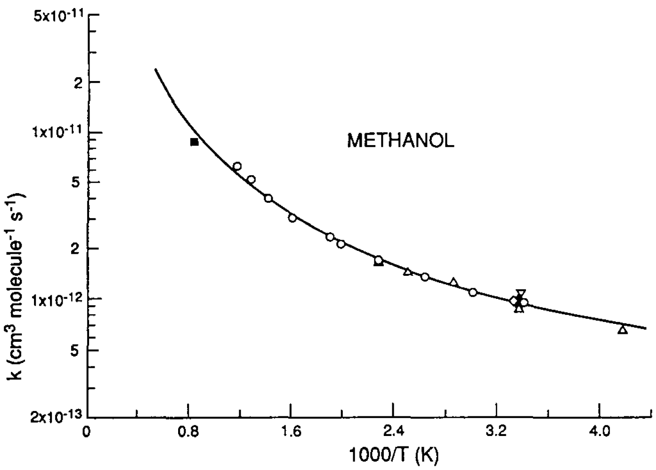
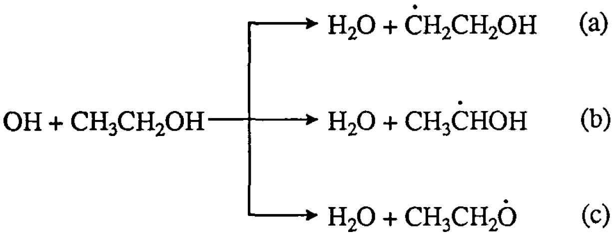


FIG. 37. Arrhenius plot of selected rate constants for the reaction of the OH radical with methanol. (▽) Overend and Paraskevopoulos;[43] (▲) Ravishankara and Davis,[44] McCaulley *et al.*;[48] (◇) Tuazon *et al.*;[45] (△) Wallington and Kurylo;[46] (○) Hess and Tully;[47] (■) Bott and Cohen;[3] (●) Pagsberg *et al.*,[17] Nelson *et al.*[18] (absolute rate constant); (—) recommendation (see text).

Ethanol. The rate constants of Nelson *et al.*[18] and Bott and Cohen[3] are given in Table 41. The 298 K absolute and relative rate constants of Nelson *et al.*[18] are in good agreement with the previous recommendation of Atkinson[1] of 3.27×10^{-12} cm^3 molecule^{-1} s^{-1}. As discussed previously,[1,49] at temperatures >500 K the $HOCH_2\dot{C}H_2$ radical formed from pathway (a)



$$OH + CH_3CH_2OH \rightarrow H_2O + \dot{C}H_2CH_2OH \quad \text{(a)}$$
$$OH + CH_3CH_2OH \rightarrow H_2O + CH_3\dot{C}HOH \quad \text{(b)}$$
$$OH + CH_3CH_2OH \rightarrow H_2O + CH_3CH_2\dot{O} \quad \text{(c)}$$

rapidly thermally decomposes, and hence only the rate constants for pathways (b) and (c) were measured in the kinetic study of Bott and Cohen.[3] Using an estimated rate constant[1] for H-atom abstraction from the $-CH_3$ group of $k_a = 4.47 \times 10^{-18}\ T^2\ e^{-227/T}$ cm^3 molecule^{-1} s^{-1}, a rate constant at 1205 K of $k_a = 5.4 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} is calculated. This calculated rate constant k_a at 1205 K is in agreement with that of $k_a \sim 5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} derived from the previous recommendation of Atkinson[1] for $(k_a + k_b + k_c)$, based on the rate constants of Hess and Tully[49] for the reactions of ^{16}OH and ^{18}OH radicals with ethanol (and using only the ^{18}OH radical rate constants at temperatures >500 K[1]), and the measured value of $(k_b + k_c)$ at 1205 K of Bott and Cohen.[3] Accordingly, the previous recommendation of Atkinson[1] for the overall rate constant, $(k_a + k_b + k_c)$, of

$$k(\text{ethanol}) = 6.18 \times 10^{-18}\ T^2\ e^{532/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 293–599 K, with a 298 K rate constant of 3.27×10^{-12} cm^3 molecule^{-1} s^{-1}, is unchanged.

1-Propanol. The rate constants of Nelson *et al.*[18] and Tully[19] are given in Table 41. These rate constants are in reasonable agreement with the previous recommendation of Atkinson,[1] and a unit-weighted average of the rate constants of Overend and Paraskevopoulos,[43] Wallington and Kurylo,[46] Nelson *et al.*[18] and Tully[19] leads to the recommendation of

$$k(\text{1-propanol}) = 5.53 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

with an estimated overall uncertainty of ±30%. This recommendation supersedes that previously recommended by Atkinson[1] of 5.34×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K, using the rate constants of Overend and Paraskevopoulos[43] and Wallington and Kurylo.[46]

2-Propanol. The rate constants of Nelson *et al.*[18] and Tully[19] are given in Table 41 and are plotted in Arrhenius form, together with the rate constants of Overend and Paraskevopoulos[43] and Wallington and Kurylo,[46] in Fig. 38. A unit-weighted least-squares analysis of the absolute rate constants of Overend and Paraskevopoulos,[43] Wallington and Kurylo,[46] Nelson *et al.*[18] and Tully[19] and the relative rate constant of Nelson *et al.*,[18] using the expression $k = CT^2\ e^{-D/T}$, yields the recommendation of

$$k(\text{2-propanol}) = (7.21^{+2.67}_{-1.95}) \times 10^{-18}\ T^2\ e^{(631 \pm 98)/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 240–440 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{2-propanol}) = 5.32 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

with an estimated overall uncertainty at 298 K of ±35%. This recommended expression is similar to that of Atkinson[1] of

$$k(\text{2-propanol}) = 7.32 \times 10^{-18}\ T^2\ e^{620/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the same temperature range of 240–440 K, with a 298 K rate constant of 5.21×10^{-12} cm^3 molecule^{-1} s^{-1}.

1-Butanol. The room temperature rate constants of Nelson *et al.*[18] and Tully[19] are given in Table 41. A unit-weighted average of the absolute rate constants of Wallington and Kurylo,[46] Nelson *et al.*[18] and Tully[19] and the relative rate constant of Nelson *et al.*[18] leads to the recommendation of

$$k(\text{1-butanol}) = 8.57 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

with an estimated overall uncertainty of ±35%.

1-Pentanol, 1-Hexanol and 1-Heptanol. The rate constants of Nelson *et al.*[18] are given in Table 41. These rate constants of Nelson *et al.*[18] are in good agreement with the absolute room temperature rate constants of Wallington and Kurylo[46] for 1-pentanol and Wallington *et al.*[50] for 1-hexanol and 1-heptanol. Unit-weighted least-squares averages of the rate constants of Wallington and Kurylo[46] (for 1-pentanol), Wallington *et al.*[50] (for 1-hexanol and 1-heptanol) and Nelson *et al.*[18] lead to the recommendations of

$$k(\text{1-pentanol}) = 1.11 \times 10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1},$$

$$k(\text{1-hexanol}) = 1.25 \times 10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1},\ \text{and}$$

$$k(\text{1-heptanol}) = 1.37 \times 10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1},$$

all at 298 K and with estimated overall uncertainties of ±35%.

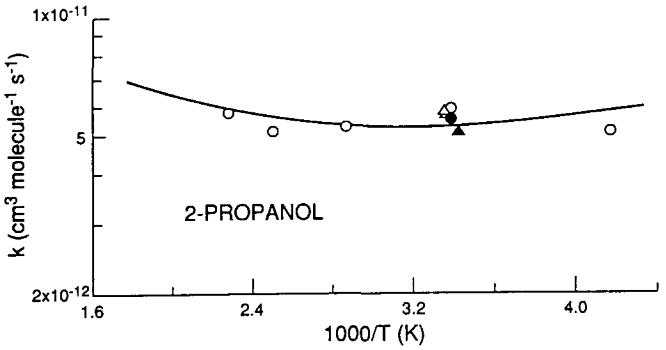


FIG. 38. Arrhenius plot of selected rate constants for the reaction of the OH radical with 2-propanol. (●) Overend and Paraskevopoulos;[43] (○) Wallington and Kurylo;[46] (△) Nelson *et al.*;[18] (▲) Tully;[19] (—) recommendation (see text).

3.6.5. Ethers

Dimethyl ether. The room temperature rate constants of Wallington *et al.*[21] and Nelson *et al.*[18] are given in Table 41. These rate constants range over a factor of 1.4, and are reasonably consistent with the previous recommendation of Atkinson[1] of

$$k(\text{dimethyl ether}) = 1.04 \times 10^{-11}\ e^{-372/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 295–442 K, with a 298 K rate constant of 2.98×10^{-12} cm^3 molecule^{-1} s^{-1}. This previous recommendation[1] is hence unchanged.

Diethyl ether. The absolute rate constant of Nelson *et al.*[18] and the relative rate constants of Bennett and Kerr,[22] Nelson *et al.*[18] and Semadeni *et al.*[23] are given in Table 41 and those of Nelson *et al.*[18] and Bennett and Kerr[22] are plotted, together with the rate constants of Tully and Droege,[51] Wallington *et al.*[52] and Bennett and Kerr,[53] in Fig. 39. There is a significant amount of scatter between the data from the various studies, with the rate constants of Bennett and Kerr,[22] obtained relative to the rate constant for the reaction of the OH radical with 2,3-dimethylbutane, being ~30% lower than the absolute rate constants of Tully and Droege[51] and Wallington *et al.*[52] The relative rate constants of Semadeni *et al.*[23] are in good agreement with (~10% lower than) those of

Tully and Droege[51] and Wallington *et al.*[52] A unit-weighted least-squares analysis of the absolute rate constants of Tully and Droege,[51] Wallington *et al.*[52] and Nelson *et al.*[18] and the relative rate constant of Nelson *et al.*,[18] using the expression $k = CT^2 \, e^{-D/T}$, leads to the recommendation of

$$k(\text{diethyl ether}) = (8.91^{+2.11}_{-1.71}) \times 10^{-18} \, T^2 \, e^{(837 \pm 70)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 240–442 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{diethyl ether}) = 1.31 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K},$$

with an estimated overall uncertainty at 298 K of ±35%. This recommendation supersedes, but is similar to, that of Atkinson[1] of

$$k(\text{diethyl ether}) = 8.80 \times 10^{-18} \, T^2 \, e^{844/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the same temperature range of 240–442 K, with a 298 K rate constant of 1.33×10^{-11} cm^3 molecule^{-1} s^{-1}.

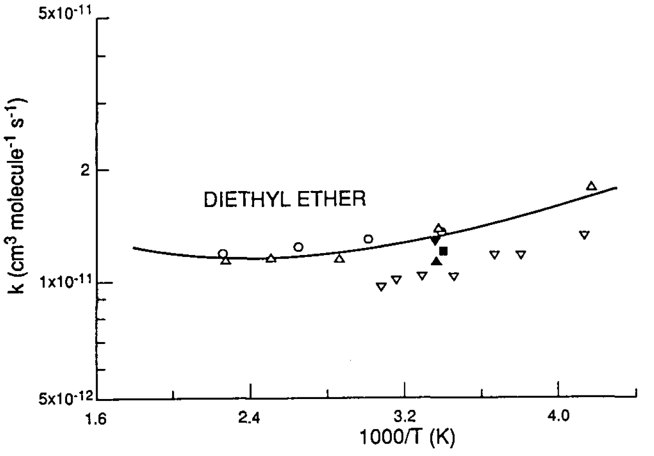


FIG. 39. Arrhenius plot of selected rate constants for the reaction of the OH radical with diethyl ether. (○) Tully and Droege;[51] (△) Wallington *et al.*;[52] (■) Bennett and Kerr;[53] (▲) Nelson *et al.*,[18] absolute rate constant; (▼) Nelson *et al.*,[18] relative rate constant; (▽) Bennett and Kerr;[22] (—) recommendation (see text).

Di-n-propyl ether. The rate constants of Wallington *et al.*,[21] Bennett and Kerr[22] and Nelson *et al.*[18] are given in Table 41 and are plotted, together with the rate constants of Wallington *et al.*[52] and Bennett and Kerr,[53] in Arrhenius form in Fig. 40. The rate constants of Wallington *et al.*,[21] Bennett and Kerr[22] and Nelson *et al.*,[18] especially those of Bennett and Kerr,[22] are higher than the previously reported rate constants of Wallington *et al.*[52] and Bennett and Kerr.[53] A unit-weighted least-squares analysis of the absolute rate constants of Wallington *et al.*[52] and Nelson *et al.*[18] and the relative rate constants of Wallington *et al.*[21] and Nelson *et al.*,[18] using the expression $k = CT^2 \, e^{-D/T}$, leads to the recommendation of

$$k(\text{di-}n\text{-propyl ether}) = (1.31^{+0.39}_{-0.30}) \times 10^{-17} \, T^2 \, e^{(825 \pm 80)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 240–440 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{di-}n\text{-propyl ether}) = 1.85 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty at 298 K of ±40%. This recommendation is slightly different from the previous recommendation of Atkinson[1] of

$$k(\text{di-}n\text{-propyl ether}) = 1.42 \times 10^{-17} \, T^2 \, e^{778/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the same temperature range, with a 298 K rate constant of 1.72×10^{-11} cm^3 molecule^{-1} s^{-1}.

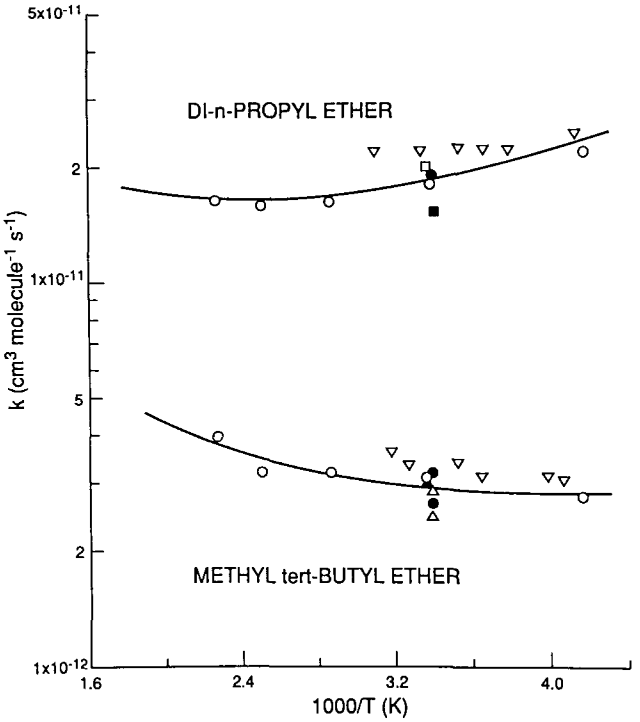


FIG. 40. Arrhenius plots of selected rate constants for the reactions of the OH radical with di-*n*-propyl ether and methyl *tert*-butyl ether. (○) Wallington *et al.*[52] (for di-*n*-propyl ether) and Wallington *et al.*[54] (for methyl *tert*-butyl ether); (■) Bennett and Kerr;[53] (△) Cox and Goldstone;[55] (●) Wallington *et al.*;[21] (□) Nelson *et al.*;[18] (▽) Bennett and Kerr;[22] (▲) Smith *et al.*;[24] (—) recommendations (see text).

Methyl tert-butyl ether. The rate constants of Wallington *et al.*,[21] Bennett and Kerr[22] and Smith *et al.*[24] are given in Table 41 and are plotted, together with those of Wallington *et al.*[54] and Cox and Goldstone,[55] in Arrhenius form in Fig. 40. As for di-*n*-propyl ether, the rate constants of Bennett and Kerr[22] are consistently higher than those of

Wallington *et al.*,[21,54] Cox and Goldstone[55] and Smith *et al.*[24] A unit-weighted least-squares analysis of the absolute rate constants of Wallington *et al.*[54] and the relative rate constants of Wallington *et al.*[21] and Smith *et al.*,[24] using the expression $k = CT^2 \mathrm{e}^{-D/T}$, leads to the recommendation of

$$k(\text{methyl } tert\text{-butyl ether}) = (6.54^{+2.13}_{-1.61}) \times 10^{-18}\, T^2\, \mathrm{e}^{(483 \pm 88)/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 240–440 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{methyl } tert\text{-butyl ether}) = 2.94 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \text{ at } 298\ \text{K},$$

with an estimated overall uncertainty at 298 K of ±40%. This recommendation supersedes that of Atkinson[1] of

$$k(\text{methyl } tert\text{-butyl ether}) = 6.81 \times 10^{-18}\, T^2\, \mathrm{e}^{460/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the same temperature range of 240–440 K, with a 298 K rate constant of 2.83×10^{-12} cm^3 molecule^{-1} s^{-1}.

Methyl n-butyl ether, ethyl n-butyl ether, ethyl tert-butyl ether, di-n-butyl ether and *di-n-pentyl ether*. The rate constants of Wallington *et al.*,[21] Bennett and Kerr[22] (ethyl *n*-butyl ether and ethyl *tert*-butyl ether), Nelson *et al.*[18] (ethyl *n*-butyl ether, di-*n*-butyl ether and di-*n*-pentyl ether), Smith *et al.*[25] (ethyl *tert*-butyl ether) and Semadeni *et al.*[23] (methyl *n*-butyl ether, ethyl *n*-butyl ether, di-*n*-butyl ether and di-*n*-pentyl ether) are given in Table 41. For di-*n*-pentyl ether, Semadeni *et al.*[23] determined rate constants relative to those for di-*n*-butyl ether over the temperature range 263–373 K; only the 298 K rate constant is given in Table 41 since no temperature dependent recommendation is given for di-*n*-butyl ether. The absolute and relative rate constants of Wallington *et al.*,[21,50,52] Nelson *et al.*,[18] Smith *et al.*[25] and Semadeni *et al.*[23] are in good agreement, while the relative rate constants of Bennett and Kerr[22,53] are generally significantly lower. The following recommendations are made from unit-weighted averages:

$$k(\text{methyl } n\text{-butyl ether}) = 1.48 \times 10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

based on the rate constants of Wallington *et al.*[21,50] and Semadeni *et al.*,[23]

$$k(\text{ethyl } n\text{-butyl ether}) = 2.13 \times 10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

based on the rate constants of Wallington *et al.*,[21,50] Nelson *et al.*[18] and Semadeni *et al.*,[23]

$$k(\text{ethyl } tert\text{-butyl ether}) = 8.84 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

based on the rate constants of Wallington *et al.*[21,50] and Smith *et al.*,[25]

$$k(\text{di-}n\text{-butyl ether}) = 2.88 \times 10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

based on the rate constants of Wallington *et al.*,[21,52] Nelson *et al.*[18] and Semadeni *et al.*,[23] and

$$k(\text{di-}n\text{-pentyl ether}) = 3.32 \times 10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

based on the rate constants of Wallington *et al.*,[21,52] Nelson *et al.*[18] and Semadeni *et al.*,[23] all at 298 K and with estimated overall uncertainties of ± ~35%.

Furan. The room temperature rate constant of Bierbach *et al.*[30] is given in Table 41. This rate constant is in excellent agreement with the previously recommended[1] value of 4.02×10^{-11} cm^3 molecule^{-1} s^{-1} at 300 K. The previous recommendation of Atkinson[1] of

$$k(\text{furan}) = 1.32 \times 10^{-11}\ \mathrm{e}^{334/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 254–424 K, with a 298 K rate constant of 4.05×10^{-11} cm^3 molecule^{-1} s^{-1}, is hence unchanged.

3.6.6. Carboxylic acids

Acetic Acid. The absolute rate constants of Singleton *et al.*[31] for the reactions of the OH radical with CH_3COOH, CD_3COOH and CD_3COOD are given in Table 41. While the room temperature rate constant of Singleton *et al.*[31] for CH_3COOH is in reasonable agreement with the previous measurement of Dagaut *et al.*,[56] the rate constants of Singleton *et al.*[31] for CH_3COOH decrease with increasing temperature, in contrast to the study of Dagaut *et al.*[56] in which the rate constants increased with increasing temperature. A unit-weighted average of the room temperature rate constants from these two studies[31,56] leads to the recommendation of

$$k(\text{acetic acid}) = 8 \times 10^{-13}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \text{ at } 298\ \text{K},$$

with an estimated overall uncertainty of a factor of 1.5. No temperature dependence is recommended.

Singleton *et al.*[31] determined that the rate constant for the reaction of the OH radical with CD_3COOH is essentially identical to that for CH_3COOH, and that the rate constant for the reaction of the OH radical with CD_3COOD is uniformly a factor of ~3.5 lower than those for CH_3COOH and CD_3COOH over the temperature range 297–445 K. These observations indicate that the reaction proceeds by H– (or D–) atom abstraction from the –OH (or –OD) bond. For example, for CD_3COOH

$$OH + CD_3COOH \rightarrow H_2O + CD_3CO_2$$

Propionic acid. The absolute rate constants of Singleton *et al.*[31] are given in Table 41. In this case, the agreement of the rate constants of Singleton *et al.*[31] with those of Dagaut *et al.*[56] and Zetzsch and Stuhl[57] is reasonable. Both of the temperature dependent studies of Dagaut *et al.*[56] and Singleton *et al.*[31] indicate that the rate constant is essentially independent of temperature over the range 298–445 K. A unit-weighted average of all of the rate constants of Dagaut *et al.*[56] and Singleton *et al.*[31] leads to the recommendation of

$$k(\text{propionic acid}) = 1.16 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1},$$

independent of temperature over the range 298–445 K, with an estimated overall uncertainty of a factor of 2.

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3.7. Sulfur-Containing Organic Compounds

The rate constants reported since the review and evaluation of Atkinson[1] are given in Table 42. In addition to these kinetic data, Tyndall and Ravishankara[7] have shown that the yield of $CH_3\dot{S}$ radicals from the OH radical reaction with CH_3SH is 1.1 ± 0.2 at 298 K. These data, combined with the lack of any significant deuterium atom isotope effect on the rate constants for the reactions of the OH radical with CH_3SD[8] and CD_3SH[9] show that the OH radical reaction with CH_3SH proceeds by

$$OH + CH_3SH \rightarrow [CH_3S(OH)H] \rightarrow H_2O + CH_3\dot{S}$$

Dimethyl sulfide. The absolute rate constants of Nielsen *et al.*[2] and Abbatt *et al.*[3] determined in the absence of O_2 are given in Table 42 and are plotted, together with the rate constants of Wine *et al.*,[10] Hynes *et al.*,[11] Hsu *et al.*[12] and Barnes *et al.*[13] (all of which were also obtained in the absence of O_2), in Arrhenius form in Fig. 41. There is an appreciable amount of scatter in these data, and the absolute rate constant of Nielsen *et al.*[2] appears to be significantly low. A unit-weighted least-squares analysis of the absolute rate constants of Wine *et al.*,[10] Hynes *et al.*,[11] Hsu *et al.*[12] and Abbatt *et al.*[3] leads to the recommended Arrhenius expression of

$$k(CH_3SCH_3) = (1.13^{+0.37}_{-0.28}) \times 10^{-11}\, e^{-(254 \pm 87)/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the temperature range 248–397 K, where the indicated errors are two least-squares standard deviations, and

$$k(CH_3SCH_3) = 4.82 \times 10^{-12}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ \text{at 298 K},$$

with an estimated overall uncertainty at 298 K of ±35%. This recommendation supersedes the previous recommendation of Atkinson[1] of

$$k(CH_3SCH_3) = 1.03 \times 10^{-11}\, e^{-243/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the same temperature range of 248–397 K, with a 298 K rate constant of 4.56×10^{-12} cm^3 molecule^{-1} s^{-1}.

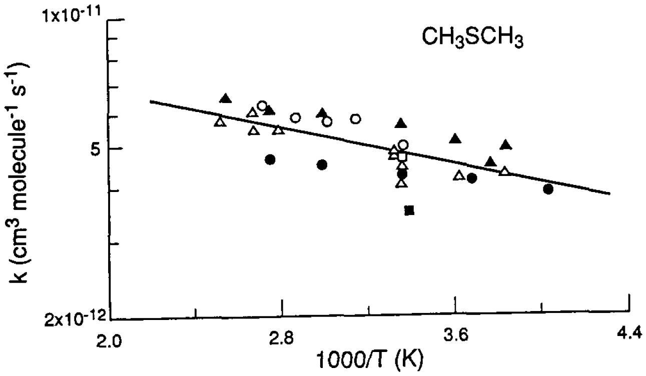

FIG. 41. Arrhenius plot of selected rate constants for the reaction of the OH radical with dimethyl sulfide, obtained in the absence of O_2. (●) Wine *et al.*;[10] (△) Hynes *et al.*;[11] (▲) Hsu *et al.*;[12] (□) Barnes *et al.*;[13] (■) Nielsen *et al.*;[2] (○) Abbatt *et al.*;[3] (—) recommendation (see text).

As discussed previously,[1] the rate constant determined in the absence of O_2 is that for the H-atom abstraction pathway

$$OH + CH_3SCH_3 \rightarrow H_2O + CH_3S\dot{C}H_2$$

In the presence of O_2, the reaction of the OH-CH_3SCH_3 adduct with O_2 occurs in competition with the back-decomposition of the adduct to reactants.[1,11]

$$OH + CH_3SCH_3 \rightleftharpoons [CH_3S(OH)CH_3] \xrightarrow{O_2} \text{products}$$

Kinetic data for the addition pathway have been presented previously.[1]

Diethyl sulfide. The rate constant of Nielsen *et al.*[4] is given in Table 42. This room temperature rate constant of Nielsen *et al.*[4] is in reasonable agreement with the rate constants of Martin *et al.*,[14] Barnes *et al.*[15] and Hynes *et al.*[11] The previous recommendation of Atkinson[1] of

$$k(CH_3CH_2SCH_2CH_3) = 1.5 \times 10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}},$$

independent of temperature over the range 255–370 K, is hence unchanged.

Di-n-propyl sulfide. The room temperature rate constant of Nielsen *et al.*[4] is given in Table 42. This rate constant[4] is in good agreement with that of Barnes *et al.*[15] of $(2.00 \pm 0.22) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 300 K. A unit-weighted average of these rate constants of Barnes *et al.*[15] and Nielsen *et al.*[4] leads to the recommendation of

$$k(\text{di-}n\text{-propyl sulfide}) = 2.1 \times 10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ \text{at 298 K},$$

with an estimated overall uncertainty of ±40%.

Dimethyl disulfide. The absolute rate constants of Abbatt *et al.*[3] are given in Table 42 and are plotted, together with the rate constants of Cox and Sheppard,[16] Wine *et al.*[10] and Barnes *et al.*,[15,17] in Arrhenius form in Fig. 42.

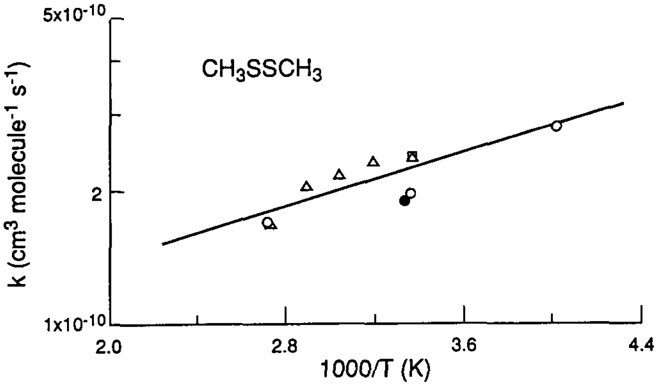

FIG. 42. Arrhenius plot of rate constants for the reaction of the OH radical with dimethyl disulfide. (□) Cox and Sheppard;[16] (○) Wine *et al.*;[10] (●) Barnes *et al.*;[15,17] (△) Abbatt et al.;[3] (—) recommendation (see text).

The agreement between these absolute[3,10] and relative[15–17] rate studies is reasonable, and a unit-weighted least-squares analysis of the absolute rate constants of Wine *et al.*[10] and Abbatt *et al.*[3] leads to the recommended Arrhenius expression of

$$k(CH_3SSCH_3) = (7.00^{+4.63}_{-2.79}) \times 10^{-11}\, e^{(350 \pm 160)/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the temperature range 249–367 K, where the indicated errors are two least-squares standard deviations, and

TABLE 42. Rate constants k and temperature-dependent parameters, $k = A e^{-B/T}$, for the gas-phase reactions of the OH radical with sulfur-containing organics

Organic	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
Dimethyl sulfide			3.5 ± 0.2	295 ± 2	PR-RA	Nielsen *et al.*[2]	
			4.98 ± 0.23	297 ± 2	DF-LIF	Abbatt *et al.*[3]	297–368
			5.73 ± 0.25	317			
			5.69 ± 0.25	331			
			5.81 ± 0.30	348			
	13.5 ± 6.2	285 ± 135	6.22 ± 0.35	368			
Diethyl sulfide			11.6 ± 2.5	295 ± 3	PR-RA	Nielsen *et al.*[4]	
Di-*n*-propyl sulfide			21.5 ± 3	295 ± 3	PR-RA	Nielsen *et al.*[4]	
Di-*n*-butyl sulfide			37.4 ± 5	295 ± 3	PR-RA	Nielsen *et al.*[4]	
Dimethyl disulfide			239 ± 15	297	DF-LIF	Abbatt *et al.*[3]	297–366
			233 ± 16	313			
			219 ± 16	329			
			207 ± 18	346			
	62 ± 49	−410 ± 210	169 ± 22	366			
Dimethyl sulfate			<0.5	a	RR [relative to k(ethene) = 8.52 × 10^{-12}][b]	Japar *et al.*[5]	
Diethyl sulfate			2.18 ± 0.31	a	RR [relative to k(ethene) = 8.52 × 10^{-12}][b]	Japar *et al.*[6]	
			1.43 ± 0.32	a	RR [relative to k(acetylene) = 8.15 × 10^{-13}][b]	Japar *et al.*[6]	

[a] Room temperature; 298 K assumed.
[b] From previous[1] recommendations.

$$k(\mathrm{CH_3SSCH_3}) = 2.27 \times 10^{-10}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ \text{at 298 K},$$

with an estimated overall uncertainty at 298 K of ±25%. This recommendation supersedes that of Atkinson[1] of

$$k(\mathrm{CH_3SSCH_3}) = 5.83 \times 10^{-11}\ e^{383/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the same temperature range of 249–367 K, with a 298 K rate constant of 2.11×10^{-10} cm^3 molecule^{-1} s^{-1}.

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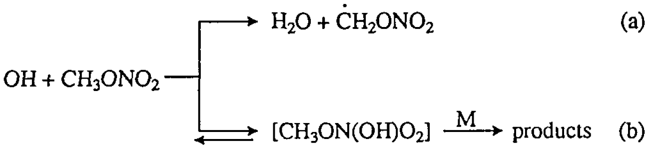
3.8. Nitrogen-Containing Organic Compounds

The rate constants reported since the review and evaluation of Atkinson[1] are given in Tables 43 (OH radical reactions) and 44 (OD radical reactions). For several nitrogen-containing compounds, the rate constants given in Table 43 are the first reported.

3.8.1 Nitrates

Methyl nitrate. The absolute and relative rate constants of Nielsen *et al.*[2] are given in Table 43. These rate constants were obtained at one atmosphere total pressure of air or argon. The room temperature absolute and relative rate constants of Nielsen *et al.*[2] are in agreement with the relative rate constant of Kerr and Stocker,[12] also obtained at one atmosphere total pressure, but are a factor of ~10 higher than the rate constant obtained at a total pressure of 2–3 Torr by Gaffney *et al.*[13] These observations indicate that at room temperature the rate constant for the reaction of the OH radical with methyl nitrate is pressure dependent, and that the reaction proceeds by an H-atom abstraction pathway (a) and an addition pathway (b),



$$\mathrm{OH + CH_3ONO_2 \rightarrow H_2O + \dot{C}H_2ONO_2} \qquad \text{(a)}$$

$$\mathrm{OH + CH_3ONO_2 \rightleftharpoons [CH_3ON(OH)O_2] \xrightarrow{M} products} \qquad \text{(b)}$$

where the products of the addition pathway may include $\mathrm{CH_3\dot{O} + HONO_2}$.[2] This situation is similar to the OH radical reactions with the alkyl nitrites and nitroalkanes (see below). Comparison of the low pressure[13] and atmospheric pressure[2,12] rate constants at room temperature further indicates that at atmospheric pressure and room temperature the OH radical reaction with methyl nitrate proceeds mainly (~90%) by the addition pathway (b).[2] This conclusion is consistent with the observation of a marked negative temperature dependence of the rate constant at atmospheric pressure (Table 43 and Ref. 2).

At the present time the total pressure at which the high-pressure limiting rate constant is attained is not known. A unit-weighted average of the atmospheric pressure absolute rate constant of Nielsen *et al.*[2] and the atmospheric pressure relative rate constants of Kerr and Stocker[12] and Nielsen *et al.*[2] leads to the recommendation of

$$k(\text{methyl nitrate}) = 3.5 \times 10^{-13}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

at 298 K and 760 Torr total pressure of air, with an estimated overall uncertainty of a factor of 1.5. In the absence of kinetic and mechanistic data for this reaction as a function of temperature and pressure, no recommendations are made concerning the temperature or pressure dependence of the rate constant.

Ethyl nitrate. The absolute and relative rate constants of Nielsen *et al.*[2] are given in Table 43. At room temperature, these rate constants, obtained at one atmosphere total pressure of argon or air, are in agreement with the atmospheric pressure relative rate constant of Kerr and Stocker.[12] Accordingly, a unit-weighted average of the absolute rate constant of Nielsen *et al.*[2] and the relative rate constants of Kerr and Stocker[12] and Nielsen *et al.*[2] leads to the recommendation of

$$k(\text{ethyl nitrate}) = 4.9 \times 10^{-13}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

at 298 K and 760 Torr total pressure of air, with an estimated overall uncertainty of a factor of 1.5. Analogous to the OH radical reaction with methyl nitrate, the room temperature rate constant for the reaction of the OH radical with ethyl nitrate is expected to be pressure dependent, and the negative temperature dependence determined by Nielsen *et al.*[2] at atmospheric pressure of argon diluent is consistent with the reaction proceeding mainly by OH radical addition at 298 K and 760 Torr total pressure of air, as also concluded by Nielsen *et al.*[2]

1-Propyl nitrate. The absolute and relative rate constants of Nielsen *et al.*[2] are given in Table 43. The room temperature rate constants of Nielsen *et al.*,[2] obtained at one atmosphere total pressure of argon or air, are in agreement with the atmospheric pressure relative rate measurements of Kerr and Stocker[12] and Atkinson and Aschmann.[14] A unit-weighted average of the absolute rate constant of Nielsen *et al.*[2] and the relative rate constants of Kerr and Stocker,[12] Atkinson and Aschmann[14] and Nielsen *et al.*[2] leads to the recommendation of

$$k(\text{1-propyl nitrate}) = 7.3 \times 10^{-13}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

at 298 K and 760 Torr total pressure of air, with an estimated overall uncertainty of a factor of 1.5. Consistent with the observed lack of a temperature dependence for the rate constant at one atmosphere total pressure of argon diluent,[2] the reaction of the OH radical with 1-propyl nitrate is expected to proceed by both H-atom abstraction and initial OH radical addition, with the two pathways possibly being of approximately comparable importance at 298 K and one atmosphere total pressure of air.[2]

2-Propyl nitrate. The room temperature relative rate constant of Becker and Wirtz[3] is given in Table 43. This rate constant[3] is in agreement, within the experimental errors, with the relative rate constant of Atkinson and Aschmann[14] (which supersedes the previous measurement of Atkinson *et al.*[15]). A unit-weighted average of the rate constants of Atkinson and Aschmann[14] and Becker and Wirtz[3] leads to the recommendation of

$$k(\text{2-propyl nitrate}) = 4.9 \times 10^{-13}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

at 298 K and 760 Torr total pressure of air, with an estimated overall uncertainty of a factor of 2. The OH radical reaction with 2-propyl nitrate at room temperature and atmospheric pressure is again expected to proceed by H-atom abstraction and initial OH radical addition.

1-Butyl nitrate. The room temperature absolute and relative rate constants of Nielsen *et al.*[2] are given in Table 43. These rate constants, obtained at a total pressure of one atmosphere of argon or air, are in good agreement with the previous relative rate constant of Atkinson and Aschmann[14] (which supersedes the earlier measurement of Atkinson *et al.*[15]). Accordingly, a unit-weighted average of the absolute rate constant of Nielsen *et al.*[2] and the relative rate constants of Atkinson and Aschmann[14] and Nielsen *et al.*[2] leads to the recommendation of

$$k(\text{1-butyl nitrate}) = 1.71 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

at 298 K and 760 Torr total pressure of air, with an estimated overall uncertainty of ±35%. Based on the correlation of Nielsen *et al.*[2] of the Cl atom and OH radical reaction rate constants with a series of alkyl nitrates, it is expected that the OH radical reaction with 1-butyl nitrate proceeds mainly by H-atom abstraction at 298 K and atmospheric pressure.

2-Methyl-3-butyl nitrate. The relative rate constant of Becker and Wirtz[3] obtained at room temperature and atmospheric pressure is given in Table 43. This rate constant[3] is in good agreement with that of Atkinson *et al.*,[16] and a unit-weighted average of these rate constants[3,16] leads to the recommendation of

$$k(\text{2-methyl-3-butyl nitrate}) = 1.82 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

at 298 K and atmospheric pressure of air, with an estimated overall uncertainty of ±35%. It is expected that this OH radical reaction proceeds mainly by H-atom abstraction under atmospheric conditions.

Other alkyl nitrates. Only single studies have been conducted for the alkyl nitrates other than those discussed above and 2-butyl nitrate (for which the study of Atkinson and Aschmann[14] supersedes that of Atkinson *et al.*[15]). While no firm recommendations are made, the rate constants of Atkinson *et al.*,[15,16] (other than for 2-butyl nitrate for which the rate constant of Atkinson and Aschmann[14] should be used), Becker and Wirtz[3] and Nielsen *et al.*[2] should be used.

3.8.2. Alkyl nitrites

Methyl nitrite. The absolute and relative rate constants of Nielsen *et al.*[5] are given in Table 43. The room temperature rate constants of Nielsen *et al.*,[5] obtained at one atmosphere total pressure of argon or air, are consistent with the previous relative rate constants of Tuazon *et al.*,[17] but are lower by a factor of ~4 than the rate constants of Campbell and Goodman,[18] Audley *et al.*[19] and Baulch *et al.*[20] Consistent with the previous discussion by Atkinson,[1] a unit-weighted average of the absolute and relative rate constants of Tuazon *et al.*[17] and Nielsen *et al.*[5] leads to the recommendation of

$$k(\text{methyl nitrite}) = 2.2 \times 10^{-13}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

at 298 K and 760 Torr total pressure of air, with an estimated overall uncertainty of a factor of 3. It is likely that at room temperature and atmospheric pressure the OH radical reaction with methyl nitrite proceeds by both H-atom abstraction and initial OH radical addition.[5]

Other alkyl nitrites. Rate constants for the C_2 through C_5 *n*-alkyl nitrites have been determined by Nielsen *et al.*[5] (Table 43) at room temperature and atmospheric pressure. These rate constants for ethyl nitrite, 1-propyl nitrite and 1-butyl nitrite[5] are significantly lower (by factors of ~2) than the previous rate constants of Audley *et al.*[19] and Baulch *et al.*[20] Consistent with the above recommendation for methyl nitrite, the rate constants of Nielsen *et al.*[5] are preferred.

TABLE 43. Rate constants k and temperature-dependent parameters at, or close to, the high-pressure limit for the gas-phase reactions of the OH radical with nitrogen-containing organics

Organic	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
Methyl nitrate			0.32 ± 0.05	298 ± 2	PR-RA	Nielsen *et al.*[2]	298–393
			0.22 ± 0.06	323			
			0.15 ± 0.03	358			
		−1057	0.14 ± 0.03	393			
			0.339 ± 0.070	298 ± 2	RR [relative to k(2-methylpropane) = 2.33×10^{-12}]^a	Nielsen *et al.*[2]	
Ethyl nitrate			0.53 ± 0.06	298 ± 2	PR-RA	Nielsen *et al.*[2]	298–373
			0.37 ± 0.05	338			
		−705	0.33 ± 0.05	373			
			0.458 ± 0.030	298 ± 2	RR [relative to k(2-methylpropane) = 2.33×10^{-12}]^a	Nielsen *et al.*[2]	
1-Propyl nitrate			0.82 ± 0.08	298 ± 2	PR-RA	Nielsen *et al.*[2]	298–368
			0.72 ± 0.15	338			
		~0	0.76 ± 0.05	368			
			0.767 ± 0.080	298 ± 2	RR [relative to k(2-methylpropane) = 2.33×10^{-12}]^a	Nielsen *et al.*[2]	
2-Propyl nitrate			0.575 ± 0.225	295 ± 2	RR [relative to k(n-butane) = 2.50×10^{-12}]^a	Becker and Wirtz[3]	
1-Butyl nitrate			1.74 ± 0.19	298 ± 2	PR-RA	Nielsen *et al.*[2]	
			1.61 ± 0.08	298 ± 2	RR [relative to k(2-methylpropane) = 2.33×10^{-12}]^a	Nielsen *et al.*[2]	
2-Methyl-1-propyl nitrate			1.63 ± 0.20	295 ± 2	RR [relative to k(n-butane) = 2.50×10^{-12}]^a	Becker and Wirtz[3]	
1-Pentyl nitrate			3.32 ± 0.30	298 ± 2	PR-RA	Nielsen *et al.*[2]	
			2.95 ± 0.09	298 ± 2	RR [relative to k(2-methylpropane) = 2.33×10^{-12}]^a	Nielsen *et al.*[2]	
2-Methyl-3-butyl nitrate			1.93 ± 0.15	295 ± 2	RR [relative to k(n-butane) = 2.50×10^{-12}]^a	Becker and Wirtz[3]	
2-Methyl-1-butyl nitrate			2.48 ± 0.15	295 ± 2	RR [relative to k(n-butane) = 2.50×10^{-12}]^a	Becker and Wirtz[3]	

TABLE 43. Rate constants k and temperature-dependent parameters at, or close to, the high-pressure limit for the gas-phase reactions of the OH radical with nitrogen-containing organics — Continued

Organic	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
3-Methyl-1-butyl nitrate			2.53 ± 0.35	295 ± 2	RR [relative to k(n-butane) = 2.50×10^{-12}]^a	Becker and Wirtz[3]	
$CH_3C(O)CH_2ONO_2$			<0.44	298 ± 2	RR [relative to k(n-butane) = 2.54×10^{-12}]^a	Zhu *et al.*[4]	
$CH_3CH_2C(O)CH_2ONO_2$			0.907 ± 0.153	298 ± 2	RR [relative to k(n-butane) = 2.54×10^{-12}]^a	Zhu *et al.*[4]	
$CH_3CH(ONO_2)C(O)CH_3$			1.27 ± 0.15	298 ± 2	RR [relative to k(n-butane) = 2.54×10^{-12}]^a	Zhu *et al.*[4]	
$CH_3CH(ONO_2)CH_2ONO_2$			<0.32	298 ± 2	RR [relative to k(propane) = 1.15×10^{-12}]^a	Zhu *et al.*[4]	
$CH_3CH_2CH(ONO_2)CH_2ONO_2$			1.70 ± 0.33	298 ± 2	RR [relative to k(propane) = 1.15×10^{-12}]^a	Zhu *et al.*[4]	
$CH_3CH(ONO_2)CH(ONO_2)CH_3$			1.07 ± 0.26	298 ± 2	RR [relative to k(propane) = 1.15×10^{-12}]^a	Zhu *et al.*[4]	
$O_2NOCH_2CH=CHCH_2ONO_2$			15.1 ± 1.6	298 ± 2	RR [relative to k(ethene) = 8.52×10^{-12}]^a	Zhu *et al.*[4]	
$O_2NOCH_2CH(ONO_2)CH=CH_2$			10.1 ± 0.6	298 ± 2	RR [relative to k(ethene) = 8.52×10^{-12}]^a	Zhu *et al.*[4]	
Methyl nitrite			0.26 ± 0.05	298 ± 2	PR-RA	Nielsen *et al.*[5]	298–393
			0.42 ± 0.03	323			
			0.74 ± 0.10	353			
	100^{+130}_{-50}	1764 ± 300	1.05 ± 0.10	393			
			0.30 ± 0.10	298 ± 2	RR [relative to k(2-methyl-propane) = 2.33×10^{-12}]^a	Nielsen *et al.*[5]	
Ethyl nitrite			0.70 ± 0.11	298 ± 2	PR-RA	Nielsen *et al.*[5]	
			0.70 ± 0.15	298 ± 2	RR [relative to k(2-methyl-propane) = 2.33×10^{-12}]^a	Nielsen *et al.*[5]	
1-Propyl nitrite			1.20 ± 0.05	298 ± 2	PR-RA	Nielsen *et al.*[5]	
			1.10 ± 0.15	298 ± 2	RR [relative to k(2-methyl-propane) = 2.33×10^{-12}]^a	Nielsen *et al.*[5]	

TABLE 43. Rate constants k and temperature-dependent parameters at, or close to, the high-pressure limit for the gas-phase reactions of the OH radical with nitrogen-containing organics — Continued

Organic	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
1-Butyl nitrite			2.72 ± 0.60	298 ± 2	PR-RA	Nielsen *et al.*[5]	
			2.26 ± 0.08	298 ± 2	RR [relative to k(2-methylpropane) = 2.33 × 10^{-12}][a]	Nielsen *et al.*[5]	
1-Pentyl nitrite			4.25 ± 0.80	298 ± 2	PR-RA	Nielsen *et al.*[5]	
			3.72 ± 0.50	298 ± 2	RR [relative to k(2-methylpropane) = 2.33 × 10^{-12}][a]	Nielsen *et al.*[5]	
Nitromethane			0.16 ± 0.05	295 ± 3	PR-RA	Nielsen *et al.*[6]	
			0.107 ± 0.010	295 ± 3	RR [relative to k(2,2-dimethylpropane) = 8.26 × 10^{-13}][a]	Nielsen *et al.*[6]	
			0.0158 ± 0.0009 0.0321 ± 0.0057	298 400	FP-RF	Liu *et al.*[7]	298–400
Nitromethane-d_3			0.10 ± 0.02	295 ± 3	PR-RA	Nielsen *et al.*[6]	
			0.087 ± 0.010	295 ± 3	RR [relative to k(2,2-dimethylpropane) = 8.26 × 10^{-13}][a]	Nielsen *et al.*[6]	
			0.0090 ± 0.0004 0.0119 ± 0.0003	298 400	FP-RF	Liu *et al.*[7]	298–400
Nitroethane			0.15 ± 0.05	295 ± 3	PR-RA	Nielsen *et al.*[6]	
			0.145 ± 0.010	295 ± 3	RR [relative to k(2,2-dimethylpropane) = 8.26 × 10^{-13}][a]	Nielsen *et al.*[6]	
	1.9 ± 0.5	960 ± 90	0.0438 ± 0.003 0.0722 ± 0.0082 0.100 ± 0.004 0.112 ± 0.009 0.175 ± 0.007	253 298 330 350 400	FP-RF	Liu *et al.*[7]	253–400
1-Nitropropane			0.34 ± 0.08	295 ± 3	PR-RA	Nielsen *et al.*[6]	
			0.533 ± 0.078	295 ± 3	RR [relative to k(2,2-dimethylpropane) = 8.26 × 10^{-13}][a]	Nielsen *et al.*[6]	

TABLE 43. Rate constants k and temperature-dependent parameters at, or close to, the high-pressure limit for the gas-phase reactions of the OH radical with nitrogen-containing organics — Continued

Organic	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
			0.207 ± 0.016	240	FP-RF	Liu *et al.*[7]	240–400
			0.364 ± 0.018	298			
			0.448 ± 0.032	330			
			0.514 ± 0.031	350			
	3.7 ± 0.2	690 ± 17	0.663 ± 0.055	400			
2-Nitropropane			0.145 ± 0.014	240	FP-RF	Liu *et al.*[7]	240–400
			0.259 ± 0.011	298			
			0.314 ± 0.020	330			
			0.322 ± 0.015	350			
	2.1 ± 0.7	630 ± 106	0.439 ± 0.018	400			
1-Nitrobutane			1.55 ± 0.09	295 ± 3	PR-RA	Nielsen *et al.*[6]	
			1.68 ± 0.11	295 ± 3	RR [relative to k(2,2-dimethylpropane) = 8.26×10^{-13}][a]	Nielsen *et al.*[6]	
			0.404 ± 0.032	240	FP-RF	Liu *et al.*[7]	240–400
			0.658 ± 0.042	298			
			0.790 ± 0.074	330			
			0.930 ± 0.054	350			
	6.1 ± 0.9	660 ± 49	1.20 ± 0.06	400			
1-Nitropentane			3.30 ± 0.05	295 ± 3	PR-RA	Nielsen *et al.*[6]	
			3.17 ± 0.15	295 ± 3	RR [relative to k(2,2-dimethylpropane) = 8.26×10^{-13}][a]	Nielsen *et al.*[6]	
			0.574 ± 0.033	240	FP-RF	Liu *et al.*[7]	240–440
			1.00 ± 0.06	298			
			1.33 ± 0.07	330			
			1.48 ± 0.09	350			
	10.9 ± 1.7	710 ± 47	1.81 ± 0.13	400			
Nitroethene [$CH_2=CHNO_2$]			1.2 ± 0.2	298 ± 2	PR-RA	Nielsen *et al.*[8]	
3-Nitropropene [$CH_2=CHCH_2NO_2$]			12.2 ± 2.1	298 ± 2	PR-RA	Nielsen *et al.*[8]	
1-Nitrocyclohexene			43.7 ± 4.3	298 ± 2	RR [relative to k(*cis*-2-butene) = 5.64×10^{-11}][a]	Nielsen *et al.*[8]	

TABLE 43. Rate constants k and temperature-dependent parameters at, or close to, the high-pressure limit for the gas-phase reactions of the OH radical with *nitrogen-containing organics* – Continued

Organic	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
CH_3CN			0.0138 ± 0.0008	256.5	LP-LIF	Hynes and Wine[9]	256–388
			0.0146 ± 0.0009	256.5			
			0.0199 ± 0.0013	273			
			0.0184 ± 0.0018	274.5			
			0.0188 ± 0.0024	274.5			
			0.0230 ± 0.0013	278			
			0.0248 ± 0.0038	298			
			0.0330 ± 0.0055	318			
			0.0315 ± 0.0013	318			
			0.0368 ± 0.0050	336			
			0.0361 ± 0.0091	338.5			
			0.0540 ± 0.007	345.5			
			0.0471 ± 0.0024	352.5			
			0.0507 ± 0.0019	366.5			
			0.0571 ± 0.0052	370.5			
			0.0611 ± 0.0069	377			
	$1.1^{+0.5}_{-0.3}$	1130 ± 90	0.0594 ± 0.0020	388			
CD_3CN			0.00941 ± 0.00041[b]	256	LP-LIF	Hynes and Wine[9]	256–379
			0.0126 ± 0.0013[b]	275			
			0.0216 ± 0.0011[b]	298			
			0.0259 ± 0.0023[b]	335			
	$0.94^{+1.34}_{-0.50}$	1180 ± 250	0.0364 ± 0.0051[b]	358.5			
2-Vinylpyridine			56.7 ± 3.7	298 ± 2	RR [relative to k(2-methyl-1,3-butadiene) = 1.01×10^{-10}][a]	Tuazon *et al.*[10]	
$(CH_3)_2NC(O)SCH_3$			13.3 ± 0.6	298 ± 2	RR [relative to k(cyclohexane) = 7.49×10^{-12}][a]	Kwok *et al.*[11]	
$(CH_3CH_2CH_2)_2NC(O)SCH_2CH_3$			31.0 ± 2.9	298 ± 2	RR [relative to k(propene) = 2.63×10^{-11}][a]	Kwok *et al.*[11]	
			34.0 ± 3.8	298 ± 2	RR [relative to k(2-methyl-1,3-butadiene) = 1.01×10^{-10}][a]	Kwok *et al.*[11]	
$CH_3CH_2(c\text{-}C_6H_{11})NC(O)SCH_2CH_3$			35.4 ± 5.7	298 ± 2	RR [relative to k(2-methyl-1,3-butadiene) = 1.01×10^{-10}][a]	Kwok *et al.*[11]	

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[a] From present and previous[1] recommendations.

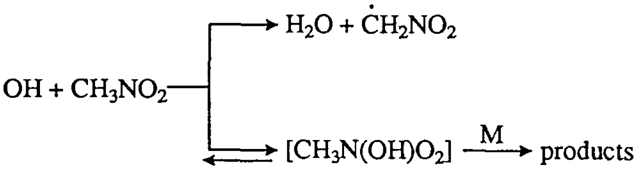
[b] At total pressures of $N_2 \geq 550$ Torr.

3.8.3. Nitroalkanes

The absolute and relative rate constants determined by Nielsen *et al.*[6] at one atmosphere of argon or air and the absolute rate constants of Liu *et al.*,[7] obtained at total pressures of argon diluent of 25–50 Torr, are given in Table 43 (the absolute rate constants of Nielsen *et al.*[6] were included in the review of Atkinson,[1] but are included here for completeness). The data from this study of Nielsen *et al.*[6] supersede those reported earlier.[21]

The rate constants of Liu *et al.*[7] for CH_3NO_2 are in reasonable agreement with the absolute rate constants of Zabarnick *et al.*,[22] and those of Liu *et al.*[7] for the nitroalkanes studied are generally significantly lower than the atmospheric pressure rate constants of Nielsen *et al.*[6] (Table 43). While these observations suggest an effect of total pressure on the rate constant, neither Zabarnick *et al.*[22] or Liu *et al.*[7] observed an effect of the pressure of the argon diluent on the measured rate constants over total pressure ranges of 100–300 Torr[22] and 25–50 Torr.[7]

Only for the reaction of the OH radical with 1-nitrobutane have studies been conducted at atmospheric pressure by more than one research group, and the rate constants of Atkinson and Aschmann[14] and Nielsen *et al.*[6] are in reasonable agreement. While definitive experimental evidence still remains to be obtained, the experimental data suggest that the rate constants for the reactions of the OH radical with the $< C_4$ nitroalkanes studied to date are pressure dependent at around room temperature, and that these reactions proceed by both H-atom abstraction and initial OH radical addition



$$OH + CH_3NO_2 \rightarrow H_2O + \dot{C}H_2NO_2$$
$$OH + CH_3NO_2 \rightleftarrows [CH_3N(OH)O_2] \xrightarrow{M} \text{products}$$

Based on unit-weighted averages of the absolute and relative rate constants of Nielsen *et al.*[6] for nitromethane, nitromethane-d_3, nitroethane, 1-nitropropane and 1-nitropentane, and of the rate constants of Atkinson and Aschmann[14] and Nielsen *et al.*[6] for 1-nitrobutane, the following recommendations are made for 298 K and 760 Torr total pressure of air:

$$k(\text{nitromethane}) = 1.3 \times 10^{-13}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1},$$

$$k(\text{nitromethane-}d_3) = 9 \times 10^{-14}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1},$$

$$k(\text{nitroethane}) = 1.5 \times 10^{-13}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1},$$

$$k(\text{1-nitropropane}) = 4.4 \times 10^{-13}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1},$$

all with estimated overall uncertainties of a factor of 2,

$$k(\text{1-nitrobutane}) = 1.5 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1},$$

and

$$k(\text{1-nitropentane}) = 3.2 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1},$$

both with estimated overall uncertainties of ±35%.

3.8.4. Nitriles

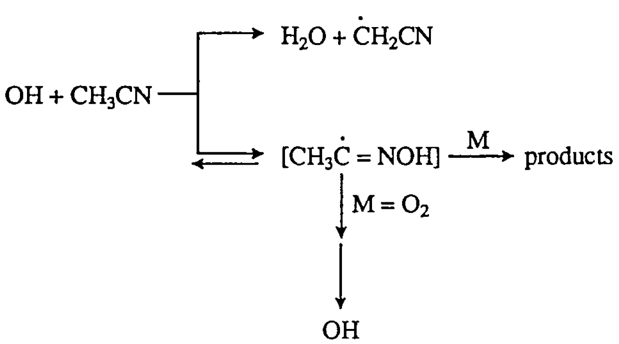
Acetonitrile (CH_3CN). The absolute rate constants of Hynes and Wine[9] for the reactions of the OH radical with CH_3CN and CD_3CN are given in Table 43, and the rate constants for the reactions of the OD radical with CH_3CN and CD_3CN[9] are given in Table 44.

At 298 K, rate constants for the reaction of the OH radical with CH_3CN were obtained over the total pressure range 46–700 Torr of N_2 and at 580–630 Torr total pressure of He. The measured rate constants were independent of total pressure within the experimental uncertainties, although a tendency for the rate constant to decrease for total pressures of N_2 of $<$ 100–200 Torr was observed.[9] In contrast, the rate constant for the reaction of the OH radical with CD_3CN increased with increasing pressure at 298 K, from $\sim 1.3 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at $\sim$50 Torr total pressure of N_2 to 2.16×10^{-14} cm^3 molecule^{-1} s^{-1} at 680 Torr total pressure of N_2.[9] The 298 K rate constants for the reactions of the OD radical with CH_3CN and CD_3CN were observed to be independent of total pressure of N_2 diluent over the pressure range 50–700 Torr.[9] In the presence of O_2, OH radical regeneration was observed[9] from both of the OH radical reactions with CH_3CN and CD_3CN, and similarly OD radical regeneration was observed from the reactions of the OD radical with both CH_3CN and CD_3CN.[9]

These data show that these reactions are complex,[9] with bimolecular and termolecular channels. The essential lack of deuterium isotope effects for the reactions of the OH radical with CH_3CN and CD_3CN also indicates that an addition reaction is important. It is possible that the reactions proceed by, for example,

TABLE 44. Rate constants k at, or close to, the high-pressure limit for the gas-phase reactions of the OD radical with nitrogen-containing organics

Organic	$10^{12} \times k$(cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference
CH_3CN	0.0318 ± 0.0040	298	LP-LIF	Hynes and Wine[9]
CD_3CN	0.0225 ± 0.0028	298	LP-LIF	Hynes and Wine[9]



The rate constants of Hynes and Wine[9] for the reaction of the OH radical with CH_3CN are plotted, together with those of Fritz *et al.*,[23] Zetzsch,[24] Kurylo and Knable[25] and Poulet *et al.*,[26] in Arrhenius form in Fig. 43 (the 100–300 Torr total pressure rate constant of Zetzsch[24] is plotted, since Zetzsch[24] also observed the rate constant to be pressure dependent, especially at total pressures (of argon) below 100 Torr). The agreement between these studies is reasonable.

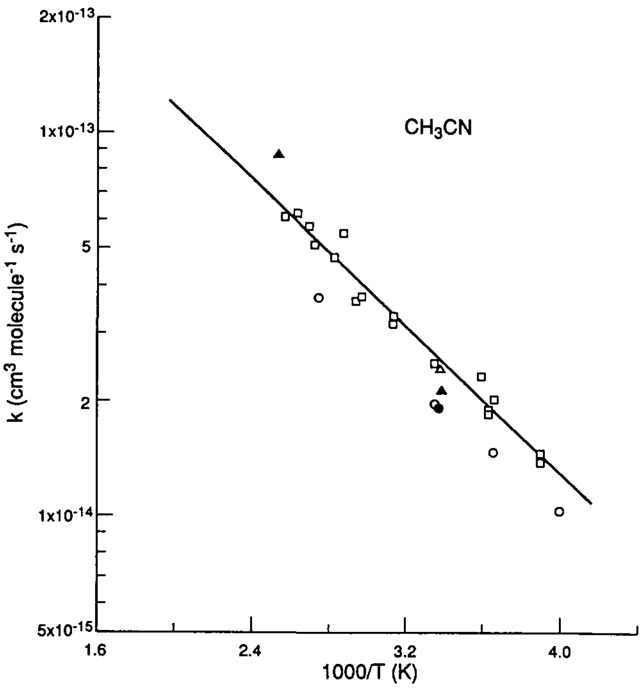


FIG. 43. Arrhenius plot of selected rate constants for the reaction of the OH radical with CH_3CN. (△) Fritz *et al.*;[23] (●) Zetzsch[24] (for total pressures 100–300 Torr of argon); (○) Kurylo and Knable;[25] (▲) Poulet *et al.*;[26] (□) Hynes and Wine;[9] (—) recommendation (see text).

Because of the much more extensive study of Hynes and Wine,[9] the data from that study are preferred, and a unit-weighted least-squares analysis of the rate constants of Hynes and Wine[9] leads to the recommendation of

$$k(CH_3CN) = (1.08^{+0.39}_{-0.29}) \times 10^{-12}\, e^{-(1107 \pm 95)/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the temperature range 256–388 K, where the indicated errors are two least-squares standard deviations, and

$$k(CH_3CN) = 2.63 \times 10^{-14}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}\ at\ 298\ K},$$

with an estimated overall uncertainty at 298 K of ±40%. This recommended expression should not be used outside of the stated temperature range (256–388 K) or at total pressures $\leq$100 Torr.

3.8.5. Miscellaneous

2-Vinylpyridine. The rate constant of Tuazon *et al.*[10] is given in Table 43. The magnitude of the rate constant, when compared to that for pyridine,[1] and the product data of Tuazon *et al.*[10] show that the reaction proceeds by initial OH radical addition to the $-CH=CH_2$ substituent group as shown below [Reaction Scheme (16)] with subsequent reactions of these initially formed radicals leading to the formation of 2-pyridinecarboxaldehyde with a yield of 0.78 ± 0.14.[10]

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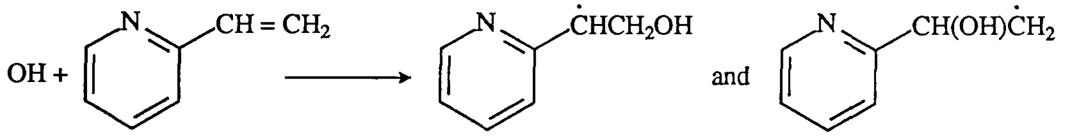

Reaction Scheme (16)

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3.9 Silicon-Containing Organic Compounds

The rate constants for the room temperature reactions of the OH radical with tetramethylsilane, a series of siloxanes and $(CH_3)_3SiOSi(CH_3)_2OH$ determined by Atkinson[1] and Atkinson *et al.*[2] from relative rate studies are given in Table 45. The magnitude of these rate constants[1,2] indicates that these reactions proceed by H-atom abstraction:

$$\mathrm{OH} + {\succ}\mathrm{SiCH_3} \rightarrow \mathrm{H_2O} + {\succ}\mathrm{Si\dot{C}H_2}.$$

References

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3.10. Selenium-Containing Organic Compounds

The room temperature rate constant determined for dimethyl selenide by Atkinson *et al.*[1] from a relative rate study is given in Table 46. The magnitude of this rate constant suggests that the reaction proceeds by initial addition of the OH radical to the Se atom,

$$\mathrm{OH} + \mathrm{CH_3SeCH_3} \rightleftarrows [\mathrm{CH_3Se(OH)CH_3}] \rightarrow \text{products}$$

where the products may include $H_2O + CH_3Se\dot{C}H_2$.

References

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3.11. Aromatic Compounds

The rate constants reported since the review and evaluation of Atkinson[1] are given in Table 47. The study of Atkinson *et al.*[7] concerning the kinetics of the reactions of the OH radical with 1,4-benzodioxan, 2,3-dihydrobenzofuran and 2,3-benzofuran at 298 ± 2 K, the data being given in the review of Atkinson,[1] has now been published.[7] In addition to the rate constants given in Table 47, Goumri *et al.*[8] have investigated the reaction of the OH radical with benzene at low total pressures (0.5–9 Torr) at 297 ± 3 K and 353 K.

TABLE 45. Rate constants k for the gas-phase reactions of the OH radical with silicon-containing organic compounds

Organic	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference
Tetramethylsilane $[(CH_3)_4Si]$	1.00 ± 0.09	297 ± 2	RR [relative to k(cyclohexane) = 7.47×10^{-12}]^a	Atkinson[1]
Hexamethyldisiloxane $[(CH_3)_3SiOSi(CH_3)_3]$	1.38 ± 0.09	297 ± 2	RR [relative to k(cyclohexane) = 7.47×10^{-12}]^a	Atkinson[1]
Hexamethylcyclotrisiloxane $[(-(CH_3)_2SiO-)_3]$	0.52 ± 0.11	297 ± 2	RR [relative to k(cyclohexane) = 7.47×10^{-12}]^a	Atkinson[1]
Octamethylcyclotetrasiloxane $[(-CH_3)_2SiO-)_4]$	1.01 ± 0.20	297 ± 2	RR [relative to k(cyclohexane) = 7.47×10^{-12}]^a	Atkinson[1]
Decamethylcyclopentasiloxane $[(-(CH_3)_2SiO-)_5]$	1.55 ± 0.30	297 ± 2	RR [relative to k(cyclohexane) = 7.47×10^{-12}]^a	Atkinson[1]
$(CH_3)_3SiOSi(CH_3)_2OH$	1.89 ± 0.36	297 ± 2	RR [relative to k(cyclohexane) = 7.47×10^{-12}]^a	Atkinson *et al.*[2]

[a]From present and previous[3] recommendations.

Benzene. The absolute rate constants of Knispel *et al.*[2] are given in Table 47. These rate constants, obtained at 100 Torr total pressure of argon, are in generally good agreement with the previous literature data[1] and with the recommended 298 K rate constant at ~100 Torr total pressure of Atkinson[1] of 1.23×10^{-12} cm^3 molecule^{-1} s^{-1}. These rate constants of Knispel *et al.*[2] are essentially independent of temperature over the temperature range 298–354 K, in contrast to the recommended Arrhenius expression of Atkinson[1] for the temperature range 234–354 K which has a small positive temperature dependence, of $B = 207$ K. The previous recommendations[1] are unchanged.

Goumri *et al.*[8] used a discharge flow technique with resonance fluorescence detection of the OH radical to study the reaction of the OH radical with benzene at 297 ± 3 K and 353 K over the total pressure range of helium diluent of 0.5–9 Torr. Under these conditions, the rate constants are in the fall-off region between second- and third-order kinetics, and fits of the experimental data to the Troe fall-off expression led to limiting low-pressure and high-pressure rate constants k_0 and k_∞, respectively, of k_0 (cm^6 molecule^{-2} s^{-1} units), $(1.7 \pm 0.5) \times 10^{-29}$ at 297 ± 3 K and $(1 \pm 0.2) \times 10^{-29}$ at 353 K; and of k_∞ (cm^3 molecule^{-1} s^{-1} units), $(1.0 \pm 0.2) \times 10^{-12}$ at 297 ± 3 K and $(1.0 \pm 0.1) \times 10^{-12}$ at 353 K. The high-pressure rate constants are in good agreement with the literature data (Table 47 and Ref. 1) and the low-pressure rate constant k_0 for M = He at 297 K is consistent with the literature data[9,10] for M = Ar of $k_0(\mathrm{M} = \mathrm{Ar}) = 3 \times 10^{-29}$ cm^6 molecule^{-2} s^{-1}.[10] The rate constant for the reaction of the OH radical with benzene-d_6 at 353 K and 1 Torr total pressure of helium was observed to be within 10% of that for benzene-h_6.

Toluene. The rate constants of Knispel *et al.*,[2] obtained at 100 Torr total pressure of argon, are given in Table 47. These rate constants, which are for the overall H-atom abstraction and OH radical addition reactions, are in reasonable agreement with the previous recommendation of Atkinson[1] of

$$k_\infty(\text{toluene}) = 1.81 \times 10^{-12}\, e^{355/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 213–324 K, with a 298 K rate constant of 5.96×10^{-12} cm^3 molecule^{-1} s^{-1}. The previous recommendation[1] is hence unchanged.

Phenol. The rate constants of Knispel *et al.*[2] are given in Table 47. These rate constants for the overall H-atom abstraction and OH radical addition reactions are in agreement within the experimental errors with the recommendation of Atkinson[1] of

$$k(\text{phenol}) = 6.75 \times 10^{-12}\, e^{405/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 245–296 K, with a 298 K rate constant of 2.63×10^{-11} cm^3 molecule^{-1} s^{-1}. The previous recommendation[1] is hence unchanged.

Decomposition rates of the hydroxycyclohexadienyl-type radicals. Knispel *et al.*[2] derived the thermal decomposition rate constants at 100 Torr total pressure of argon for three OH-aromatic adduct radicals. The decomposition rate constants (s^{-1}) for the OH-benzene, OH-toluene and OH-phenol adducts at the various temperatures studied were: benzene, 3.3 ± 0.3 at 298 K, 13.8 ± 0.6 at 315 K, 61 ± 8 at 333 K, and 301 ± 31 at 354 K; toluene, 4.8 ± 1.8 at 299 K, 14.4 ± 1.5 at 311 K, 38.8 ± 3.3 at 323 K, and 118 ± 30 at 340 K; and phenol, 0.7 ± 1 at 300 K, 2.3 ± 1 at 308 K, 9.4 ± 1 at 323 K, 36.0 ± 3 at 339 K, 123 ± 15 at 354 K, and 480 ± 70 at 374 K. These thermal decomposition rates for the hydroxycyclohexadienyl radical (the OH-benzene adduct) are in good agreement with the recommendation of Atkinson[1] of $k_d(\text{hydroxycyclohexadienyl}) = 9.4 \times 10^{12}\, e^{-8540/T}$ s^{-1}, and the Arrhenius expression of Knispel *et al.*[2] of $k_d(\text{hydroxycyclohexadienyl}) = 9.0 \times 10^{12}\, e^{-8570/T}$ s^{-1} is virtually identical to that of Atkinson.[1]

The decomposition rates of Knispel *et al.*[2] for the OH-toluene adduct are within 30% of those calculated from the recommendation of Atkinson[1] for the hydroxycyclohexadienyl radical, as expected. The Arrhenius expression of Knispel *et al.*[2] is $k_d(\text{OH-toluene}) = 1.49 \times 10^{12}\, e^{-7880/T}$ s^{-1}. For the OH-phenol adduct, Knispel *et al.*[2] obtained $k_d(\text{OH-phenol}) = 1.33 \times 10^{14}\, e^{-9770/T}$ s^{-1}.

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TABLE 46. Rate constants k for the gas-phase reactions of the OH radical with selenium-containing organics

Organic	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference
Dimethyl selenide [CH_3SeCH_3]	67.8 ± 0.5	296 ± 2	RR [relative to k(2-methyl-1,3-butadiene) = 1.01×10^{-10}][a]	Atkinson *et al.*[1]

[a] From present and previous[2] recommendations.

TABLE 47. Rate constants k for the gas-phase reactions of the OH radical with aromatic compounds at, or close to, the high-pressure limit

Aromatic	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
Benzene	1.11 ± 0.12	298	FP-RF	Knispel *et al.*[2]	298–354
	1.04 ± 0.05	315			
	1.06 ± 0.13	333			
	0.90 ± 0.24	354			
Toluene	7.0 ± 2.3	299	FP-RF	Knispel *et al.*[2]	299–340
	6.05 ± 0.61	311			
	5.50 ± 0.36	323			
	4.42 ± 0.99	340			
1-Methyl-4-isopropyl benzene (p-cymene)	15.1 ± 1.5	295 ± 2	RR [relative to k(cyclohexane) = 7.43×10^{-12}][a]	Corchnoy and Atkinson[3]	
Phenol	29 ± 3.5	300	FP-RF	Knispel *et al.*[2]	300–374
	26 ± 3.5	308			
	22.4 ± 2.5	323			
	18.6 ± 2.5	339			
	17.6 ± 2.4	354			
	17.1 ± 2.4	374			
Indan	9.2 ± 1.4	295	DF-RF	Baulch *et al.*[4]	
Indene	$\geqslant 51$	295	DF-RF	Baulch *et al.*[4]	
Styrene	$\geqslant 43$	295	DF-RF	Baulch *et al.*[4]	
p-Dichlorobenzene	0.384 ± 0.028	297 ± 2	RR [relative to k(ethane) = 2.54×10^{-13}][a]	Arnts *et al.*[5]	
Nitrobenzene	<0.6	297 ± 2	RR [relative to k(ethane) = 2.54×10^{-13}][a]	Arnts *et al.*[5]	
Azulene	273 ± 10	298 ± 2	RR [relative to k(2,3-dimethyl-2-butene) = 1.10×10^{-10}][a]	Atkinson *et al.*[6]	

[a] From present and previous[1] recommendations.

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3.12. Organometallic Compounds

The rate constants reported since the review and evaluation of Atkinson[1] are given in Table 48. The absolute and relative rate constants determined by Nielsen *et al.*[2] are judged to supersede the previous absolute measurements of Nielsen *et al.*[3] at 296 K, of $(6.3 \pm 1.4) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} for $(CH_3)_4Pb$ and $(1.16 \pm 0.17) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} for $(C_2H_5)_4Pb$. In fact, the most recent data of Nielsen *et al.*[2] are more consistent with the relative rate measurements of Harrison and Laxen[4] at 295 ± 3 K, of 9.0×10^{-12} cm^3 $molecule^{-1}$ s^{-1} for $(CH_3)_4Pb$ and 8.0×10^{-11} cm^3 $molecule^{-1}$ s^{-1} for $(C_2H_5)_4Pb$. Based on the absolute and relative rate constants of Nielsen *et al.*,[2] recommendations of

$$k((CH_3)_4Pb) = 4.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

and

$$k((C_2H_5)_4Pb) = 6.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

both at 298 K and with estimated overall uncertainties of a factor of 2, are made.

The reaction mechanisms and products formed are not presently known.[1,2]

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3.13. Organic Radicals

Rate constants for the reaction of the CH_3 radical with the OH radical have been obtained at room temperature by Anastasi *et al.*[1] and Oser *et al.*[2] and by Bott and Cohen[3] at 1212 K and one atmosphere total pressure (Table 49). Anastasi *et al.*[1] used a pulsed radiolysis technique at 750 Torr total pressure of argon and 294 K and derived a rate constant for the reaction

$$OH + CH_3 \xrightarrow{M} CH_3OH$$

of $(9.4 \pm 1.3) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} from computer modeling the data obtained.

Oser *et al.*[2] used a discharge flow system with mass spectrometric detection of reactants over the total pressure range 0.22–4.7 Torr at 300 K. The rate constant for the combination reaction of CH_3 and OH radicals increased with increasing total pressure from 8.0×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 0.225 Torr to 6.0×10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 4.65 Torr total pressure of helium. The rate constants obtained were consistent with a limiting high-pressure rate constant of $\sim(9\text{–}10) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 300 K,[2] effectively attained at total pressures ≥ 100 Torr.[2] The room temperature rate constants of Sworski *et al.*,[4] Anastasi *et al.*[1] and Oser *et al.*[2] are all reasonably consistent with a recommended high-pressure rate constant of

TABLE 48. Rate constants k for the gas-phase reactions of the OH radical with organometallic compounds

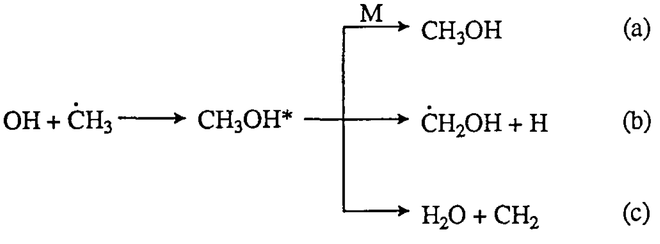
Organometallic	$10^{12} \times k$ (cm^3 $molecule^{-1}$ s^{-1})	at T (K)	Technique	Reference
$(CH_3)_4Pb$	5.9 ± 1.2	298 ± 2	PR-RA	Nielsen *et al.*[2]
	3.98 ± 0.29	298 ± 2	RR [relative to k(*n*-hexane) $= 5.61 \times 10^{-12}$][a]	Neilsen *et al.*[2]
	3.82 ± 0.38	298 ± 2	RR [relative to k(cyclohexane) $= 7.49 \times 10^{-12}$][a]	Nielsen *et al.*[2]
$(C_2H_5)_4Pb$	68 ± 16	298 ± 2	PR-RA	Nielsen *et al.*[2]
	54.9 ± 14.3	298 ± 2	RR [relative to k(*n*-nonane) $= 1.02 \times 10^{-11}$][a]	Nielsen *et al.*[2]
	66.3 ± 1.1	298 ± 2	RR [relative to k(propene) $= 2.63 \times 10^{-11}$][a]	Nielsen *et al.*[2]

[a] From the present and previous[1] recommendations.

$$k_\infty(CH_3) = 1.0 \times 10^{-10}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

which is applicable to a total pressure of air ≥100 Torr and has an estimated overall uncertainty of a factor of 2.

Bott and Cohen[3] derived a rate constant of (1.8 ± 0.5) × 10^{-11} cm^3 molecule^{-1} s^{-1} at 1212 K and ~800 Torr total pressure of argon, and concluded that the major reaction pathway under the conditions employed was the combination channel (a),



with channels (b) and (c) possibly being of minor importance.

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4. Kinetics and Mechanisms of the Gas-Phase Reactions of the NO_3 Radical with Organic Compounds

Recent kinetic and mechanistic data for the gas-phase reactions of the NO_3 radical with organic compounds are presented and discussed in the following sections. Temperature-dependent rate constants are generally given in the recommendations using the Arrhenius expression $k = A\ e^{-B/T}$.

4.1. Alkanes

The rate constants reported since the previous review of Atkinson[1] are given in Table 50 (the data of Bagley *et al.*[3] were reported in an Addendum in the Atkinson[1] review, but were not used in the recommendations). The upper limits to the rate constants reported by Boyd *et al.*[2] for ethane, propane and 2-methylbutane were derived by assuming that the stoichiometry factors were ≥2 under the stopped-flow reaction conditions employed. For methane, no enhanced decay rate of the NO_3 radical was observed,[2] and the upper limit reported was derived from the observed lack of an increased NO_3 radical decay rate in the presence of methane.

Ethane. Absolute rate constants have been determined by Bagley *et al.*[3] over the temperature range 453–553 K, and an upper limit has been derived by Boyd *et al.*[2] at room temperature (Table 50). The extrapolated 298 K rate constant from the data of Bagley *et al.*[3] is 2.0 × 10^{-18} cm^3 molecule^{-1} s^{-1} (subject to an uncertainty of a factor of ≥2), which is consistent with the upper limits to the rate constant of 4 × 10^{-18} cm^3 molecule^{-1} s^{-1} measured by Wallington *et al.*[4] (which may however be erroneously low due to removal of the ethane by reaction with F_2 in the experimental system used) and 2.9 × 10^{-17} cm^3 molecule^{-1} s^{-1} by Boyd *et al.*[2] This extrapolated rate constant of Bagley *et al.*[3] of 2.0 × 10^{-18} cm^3 molecule^{-1} s^{-1} at 298 K is also in reasonable agreement with the rate constant calculated using a group rate constant for H-atom abstraction from a $-CH_3$ group of $k_{\text{prim}} = 7.0 \times 10^{-19}$ cm^3 molecule^{-1} s^{-1} at 298 K[1] [leading to k(ethane) = 1.4 × 10^{-18} cm^3 molecule^{-1} s^{-1} at 298 K]. However, Boyd *et al.*[2] also derived from modeling their data a lower limit to the rate constant of 9 × 10^{-18} cm^3 molecule^{-1} s^{-1} at 302 K, significantly higher than that obtained from extrapolation of the elevated temperature data of Bagley *et al.*[3] or the estimated[1] rate constant.

Because of the small, and elevated, temperature range for which apparently reliable absolute rate constants are available,[3] no recommendation is made for this reaction. The previously derived 298 K $-CH_3$ group rate constant[1] of $k_{\text{prim}} = 7.0 \times 10^{-19}$ cm^3 molecule^{-1} s^{-1} is unchanged.

n-Butane. The rate constants measured by Bagley *et al.*[3] over the temperature range 298–523 K are given in Table 50. The 298 K rate constant of Bagley *et al.*[3] of (4.5 ± 0.6) × 10^{-17} cm^3 molecule^{-1} s^{-1} is in agreement within the error limits with the relative rate constant of Atkinson *et al.*[5] of (6.6 ± 1.7) × 10^{-17} cm^3 molecule^{-1} s^{-1} but is a factor of ~2 higher than the upper limit reported by Wallington *et al.*[4] At temperatures >423 K the Arrhenius plot exhibits upward curvature, especially above

TABLE 49. Rate constants k for the gas-phase reactions of the OH radical with organic radicals at ~1 atmosphere total pressure

Organic Radical	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference
CH_3	94 ± 13[a]	294	PR-Modeling	Anastasi *et al.*[1]
	18 ± 5[b]	1212	SH-RA	Bott and Cohen[3]

[a] At 750 Torr total pressure of argon diluent.

[b] At ~800 Torr total pressure of argon.

TABLE 50. Rate constants k and temperature-dependent parameters, $k = A e^{-B/T}$, for the gas-phase reactions of the NO_3 radical with alkanes

Alkane	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	k (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
Methane			$\leq 8 \times 10^{-19}$	302	SF-A	Boyd *et al.*[2]	
Ethane			$(3.0 \pm 0.5) \times 10^{-16}$	453	DF-A	Bagley *et al.*[3]	453-553
			$(4.7 \pm 0.8) \times 10^{-16}$	473			
			$(1.4 \pm 0.3) \times 10^{-15}$	523			
	5.7 ± 4.0	4426 ± 337	$(1.6 \pm 0.3) \times 10^{-15}$	553			
			$\leq 2.9 \times 10^{-17}$	302	SF-A	Boyd *et al.*[2]	
Propane			$\leq 6.5 \times 10^{-17}$	298	SF-A	Boyd *et al.*[2]	
n-Butane			$(4.5 \pm 0.6) \times 10^{-17}$	298	DF-A	Bagley *et al.*[3]	298-523
			$(1.44 \pm 0.12) \times 10^{-16}$	333			
			$(4.6 \pm 1.2) \times 10^{-16}$	373			
			$(1.12 \pm 0.12) \times 10^{-15}$	423			
			$(3.2 \pm 0.3) \times 10^{-15}$	473			
			$(9.0 \pm 0.4) \times 10^{-15}$	523			
2-Methylpropane			$(1.1 \pm 0.2) \times 10^{-16}$	298	DF-A	Bagley *et al.*[3]	298-523
			$(4.5 \pm 1.6) \times 10^{-16}$	348			
			$(8.0 \pm 0.8) \times 10^{-16}$	373			
			$(2.3 \pm 0.4) \times 10^{-15}$	423			
			$(5.4 \pm 1.2) \times 10^{-15}$	473			
			$(1.30 \pm 0.24) \times 10^{-14}$	523			
			$\leq 7.0 \times 10^{-16}$	298	SF-A	Boyd *et al.*[2]	
2-Methylbutane			$(1.6 \pm 0.2) \times 10^{-16}$	298	DF-A	Bagley *et al.*[3]	298-523
			$(3.9 \pm 1.4) \times 10^{-16}$	323			
			$(1.04 \pm 0.12) \times 10^{-15}$	373			
			$(2.5 \pm 0.4) \times 10^{-15}$	423			
			$(6.1 \pm 1.4) \times 10^{-15}$	473			
			$(1.29 \pm 0.37) \times 10^{-14}$	523			

473 K.[3] A unit-weighted least-squares analysis of the absolute rate constants of Bagley *et al.*[3] obtained over the restricted temperature range 298–423 K yields the recommended Arrhenius expression of

$$k(n\text{-butane}) = (2.76^{+2.30}_{-1.26}) \times 10^{-12}\, e^{-(3279 \pm 211)/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 298–423 K, where the indicated errors are two least-squares standard deviations, and

$$k(n\text{-butane}) = 4.59 \times 10^{-17}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at}\ 298\ \text{K},$$

with an estimated overall uncertainty at 298 K of a factor of 1.5. While the relative rate constant of Atkinson *et al.*[5] is in reasonable agreement with this recommendation, it is possible that the rate constant of Atkinson *et al.*[5] is somewhat high[1] due to secondary reactions involving OH radicals.[6]

2-Methylpropane. The rate constants determined by Bagley *et al.*[3] over the temperature range 298–523 K are given in Table 50, and are plotted in Arrhenius form in Fig. 44 together with the room temperature relative rate constant of Atkinson *et al.*[5] In addition, Boyd *et al.*[2] derived an upper limit to the rate constant of 7.0×10^{-17} cm^3 molecule^{-1} s^{-1} at 298 K, consistent with the data of Bagley *et al.*[3] and Atkinson *et al.*[5] The room temperature rate constants of Atkinson *et al.*[5] and Bagley *et al.*[2] are in excellent agreement. Since the Arrhenius plot appears to exhibit a significant degree of curvature at temperatures >423 K, a unit-weighted least-squares analysis of the room temperature relative rate constant of Atkinson *et al.*[5] and the 298–423 K absolute rate constants of Bagley *et al.*[3] has been carried out to yield the recommended Arrhenius expression of

$$k(\text{2-methylpropane}) = (3.05^{+1.04}_{-0.78}) \times 10^{-12}\, e^{-(3060 \pm 99)/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 296–423 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{2-methylpropane}) = 1.06 \times 10^{-16}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at}\ 298\ \text{K},$$

with an estimated overall uncertainty at 298 K of ±40%.

Other Alkanes. The upper limit to the rate constant for the reaction of the NO_3 radical with methane of 8×10^{-19} cm^3 molecule^{-1} s^{-1} at 302 K reported by Boyd *et al.*[2] is consistent with the upper limit to the rate constant recommended by Atkinson[1] of 1×10^{-18} cm^3 molecule^{-1} s^{-1} at 298 K. Since only a single study has been carried out for 2-methylbutane,[3] no recommendation is made for this reaction. However, the measured 298 K rate constant[3] of $(1.6 \pm 0.2) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} is totally consistent with the rate constants for H-atom abstraction from primary, secondary and tertiary C–H bonds derived by Bagley *et al.*[3] from their rate data for ethane, *n*-butane and 2-methylpropane, and is in excellent agreement with the rate constant of 1.5×10^{-16} cm^3 molecule^{-1} s^{-1} calculated from the $-CH_3$, $-CH_2-$ and $>CH-$ group rate constants derived by Atkinson[1]. Moreover, the predicted 298 K rate constants for *n*-butane and 2-methylpropane of 4.7×10^{-17} cm^3 molecule^{-1} s^{-1} and 8.5×10^{-17} cm^3 molecule^{-1} s^{-1}, respectively, are in good agreement with the recommended values, and the calculated rate constant for propane of 1.7×10^{-17} cm^3 molecule^{-1} s^{-1} at 298 K[1] is reasonably consistent with the lower limit to the rate constant of 2.0×10^{-17} cm^3 molecule^{-1} s^{-1} at 298 K derived by Boyd *et al.*[2] from modeling their data. These observations indicate that the group rate constants at 298 K (in cm^3 molecule^{-1} s^{-1} units) of: $k_{\text{prim}} = 7.0 \times 10^{-19}$, $k_{\text{sec}} = 1.5 \times 10^{-17}$, and $k_{\text{tert}} = 8.2 \times 10^{-17}$, together with the substituent factors of $F(-CH_3) = 1.00$ and $F(-CH_2-) = F(>CH-) = F(>C<) = 1.5$, all at 298 K, can be used to calculate room temperature rate constants for the gas-phase reactions of the NO_3 radical with alkanes. In addition to allowing the overall reaction rate constants to be calculated, the distribution of alkyl radicals formed can be calculated.

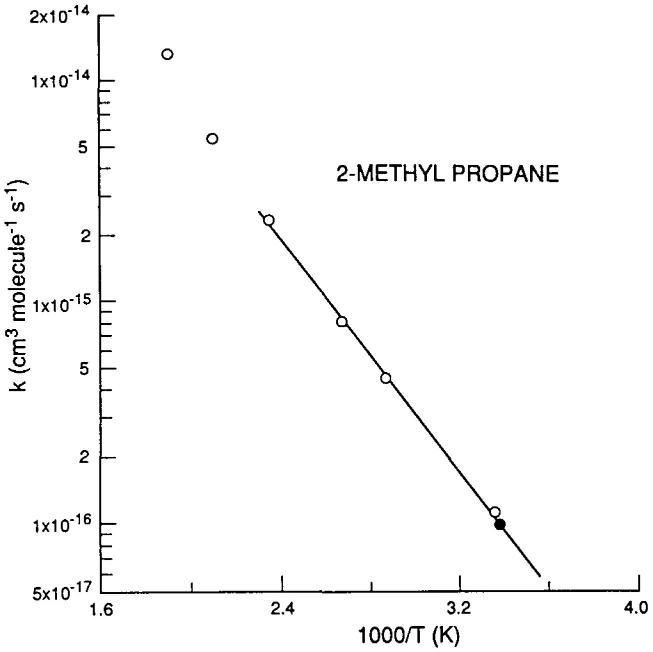

FIG. 44. Arrhenius plot of rate constants for the reaction of the NO_3 radical with 2-methylpropane. (○) Bagley *et al.*;[3] (●) Atkinson *et al.*;[5] (—) recommendation (see text).

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4.2. Haloalkanes

The kinetic data reported since the review of Atkinson[1] are given in Table 51. The upper limits to the rate constants obtained by Boyd *et al.*[2] using a stopped flow system with optical absorption of the NO_3 radical assumed a minimum stoichiometric factor of 2 for reactions of the NO_3 radical under these conditions.

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4.3. Alkenes

The rate constants reported since the review and evaluation of Atkinson[1] are given in Table 52, with the data of Wille *et al.*[6] being obtained from observation of the oxirane product formation profiles. The rate constants for the reactions of the NO_3 radical with 2,3-dimethyl-2-butene, 1,3-butadiene, 2-methyl-1,3-butadiene (isoprene) and 2,3-dimethyl-1,3-butadiene reported by Poulet and Le Bras,[10] and used by Atkinson[1] in the evaluations of the rate constants for these reactions, have been published[8,11] (that for isoprene is included in the publication of Wille *et al.*[8] and is also given in Table 52).

Ethene. The room temperature rate constant of Biggs *et al.*,[2] of $(1.7 \pm 0.5) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 300 K, is given in Table 52. This rate constant is in reasonable agreement with the recommended rate constant of Atkinson[1] of 2.18×10^{-16} cm^3 molecule^{-1} s^{-1} at this temperature. Hence the previous recommendation,[1] of

$$k(\text{ethene}) = 4.88 \times 10^{-18}\, T^2\, e^{-2282/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 295–523 K, with a 298 K rate constant of 2.05×10^{-16} cm^3 molecule^{-1} s^{-1}, is unchanged.

Propene. The absolute rate constants of Canosa-Mas *et al.*[3] are given in Table 52 and are plotted, together with the room temperature relative rate constant of Atkinson *et al.*,[12] in Arrhenius form in Fig. 45. The agreement between the room temperature rate constants[3,12] is excellent. The Arrhenius plot exhibits distinct non-Arrhenius behavior above 423 K, and a unit-weighted least-squares analysis of the 298–423 K absolute rate constants of Canosa-Mas *et al.*[3] and the relative rate constant of Atkinson *et al.*[12] leads to the recommended Arrhenius expression of

$$k(\text{propene}) = (4.59^{+1.22}_{-0.96}) \times 10^{-13}\, e^{-(1156 \pm 79)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 296–423 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{propene}) = 9.49 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K},$$

with an estimated overall uncertainty at 298 K of ±35%. This recommendation is in excellent agreement with, but supersedes, that of Atkinson[1] of

$$k(\text{propene}) = 9.45 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K}.$$

1-Butene. The absolute rate constants of Canosa-Mas *et al.*[4] are given in Table 52 and are plotted, together with those of Atkinson *et al.*,[12,13] Andersson and Ljungström[14] and Barnes *et al.*,[15] in Arrhenius form in Fig. 46. The agreement between these studies is good, and a unit-weighted least-squares analysis of the absolute rate constants of Canosa-Mas *et al.*[4] and the relative rate constants of Atkinson *et al.*[12,13] and Barnes *et al.*[15] leads to the recommended Arrhenius expression of

$$k(\text{1-butene}) = (2.04^{+1.06}_{-0.70}) \times 10^{-13}\, e^{-(843 \pm 139)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 296–473 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{1-butene}) = 1.21 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K},$$

with an estimated overall uncertainty at 298 K of ±30%. This recommendation is in excellent agreement with, but supersedes, that of Atkinson[1] of

$$k(\text{1-butene}) = 1.25 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K}.$$

TABLE 51. Rate constants for the gas-phase reactions of the NO_3 radical with haloalkanes

Haloalkane	k (cm^3 molecule^{-1} s^{-1})	at T(K)	Technique	Reference
CH_3Cl	$\leq 8 \times 10^{-19}$	300	SF-A	Boyd *et al.*[2]
CH_2Cl_2	$\leq 5.8 \times 10^{-18}$	300	SF-A	Boyd *et al.*[2]
$CHCl_3$	$\leq 6.5 \times 10^{-17}$	304	SF-A	Boyd *et al.*[2]

TABLE 52. Rate constants and temperature-dependent parameters for the gas-phase reactions of the NO_3 radical with alkenes

Alkene	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	k (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
Ethene			$(1.7 \pm 0.5) \times 10^{-16}$	300	SF-A	Biggs *et al.*[2]	
Propene			$(9.3 \pm 1.2) \times 10^{-15}$	298	DF-A	Canosa-Mas *et al.*[3]	298–523
			$(1.45 \pm 0.36) \times 10^{-14}$	333			
			$(1.98 \pm 0.44) \times 10^{-14}$	373			
			$(3.06 \pm 0.84) \times 10^{-14}$	423			
			$(5.05 \pm 0.34) \times 10^{-14}$	473			
	$0.474^{+0.106}_{-0.085}$	1171 ± 66 (298–423 K)	$(9.3 \pm 2.4) \times 10^{-14}$	523			
1-Butene			$(1.1 \pm 0.2) \times 10^{-14}$	299	DF-A	Canosa-Mas *et al.*[4]	299–473
			$(1.6 \pm 0.5) \times 10^{-14}$	323			
			$(1.8 \pm 0.4) \times 10^{-14}$	373			
			$(2.9 \pm 1.0) \times 10^{-14}$	423			
	0.25	940	$(3.6 \pm 0.8) \times 10^{-14}$	473			
2-Methylpropene			$(3.87 \pm 0.42) \times 10^{-13}$	298	DF-MS	Benter *et al.*[5]	
			$(3.6 \pm 0.4) \times 10^{-13}$	298	DF-MS	Wille *et al.*[6]	
cis-2-Butene			$(3.75 \pm 0.24) \times 10^{-13}$	298	DF-MS	Benter *et al.*[5]	
			$(3.3 \pm 0.8) \times 10^{-13}$	298	DF-MS	Wille *et al.*[6]	
trans-2-Butene			$(3.88 \pm 0.30) \times 10^{-13}$	298	DF-MS	Benter *et al.*[5]	
2-Methyl-2-butene			$(8.42 \pm 0.60) \times 10^{-12}$	298	DF-MS	Benter *et al.*[5]	
			$(7.0 \pm 2.0) \times 10^{-12}$	298	DF-MS	Wille *et al.*[6]	
2,3-Dimethyl-2-butene			$(4.07 \pm 0.40) \times 10^{-11}$	298	DF-MS	Benter *et al.*[5]	
			$(3.8 \pm 0.8) \times 10^{-11}$	298	DF-MS	Wille *et al.*[6]	
			$(5.71 \pm 0.28) \times 10^{-11}$	296 ± 2	RR [relative to k(2-methyl-2-butene) = 9.37×10^{-12}][a]	Atkinson *et al.*[7]	
2-Methyl-1,3-butadiene (isoprene)			$(8.26 \pm 0.60) \times 10^{-13}$	298	DF-MS	Wille *et al.*[8]	
			$(7.30 \pm 0.44) \times 10^{-13}$	298	DF-MS	Wille *et al.*[8]	
β-Phellandrene			$(7.96 \pm 0.44) \times 10^{-12}$	297 ± 2	RR [relative to k(2-methyl-2-butene) = 9.37×10^{-12}][a]	Shorees *et al.*[9]	

[a] From present and previous[1] recommendations.

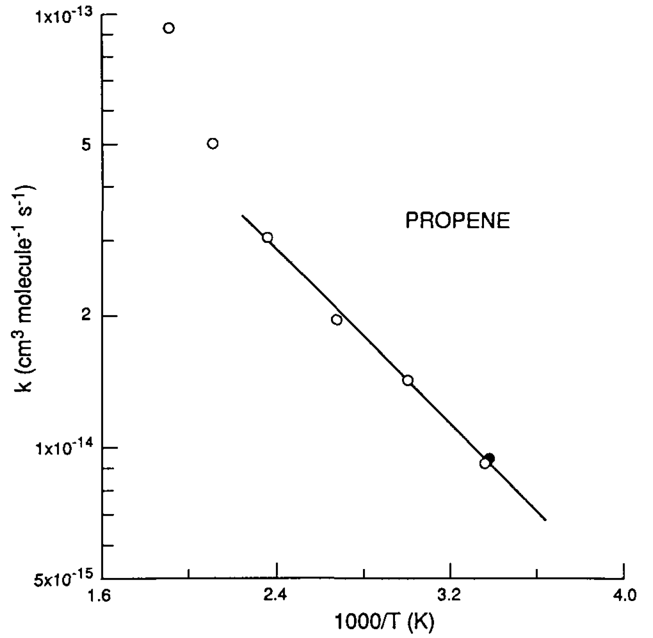


FIG. 45. Arrhenius plot of selected rate constants for the reaction of the NO_3 radical with propene. (●) Atkinson *et al.*;[12] (○) Canosa-Mas *et al.*;[3] (—) recommendation (see text).

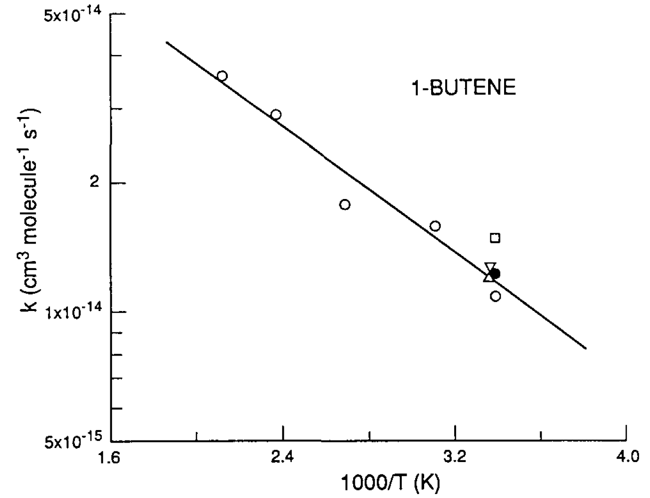


FIG. 46. Arrhenius plot of selected rate constants for the reaction of the NO_3 radical with 1-butene. (△) Atkinson *et al.*;[13] (●) Atkinson *et al.*;[12] (□) Andersson and Ljungström;[14] (▽) Barnes *et al.*;[15] (○) Canosa-Mas *et al.*;[4] (—) recommendation (see text).

2-Methylpropene. The rate constants determined by Benter *et al.*[5] and Wille *et al.*[6] (the latter from the oxirane product formation rate) are given in Table 52. These rate constants[5,6] are in good agreement with the previous recommendation of Atkinson[1] of

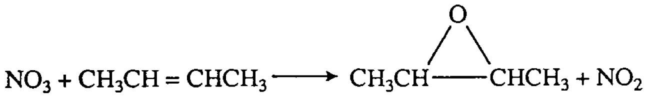
$$k(\text{2-methylpropene}) = 3.32 \times 10^{-13}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

which is therefore unchanged.

cis-2-Butene. The rate constants determined by Benter *et al.*[5] and Wille *et al.*[6] (the latter from the oxirane product formation rate) are given in Table 52. These rate constants[5,6] are in excellent agreement with the previous recommendation of Atkinson[1] of

$$k(cis\text{-2-butene}) = 3.50 \times 10^{-13}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

which is therefore unchanged. Wille *et al.*[6] showed that at 298 K and 2.2–7.5 Torr total pressure that the pathway



$$NO_3 + CH_3CH=CHCH_3 \longrightarrow CH_3CH\overset{O}{\frown}CHCH_3 + NO_2$$

accounted for 90 ± 10% of the overall reaction. This observation is in agreement with the previous results of Dlugokencky and Howard[16] for the NO_3 radical reaction with *trans*-2-butene at low total pressures.

trans-2-Butene. The rate constant reported by Benter *et al.*[5] is given in Table 52. This rate constant is in excellent agreement with the previous recommendation of Atkinson[1] of

$$k(trans\text{-2-butene}) = 3.90 \times 10^{-13}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

which is therefore unchanged.

2-Methyl-2-butene. The rate constants reported by Benter *et al.*[5] and Wille *et al.*[6] (the latter from the oxirane product formation rate) are given in Table 52. The more precise rate constant of Benter *et al.*[5] is 20% lower than the previous recommendation of Atkinson[1] of

$$k(\text{2-methyl-2-butene}) = 9.37 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

at 298 K. Until further absolute rate constant studies confirm a lower rate constant for this reaction, the previous recommendation[1] is unchanged.

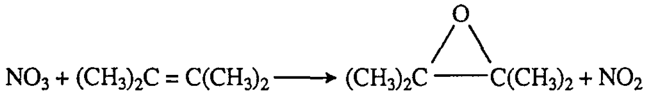
2,3-Dimethyl-2-butene. The rate constants obtained by Benter *et al.*[5] and Wille *et al.*[6] at low total pressures (2.3 Torr) are given in Table 52 (the rate constant of Wille *et al.*[6] was obtained from the oxirane product formation rate). These absolute rate constants[5,6] are ~30% lower than the previous recommendation of Atkinson[1] of

$$k(\text{2,3-dimethyl-2-butene}) = 5.72 \times 10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K}.$$

In contrast, the relative rate constant of Atkinson *et al.*[7] is in excellent agreement with the previous recommendation of Atkinson.[1]

However, the rate constants of Benter *et al.*[5] and Wille *et al.*[6] are in good agreement with the previously reported low pressure absolute rate constants of Rahman *et al.*[17] and Lancar *et al.*,[11] also obtained using discharge flow-mass spectrometry techniques. Until this discrepancy is resolved, possibly through the use of other experimental approaches, the previous recommendation is unchanged.

It should also be noted that the rate constant ratio of k(2,3-dimethyl-2-butene)/k(2-methyl-2-butene) = 4.83 ± 0.59 at 298 K derived from the rate constants of Benter *et al.*[5] is significantly lower than the ratios of 6.10 ± 0.16 at 298 ± 1 K,[13] 6.13 ± 0.16 at 295 ± 1 K[18] and 6.09 ± 0.29 at 296 ± 2 K[7] obtained by Atkinson *et al.*[7,13,18] from relative rate studies conducted at atmospheric pressure of air. Wille *et al.*[6] observed the formation of the oxirane from the reaction pathway



to account for 90 ± 10% of the overall reaction.

2-Methyl-1,3-butadiene (isoprene). The rate constants reported by Wille *et al.*[8] at 298 K originate from studies conducted at two laboratories, with that of Lancar *et al.*[11] being reported previously[10] and used in the review and evaluation of Atkinson.[1] The rate constant determined at Kiel, Germany[8] of (7.30 ± 0.44) × 10^{-13} cm^3 $molecule^{-1}$ s^{-1} at 298 K is in good agreement with the recommendation of Atkinson[1] of

$$k(\text{isoprene}) = 6.78 \times 10^{-13}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \text{ at } 298\ \text{K},$$

and hence this previous recommendation[1] of

$$k(\text{isoprene}) = 3.03 \times 10^{-12}\ e^{-446/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 251–381 K is unchanged.

References

[1] R. Atkinson, J. Phys. Chem. Ref. Data **20**, 459 (1991).
[2] P. Biggs, A. A. Boyd, C. E. Canosa-Mas, D. M. Joseph, and R. P. Wayne, Meas. Sci. Technol. **2**, 675 (1991).
[3] C. E. Canosa-Mas, S. J. Smith, S. J. Waygood, and R. P. Wayne, J. Chem. Soc. Faraday Trans. **87**, 3473 (1991).
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[11] I. T. Lancar, V. Daele, G. Le Bras, and G. Poulet, J. Chim. Phys. **88**, 1777 (1991).
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[14] Y. Andersson and E. Ljungström, Atmos. Environ. **23**, 1153 (1989).
[15] I. Barnes, V. Bastian, K. H. Becker, and Z. Tong, J. Phys. Chem. **94**, 2413 (1990).
[16] E. J. Dlugokencky and C. J. Howard, J. Phys. Chem. **93**, 1091 (1989).
[17] M. M. Rahman, E. Becker, Th. Benter, and R. N. Schindler, Ber. Bunsenges. Phys. Chem. **92**, 91 (1988).
[18] R. Atkinson, S. M. Aschmann, A. M. Winer, and J. N. Pitts, Jr., Environ. Sci. Technol. **18**, 370 (1984).

4.4. Haloalkenes

The rate constants reported since the review and evaluation of Atkinson[1] are given in Table 53 (the data of Wängberg *et al.*[3] were included in the Addendum in Atkinson[1]). The rate constants for the reaction of the NO_3 radical with 2-chloro-1-butene at room temperature[2,3] are in good agreement. The trends in the rate constants for the reactions of the NO_3 radical with haloalkenes with the number and configuration of the halogen substituent(s) around the $>C=C<$ bond are discussed by Aird *et al.*[2]

References

[1] R. Atkinson, J. Phys. Chem. Ref. Data **20**, 459, (1991).
[2] R. W. S. Aird, C. E. Canosa-Mas, D. J. Cook, G. Marston, P. S. Monks, R. P. Wayne, and E. Ljungström, J. Chem. Soc. Faraday Trans. **88**, 1093 (1992).
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4.5. Alkynes

The rate constants reported since the review and evaluation of Atkinson[1] are given in Table 54.

References

[1] R. Atkinson, J. Phys. Chem. Ref. Data **20**, 459 (1991).
[2] Th. Benter, E. Becker, U. Wille, R. N. Schindler, C. E. Canosa-Mas, S. J. Smith, S. J. Waygood, and R. P. Wayne, J. Chem. Soc. Faraday Trans. **87**, 2141 (1991).

4.6. Oxygen-Containing Organic Compounds

The kinetic data reported since the review and evaluation of Atkinson[1] are given in Table 55.

References

[1] R. Atkinson, J. Phys. Chem. Ref. Data **20**, 459 (1991).
[2] A. A. Boyd, C. E. Canosa-Mas, A. D. King, R. P. Wayne, and M. R. Wilson, J. Chem. Soc. Faraday Trans. **87**, 2913 (1991).
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4.7. Sulfur-Containing Organic Compounds

Jensen *et al.*[1,2] have conducted product studies of the gas-phase reactions of the NO_3 radical with CH_3SCH_3[1,2], CD_3SCD_3,[2] CH_3SH[2] and CH_3SSCH_3,[2] using Fourier transform infrared (FT-IR) absorption spectroscopy to monitor the reactants and products. By monitoring the relative disappearance rates of CH_3SCH_3 and CD_3SCD_3, a rate constant ratio of $k(CH_3SCH_3)/k(CD_3SCD_3)$ = 3.8 ± 0.6 at 295 ± 2 K was determined,[2] in excellent agreement with the absolute rate constants of Daykin and Wine[3] for CH_3SCH_3 and CD_3SCD_3. This deuterium isotope effect[2] and the products observed[1,2] led Jensen *et al.*[1,2] to conclude that these NO_3 radical reactions proceed exclusively (or mainly) by,

$$NO_3 + CH_3SCH_3 \rightleftarrows [CH_3S(ONO_2)CH_3] \rightarrow HONO_2 + CH_3S\dot{C}H_2$$

$$NO_3 + CH_3SH \rightleftarrows [CH_3S(ONO_2)H] \rightarrow HONO_2 + CH_3S^{\bullet}$$

$$NO_3 + CH_3SSCH_3 \rightleftarrows [CH_3SS(ONO_2)CH_3] \rightarrow CH_3\dot{S} + CH_3\dot{S}O + NO_2$$

in agreement with previous discussions.[4]

Analogous product studies have been conducted by Jensen *et al.*[5] for the gas-phase reactions of the NO_3 radical with CH_3CH_2SH, $CH_3CH_2SCH_3$, $CH_3CH_2SCH_2CH_3$ and $CH_3CH_2SSCH_2CH_3$ in air at 295 ± 2 K. Jensen *et al.*[5] concluded that the reaction mechanisms for these organosulfur compounds were analogous to those for CH_3SH, CH_3SCH_3 and CH_3SSCH_3.[1,2,4]

References

[1]N. R. Jensen, J. Hjorth, C. Lohse, H. Skov, and G. Restelli, Atmos. Environ. **25A**, 1897 (1991).

[2]N. R. Jensen, J. Hjorth, C. Lohse, H. Skov, and G. Restelli, J. Atmos. Chem. **14**, 95 (1992).

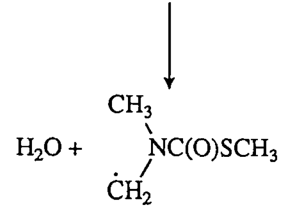
[3]E. P. Daykin and P. H. Wine, Int. J. Chem. Kinet. **22**, 1083 (1990).

[4]R. Atkinson, J. Phys. Chem. Ref. Data **20**, 459 (1991).

[5]N. R. Jensen, J. Hjorth, C. Lohse, H. Skov, and G. Restelli, Int. J. Chem. Kinet. **24**, 839 (1992).

4.8. Nitrogen- and Silicon-Containing Organic Compounds

The rate constants reported since the review and evaluation of Atkinson[1] are given in Table 56. From a product study, Kwok *et al.*[2] showed that the major reaction pathway for the NO_3 radical reaction with $(CH_3)_2NC(O)SCH_3$ proceeds by overall H-atom abstraction to form the $\dot{C}H_2(CH_3)NC(O)SCH_3$ radical (presumably by initial NO_3 radical interaction with the N atom), ultimately leading to the formation of $CH_3(CHO)NC(O)SCH_3$ in 87 ± 13% yield.



$$NO_3 + (CH_3)_2NC(O)SCH_3 \longrightarrow [(CH_3)_2N(OH)C(O)SCH_3] \longrightarrow H_2O + CH_3(\dot{C}H_2)NC(O)SCH_3$$

References

[1]R. Atkinson, J. Phys. Chem. Ref. Data **20**, 459 (1991).

[2]E. S. C. Kwok, R. Atkinson, and J. Arey, Environ. Sci. Technol. **26**, 1798 (1992).

[3]R. Atkinson, S. M. Aschmann, and J. Arey, unpublished data (1993).

4.9. Aromatic Compounds

The rate constants reported since the review and evaluation of Atkinson[1] are given in Table 57.

Phenol, o-Cresol, m-Cresol and p-Cresol. The room temperature rate constants of Atkinson *et al.*[2] are given in Table 57. These rate constants are in general agreement (within ±40%) with the relative rate constants of Carter *et al.*,[3] and that for phenol[2] is also in excellent agreement with the rate constant of Atkinson *et al.*[4] determined relative to the rate constant for the reaction of the NO_3 radical with 2-methyl-2-butene. There are, however, significant discrepancies between the rate constants for *o*-, *m*- and *p*-cresol obtained from the two studies of Atkinson *et al.*[2,4] (the rate constants for *o*- and *p*-cresol[4] were relative to that for *m*-cresol, which in turn was relative to that for phenol,[4] all determined using FT-IR absorption spectroscopy).[4]

A unit-weighted average of the rate constants for phenol of Atkinson *et al.*[2,4] leads to the recommendation of

$$k(\text{phenol}) = 3.78 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

with an estimated overall uncertainty of ±35%. This recommendation supersedes that of Atkinson[1] of

$$k(\text{phenol}) = 3.64 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

which was based on the study of Atkinson *et al.*[4] For the three cresol isomers, the rate constants of Atkinson *et al.*[2] are recommended:

$$k(\text{o-cresol}) = 1.37 \times 10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K}$$

with an estimated overall uncertainty of ±35%,

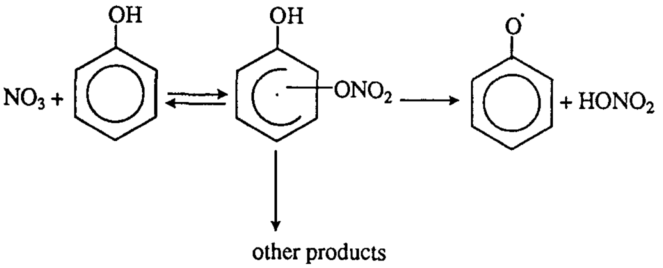
$$k(m\text{-cresol}) = 9.74 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K}$$

with an estimated overall uncertainty of ±35%, and

$$k(p\text{-cresol}) = 1.07 \times 10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K}$$

with an estimated overall uncertainty of a factor of 1.5.

Atkinson *et al.*[2] also measured the nitrophenol and nitrocresol yields from these NO_3 radical reactions, and observed yields significantly lower than unity for phenol and *o*- and *m*-cresol (Sec. 2.4). These product data suggest that these NO_3 radical reactions proceed by,



with the phenoxy radicals reacting with NO_2 to form the nitrophenols.[2]

Miscellaneous

Rindone *et al.*[5] have investigated the gas-phase reactions of the NO_3 radical with *o*-xylene-h_{10}, *o*-xylene-d_{10},

TABLE 53. Rate constants k for the gas-phase reactions of the NO_3 radical with haloalkenes

Haloalkene	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	k (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
1-Chloro-1-butene [$CH_3CH_2CH=CHCl$]			$(1.2 \pm 0.4) \times 10^{-14}$	298	DF-A	Aird *et al.*[2]	
2-Chloro-1-butene [$CH_3CH_2CCl=CH_2$]			$(1.73 \pm 0.31) \times 10^{-14}$	299	DF-A	Wängberg *et al.*[3]	
			$(2.21 \pm 0.53) \times 10^{-14}$	296	RR [relative to $k(NO_3 + NO_2 \rightleftarrows N_2O_5) = 4.40 \times 10^{-11}$][a]	Wängberg *et al.*[3]	
			$(1.7 \pm 0.3) \times 10^{-14}$	299	DF-A	Aird *et al.*[2]	
3-Chloro-1-butene [$CH_3CHClCH=CH_2$]			$(3.0 \pm 0.7) \times 10^{-15}$	296	DF-A	Aird *et al.*[2]	296–473
			$(1.2 \pm 0.1) \times 10^{-14}$	373			
	2.4×10^{-12}	1992 ± 241	$(3.5 \pm 1.2) \times 10^{-14}$	473			
1-Chloro-2-butene [$CH_3CH=CHCH_2Cl$]			$(2.0 \pm 0.7) \times 10^{-14}$	298	DF-A	Aird *et al.*[2]	298–473
			$(5.0 \pm 1.7) \times 10^{-14}$	373			
	6.0×10^{-13}	981 ± 349	$(7.0 \pm 5.5) \times 10^{-14}$	473			
2-Chloro-2-butene [$CH_3CH=CClCH_3$]			$(1.10 \pm 0.40) \times 10^{-13}$	298	DF-A	Aird *et al.*[2]	
1-Chloro-2-methylpropene [$(CH_3)_2C=CHCl$]			$(9.0 \pm 2.3) \times 10^{-14}$	298	DF-A	Aird *et al.*[2]	
2-Chloromethylpropene [$CH_3C(CH_2Cl)=CH_2$]			$(2.5 \pm 0.4) \times 10^{-14}$	298	DF-A	Aird *et al.*[2]	298–473
			$(4.7 \pm 0.5) \times 10^{-14}$	373			
	1.6×10^{-12}	1277 ± 205	$(1.23 \pm 0.06) \times 10^{-13}$	473			
3-Bromo-1-butene [$CH_3CHBrCH=CH_2$]			$(4 \pm 1) \times 10^{-15}$	298	DF-A	Aird *et al.*[2]	
4-Bromo-1-butene [$CH_2BrCH_2CH=CH_2$]			$(5 \pm 1) \times 10^{-15}$	298	DF-A	Aird *et al.*[2]	
2-Bromo-2-butene [$CH_3CH=CBrCH_3$]			$(1.34 \pm 0.01) \times 10^{-13}$	298	DF-A	Aird *et al.*[2]	

[a] From present and previous[1] recommendations.

TABLE 54. Rate constants k for the gas-phase reactions of the NO_3 radical with alkynes

Alkyne	k(cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference
2-Hexyne	$(2.8 \pm 0.1) \times 10^{-14}$	298	DF-MS	Benter *et al.*[2]
	$\sim 3 \times 10^{-13}$	433	DF-A	Benter *et al.*[2]

TABLE 55. Rate constants k for the gas-phase reactions of the NO_3 radical with oxygen-containing organic compounds

Oxygenate	k(cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference
Acetone	$\leq 1.1 \times 10^{-17}$	302	SF-A	Boyd *et al.*[2]
4-Acetyl-1-methylcyclohexene	$(1.05 \pm 0.08) \times 10^{-11}$	296 ± 2	RR [relative to k(2-methyl-2-butene) = 9.37×10^{-12}][a]	Atkinson and Aschmann[3]

[a] From present and previous[1] recommendation.

TABLE 56. Rate constants k for the gas-phase reactions of the NO_3 radical with nitrogen- and silicon-containing organic compounds

Organic	k(cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference
Nitrogen-containing				
$(CH_3)_2NC(O)SCH_3$	$(7.10 \pm 0.31) \times 10^{-15}$	298 ± 2	RR [relative to k(1-butene) = 1.21×10^{-14}][a]	Kwok *et al.*[2]
$(CH_3CH_2CH_2)_2NC(O)SCH_2CH_3$	$(8.94 \pm 0.45) \times 10^{-15}$	298 ± 2	RR [relative to k(1-butene) = 1.21×10^{-14}][a]	Kwok *et al.*[2]
$CH_3CH_2(c\text{-}C_6H_{11})NC(O)SCH_2CH_3$	$(3.18 \pm 0.26) \times 10^{-14}$	298±2	RR [relative to k(1-butene) = 1.21×10^{-14}][a]	Kwok *et al.*[2]
Silicon-containing				
$(CH_3)_3SiOSi(CH_3)_2OH$	$< 1.7 \times 10^{-16}$	297 ± 2	RR [relative to k(n-heptane) = 1.37×10^{-16}][a]	Atkinson *et al.*[3]

[a] From present and previous[1] recommendations.

TABLE 57. Rate constants k for the gas-phase reactions of the NO_3 radical with aromatic compounds

Aromatic	k(cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference
Phenol	$(3.92 \pm 0.25) \times 10^{-12}$	296 ± 2	RR [relative to k(2-methyl-2-butene) = 9.37×10^{-12}]^a	Atkinson *et al.*[2]
o-Cresol	$(1.37 \pm 0.09) \times 10^{-11}$	296 ± 2	RR [relative to k(2-methyl-2-butene) = 9.37×10^{-12}]^a	Atkinson *et al.*[2]
m-Cresol	$(9.74 \pm 0.47) \times 10^{-12}$	296 ± 2	RR [relative to k(2-methyl-2-butene) = 9.37×10^{-12}]^a	Atkinson *et al.*[2]
p-Cresol	$(1.07 \pm 0.10) \times 10^{-11}$	296 ± 2	RR [relative to k(2-methyl-2-butene) = 9.37×10^{-12}]^a	Atkinson *et al.*[2]
2-Nitrophenol	$< 1.2 \times 10^{-14}$	296 ± 2	RR [relative to k(*trans*-2-butene) = 3.89×10^{-13}]^a	Atkinson *et al.*[2]

[a] From present and previous[1] recommendations.

p-xylene-h_{10}, *p*-xylene-d_{10} and *p*-xylene-d_6 [$C_6H_4(CD_3)_2$] at room temperature, and observed a significant deuterium isotope effect on the rate constants, with the deuterated xylenes reacting slower than the non-deuterated compounds by factors of 1.48–1.87. In agreement with the rate constants of Atkinson and Aschmann,[6] these kinetic data of Rindone *et al.*[5] confirm that the NO_3 radicals with the alkyl-substituted benzenes proceed by H-atom abstraction from the C–H (or C–D) bonds

$$NO_3 + C_6H_5CH_3 \rightarrow HONO_2 + C_6H_5CH_2$$

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5. Kinetics and Mechanisms of the Gas-Phase Reactions of Ozone with Organic Compounds

In this section, the previous review and evaluation of Atkinson and Carter[1] is updated.

5.1. Haloalkanes

Since the review and evaluation of Atkinson and Carter,[1] Tuazon *et al.*[2] have determined an upper limit to the rate constant for the reaction of O_3 with 1,2-dibromo-3-chloropropane ($CH_2BrCHBrCH_2Cl$) of $k(CH_2BrCHBrCH_2Cl) < 3 \times 10^{-20}$ cm^3 molecule^{-1} s^{-1} at 296 ± 2 K.

References

[1] R. Atkinson and W. P. L. Carter, Chem. Rev. **84**, 437 (1984).

[2] E. C. Tuazon, R. Atkinson, S. M. Aschmann, J. Arey, A. M. Winer, and J. N. Pitts, Jr., Environ. Sci. Technol. **20**, 1043 (1986).

5.2. Alkenes

The rate constants reported since the review and evaluation of Atkinson and Carter[1] are given in Table 58. Also included in this table are the corrected rate constants of Herron and Huie[4] for propene. The study of Treacy *et al.*[3] is taken to supersede the data previously reported by Donlon *et al.*[14]

Ethene. The rate constants of Bahta *et al.*[2] and Treacy *et al.*[3] are given in Table 58 (the rate constants of Bahta *et al.*[2] have been averaged at each of the four temperatures studied). Since Treacy *et al.*[3] did not tabulate the individual rate constants at the various temperatures studied, only the Arrhenius expression and 298 K rate constants can be included in Table 58. These two kinetic studies[2,3] obtained room temperature rate constants in the range $(1.37–1.45) \times 10^{-18}$ cm^3 molecule^{-1} s^{-1}, which are somewhat lower than many of the previous rate constant data,[1] including those of Su *et al.*[15] and Kan *et al.*[16] The rate constants of Bahta *et al.*[2] and Treacy *et al.*[3] are plotted in Arrhenius form in Fig. 47, together with the rate constants of DeMore,[17] Stedman *et al.*,[18] Herron and Huie,[4] Japar *et al.*,[19,20] Toby *et al.*[21] and Atkinson *et al.*[22] A unit-weighted least-squares analysis of the rate constants of DeMore,[17] Stedman *et al.*,[18] Herron and Huie,[4] Japar *et al.*,[19,20] Toby *et al.*,[21] Atkinson *et al.*,[22] Bahta *et al.*[2] and the 298 K rate constant of Treacy *et al.*[3] leads to the recommended Arrhenius expression of

$$k(\text{ethene}) = (9.14^{+3.13}_{-2.33}) \times 10^{-15}\, e^{-(2580 \pm 71)/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 178–362 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{ethene}) = 1.59 \times 10^{-18}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

with an estimated overall uncertainty at 298 K of ±30%.

This recommendation supersedes the previous recommendation of Atkinson and Carter[1] (which was also used by the NASA[23] and IUPAC[24] evaluations) of

$$k(\text{ethene}) = 1.2 \times 10^{-14}\, e^{-2630/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the same temperature range of 178–362 K, with a 298 K rate constant of 1.75×10^{-18} cm^3 molecule^{-1} s^{-1}.

Propene. The rate constants of Treacy *et al.*[3] are given in Table 58, together with the corrected rate constants of Herron and Huie[4] (the lowest temperature studied was 235.0 K and not 250.0 K as given by Herron and Huie[4] and used in the evaluation of Atkinson and Carter[1]). The rate constants of Herron and Huie[4] and Treacy *et al.*[3] are plotted in Arrhenius form in Fig. 48, together with the apparently reliable[1] rate constants of Cox and Penkett,[25] Stedman *et al.*,[18] Japar *et al.*[19,20] and Atkinson *et al.*[22] The rate constants determined by Herron and Huie[4] and Treacy *et al.*[3] for propene [and ethene (Fig. 47)] are in excellent agreement over the temperature range common to both studies (240–324 K). The rate constants obtained by Huie and Herron[26] and Treacy *et al.*[3] for 1-butene, *cis*-2-butene, *trans*-2-butene, 2-methylpropene and 2-methyl-2-butene are also in excellent agreement over the temperature range common to both studies (240–324 K).

In addition to these studies, Greene and Atkinson[5] have carried out a relative rate study of the reactions of O_3 with a series of alkenes at 296 ± 2 K. Greene and Atkinson[5] obtained relative rate constants for propene, 1-butene, 2-methylpropene, *cis*- and *trans*-2-butene, 2-methyl-2-butene, 2,3-dimethyl-2-butene and 2-methyl-1,3-butadiene,[5] and these relative rate constants are in generally excellent agreement with the absolute rate constants of Herron and Huie,[4] Huie and Herron[26] and Treacy *et al.*[3] From a unit-weighted average of the 298 K rate constants of Herron and Huie[4] and Treacy *et al.*[3] a rate constant of

$$k(\text{propene}) = 1.01 \times 10^{-17}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K}$$

is recommended. Combination of this 298 K rate constant with the temperature dependence of B = 1878 K, obtained from a unit-weighted average of the temperature dependencies of Herron and Huie[4] and Treacy *et al.*,[3] leads to the recommended Arrhenius expression of

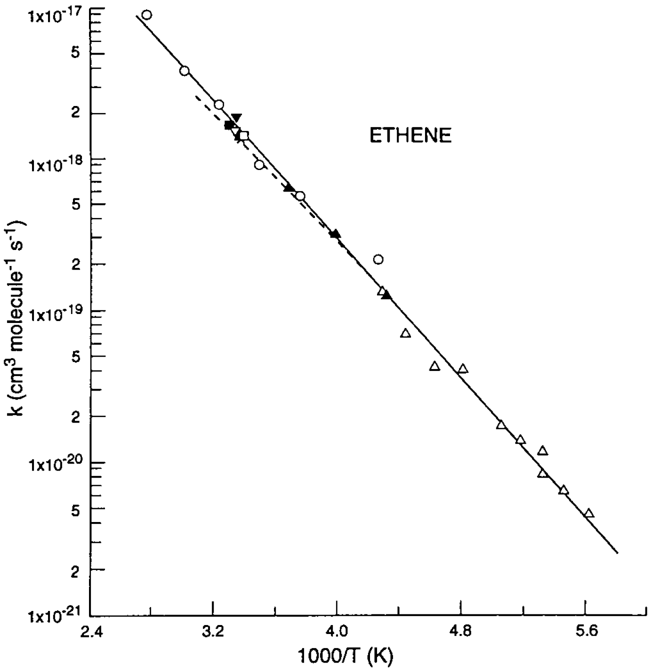

FIG. 47. Arrhenius plot of selected rate constants for the reaction of O_3 with ethene. (△) DeMore;[17] (▽) Stedman *et al.*;[18] (○) Herron and Huie;[4] (▼) Japar *et al.*;[19,20] (■) Toby *et al.*;[21] (□) Atkinson *et al.*;[22] (▲) Bahta *et al.*;[2] (–X–) Treacy *et al.*;[3] (—) recommendation (see text).

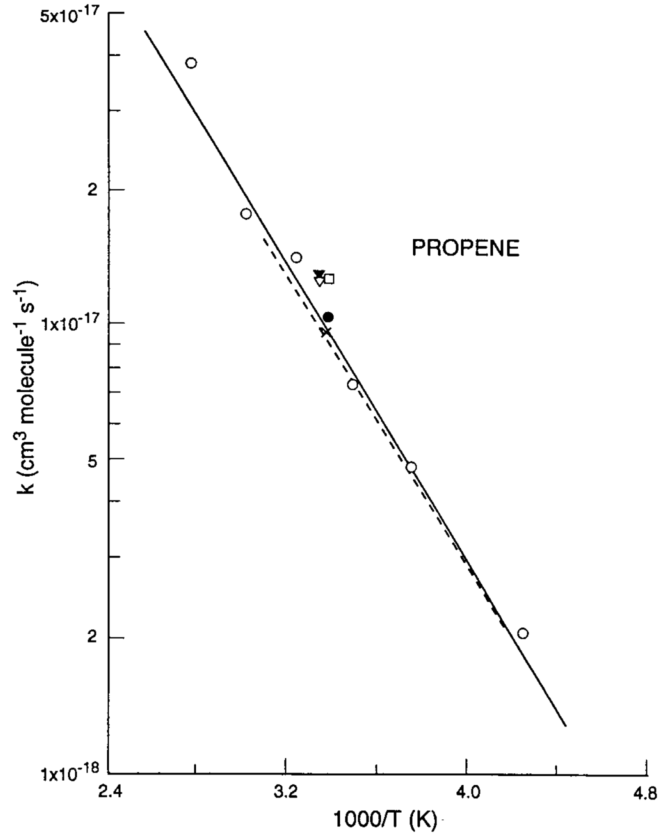

FIG. 48. Arrhenius plot of selected rate constants for the reaction of O_3 with propene. (□) Cox and Penkett;[25] (▽) Stedman *et al.*;[18] (○) Herron and Huie;[4] (▼) Japar *et al.*;[19,20] (●) Atkinson *et al.*;[22] (–X–) Treacy *et al.*;[3] (—) recommendation (see text).

$$k(\text{propene}) = 5.51 \times 10^{-15}\, e^{-1878/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 235–362 K, with an estimated overall uncertainty at 298 K of ±25%.

This recommendation supersedes the IUPAC[24] recommendation of

$$k(\text{propene}) = 6.5 \times 10^{-15}\, e^{-1880/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 230–370 K, with a 298 K rate constant of 1.2×10^{-17} cm^3 molecule^{-1} s^{-1}.

1-Butene. The rate constants of Treacy *et al.*[3] and Greene and Atkinson[5] are given in Table 58 and are plotted, together with the rate constants of Japar *et al.*[19] and Huie and Herron,[26] in Arrhenius form in Fig. 49. The agreement of the room temperature rate constants between the studies of Huie and Herron,[26] Treacy *et al.*[3] and Greene and Atkinson[5] is excellent. From a unit-weighted average of the 298 K rate constants of Huie and Herron,[26] Treacy *et al.*[3] and Greene and Atkinson[5] (corrected from 296 K to 298 K using the recommended temperature dependence), the rate constant of

$$k(\text{1-butene}) = 9.64 \times 10^{-18}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K}$$

is recommended. Combining this recommended 298 K rate constant with the unit-weighted average of the temperature dependences of Huie and Herron[26] and Treacy *et al.*,[3] of B = 1744 K, leads to the recommendation of

$$k(\text{1-butene}) = 3.36 \times 10^{-15}\, e^{-1744/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 225–363 K, with an estimated overall uncertainty at 298 K of ±25%. This recommendation supersedes that of Atkinson and Carter[1] of

$$k(\text{1-butene}) = 3.46 \times 10^{-15}\, e^{-1713/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the same temperature range of 225–363 K, with a 298 K rate constant of 1.10×10^{-17} cm^3 molecule^{-1} s^{-1}.

2-Methylpropene. The rate constants of Treacy *et al.*[3] and Greene and Atkinson[5] are given in Table 58 and are plotted, together with the rate constants of Japar *et al.*[19] and Huie and Herron,[26] in Arrhenius form in Fig. 50. The rate constants of Huie and Herron,[26] Treacy *et al.*[3] and Green and Atkinson[5] are in excellent agreement, and a unit-weighted average of the 298 K rate constants of Huie and Herron,[26] Treacy *et al.*[3] and Greene and Atkinson[5] (corrected to 298 K as described for 1-butene above) leads to the recommended 298 K rate constant of

$$k(\text{2-methylpropene}) = 1.13 \times 10^{-17}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}.$$

Combining this 298 K rate constant with the temperature dependence of B = 1632 K obtained from a unit-weighted average of the temperature dependencies of Huie and Herron[26] and Treacy *et al.*[3] leads to the recommendation of

$$k(\text{2-methylpropene}) = 2.70 \times 10^{-15}\, e^{-1632/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 225–363 K, with an estimated overall uncertainty at 298 K of ±30%. This recommendation supersedes that of Atkinson and Carter[1] of

$$k(\text{2-methylpropene}) = 3.55 \times 10^{-15}\, e^{-1693/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the same temperature range of 225–363 K, with a 298 K rate constant of 1.21×10^{-17} cm^3 molecule^{-1} s^{-1}.

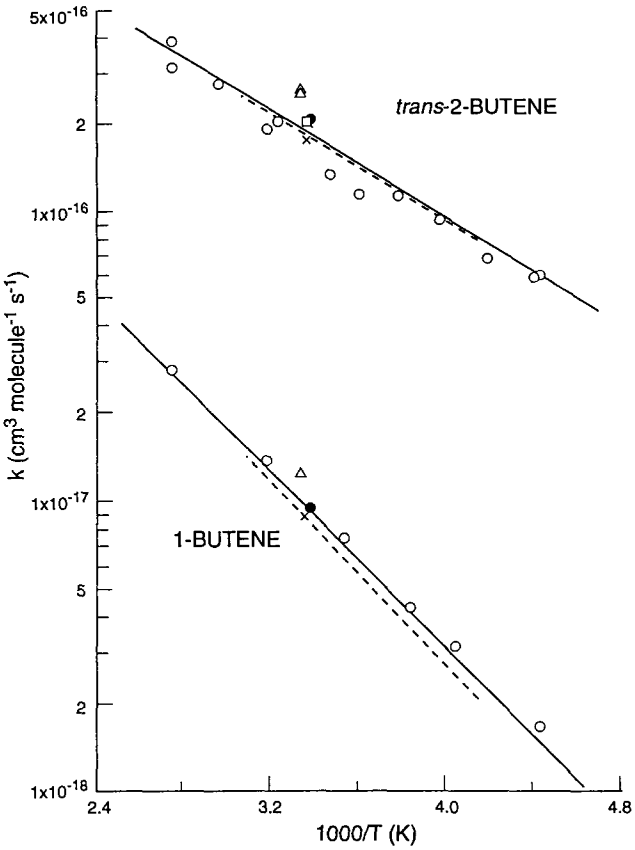

FIG. 49. Arrhenius plots of selected rate constants for the reactions of O_3 with 1-butene and *trans*-2-butene. (△) Japar *et al.*;[19] (1-butene) and Japar *et al.*[19,20] (*trans*-2-butene); (○) Huie and Herron;[26] (□) Nolting *et al.*;[6] (– X –) Treacy *et al.*;[3] (●) Greene and Atkinson;[5] (—) recommendations (see text).

cis-2-Butene. The rate constants of Treacy *et al.*[3] and Greene and Atkinson[5] are given in Table 58 and are plotted in Arrhenius form, together with the rate constants of Japar *et al.*,[19] Huie and Herron[26] and Atkinson *et al.*,[27] in Fig. 50. The room temperature rate constants of Huie and Herron,[26] Treacy *et al.*[3] and Greene and Atkinson[5] are in excellent agreement, and agree well with the literature rate constants of Cox and Penkett,[25] Japar *et al.*,[19] and Atkinson *et al.*[27] A unit-weighted average of the 298 K rate constants of Huie and Herron,[26] Treacy *et al.*[3] and Greene and Atkinson[5] (corrected to 298 K as described above for 1-butene) leads to the recommended 298 K rate constant of

TABLE 58. Rate constants k and temperature-dependent parameters, $k = Ae^{-B/T}$, for the gas-phase reactions of O_3 with alkenes

Alkene	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	k (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
Ethene			$(1.34 \pm 0.37) \times 10^{-19}$	232 ± 4	S-UV	Bahta *et al.*[2]	228–301
			$(3.31 \pm 0.88) \times 10^{-19}$	251 ± 4			
			$(6.60 \pm 1.75) \times 10^{-19}$	272 ± 3			
	$(7.72 \pm 0.89) \times 10^{-15}$	2557 ± 31	$(1.45 \pm 0.25) \times 10^{-18}$	298 ± 3			
	$(5.1 \pm 1.0) \times 10^{-15}$	2446 ± 91	$(1.37 \pm 0.08) \times 10^{-18}$	298	S-UV	Treacy *et al.*[3]	240–324
Propene			$(2.08 \pm 0.02) \times 10^{-18}$	235.0	SF-MS	Herron and Huie[4]	235–362
			$(4.83 \pm 0.10) \times 10^{-18}$	266.9			
			$(7.37 \pm 0.15) \times 10^{-18}$	286.2			
			$(1.41 \pm 0.02) \times 10^{-17}$	309.4			
			$(1.76 \pm 0.02) \times 10^{-17}$	332.4			
	6.14×10^{-15}	1897 ± 109	$(3.82 \pm 0.05) \times 10^{-17}$	362.0			
	$(4.9 \pm 1.0) \times 10^{-15}$	1858 ± 70	$(9.6 \pm 0.4) \times 10^{-18}$	298	S-UV	Treacy *et al.*[3]	240–324
1-Butene	$(3.7 \pm 1.0) \times 10^{-15}$	1801 ± 156	$(8.8 \pm 0.6) \times 10^{-18}$	298	S-UV	Treacy *et al.*[3]	240–324
			$(9.44 \pm 0.30) \times 10^{-18}$	296 ± 2	RR [relative to k(propene) = 9.68×10^{-18}][a]	Greene and Atkinson[5]	
2-Methylpropene	$(2.5 \pm 0.5) \times 10^{-15}$	1592 ± 115	$(1.09 \pm 0.18) \times 10^{-17}$	298	S-UV	Treacy *et al.*[3]	240–324
			$(1.10 \pm 0.04) \times 10^{-17}$	296 ± 2	RR [relative to k(propene) = 9.68×10^{-18}][a]	Greene and Atkinson[5]	
cis-2-Butene	$(3.4 \pm 0.7) \times 10^{-15}$	979 ± 22	$(1.23 \pm 0.18) \times 10^{-16}$	298	S-UV	Treacy *et al.*[3]	240–324
			$(1.24 \pm 0.08) \times 10^{-16}$	296 ± 2	RR [relative to k(propene) = 9.68×10^{-18}][a]	Greene and Atkinson[5]	
trans-2-Butene			$(2.02 \pm 0.10) \times 10^{-16}$	297 ± 2	RR [relative to k(*cis*-2-butene) = 1.24×10^{-16}][a]	Nolting *et al.*[6]	
	$(6.7 \pm 1.3) \times 10^{-15}$	1066 ± 115	$(1.81 \pm 0.06) \times 10^{-16}$	298	S-UV	Treacy *et al.*[3]	240–324
			$(2.08 \pm 0.15) \times 10^{-16}$	296 ± 2	RR [relative to k(propene) = 9.68×10^{-18}][a]	Greene and Atkinson[5]	

TABLE 58. Rate constants k and temperature-dependent parameters, $k = A\,e^{-B/T}$, for the gas-phase reactions of O_3 with alkenes – Continued

Alkene	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	k (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
1-Pentene	$(1.7 \pm 0.5) \times 10^{-15}$	1579 ± 81	$(9.2 \pm 0.5) \times 10^{-18}$	298	S-UV	Treacy *et al.*[3]	240–324
2-Methyl-2-butene	$(6.5 \pm 1.3) \times 10^{-15}$	831 ± 44	$(3.97 \pm 0.12) \times 10^{-16}$	298	S-UV	Treacy *et al.*[3]	240–324
			$(3.81 \pm 0.04) \times 10^{-16}$	298 ± 2	RR [relative to k(2,3-dimethyl-2-butene) = 1.13×10^{-15}][a]	Atkinson *et al.*[7]	
			$(4.08 \pm 0.28) \times 10^{-16}$	296 ± 2	RR [relative to k(propene) = 9.68×10^{-18}][a]	Greene and Atkinson[5]	
1-Hexene	$(1.4 \pm 0.5) \times 10^{-15}$	1479 ± 70	$(1.02 \pm 0.06) \times 10^{-17}$	298	S-UV	Treacy *et al.*[3]	240–324
cis-3-Methyl-2-pentene			$(4.50 \pm 0.17) \times 10^{-16}$	297 ± 2	RR [relative to k(*cis*-2-butene) = 1.24×10^{-16}][a]	Nolting *et al.*[6]	
2,3-Dimethyl-2-butene			$(1.19 \pm 0.11) \times 10^{-15}$	296 ± 2	RR [relative to k(propene) = 9.68×10^{-18}][a]	Greene and Atkinson[5]	
1-Heptene			$(1.44 \pm 0.85) \times 10^{-17}$	293–298	S-UV/GC	Grosjean[8]	
1,2-Propadiene			1.3×10^{-20}	231	S-UV	Bahta *et al.*[2]	231–298
			1.4×10^{-20}	236			
			2.4×10^{-20}	240			
			2.7×10^{-20}	243			
			3.9×10^{-20}	252			
			4.3×10^{-20}	257			
			4.9×10^{-20}	258			
			4.6×10^{-20}	259			
			4.9×10^{-20}	261			
			5.0×10^{-20}	261			
			4.6×10^{-20}	261			
			5.0×10^{-20}	263			
			6.4×10^{-20}	265			
			6.6×10^{-20}	266			
			7.0×10^{-20}	268			
			7.1×10^{-20}	268			
			8.7×10^{-20}	275			
			1.03×10^{-19}	278			
			1.08×10^{-19}	280			
			1.02×10^{-19}	280			
	$(1.54 \pm 0.25) \times 10^{-15}$	2689 ± 44	$(1.80 \pm 0.18) \times 10^{-19}$	297 ± 1			

TABLE 58. Rate constants k and temperature-dependent parameters, $k = A\,e^{-B/T}$, for the gas-phase reactions of O_3 with alkenes – Continued

Alkene	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	k (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
1,3-Butadiene			1.48×10^{-18}	254	S-UV	Bahta *et al.*[2]	254–299
			1.63×10^{-18}	256			
			1.61×10^{-18}	257			
			1.73×10^{-18}	257			
			1.79×10^{-18}	257			
			1.67×10^{-18}	258			
			1.96×10^{-18}	260			
			1.78×10^{-18}	261			
			1.86×10^{-18}	262			
			2.12×10^{-18}	263			
			1.93×10^{-18}	264			
			2.63×10^{-18}	266			
			2.83×10^{-18}	267			
			2.74×10^{-18}	268			
			2.99×10^{-18}	269			
			2.73×10^{-18}	270			
			2.78×10^{-18}	270			
			3.27×10^{-18}	271			
			3.35×10^{-18}	271			
			3.16×10^{-18}	272			
			3.05×10^{-18}	273			
			3.48×10^{-18}	274			
			3.44×10^{-18}	275			
			3.27×10^{-18}	276			
			3.29×10^{-18}	279			
			3.37×10^{-18}	279			
			3.31×10^{-18}	280			
	$(2.20 \pm 0.44) \times 10^{-14}$	2430 ± 55	$(6.27 \pm 0.63) \times 10^{-18}$	297 ± 2			
	$(8.2 \pm 1.6) \times 10^{-15}$	2136 ± 106	$(6.3 \pm 0.4) \times 10^{-18}$	298	S-UV	Treacy *et al.*[3]	240–324
trans-1,3-Pentadiene			6.3×10^{-18}	238	S-UV	Bahta *et al.*[2]	238–298
			8.1×10^{-18}	242			
			7.1×10^{-18}	243			
			8.6×10^{-18}	245			
			9.1×10^{-18}	247			
			6.6×10^{-18}	248			
			8.5×10^{-18}	249			
			9.9×10^{-18}	249			
			1.03×10^{-17}	251			
			1.25×10^{-17}	253			
			1.06×10^{-17}	253			
			1.20×10^{-17}	254			
			1.49×10^{-17}	255			

TABLE 58. Rate constants k and temperature-dependent parameters, $k = A\,e^{-B/T}$, for the gas-phase reactions of O_3 with alkenes — Continued

Alkene	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	k (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
			1.59×10^{-17}	255			
			1.50×10^{-17}	256			
			1.21×10^{-17}	256			
			1.21×10^{-17}	256			
			1.06×10^{-17}	257			
			1.30×10^{-17}	258			
			1.44×10^{-17}	258			
			1.48×10^{-17}	259			
			1.50×10^{-17}	260			
			1.75×10^{-17}	260			
			1.15×10^{-17}	260			
			1.50×10^{-17}	261			
			1.36×10^{-17}	261			
			1.61×10^{-17}	266			
			1.70×10^{-17}	266			
			1.98×10^{-17}	270			
			2.35×10^{-17}	271			
	$(1.07 \pm 0.25) \times 10^{-13}$	2319 ± 62	$(4.42 \pm 0.51) \times 10^{-17}$	297–298			
1,3-Pentadiene	$(2.1 \pm 0.4) \times 10^{-15}$	1158 ± 101	$(4.24 \pm 0.12) \times 10^{-17}$	298	S-UV	Treacy *et al.*[3]	240–324
1,4-Pentadiene			$(1.45 \pm 0.20) \times 10^{-17}$	298 ± 2	S-UV	Treacy *et al.*[3]	
2-Methyl-1,3-butadiene (isoprene)	$(7.8 \pm 1.6) \times 10^{-15}$	1913 ± 139	$(1.28 \pm 0.12) \times 10^{-17}$	298	S-UV	Treacy *et al.*[3]	240–324
			$(1.17 \pm 0.02) \times 10^{-17}$	296 ± 2	RR [relative to k(propene) = 9.68×10^{-18}][a]	Greene and Atkinson[5]	
2-Methyl-1,4-pentadiene			$(1.32 \pm 0.20) \times 10^{-17}$	298 ± 2	S-UV	Treacy *et al.*[3]	
2,3-Dimethyl-1,3-butadiene	$(6.9 \pm 1.3) \times 10^{-15}$	1668 ± 42	$(2.65 \pm 0.08) \times 10^{-17}$	298	S-UV	Treacy *et al.*[3]	240–324
2,4-Dimethyl-1,3-butadiene			$(8.0 \pm 1.4) \times 10^{-17}$	298 ± 2	S-UV	Treacy *et al.*[3]	
2,5-Dimethyl-1,5-hexadiene			$(1.42 \pm 0.20) \times 10^{-17}$	298 ± 2	S-UV	Treacy *et al.*[3]	
3-Methylene-7-methyl-1,6-octadiene (myrcene)			$(4.74 \pm 0.76) \times 10^{-16}$	296 ± 2	RR [relative to k(α-pinene) = 8.52×10^{-17}][a]	Atkinson *et al.*[9]	

TABLE 58. Rate constants k and temperature-dependent parameters, $k = A e^{-B/T}$, for the gas-phase reactions of O_3 with alkenes – Continued

Alkene	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	k (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
trans-3,7-Dimethyl-1,3,6-octatriene (*trans*-ocimene)[b]			$(5.44 \pm 0.83) \times 10^{-16}$	296 ± 2	RR [relative to k(α-pinene) = 8.52×10^{-17}][a]	Atkinson *et al.*[9]	
Cyclopentene			$(4.97 \pm 0.30) \times 10^{-16}$	291.5	S-CL	Bennett *et al.*[10]	
			$(5.95 \pm 0.34) \times 10^{-16}$	297 ± 2	RR [relative to k(*cis*-2-butene) = 1.24×10^{-16}][a]	Nolting *et al.*[6]	
			$(6.28 \pm 0.42) \times 10^{-16}$	296 ± 2	RR [relative to k(propene) = 9.68×10^{-18}][a]	Greene and Atkinson[5]	
Cyclohexene			$(1.51 \pm 0.10) \times 10^{-16}$	295	S-CL	Bennett *et al.*[10]	
			$(7.44 \pm 0.48) \times 10^{-17}$	297 ± 2	RR [relative to k(*cis*-2-butene) = 1.24×10^{-16}][a]	Nolting *et al.*[6]	
			$(9.93 \pm 0.21) \times 10^{-17}$	303 ± 1	S-CL	Izumi *et al.*[11]	
			$(7.14 \pm 0.47) \times 10^{-17}$	296 ± 2	RR [relative to k(propene) = 9.68×10^{-18}][a]	Greene and Atkinson[5]	
1,4-Cyclohexadiene			$(4.60 \pm 0.23) \times 10^{-17}$	296 ± 2	RR [relative to k(propene) = 9.68×10^{-18}][a]	Greene and Atkinson[5]	
Cycloheptene			$(2.70 \pm 0.15) \times 10^{-16}$	297 ± 2	RR [relative to k(*cis*-2-butene) = 1.24×10^{-16}][a]	Nolting *et al.*[6]	
α-Pinene			$(8.20 \pm 1.24) \times 10^{-17}$	297 ± 2	RR [relative to k(*cis*-2-butene) = 1.24×10^{-16}][a]	Nolting *et al.*[6]	
			$(9.71 \pm 1.06) \times 10^{-17}$	296 ± 2	S-CL	Atkinson *et al.*[9]	
β-Pinene			$(1.34 \pm 0.20) \times 10^{-17}$	297 ± 2	RR [relative to k(*cis*-2-butene) = 1.24×10^{-16}][a]	Nolting *et al.*[6]	

TABLE 58. Rate constants k and temperature-dependent parameters, $k = A e^{-B/T}$, for the gas-phase reactions of O_3 with alkenes – Continued

Alkene	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	k (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
			$(1.48 \pm 0.17) \times 10^{-17}$	296 ± 2	S-CL	Atkinson *et al.*[9]	
			$(1.64 \pm 0.20) \times 10^{-17}$	296 ± 2	RR [relative to k(α-pinene) = 8.52×10^{-17}]^a	Atkinson *et al.*[9]	
2-Carene			$(2.32 \pm 0.30) \times 10^{-16}$	296 ± 2	S-CL	Atkinson *et al.*[9]	
			$(2.31 \pm 0.24) \times 10^{-16}$	296 ± 2	RR [relative to k(α-pinene) = 8.52×10^{-17}]^a	Atkinson *et al.*[9]	
3-Carene			$(5.20 \pm 0.56) \times 10^{-17}$	296 ± 2	S-CL	Atkinson *et al.*[9]	
			$(3.71 \pm 0.40) \times 10^{-17}$	296 ± 2	RR [relative to k(α-pinene) = 8.52×10^{-17}]^a	Atkinson *et al.*[9]	
Camphene			$(9.0 \pm 1.7) \times 10^{-19}$	296 ± 2	S-CL	Atkinson *et al.*[12]	
Sabinene			$(8.07 \pm 0.83) \times 10^{-17}$	296 ± 2	S-CL	Atkinson *et al.*[12]	
			$(8.61 \pm 0.94) \times 10^{-17}$	296 ± 2	RR [relative to k(α-pinene) = 8.52×10^{-17}]^a	Atkinson *et al.*[9]	
Limonene			$(2.04 \pm 0.22) \times 10^{-16}$	296 ± 2	RR [relative to k(α-pinene) = 8.52×10^{-17}]^a	Atkinson *et al.*[9]	
α-Phellandrene			$(1.85 \pm 0.40) \times 10^{-15}$	296 ± 2	RR [relative to k(α-pinene) = 8.52×10^{-17}]^a	Atkinson *et al.*[9]	
β-Phellandrene			$(4.71 \pm 0.28) \times 10^{-17}$	297 ± 2	RR [relative to k(α-pinene) = 8.59×10^{-17}]^a	Shorees *et al.*[13]	
α-Terpinene			$(8.47 \pm 2.24) \times 10^{-15}$	296 ± 2	RR [relative to k(α-pinene) = 8.52×10^{-17}]^a	Atkinson *et al.*[9]	

TABLE 58. Rate constants k and temperature-dependent parameters, $k = A e^{-B/T}$, for the gas-phase reactions of O_3 with alkenes – Continued

Alkene	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	k (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
γ-Terpinene			$(1.40 \pm 0.16) \times 10^{-16}$	296 ± 2	RR [relative to k(α-pinene) = 8.52×10^{-17}]^a	Atkinson *et al.*[9]	
Terpinolene			$(1.38 \pm 0.24) \times 10^{-15}$	296 ± 2	RR [relative to k(α-pinene) = 8.52×10^{-17}]^a	Atkinson *et al.*[9]	
Azulene			$< 7 \times 10^{-17}$	298 ± 2	RR [relative to k(2,3-dimethyl-2-butene) = 1.13×10^{-15}]^a	Atkinson *et al.*[7]	

[a] From present recommendations (see text).

[b] *cis*-isomer has a rate constant 10 ± 10% lower than that for the *trans*-isomer.[9]

$$k(cis\text{-2-butene}) = 1.25 \times 10^{-16}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}.$$

Combination of this 298 K rate constant with the temperature dependence of $B = 968$ K determined from a unit-weighted average of the temperature dependencies of Huie and Herron[26] and Treacy *et al.*[3] leads to the recommendation of

$$k(cis\text{-2-butene}) = 3.22 \times 10^{-15}\ e^{-968/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the temperature range 225–364 K, with an estimated overall uncertainty at 298 K of ±25%. This recommendation supersedes that of Atkinson and Carter[1] of

$$k(cis\text{-2-butene}) = 3.52 \times 10^{-15}\ e^{-983/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the same temperature range of 225–364 K, with a 298 K rate constant of 1.30×10^{-16} cm^3 molecule^{-1} s^{-1}.

trans-2-Butene. The absolute rate constants of Treacy *et al.*[3] and the relative rate constants of Nolting *et al.*[6] and Greene and Atkinson[5] are given in Table 58 and are plotted, together with the rate constants of Japar *et al.*[19,20] and Huie and Herron,[26] in Arrhenius form in Fig. 49. The rate constants of Nolting *et al.*[6] and Greene and Atkinson[5] are in excellent agreement and are in reasonable agreement with the room temperature rate constants of Huie and Herron[26] and Treacy *et al.*[3] A unit-weighted average of the 298 K rate constants of Huie and Herron,[26] Treacy *et al.*[3] and Greene and Atkinson[5] (corrected to 298 K as described above for 1-butene) leads to the recommended 298 K rate constant of

$$k(trans\text{-2-butene}) = 1.90 \times 10^{-16}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}.$$

Combination of this 298 K rate constant with the temperature dependence of $B = 1059$ K determined from a unit-weighted average of the temperature dependencies of Huie and Herron[26] and Treacy *et al.*[3] leads to the recommendation of

$$k(trans\text{-2-butene}) = 6.64 \times 10^{-15}\ e^{-1059/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the temperature range 225–364 K, with an estimated overall uncertainty at 298 K of ±35%.

This recommendation supersedes that of Atkinson and Carter[1] of

$$k(trans\text{-2-butene}) = 9.08 \times 10^{-15}\ e^{-1136/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the same temperature range of 225–364 K, with a 298 K rate constant of 2.00×10^{-16} cm^3 molecule^{-1} s^{-1}.

1-Pentene. The rate constants of Treacy *et al.*[3] are given in Table 58. The room temperature rate constant of Treacy *et al.*[3] is in reasonable agreement with that of Japar *et al.*[19] of $(1.07 \pm 0.04) \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 299 ± 2 K. A unit-weighted average of the rate constants of Treacy *et al.*[3] and Japar *et al.*[18] leads to the recommendation of

$$k(\text{1-pentene}) = 1.00 \times 10^{-17}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}\ at\ 298\ K},$$

with an estimated overall uncertainty of ±30%.

2-Methyl-2-butene. The rate constants of Treacy *et al.*,[3] Atkinson *et al.*[7] and Greene and Atkinson[5] are given in Table 58 and those of Treacy *et al.*[3] and Green and Atkinson[5] are plotted, together with the rate constants of Japar *et al.*[19] and Huie and Herron,[26] in Arrhenius form in Fig. 50. The rate constants of Atkinson *et al.*[7] and Greene and Atkinson[5] are self-consistent and are in good agreement with the room temperature rate constants of Huie and Herron[26] and Treacy *et al.*[3] A unit-weighted average of the 298 K rate constants of Huie and Herron,[26] Treacy *et al.*[3] and Greene and Atkinson[5] (corrected to 298 K as described above for 1-butene) leads to the recommended 298 K rate constant of

$$k(\text{2-methyl-2-butene}) = 4.03 \times 10^{-16}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}.$$

Combination of this 298 K rate constant with the temperature dependence of $B = 829$ K determined from a unit-weighted average of the temperature dependencies of Huie and Herron[26] and Treacy *et al.*[3] leads to the recommendation of

$$k(\text{2-methyl-2-butene}) = 6.51 \times 10^{-15}\ e^{-829/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the temperature range 227–363 K, with an estimated overall uncertainty at 298 K of ±35%. This recommendation supersedes that of Atkinson and Carter[1] of

$$k(\text{2-methyl-2-butene}) = 6.17 \times 10^{-15}\ e^{-798/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the same temperature range of 227–363 K, with a 298 K rate constant of 4.23×10^{-16} cm^3 molecule^{-1} s^{-1}.

1-Hexene. The rate constants of Treacy *et al.*[3] are given in Table 58. These absolute rate constants are in good agreement with the previous room temperature rate constants of Stedman *et al.*,[18] Japar *et al.*,[19] Adeniji *et al.*[28] and Atkinson *et al.*[22] A unit-weighted average of the room temperature constants of Stedman *et al.*,[18] Japar *et al.*,[19] Adeniji *et al.*,[28] Atkinson *et al.*[22] and Treacy *et al.*[3] leads to the recommendation of

$$k(\text{1-hexene}) = 1.10 \times 10^{-17}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}\ at\ 298\ K},$$

with an estimated overall uncertainty of ±30%. This recommendation is similar to, but supersedes, that of Atkinson and Carter[1] of

$$k(\text{1-hexene}) = 1.17 \times 10^{-17}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}\ at\ 298\ K}.$$

2,3-Dimethyl-2-butene. The relative rate constant of Greene and Atkinson[5] is given in Table 58 and is plotted, together with the rate constants of Japar *et al.*[19] and Huie and Herron,[26] in Arrhenius form in Fig. 50. The room temperature rate constant of Greene and Atkinson[5] is in

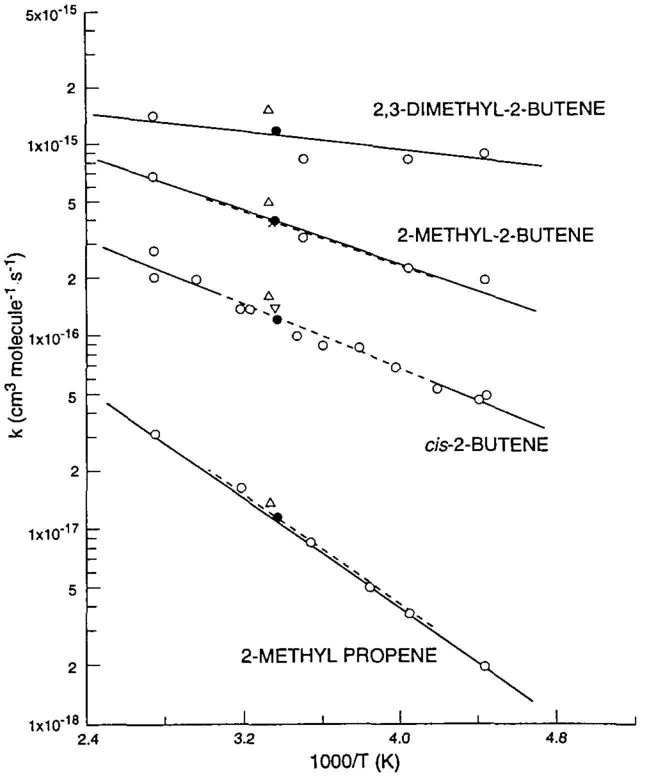

FIG. 50. Arrhenius plots of selected rate constants for the reactions of O_3 with 2-methylpropene, *cis*-2-butene, 2-methyl-2-butene and 2,3-dimethyl-2-butene. (△) Japar *et al.*;[19] (○) Huie and Herron;[26] (▽) Atkinson *et al.*;[27] (–X–) Treacy *et al.*;[3] (●) Greene and Atkinson;[5] (—) recommendations (see text). For *cis*-2-butene, the recommendation and Arrhenius line of Treacy *et al.*[3] are indistinguishable.

good agreement with the Arrhenius expression of Huie and Herron.[26] A unit-weighted average of the 298 K rate constants of Huie and Herron[26] and Greene and Atkinson[5] (corrected to 298 K as described above for 1-butene) leads to the recommended 298 K rate constant of

$$k(\text{2,3-dimethyl-2-butene}) = 1.13 \times 10^{-15}\ \text{cm}^3\ \text{molecule}^{-1}\text{s}^{-1}.$$

Combination of this 298 K rate constant with the temperature dependence of $B = 294$ K of Huie and Herron[26] leads to the recommendation of

$$k(\text{2,3-dimethyl-2-butene}) = 3.03 \times 10^{-15}\ e^{-294/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 227–363 K, with an estimated overall uncertainty at 298 K of ±35%. This recommendation is similar to, but supersedes, that of Atkinson and Carter[1] of

$$k(\text{2,3-dimethyl-2-butene}) = 3.71 \times 10^{-15}\ e^{-347/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the same temperature range of 227–363 K, with a 298 K rate constant of 1.16×10^{-15} cm^3 molecule^{-1} s^{-1}.

cis-3-Methyl-2-pentene. The room temperature relative rate constant of Nolting *et al.*[6] (Table 58) is in good agreement with that of Japar *et al.*,[19] of $(4.56 \pm 0.08) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 299 ± 2 K, and a unit-weighted average of these two rate constants[6,19] leads to the recommendation of

$$k(\textit{cis}\text{-3-methyl-2-pentene}) = 4.5 \times 10^{-16}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

with an estimated overall uncertainty of ±35%.

1,2-Propadiene. The rate constants of Bahta *et al.*[2] are given in Table 58, and are in good agreement with the Arrhenius expression reported by Toby and Toby.[29] Accordingly, the Arrhenius expression of Bahta *et al.*[2] is preferred.

1,3-Butadiene. The rate constants of Bahta *et al.*[2] and Treacy *et al.*[3] are given in Table 58. The room temperature rate constants determined by Bahta *et al.*[2] and Treacy *et al.*[3] are lower than the previous rate constant of Japar *et al.*,[19] and the temperature dependencies of Bahta *et al.*[2] and Treacy *et al.*[3] are lower than that reported by Toby and Toby.[30] The data of Bahta *et al.*[2] and Treacy *et al.*[3] are in reasonably good agreement, especially at around room temperature, and are hence preferred. A unit-weighted average of the 298 K rate constants of Bahta *et al.*[2] and Treacy *et al.*[3] yields the recommendation of

$$k(\text{1,3-butadiene}) = 6.3 \times 10^{-18}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

with an estimated overall uncertainty of ±30%. From a unit-weighted average of the temperature dependencies of Bahta *et al.*[2] and Treacy *et al.*,[3] a temperature dependence of $B = 2283$ K is recommended, leading to

$$k(\text{1,3-butadiene}) = 1.34 \times 10^{-14}\ e^{-2283/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 231–324 K. This recommendation differs significantly from that of Atkinson and Carter[1] of

$$k(\text{1,3-butadiene}) = 8.8 \times 10^{-14}\ e^{-2768/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1},$$

with a 298 K rate constant of 8.1×10^{-18} cm^3 molecule^{-1} s^{-1}.

2-Methyl-1,3-butadiene. The rate constants of Treacy *et al.*[3] and Greene and Atkinson[5] are given in Table 58 and are plotted in Arrhenius form in Fig. 51, together with the data of Arnts and Gay,[31] Adeniji *et al.*[28] and Atkinson *et al.*[32] The room temperature rate constants from these studies[3,5] are in excellent agreement with those of Arnts and Gay[31] (1.27×10^{-17} cm^3 molecule^{-1} s^{-1} at 295 ± 1 K) and Atkinson *et al.*[32] [$(1.25 \pm 0.20) \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 296 ± 1 K and $(1.17 \pm 0.19) \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 296 ± 2 K], but are significantly lower than the room temperature rate constant of Adeniji *et al.*[28] Combination of the 295–298 K rate con-

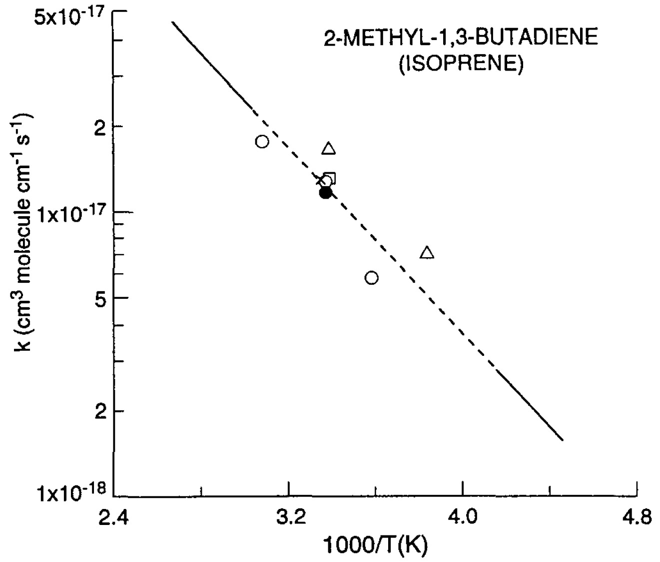

FIG. 51. Arrhenius plot of rate constants for the reaction of O_3 with 2-methyl-1,3-butadiene (isoprene). (□) Arnts and Gay;[31] (△) Adeniji *et al.*;[28] (○) Atkinson *et al.*;[32] (−X−) Treacy et al;[3] (●) Greene and Atkinson;[5] (—) recommendation (see text). [The recommendation and the Arrhenius expression of Treacy *et al.*[3] are indistinguishable].

stants of Arnts and Gay,[31] Atkinson *et al.*,[32] Treacy *et al.*[3] and Greene and Atkinson[5] with the temperature dependence of B = 1913 K determined by Tracy *et al.*[3] leads to the recommendation of

$$k(\text{2-methyl-1,3-butadiene}) = 7.86 \times 10^{-15}\ e^{-1913/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 240–324 K, and

$$k(\text{2-methyl-1,3-butadiene}) = 1.28 \times 10^{-17}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

with an estimated overall uncertainty at 298 K of ±25%. This recommendation supersedes that of Atkinson and Carter[1] of

$$k(\text{2-methyl-1,3-butadiene}) = 1.23 \times 10^{-14}\ e^{-2013/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1},$$

with a 298 K rate constant of 1.43 × 10^{-17} cm^3 molecule^{-1} s^{-1}.

Cyclopentene. The rate constants of Bennett *et al.*,[10] Nolting *et al.*[6] and Greene and Atkinson[5] are given in Table 58. As discussed previously, the previous room temperature rate constants for this reaction[19,27,28] range over a factor of 3.5. The room temperature relative rate constants of Nolting *et al.*[6] and Greene and Atkinson[5] are in excellent agreement and, based mainly on the rate constant of Greene and Atkinson,[5] it is recommended that

$$k(\text{cyclopentene}) = 6.3 \times 10^{-16}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

with an estimated overall uncertainty of ±35%.

Cyclohexene. The room temperature rate constants of Bennett *et al.*,[10] Nolting *et al.*,[6] Izumi *et al.*[11] and Greene and Atkinson[5] are given in Table 58. Somewhat analogous to the situation for cyclopentene, these[5,6,10,11] and previous[19,27,28] literature room temperature rate constants exhibit a significant degree of scatter, covering a range of ~2.7 in this case. Again, the relative rate constants of Nolting *et al.*[6] and Greene and Atkinson[5] are in good agreement and, based mainly on the rate constant of Greene and Atkinson,[5] it is recommended that

$$k(\text{cyclohexene}) = 7.2 \times 10^{-17}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

with an estimated overall uncertainty of ±30%.

1,4-Cyclohexadiene. The relative rate constant of Greene and Atkinson[5] is given in Table 58. This rate constant is 28% lower than that of Atkinson *et al.*[27] The rate constant of Greene and Atkinson[5] is recommended, of

$$k(\text{1,4-cyclohexadiene}) = 4.6 \times 10^{-17}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

with an estimated overall uncertainty of ±35%.

Cycloheptene. The relative rate constant of Nolting *et al.*[6] is given in Table 58. This rate constant of Nolting *et al.*[6] is in reasonable agreement with that of Atkinson *et al.*[27] of (3.19 ± 0.36) × 10^{-16} cm^3 molecule^{-1} s^{-1} at 297 ± 1 K. A unit-weighted average of these rate constants[6,27] leads to the recommendation of

$$k(\text{cycloheptene}) = 2.9 \times 10^{-16}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

with an estimated overall uncertainty of ±35%.

α-Pinene. The rate constants of Nolting *et al.*[6] and Atkinson *et al.*[9] are given in Table 58. In addition, the relative rate constant for sabinene relative to that for α-pinene determined in the study of Atkinson *et al.*[9] can be combined with the absolute rate constant for sabinene[12] to obtain a rate constant for α-pinene of 7.99 × 10^{-17} cm^3 molecule^{-1} s^{-1} at 296 ± 2 K.[9] The absolute rate constants of Atkinson *et al.*[9,32] and the relative rate constants of Nolting *et al.*[6] and Atkinson *et al.*[9] are in good agreement, and a unit-weighted average of these rate constants[6,9,32] leads to the recommendation of

$$k(\alpha\text{-pinene}) = 8.52 \times 10^{-17}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at } 296 \pm 1\ \text{K}.$$

Combining this 296 K rate constant with the temperature dependence of Atkinson *et al.*[32] of B = 731 ± 174 K leads to the recommendation of

$$k(\alpha\text{-pinene}) = 1.01 \times 10^{-15}\ e^{-732/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 276–324 K, and

$$k(\alpha\text{-pinene}) = 8.66 \times 10^{-17}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \text{ at 298 K},$$

with an estimated overall uncertainty at 298 K of ±30%.

β-Pinene. The room temperature rate constants of Nolting *et al.*[6] and Atkinson *et al.*[9] are given in Table 58. The rate constants from these studies[6,9] are in good agreement, and agree reasonably well with the rate constant of $(2.1 \pm 0.5) \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 296 ± 2 K determined previously by Atkinson *et al.*[32] A unit-weighted average of the absolute and relative rate constants of Nolting *et al.*[6] and Atkinson *et al.*[9] leads to the recommendation of

$$k(\beta\text{-pinene}) = 1.5 \times 10^{-17}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \text{ at 298 K},$$

with an estimated overall uncertainty of ±35%.

2-Carene, 3-Carene and Sabinene. The absolute and relative rate constants of Atkinson *et al.*[9,12] are given in Table 58. The relative rate constants are preferred,[9] leading to the recommendations of

$$k(\text{2-carene}) = 2.3 \times 10^{-16}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1},$$

$$k(\text{3-carene}) = 3.7 \times 10^{-17}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1},$$

and

$$k(\text{sabinene}) = 8.6 \times 10^{-17}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1},$$

all at 298 K and with estimated overall uncertainties of ±35%.

Other Terpenes. The rate constants of Atkinson *et al.*[9,12] and Shorees *et al.*[13] are given in Table 58. As discussed previously,[1,9] these rate constants are significantly lower than the previous literature data, but are preferred. The rate constants of Atkinson *et al.*[9,12] and Shorees *et al.*[13] should therefore be used.

Other Alkenes. For the other alkenes for which data are given in Table 58, these are the first reported data, apart from 1,3-pentadiene for which the studies of Bahta *et al.*[2] and Treacy *et al.*[3] give very different temperature dependencies (but similar room temperature rate constants).

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5.3. Haloalkenes

The rate constants reported since the review and evaluation of Atkinson and Carter[1] are given in Table 59. The rate constant of Toby and Toby[2] for $CF_2=CF_2$ was inadvertently omitted from the previous evaluation.[1] This room temperature rate constant of Toby and Toby[2] for $CF_2=CF_2$ is lower by factors of ~3 and 20 than the measurements of Adeniji *et al.*[5] and Heicklen,[6] respectively.

3-Chloro-1-propene (allyl chloride). The rate constants of Edney *et al.*[3] and Tuazon *et al.*[4] are given in Table 59. These rate constants[3,4] are in good agreement, and a unit-weighted average leads to the recommendation of

$$k(\text{allyl chloride}) = 1.55 \times 10^{-18}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \text{ at 298 K},$$

with an estimated overall uncertainty of ±30%. Product studies were also conducted by Edney *et al.*[3] and Tuazon *et al.*[4] and these references should be consulted for further details.

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5.4. Oxygen-Containing Organic Compounds

The kinetic data reported since the review and evaluation of Atkinson and Carter[1] are given in Table 60. As expected, no evidence for any reaction of 1,8-cineole (a cyclic saturated ether) was observed.[2]

Acrolein. The rate constant measured by Treacy *et al.*[3] at 298 ± 2 K is given in Table 60. This rate constant of Treacy *et al.*[3] is in excellent agreement with that of Atkinson *et al.*[5] of $(2.8 \pm 0.5) \times 10^{-19}$ cm^3 molecule^{-1} s^{-1} at 296 ± 2 K. A unit-weighted average of the rate constants of Atkinson *et al.*[5] and Treacy *et al.*[3] leads to the recommended rate constant of

$$k(\text{acrolein}) = 2.9 \times 10^{-19}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \text{ at } 298\ \text{K},$$

with an estimated overall uncertainty of ±35%.

Methacrolein. The 298 K rate constant and Arrhenius expression reported by Treacy *et al.*[3] are given in Table 60 (the individual rate constants at the temperatures studied were not tabulated). The 298 K rate constant of Treacy *et al.*[3] is in good agreement with the room temperature rate constants of Atkinson *et al.*,[5] of $(1.12 \pm 0.13) \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} at 296 ± 2 K, and Kamens *et al.*,[6] of 1.1×10^{-18} cm^3 molecule^{-1} s^{-1} at an unspecified room temperature.

A unit-weighted average of the room temperature rate constants of Atkinson *et al.*[5] and Treacy *et al.*,[3] combined with the temperature dependence of Treacy *et al.*,[3] leads to the recommended Arrhenius expression of

$$k(\text{methacrolein}) = 1.36 \times 10^{-15}\ e^{-2112/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 240–324 K, and

$$k(\text{methacrolein}) = 1.14 \times 10^{-18}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \text{ at } 298\ \text{K},$$

with an estimated overall uncertainty at 298 K of ±35%.

Methyl vinyl ketone. The 298 K rate constant and Arrhenius expression reported by Treacy *et al.*[3] are given in Table 60. The 298 K rate constant of Treacy *et al.*[3] is in reasonable agreement with the rate constants of Atkinson *et al.*,[5] of $(4.77 \pm 0.59) \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} at 296 ± 2 K, and Kamens *et al.*,[6] of 4.0×10^{-18} cm^3 molecule^{-1} s^{-1} at an unspecified room temperature. A unit-weighted average of the room temperature rate constants of Atkinson *et al.*[5] and Treacy *et al.*,[3] combined with the temperature dependence of Treacy *et al.*,[3] leads to the recommended Arrhenius expression of

$$k(\text{methyl vinyl ketone}) = 7.51 \times 10^{-16}\ e^{-1521/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 240–324 K, and

$$k(\text{methyl vinyl ketone}) = 4.56 \times 10^{-18}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \text{ at } 298\ \text{K},$$

with an estimated overall uncertainty at 298 K of ±35%.

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5.5. Nitrogen-Containing Organic Compounds

The rate constants reported since the review and evaluation of Atkinson and Carter[1] are given in Table 61. The rate constants of Tuazon *et al.*[2] for the aliphatic amines and tetramethylhydrazine are all lower, by factors of ~1.2–3, than the unpublished data of Tuazon, Atkinson, Carter and Pitts, cited in Atkinson and Carter.[1] The rate constants of Tuazon *et al.*[2] given in Table 61 are preferred.

The rate constant for 2-vinylpyridine[4] is very similar to that for styrene (see Sec. 5.7. below), indicating that the O_3 reaction proceeds by initial O_3 addition to the $-CH=CH_2$ substituent group. Under atmospheric conditions, the major products of the O_3 reaction with 2-vinylpyridine were determined to be 2-pyridinecarboxaldehyde and HCHO, with yields of 0.80 ± 0.09 and 0.34 ± 0.05, respectively,[4] together with minor amounts of pyridine, HCOOH and HC(O)OOH.[4] (See Reaction Scheme (17) on the next page.)

References

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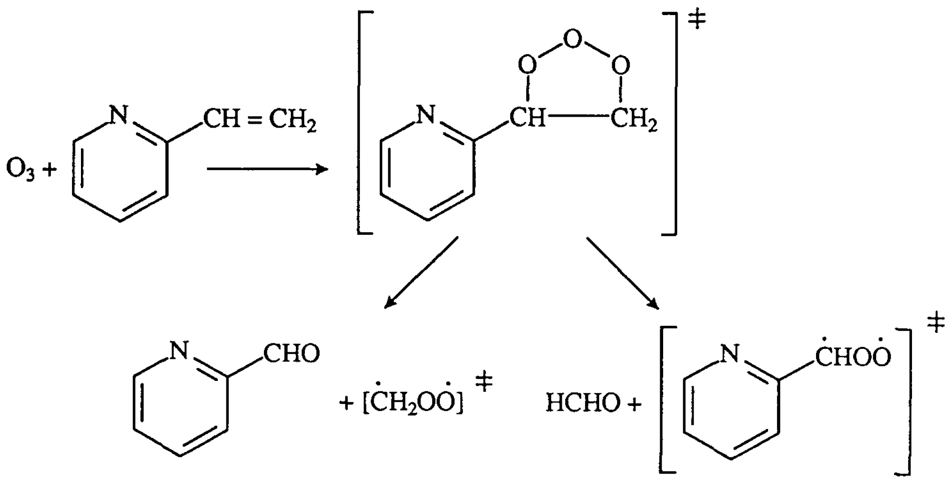

Reaction Scheme (17)

5.6. Phosphorus-, Silicon- and Selenium-Containing Organic Compunds

The rate constants reported since the review and evaluation of Atkinson and Carter[1] are given in Table 62. Only for dimethyl selenide (CH_3SeCH_3) was a reaction observed.[8]

References

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5.7. Aromatic Compounds

The rate constants reported since the review and evaluation of Atkinson and Carter[1] are given in Table 63. In most cases, only upper limits to the rate constants have been obtained.

Benzene and Alkyl-Substituted Benzenes. The rate constants of Toby *et al.*[2] for benzene, toluene and the xylenes and of Atkinson *et al.*[3] for 1-methyl-4-isopropylbenzene are given in Table 63. These reactions are extremely slow at room temperature and, consistent with the conclusions of Atkinson and Carter,[1] an upper limit of

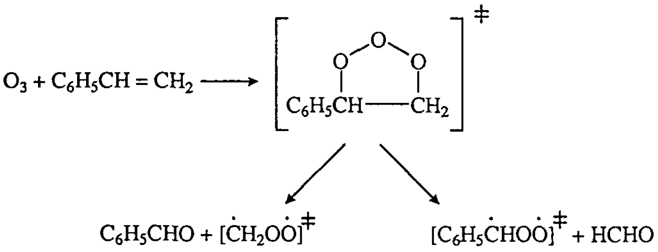
$$k(\text{benzene and alkyl-benzenes}) < 1 \times 10^{-20}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \text{ at } 298\ \text{K}$$

is recommended.

Styrene. The rate constant of Tuazon *et al.*[6] is given in Table 63. This room temperature rate constant is in good agreement with that of Atkinson *et al.*[13] of $(2.16 \pm 0.46) \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 296 ± 2 K. The study of Tuazon *et al.*[6] supersedes that of Atkinson *et al.*[13] and the rate constant of Tuazon *et al.*[6] is used to recommend that

$$k(\text{styrene}) = 1.71 \times 10^{-17}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \text{ at } 298\ \text{K},$$

with an estimated overall uncertainty of ±35%. This reaction proceeds by initial addition of O_3 to the $-CH=CH_2$ substituent group,



and both HCHO and C_6H_5CHO were observed by Tuazon *et al.*[6] in yields of 0.37 ± 0.05 and 0.41 ± 0.05, respectively.

2,3-Benzofuran and Acenaphthylene. In contrast to most of the other aromatic compunds studied (Table 63 and Atkinson and Carter[1]), these two compounds react with O_3. These O_3 reactions proceed by initial O_3 addition to the $>C=C<$ bonds in the 5-membered ring systems.[7,11]

TABLE 59. Rate constants k and temperature-dependent parameters, $k = Ae^{-B/T}$, for the gas-phase reactions of O_3 with haloalkenes

Haloalkene	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	k (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
Tetrafluoroethene	$0.26^{+0.58}_{-0.18}$	4781 ± 353	2.8×10^{-20} [a]	298	S-UV	Toby and Toby[2]	273–383
3-Chloro-1-propene (allyl chloride)			$(1.5 \pm 0.23) \times 10^{-18}$	298	S-UV	Edney *et al.*[3]	
			$(1.60 \pm 0.18) \times 10^{-18}$	298 ± 2	S-CL	Tuazon *et al.*[4]	

[a] Calculated from Arrhenius expression.

TABLE 60. Rate constants k and temperature-dependent parameters for the gas-phase reactions of O_3 with oxygen-containing compounds

Oxygenate	A (cm^3 molecule^{-1} s^{-1})	B (K)	k (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
1,8-Cineole			$< 1.5 \times 10^{-19}$	296 ± 2	S-CL	Atkinson *et al.*[2]	
Acrolein [$CH_2{=}CHCHO$]			$(3.0 \pm 0.4) \times 10^{-19}$	298 ± 2	S-UV	Treacy *et al.*[3]	
Methacrolein [$CH_2{=}C(CH_3)CHO$]	$(1.3 \pm 0.2) \times 10^{-15}$	2112 ± 131	$(1.1 \pm 0.2) \times 10^{-18}$	298	S-UV	Treacy *et al.*[3]	240–324
Methyl vinyl ketone [$CH_2{=}CHC(O)CH_3$]	$(6.9 \pm 1.4) \times 10^{-16}$	1521 ± 78	$(4.2 \pm 0.4) \times 10^{-18}$	298	S-UV	Treacy *et al.*[3]	240–324
4-Acetyl-1-methylcyclohexene			$(1.50 \pm 0.04) \times 10^{-16}$	296 ± 2	RR [relative to k(2-methyl-2-butene) = 3.96×10^{-16}][a]	Atkinson and Aschmann[4]	

[a] From present recommendation.

TABLE 61. Rate constants k for the gas-phase reactions of O_3 with nitrogen-containing organic compounds

Organic	k(cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference
Methylamine	$(7.4 \pm 2.4) \times 10^{-21}$	298 ± 2	S-CL	Tuazon *et al.*[2]
Dimethylamine	$(1.67 \pm 0.20) \times 10^{-18}$	298 ± 2	S-CL	Tuazon *et al.*[2]
Trimethylamine	$(7.84 \pm 0.87) \times 10^{-18}$	298 ± 2	S-CL	Tuazon *et al.*[2]
2-(Dimethylamino)ethanol [$(CH_3)_2NCH_2CH_2OH$]	$(6.76 \pm 0.83) \times 10^{-18}$	298 ± 2	S-CL	Tuazon *et al.*[2]
Tetramethylhydrazine	$(5.21 \pm 0.60) \times 10^{-18}$	298 ± 2	S-CL	Tuazon *et al.*[2]
Pyridine	$< 1.1 \times 10^{-20}$	296 ± 2	S-CL	Atkinson *et al.*[3]
2-Vinylpyridine	$(1.46 \pm 0.17) \times 10^{-17}$	298 ± 2	S-CL	Tuazon *et al.*[4]
1,3,5-Triazine	$< 4 \times 10^{-21}$	296 ± 2	S-CL	Atkinson *et al.*[3]
$(CH_3)_2NC(O)SCH_3$	$< 4 \times 10^{-20}$	298 ± 2	S-GC	Kwok *et al.*[5]
$(CH_3CH_2CH_2)_2NC(O)SCH_2CH_3$	$< 1.3 \times 10^{-19}$	298 ± 2	S-GC	Kwok *et al.*[5]
$CH_3CH_2(c\text{-}C_6H_{11})NC(O)SCH_2CH_3$	$< 3 \times 10^{-19}$	298 ± 2	S-GC	Kwok *et al.*[5]

TABLE 62. Rate constants k for the gas-phase reactions of O_3 with phosphorus-, selenium- and silicon- containing organic compounds

Organic	k(cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference
Phosphorus-Containing				
$(CH_3O)_3PO$	$< 6 \times 10^{-20}$	296 ± 2	S-IR	Tuazon *et al.*[2]
$(CH_3O)_2P(O)SCH_3$	$< 2 \times 10^{-19}$	298 ± 2	S-GC	Goodman *et al.*[3]
$(CH_3S)_2P(O)OCH_3$	$< 1 \times 10^{-19}$	298 ± 2	S-GC	Goodman *et al.*[3]
$(CH_3O)_3PS$	$< 3 \times 10^{-19}$	298 ± 2	S-GC	Goodman *et al.*[3]
$(CH_3O)_2P(S)SCH_3$	$< 2 \times 10^{-19}$	298 ± 2	S-GC	Goodman *et al.*[3]
$(CH_3O)_2P(S)Cl$	$< 2 \times 10^{-19}$	296 ± 2	S-GC	Atkinson *et al.*[4]
$(CH_3O)_2P(O)N(CH_3)_2$	$< 2 \times 10^{-19}$	296 ± 2	S-GC	Goodman *et al.*[5]
$(CH_3O)_2P(S)N(CH_3)_2$	$< 2 \times 10^{-19}$	296 ± 2	S-GC	Goodman *et al.*[5]
$(CH_3O)_2P(S)NHCH_3$	$< 2 \times 10^{-19}$	296 ± 2	S-GC	Goodman *et al.*[5]
$(CH_3O)_2P(S)NH_2$	$< 4 \times 10^{-19}$	296 ± 2	S-GC	Goodman *et al.*[5]
Silicon-Containing				
Tetramethylsilane [$(CH_3)_4Si$]	$< 7 \times 10^{-21}$	297 ± 2	S-GC	Atkinson[6]
Hexamethyldisiloxane [$(CH_3)_3SiOSi(CH_3)_3$]	$< 7 \times 10^{-21}$	297 ± 2	S-GC	Atkinson[6]
Hexamethylcyclotrisiloxane [$\text{-}(CH_3)_2SiO\text{-}]_3$	$< 3 \times 10^{-20}$	297 ± 2	S-GC	Atkinson[6]
Octamethylcyclotetrasiloxane [$\text{-}(CH_3)_2SiO\text{-}]_4$	$< 3 \times 10^{-20}$	297 ± 2	S-GC	Atkinson[6]
Decamethylcyclopentasiloxane [$\text{-}(CH_3)_2SiO\text{-}]_5$	$< 3 \times 10^{-20}$	297 ± 2	S-GC	Atkinson[6]
$(CH_3)_3SiOSi(CH_3)_2OH$	$< 7 \times 10^{-20}$	297 ± 2	S-GC	Atkinson *et al.*[7]
Selenium-Containing				
Dimethyl selenide $(CH_3)_2Se$	$(6.80 \pm 0.72) \times 10^{-17}$	296 ± 2	S-CL	Atkinson *et al.*[8]

TABLE 63. Rate constants k and temperature dependent parameters, $k = A e^{-B/T}$, for the gas-phase reactions of O_3 with aromatic compounds

Aromatic	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	k (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
Benzene	$10.5^{+15.9}_{-6.4}$	7398 ± 353	1.7×10^{-22} [a]	298	S-UV	Toby *et al.*[2]	298–423
Toluene	$2.34^{+5.98}_{-1.68}$	6694 ± 403	4.1×10^{-22} [a]	298	S-UV	Toby *et al.*[2]	298–398
o-Xylene	$0.240^{+0.832}_{-0.187}$	5586 ± 453	1.7×10^{-21} [a]	298	S-UV	Toby *et al.*[2]	298–423
m-Xylene	$0.537^{+0.876}_{-0.333}$	6039 ± 202	8.5×10^{-22} [a]	298	S-UV	Toby *et al.*[2]	298–423
p-Xylene	$0.191^{+0.568}_{-0.144}$	5586 ± 302	1.4×10^{-21} [a]	298	S-UV	Toby *et al.*[2]	298–423
1-Methyl-4-isopropylbenzene (*p*-cymene)			$< 5 \times 10^{-20}$	296 ± 2	S-CL	Atkinson *et al.*[3]	
			$\leq 2.1 \times 10^{-18}$	296 ± 2	RR [relative to k(α-pinene) = 8.52×10^{-17}][b]	Atkinson *et al.*[3]	
Benzylchloride			$< 6 \times 10^{-20}$	298 ± 2	S-CL	Tuazon *et al.*[4]	
Nitrobenzene			$< 7 \times 10^{-21}$	296 ± 2	S-CL	Atkinson *et al.*[5]	
Aniline			$(1.12 \pm 0.14) \times 10^{-18}$	296 ± 2	S-CL	Atkinson *et al.*[5]	
N,*N*-Dimethylaniline			$(9.1 \pm 1.0) \times 10^{-18}$	296 ± 2	S-CL	Atkinson *et al.*[5]	
Styrene			$(1.71 \pm 0.18) \times 10^{-17}$	296 ± 2	S-CL	Tuazon *et al.*[6]	
1,4-Benzodioxan			$< 1.2 \times 10^{-20}$	298 ± 2	S-CL	Atkinson *et al.*[7]	
2,3-Dihydrobenzofuran			$< 1 \times 10^{-19}$	298 ± 2	S-CL	Atkinson *et al.*[7]	
2,3-Benzofuran			$(1.83 \pm 0.21) \times 10^{-18}$	298 ± 2	S-CL	Atkinson *et al.*[7]	
1,4-Naphthoquinone			$< 2 \times 10^{-19}$	298 ± 2	S-GC	Atkinson *et al.*[8]	
Naphthalene			$< 3 \times 10^{-19}$	295 ± 1	S-GC	Atkinson and Aschmann[9]	
1-Methylnaphthalene			$< 1.3 \times 10^{-19}$	298 ± 2	S-GC	Atkinson and Aschmann[10]	
2-Methylnaphthalene			$< 4 \times 10^{-19}$	295 ± 1	S-GC	Atkinson and Aschmann[9]	
2,3-Dimethylnaphthalene			$< 4 \times 10^{-19}$	295 ± 1	S-GC	Atkinson and Aschmann[9]	
Acenaphthene			$< 5 \times 10^{-19}$	296 ± 2	S-GC	Atkinson and Aschmann[11]	
Acenaphthylene			$(5.5^{+5.5}_{-2.8}) \times 10^{-16}$	296 ± 2	S-GC	Atkinson and Aschmann[11]	
1-Nitronaphthalene			$< 6 \times 10^{-19}$	298 ± 2	S-GC	Atkinson *et al.*[8]	
2-Nitronaphthalene			$< 6 \times 10^{-19}$	298 ± 2	S-GC	Atkinson *et al.*[8]	
2-Methyl-1-nitronaphthalene			$< 3 \times 10^{-19}$	298 ± 2	S-GC	Arey *et al.*[12]	

[a] Calculated from cited Arrhenius expression.

[b] From present recommendation.

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6. Acknowledgments

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7. Addendum

Updated literature

In this section, literature data appearing since the final version of this article was prepared are presented and discussed. The format of this Addendum follows that of the article.

7.1. Gas-Phase Tropospheric Chemistry of Organic Compounds

7.1.1. Alkanes

Kinetic data concerning the OH radical reactions with the alkanes which have appeared since the final version of this article was prepared are presented and discussed in Sec. 7.2.1 (this addendum). In this section, new data concerning the reaction mechanisms and products of the reactions subsequent to the initial OH radical and/or NO_3 radical reactions are given.

Reactions of Alkyl Radicals with HO_2 Radicals

Wallington and Hurley[1] have used FT-IR absorption spectroscopy to study the products of the gas-phase reaction of the $CD_3\dot{O}_2$ radical with the HO_2 radical at 295 ± 2 K over the total pressure range 10–700 Torr of O_2 or $O_2 + N_2$. $CD_3\dot{O}_2$ and HO_2 radicals were generated[1] by the photolysis of F_2–CD_4–H_2–O_2–N_2 mixtures at wavelengths >290 nm. CD_3OOH was the major product observed and, taking into account the self-reaction of $CD_3\dot{O}_2$ radicals (calculated to be 9–11% of the overall removal of $CD_3\dot{O}_2$ radicals), then a formation yield of CD_3OOH from the reaction of HO_2 radicals with $CD_3\dot{O}_2$ radicals of 1.00 ± 0.04 was obtained.[1] These data show that the $CD_3\dot{O}_2$ radical reaction with the HO_2 radical proceeds through the single channel,

$$CD_3\dot{O}_2 + HO_2 \rightarrow CD_3OOH + O_2$$

in agreement with the data presented in Sec. 2.1.

Fenter *et al.*[2] have used a flash photolysis system with ultraviolet absorption spectroscopy to determine rate constants for the reactions

$$2\ C_2H_5\dot{O}_2 \rightarrow \text{products}$$

and

$$C_2H_5\dot{O}_2 + HO_2 \rightarrow C_2H_5OOH + O_2$$

The rate constant obtained for the self reaction of ethyl peroxy radicals of $(6.7 \pm 0.6) \times 10^{-14}\ e^{(60 \pm 40)/T}$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 248–460 K is in good agreement with that recommended in Sec. 2.1 from the IUPAC recommendation.[3] For the reaction of the $C_2H_5\dot{O}_2$ radical with the HO_2 radical, however, Fenter *et al.*[2] obtained a rate constant at atmospheric pressure of

$$k(C_2H_5\dot{O}_2 + HO_2) = (1.60 \pm 0.40) \times 10^{-13}\ e^{(1260 \pm 130)/T}\ cm^3\ molecule^{-1}\ s^{-1}$$

over the temperature range 248–480 K, with $k(C_2H_5\dot{O}_2 + HO_2) = (1.10 \pm 0.21) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.[2] This rate constant is a factor of ~2 higher than previous measurements (Sec. 2.1) but is close to the general recommendation made in Sec. 2.1 of

$$k(R\dot{O}_2 + HO_2) = 1.0 \times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}\ \text{at 298 K.}$$

Rowley *et al.*[4] have studied the kinetics and products of the gas-phase reaction of the neopentyl peroxy $[(CH_3)_3CCH_2\dot{O}_2]$ radical with the HO_2 radical. A rate constant k of $k = (1.43 \pm 0.46) \times 10^{-13}\ e^{(1380 \pm 100)/T}$ cm^3 $molecule^{-1}$ s^{-1} was determined over the temperature range 248–365 K, with $k = (1.5 \pm 0.4) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.[4] This rate constant is similar to those determined by Rowley *et al.*[5] for the reactions of the HO_2 radical with cyclopentyl peroxy and cyclohexyl peroxy radicals of $2.1 \times 10^{-13}\ e^{1323/T}$ cm^3 $molecule^{-1}$ s^{-1} and $2.6 \times 10^{-13}\ e^{1245/T}$ cm^3 $molecule^{-1}$ s^{-1}, respectively.

Using FT-IR absorption spectroscopic analysis at 296 ± 2 K and 700 Torr total pressure of $O_2 + N_2$, Rowley *et al.*[4] observed neopentyl hydroperoxide, $(CH_3)_3CCH_2OOH$, to be the major product of the HO_2 radical reaction with the neopentyl peroxy radical, with a formation yield of 0.92 ± 0.15.

These data[4] again show that the reactions of the alkyl peroxy radicals with the HO_2 radical proceed by

$$R\dot{O}_2 + HO_2 \rightarrow ROOH + O_2 \ .$$

Based on the rate constants for the alkyl peroxy radicals other than methyl peroxy, the recommendation for the reaction of HO_2 radicals with $R\dot{O}_2$ radicals given in Sec. 2.1 of

$$k(HO_2 + R\dot{O}_2) = 3.5 \times 10^{-13}\, e^{1000/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1},$$

with $k(HO_2 + R\dot{O}_2) = 1.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K, uncertain by a factor of 2, is revised to

$$k(HO_2 + R\dot{O}_2) = 1.5 \times 10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

uncertain to a factor of 2, and

$$k(HO_2 + R\dot{O}_2) = 1.9 \times 10^{-13}\, e^{1300/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 250–370 K. Obviously, the data for the individual alkyl peroxy radicals should be used, when available.

Reactions of Alkyl Peroxy Radicals with $R\dot{O}_2$ Radicals

Rowley *et al.*[6] have carried out a kinetic and product study of the self-reaction of cyclopentyl peroxyl radicals. At 295 ± 2 K and 700 Torr total pressure of $N_2 + O_2$, cyclopentanone and cyclopentanol were observed with similar yields (0.18 ± 0.01 and 0.16 ± 0.02, respectively), independent of the O_2 partial pressure over the range 5–700 Torr.[6] These data, together with the small yield of hydroperoxide(s) observed [0.07 ± 0.02], indicate that the major reaction pathway involves formation of the cyclopentoxy radical with subsequent ring cleavage[6] [see Reaction Scheme (18)] followed by the various reactions of the $\dot{C}H_2CH_2CH_2CH_2CHO$ radical, as discussed in Sec. 2.1.

Rate constants k_{obs} were determined[6] over the temperature range 243–373 K from the flash photolysis of Cl_2–cyclopentane–O_2–N_2 mixtures by monitoring the second-order decays of the cyclopentyl peroxy radical absorption. At a given temperature, values of k_{obs} was observed to depend on the O_2/Cl_2 concentration ratios used, increasing with the O_2/Cl_2 concentration ratio.[6] This behavior was explained[6] by reaction of the $\dot{C}H_2CH_2CH_2CH_2CHO$ radical with Cl_2 in competion with reaction of the $\dot{C}H_2CH_2CH_2CH_2CHO$ radical with O_2 (and possibly isomerization). From these data, Rowley *et al.*[6] obtained rate constants for the reaction pathways of

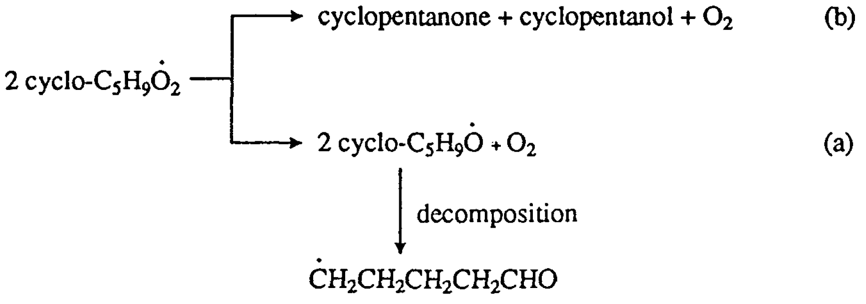
$$k_b = (1.3 \pm 0.4) \times 10^{-14}\, e^{(188\ \pm\ 83)/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

$$(k_b = 2.19 \times 10^{-14}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K}),\ \text{and}$$

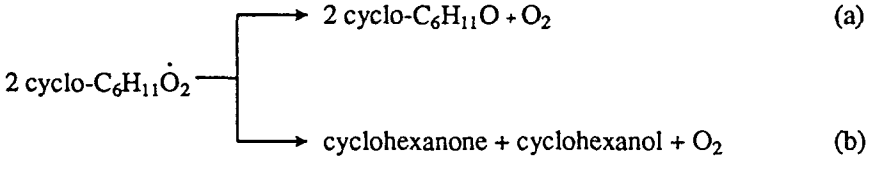
$$k_a + k_b \leq (2.9 \pm 0.8) \times 10^{-13}\, e^{-(555\ \pm\ 77)/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

$$(k_a + k_b \leq 6.73 \times 10^{-14}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K}).$$

Additional kinetic experiments for the self-reactions of cyclohexyl peroxy radicals were also conducted by Rowley *et al.*,[6] to augment those previously reported.[7] For the reactions shown by Reaction Scheme (19), rate constants of



Reaction Scheme (18)



Reaction Scheme (19)

$k_b = (1.3 \pm 0.3) \times 10^{-14}\, e^{(185 \pm 15)/T}$ cm^3 molecule^{-1} s^{-1}

over the temperature range 253–323 K and

$$k_a + k_b = 7.7 \times 10^{-14}\, e^{-184/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 253–373 K were obtained.[6] The overall rate constant $(k_a + k_b)^6$ is similar to that previously reported.[7]

Horie and Moortgat[8] have carried out a product study of the reaction of $CH_3\dot{O}_2$ radicals with the acetylperoxy $(CH_3C(O)O\dot{O})$ radical over the temperature range 263–333 K, using matrix-isolation FT-IR spectroscopy.

$$CH_3C(O)O\dot{O} + CH_3\dot{O}_2 \rightarrow CH_3C(O)\dot{O} + CH_3\dot{O} + O_2 \text{ (a)}$$

$$CH_3C(O)O\dot{O} + CH_3\dot{O}_2 \rightarrow CH_3C(O)OH + HCHO + O_2 \text{ (b)}$$

A rate constant ratio of $k_a/k_b = 2.2 \times 10^6\, e^{-(3870 \pm 950)/T}$ ($k_a/k_b = 5.0$ at 298 K) was obtained.[8] This rate constant ratio is a factor of ~5 higher than the 298 K IUPAC recommendation[3] given in Sec. 2.1.

Heimann and Warneck[9] have investigated the products of the OH radical-initiated reaction of 2,3-dimethylbutane in the presence of 750 Torr total pressure of air at 297 K. OH radicals were produced by the photolysis of H_2O_2, and the products observed were consistent with expectations. The data obtained[9] allowed derivation of rate constant ratios k_a/k ($k = k_a + k_b$) for the reactions

$$2\, R\dot{O}_2 \rightarrow 2\, R\dot{O} + O_2 \qquad \text{(a)}$$

$$2\, R\dot{O}_2 \rightarrow \text{alcohol} + \text{carbonyl} + O_2 \qquad \text{(b)}$$

of $k_a/k = 0.39 \pm 0.08$ for the self-reaction of 2-propyl peroxy radicals (in good agreement with the IUPAC recommendation[3] of $k_a/k = 0.34$ at 298 K) and $k_a/k = 0.44 \pm 0.07$ for the self-reaction of 2,3-dimethyl-2-butyl peroxy radicals. Rate constants for the cross-combination reactions of 2,3-dimethyl-2-butyl peroxy radicals with 2-propyl peroxy and 2,3-dimethyl-1-butyl peroxy radicals were also derived from computer simulations.[9]

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7.1.2. Alkenes

Kinetic data concerning the OH radical, NO_3 radical and O_3 reactions with the alkenes which have appeared since the final version of this article was prepared are given in Secs. 7.2.3, 7.3.1 and 7.4.1 (this addendum). In this section, new data concerning the products and reaction mechanisms of these reactions are given.

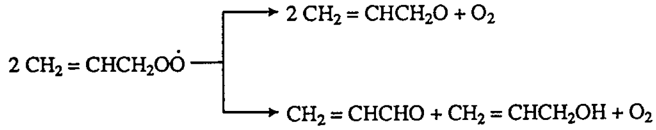
OH Radical Reactions

Jenkin *et al.*[1] have measured a rate constant at 296 ± 2 K and 740–800 Torr total pressure for the addition of O_2 to the allyl radical

$$CH_2{=}CH\dot{C}H_2 + O_2 \xrightarrow{M} CH_2{=}CHCH_2O\dot{O}$$

of $(6 \pm 2) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. This room temperature rate constant is similar to that of $\sim 4 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} measured by Morgan *et al.*[2] at 380 K and 50 Torr total pressure of Ar diluent, suggesting that the rate constant for this addition reaction is essentially independent of temperature over the range ~290–400 K.

Jenkin *et al.*[1] also investigated the kinetics and products of the self-reaction of the allyl peroxy $(CH_2{=}CHCH_2O\dot{O})$ radical, and concluded that the rate constants for the reactions



$$2\, CH_2{=}CHCH_2O\dot{O} \rightarrow 2\, CH_2{=}CHCH_2\dot{O} + O_2$$

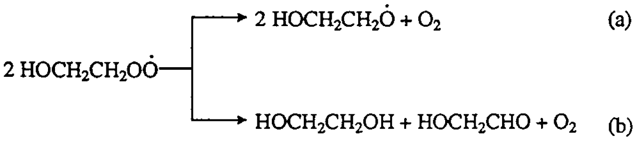
$$2\, CH_2{=}CHCH_2O\dot{O} \rightarrow CH_2{=}CHCHO + CH_2{=}CHCH_2OH + O_2$$

are $(k_a + k_b) = (6.8 \pm 1.3) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} and $k_a/(k_a + k_b) = 0.61 \pm 0.07$ at 296 ± 2 K. FT-IR absorption spectroscopy showed[1] that, as expected, the alkoxy radical $CH_2{=}CHCH_2\dot{O}$ reacts with O_2,

$$CH_2{=}CHCH_2\dot{O} + O_2 \rightarrow CH_2{=}CHCHO + HO_2$$

and no evidence for decomposition of this alkoxy radical was observed.[1]

Barnes *et al.*[3] have used FT-IR absorption spectroscopy to study the products of the self-reaction of β-hydroxyethyl peroxy $(HOCH_2CH_2O\dot{O})$ radicals at 295 ± 3 K as a function of total pressure (11–675 Torr) and O_2 concentration. The major products observed[3] were glycolaldehyde $(HOCH_2CHO)$, HCHO and $HOCH_2CH_2OH$. Barnes *et al.*[3] concluded that the reactions involved are:



$$2\, HOCH_2CH_2O\dot{O} \rightarrow 2\, HOCH_2CH_2\dot{O} + O_2 \qquad \text{(a)}$$

$$2\, HOCH_2CH_2O\dot{O} \rightarrow HOCH_2CH_2OH + HOCH_2CHO + O_2 \qquad \text{(b)}$$

followed by

$$HOCH_2CH_2\dot{O} + O_2 \rightarrow HOCH_2CHO + HO_2$$

$$\begin{array}{l} HOCH_2CH_2\dot{O} \rightarrow HCHO + \dot{C}H_2OH \\ \qquad\qquad\qquad\qquad\qquad\quad \downarrow O_2 \\ \qquad\qquad\qquad\qquad\qquad HO_2 + HCHO \end{array}$$

with $k_a/(k_a + k_b) = 0.50 \pm 0.06$. Furthermore, the rate constant ratio for reaction with O_2 versus decomposition of the $HOCH_2CH_2\dot{O}$ radical was in excellent agreement with the ratio measured by Niki *et al.*[4] from a product study of the OH radical reaction with ethene in the presence of NO_x.

Grosjean *et al.*[5] studied the products formed during NO_x-air irradiations of isoprene, and observed HCHO, methyl vinyl ketone and methacrolein to be the major products formed during the OH radical-dominated reaction period. The reported yields of these three products, which were not corrected for secondary reactions with the OH radical, were 0.50, 0.22 and 0.31, respectively.[5] These yields are consistent with the more extensive product data of Tuazon and Atkinson[6] and Paulson *et al.*[7]

Aerosol formation from the OH radical-initiated reactions of α- and β-pinene in air has been further studied by Zhang *et al.*[8]

O_3 Reactions

Hatakeyama and Akimoto[9] has investigated the oxidation of SO_2 in reacting O_3-ethene-SO_2-H_2O-air systems through the formation of formic acid (HC(O)OH). The HC(O)OH formation yield data obtained[9] were in accord with Reaction Scheme (20), and a rate constant ratio $k_b/k_a = 6.0 \times 10^{-3}$ was derived.[9]

Becker *et al.*[10] have reinvestigated the formation of H_2O_2 in the reactions of O_3 with a series of alkenes using tunable diode laser absorption spectroscopy and FT-IR absorption spectroscopy in 130–1080 liter volume reaction chambers. The H_2O_2 yields of Becker *et al.*[10] are in agreement with their previous data,[11] being (on a molar basis) 0.001 for ethene and isoprene, 0.0015 for β-pinene, 0.0028 for propene, 0.005 for *trans*-2-butene and α-pinene, 0.006 for 3-carene, 0.018 for limonene and 0.027 for 2,3-dimethyl-2-butene. These yields are in approximate agreement with those reported in the gas-phase by Hewitt and Kok,[12] but are much lower than those of Simonaitis *et al.*[13] From the H_2O_2 formation yields obtained in experiments conducted in the presence and absence of SO_2 at various water vapor concentrations, Becker *et al.*[10] derived rate constant ratios for the processes

$$\dot{C}H_2O\dot{O} + H_2O \rightarrow H_2O_2 + HCHO \qquad (a)$$

$$\dot{C}H_2O\dot{O} + H_2O \rightarrow HC(O)OH + H_2O \qquad (b)$$

$$\dot{C}H_2O\dot{O} + SO_2 \longrightarrow \text{products} \qquad (c)$$

of $(k_a + k_b)/k_c = (8.3 \pm 3.6) \times 10^{-4}$ and $k_a/(k_a + k_b) = 0.005$. For the corresponding reactions of the $(CH_3)_2\dot{C}O\dot{O}$ biradical, values of $(k_a + k_b)/k_c = (4.1 \pm 2.2) \times 10^{-4}$ and $k_a/(k_a + k_b) = 0.13$ were derived.[10] These rate constant ratios $(k_a + k_b)/k_c$ are within a factor of 4 of that reported by Suto *et al.*[14] for the $\dot{C}H_2O\dot{O}$ biradical. The discrepancies between the H_2O_2 yields measured in the studies of Becker *et al.*[10,11] and Simonaitis *et al.*[13] need to be resolved.

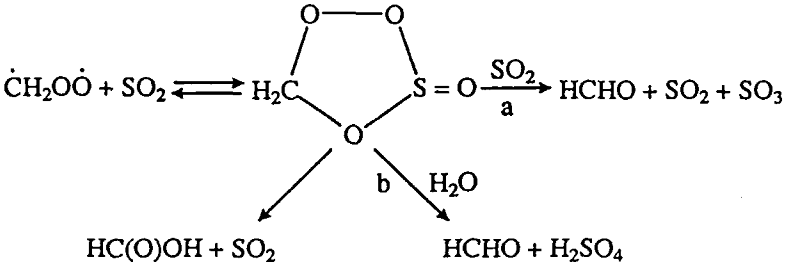
Grosjean *et al.*[5] have investigated the products formed from the gas-phase reaction of O_3 with isoprene in the presence of an excess concentration of cyclohexane to scavenge the OH radicals formed from the O_3-isoprene reaction. The molar yields of HCHO, methyl vinyl ketone and methacrolein were 0.90, 0.17 and 0.44, respectively,[5] similar to those reported by Kamens *et al.*[15] and Niki *et al.*[16] in the absence of an OH radical scavenger but lower than the methyl vinyl ketone and methacrolein yields derived from the primary reaction by Paulson *et al.*[17] Further studies are clearly required.

Atkinson *et al.*[18] have carried out a product study of the reaction of O_3 with isoprene in the presence of cyclohexane (to scavenge OH radicals) in N_2 and air diluents, and shown that the epoxides observed by Paulson *et al.*[17] arise from a direct reaction (see Reaction Scheme (21) on next page) and not via the intermediary of $O(^3P)$ atoms. An $O(^3P)$ atom formation yield of <0.1, and probably <0.01, was obtained,[18] much lower than that of 0.45 ± 0.20 derived by Paulson *et al.*[17]

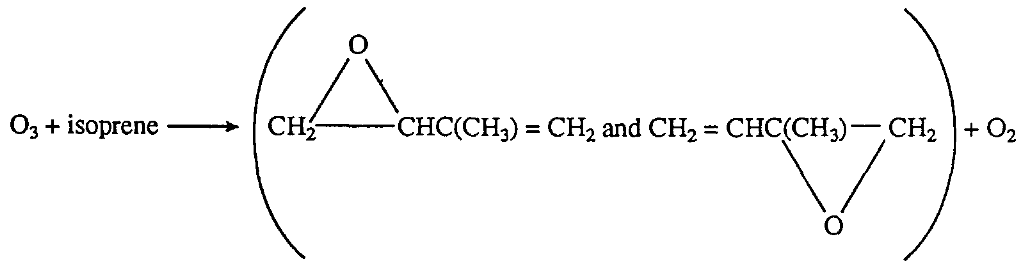
Aerosol formation from the O_3 reactions with α- and β-pinene has been investigated by Zhang *et al.*[8]

NO_3 Radical Reactions

Skov *et al.*[19] have investigated the products and mechanisms of the gas-phase reactions of the NO_3 radical with isoprene, 1,3-butadiene, 2,3-dimethyl-1,3-butadiene, 1,3-butadiene-1,1,4,4-d_4, 1,3-butadiene-d_6 and 2-methyl-1,3-butadiene-4,4-d_2 in air at 295 ± 2 K and 740 ± 5 Torr total pressure. The products observed were in general accord with the reaction schemes discussed in Sec. 2.2, and



Reaction Scheme (20)



Reaction Scheme (21)

the article of Skov *et al.*[19] should be consulted for further details.

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7.1.3. Aromatic Compounds

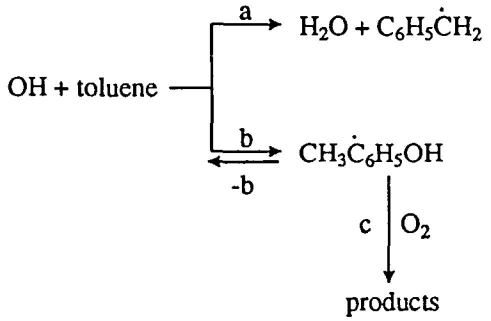
Kinetic data for the OH radical and NO_3 reactions with aromatic compounds which have appeared since the final version of this article was prepared are presented and discussed in Secs. 7.2.6 and 7.3.3. In this section, new data concerning the products and reaction mechanisms of these reactions are given.

The rate constants for the reactions of the OH-phenol adduct with NO and NO_2 determined by Knispel *et al.*[1] were inadvertently omitted from Sec. 2.4. An upper limit for reaction of the OH-phenol adduct with NO of 7×10^{-14} cm^3 molecule^{-1} s^{-1} at 316–332 K was obtained.[1] Rate constants for reaction of the OH-phenol adduct with NO_2 of $(2.8 \pm 0.4) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 331 K and $(3.6 \pm 0.3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 353 K were determined, these rate constants being similar to those for the corresponding reactions of NO_2 with the OH-benzene and OH-toluene adducts.[1]

Zetzsch and coworkers[2] have reported updated rate constants for the reactions of hydroxycyclohexadienyl and substituted-hydroxycyclohexadienyl radicals with O_2. The rate constants (in units of 10^{-16} cm^3 molecule^{-1} s^{-1} at 100 Torr total pressure of Ar diluent) are[2]: for the hydroxycyclohexadienyl radical formed from the OH radical reaction with benzene; 1.6 ± 0.6 at 299 K, 2.1 ± 0.4 at 314 K, 3.0 ± 0.3 at 333 K, and 3.7 ± 0.4 at 354 K; for the methylhydroxycyclohexadienyl radical(s) formed from the OH radical reaction with toluene; 5.6 ± 1.5 at 299 K, 5.6 ± 0.6 at 321 K, 5.6 ± 0.6 at 339 K, 5.3 ± 0.7 at 347 K, and 5.9 ± 0.8 at 354 K; and for the dihydroxycyclohexadienyl radical(s) formed from the OH radical reaction with phenol; 300 ± 70 at 323 K, 260 ± 60 at 333 K, 270 ± 50 at 337 K, 290 ± 60 at 343 K, 270 ± 60 at 353 K, and 360 ± 50 at 363 K. Additional experiments showed the formation of HO_2 radicals in >90% yield from reaction of the OH-phenol adduct with O_2 at room temperature,[2] although the reaction sequence was concluded[2] to be more complex than the direct formation of HO_2 radicals via

$$\text{OH-phenol adduct} + O_2 \rightarrow \text{dihydroxybenzene} + HO_2$$

Using a 2400 liter volume reaction chamber at 300 K and atmospheric pressure of N_2, Zetzsch *et al.*[2] used a relative rate technique to show that the rate constants for the reactions of benzene, toluene and *p*-xylene with the OH radical increased with increasing concentrations of O_2, as expected from the reaction sequence (taking toluene as an example)



and the previously measured rate constants k_a, k_b, k_{-b} and k_c. For *p*-xylene, the experimental data allowed a rate constant k_c for reaction of O_2 with the dimethylhydroxycyclohexadienyl radical of $\sim 1.9 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} to be derived.[2]

Atkinson and Aschmann[3] have generated OH radicals from the dark O_3 reactions with propene and α-pinene at 296 ± 2 K and atmospheric pressure of air (Sec. 2.2), and shown that *o*-cresol is formed from toluene with a slightly lower yield in the absence of NO_x than in the presence of NO_x. The formation yields of 2,3-butanedione (biacetyl) were also measured from the OH radical reactions with *o*-xylene and 1,2,3-trimethylbenzene in the presence and absence of NO_x. For 1,2,3-trimethylbenzene, the 2,3-butanedione formation yield[3] increased from ~ 0.18 in the absence of NO_x to ~ 0.45 in the presence of NO_2 at concentrations $\geq 5 \times 10^{12}$ molecule cm^{-3}. The product data of Atkinson and Aschmann[3] are consistent with the kinetic data of Zetzsch and coworkers[1,2] and indicate that the OH-benzene, OH-toluene, OH-xylene and OH-trimethylbenzene adducts will react with O_2 under most atmospheric conditions.

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87.1.4. Oxygen-Containing Organic Compounds

The kinetics of the OH radical, NO_3 radical and O_3 reactions with oxygen-containing organic compounds which have appeared since the final version of this article was prepared are presented and discussed in Secs. 7.2.5, 7.3.2 and 7.4.2. In this section new data concerning the products and reaction mechanisms of these reactions are given.

Horie and Moortgat[1] have obtained, from a product study of the reaction of the $CH_3C(O)O\dot{O}$ radical with HO_2,

$$CH_3C(O)O\dot{O} + HO_2 \rightarrow CH_3C(O)OOH + O_2 \quad (a)$$

$$CH_3C(O)O\dot{O} + HO_2 \rightarrow CH_3C(O)OH + O_3 \quad (b)$$

the rate constant ratio of $k_a/k_b = 330\ e^{-(1430 \pm 480)/T}$ over the temperature range 263–333 K ($k_a/k_b = 2.7$ at 298 K). This rate constant ratio[1] is in agreement with the recommendation of Atkinson *et al.*[2] (Sec. 2.5) of $k_a/k_b = 2.3$ at 298 K, but disagrees with the previous recommendation[2] that $k_a/k_b = 2.3$, independent of temperature over the range 250–370 K.

Cox *et al.*[3] have used a pulsed radiolysis technique to obtain rate constants for the reactions

$$CH_3C(O)\dot{C}H_2 + O_2 \xrightarrow{M} CH_3C(O)CH_2O\dot{O}$$

and

$$2\ CH_3C(O)CH_2O\dot{O} \rightarrow \text{products}$$

at 298 K and one atmosphere total pressure of SF_6, of $(1.5 \pm 0.3) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} and $(8.3 \pm 1.6) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, respectively. The O_2 addition reaction to the $CH_3C(O)\dot{C}H_2$ radical has a rate constant of a similar magnitude to the reactions of O_2 with alkyl radicals (Sec. 2.1), as expected.

Grosjean *et al.*[4] have shown that the atmospheric photooxidation of *cis*-3-hexen-1-ol ($CH_3CH_2CH = CHCH_2CH_2OH$) leads to the formation of propanal and peroxypropionyl nitrate, as expected.[5] Based on analogy with the reaction of propene with OH radicals and O_3, propanal is expected to be a first-generation product, with subsequent OH radical reaction with propanal in the presence of NO_x leading to the formation of peroxypropionyl nitrate ($CH_3CH_2C(O)OONO_2$) [Sec. 2.6].

Wallington *et al.*[6] have used FT-IR absorption spectroscopy to investigate the products formed from the OH radical and Cl atom-initiated reactions of di-isopropyl ether at 295 ± 2 K and 700 Torr total pressure of air. The major product of both the OH radical (in the presence of NO_x) and Cl atom reactions was isopropyl acetate [$(CH_3)_2CHOC(O)CH_3$], with a yield of 1.05 ± 0.06 from the OH radical reaction.[6] An isopropyl acetate yield of 0.92 ± 0.13 was obtained from the Cl atom-initiated reaction in the presence of NO_x and a yield of the products arising from the reactions of the $CH_3\dot{O}$ radical (HCHO, CH_3ONO and CH_3ONO_2) of ~ 1.1 was determined. The OH radical reaction is expected to proceed mainly at the $>$CH– group,[6,7] and hence the OH radical reaction in the presence of NO_x must proceed by Reaction Scheme (22).

Temperature-dependent absorption cross-sections for acetone and 2-butanone have been measured by Hynes *et al.*[8]

The gas-phase reaction of the HO_2 radical with HCHO has been theoretically investigated by Evleth *et al.*,[9] and it was concluded that the reaction proceeds by

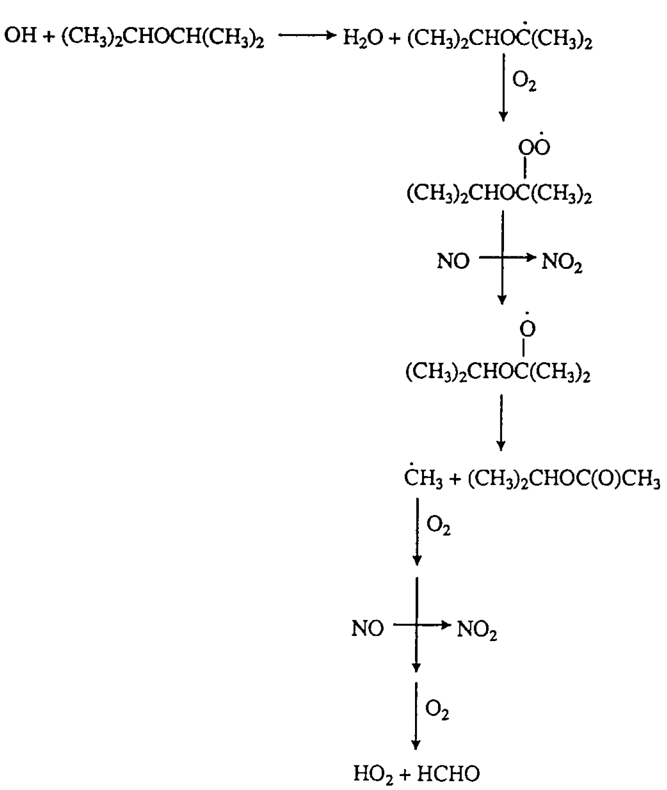
$$HO_2 + HCHO \rightleftarrows [H_2C{=}OHOO] \rightleftarrows HOCH_2O\dot{O}$$

and that the intermediate alkoxy radical $HOOCH_2\dot{O}$ is not involved.

Barnes *et al.*[10] have studied the products of the OH radical reaction with $HOCH_2CH_2OH$ and shown that glycolaldehyde ($HOCH_2CHO$) is the major product, together with lesser yields of HCHO and HC(O)OH. The reaction then proceeds mainly by[10]

$$OH + HOCH_2CH_2OH \rightarrow H_2O + HOCH_2\dot{C}HOH$$

$$HOCH_2\dot{C}HOH + O_2 \rightarrow HOCH_2CHO + HO_2$$



Reaction Scheme (22)

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7.1.5. Nitrogen-Containing Organic Compounds

Kinetic data for the gas-phase reactions of O_3 with nitrogen-containing organic compounds which has appeared since the finalization of this article are presented in Sec. 7.4.3 below. The product and mechanistic data for nitrogen-containing organic compounds are presented below.

Langer *et al.*[1] and Orlando *et al.*[2] have investigated the thermal decomposition of peroxyactyl nitrate (PAN) in the presence of NO_2. Orlando *et al.*[2] showed that the reaction channels

$$CH_3C(O)OONO_2 \rightarrow CH_3ONO_2 + CO_2$$

and

$$CH_3C(O)OONO_2 \rightarrow CH_3C(O)\dot{O} + NO_3$$

are of negligible importance compared to the reaction pathway,

$$CH_3C(O)OONO_2 \rightarrow CH_3C(O)O\dot{O} + NO_2$$

and that the thermal decomposition of PAN is not a significant source of CH_3ONO_2 in the atmosphere. Langer *et al.*[1] concluded that the heterogeneous decomposition of PAN is not important under atmospheric conditions.

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7.2. Kinetics and Mechanisms of the Gas-Phase Reactions of the OH Radical with Organic Compounds

The rate constants for the reactions of the OH radical with organic compounds reported since Sec. 3 of this article was finalized are presented and discussed in the sections below.

7.2.1. Alkanes

The rate constants reported since Table 36 was finalized are given in Table 64.

Methane. The absolute rate constants reported by Lancar *et al.*[1] and Sharkey and Smith[2] at 378–422 K[1] and 298 K[2] are within ±20% of the recommendation given in Sec. 3.1, of $k(CH_4) = 7.44 \times 10^{-18} T^2 e^{-1361/T}$ cm^3 molecule^{-1} s^{-1} over the temperature range 223–1512 K. The upper limit obtained by Sharkey and Smith[2] at 178 K is also consistent with this recommended rate constant. However, the rate constant reported by Sharkey and Smith[2] at 216 K is a factor of 2.6 higher than the recommended rate constant. The recommended rate constant from Sec. 3.1 is unchanged. The 378 and 422 K rate constants of Lancar *et al.*[1] together with the 295–420 K data of Vaghjiani and Ravishankara[6] and the 333–378 K data of Finlayson-Pitts *et al.*[7] may indicate that the value of n in the three-parameter expression $k(CH_4) = CT^n e^{-D/T}$ is >2, leading to slightly lower rate constants in the range ~330–600 K than presently recommended.

Ethane. The absolute rate constants reported by Sharkey and Smith[2] at 178–298 K are 9 ± 6 to 20 ± 10% higher than those calculated from the recommendation of Sec. 3.1. of $k(\text{ethane}) = 1.51 \times 10^{-17} T^2 e^{-492/T}$ cm^3

Table 64. Rate constants k for the gas-phase reactions of the OH radical with alkanes

Alkane	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference
Methane	0.0262 ± 0.0027	378	DF-EPR	Lancar *et al.*[1]
	0.0427 ± 0.0018	422		
	<0.0003	178	LP-LIF	Sharkey and Smith[2]
	0.00165 ± 0.0002	216		
	0.0076 ± 0.0003	298		
Ethane	0.013 ± 0.002	138	LP-LIF	Sharkey and Smith[2]
	0.025 ± 0.003	178		
	0.0785 ± 0.004	216		
	0.295 ± 0.014	298		
	0.291 ± 0.007	298	RR [relative to k(propane) = $1.50 \times 10^{-17}\,T^2\,e^{-44/T}$][a]	Finlayson-Pitts *et al.*[3]
	0.285 ± 0.013	298		
	0.377 ± 0.014	323		
	0.480 ± 0.013	348		
	0.590 ± 0.010	373		
Propane	1.15 ± 0.06	298	RR [relative to k(n-butane) = 2.54×10^{-12}][a]	Finlayson-Pitts *et al.*[3]
	1.15 ± 0.06	298		
	1.04 ± 0.07	298	RR [relative to k(2-methylpropane) = 2.33×10^{-12}][a]	Finlayson-Pitts *et al.*[3]
	1.22 ± 0.04	298		
	1.16 ± 0.06	298		
n-Pentane	4.22 ± 0.05	302	RR [relative to k(2-methylpropane) = 2.36×10^{-12}][a]	Donaghy *et al.*[4]
n-Hexane	5.55 ± 0.20	301 ± 2	RR [relative to k(n-pentane) = 3.99×10^{-12}][a]	McLoughlin *et al.*[5]

[a] From recommendations in Sec. 3.1.

molecule^{-1} s^{-1} over the temperature range 226–800 K. The rate constant reported by Sharkey and Smith[2] at 138 K is 60 ± 25% higher than the present recommendation. Finlayson-Pitts *et al.*[3] have employed a relative rate method, using the dark reaction of O_3 in the presence of alkanes and the photolysis of O_3–H_2O–alkane mixtures to generate OH radicals, to obtain rate constants for ethane versus propane. The rate constants obtained by Finlayson-Pitts *et al.*[3] over the temperature range 298–373 K (Table 64) are within 13% of the recommendation given in Sec. 3.1, which is hence unchanged.

Propane. Finlayson-Pitts *et al.*[3] have used relative rate methods to obtain rate constants for the OH radical reaction with propane relative to those for the OH radical reactions with n-butane and 2-methylpropane. For the measurements relative to 2-methylpropane, OH radicals were generated from the dark reactions of O_3 in alkane–O_2 or alkane–H_2O–O_2 mixtures, the photolysis of O_3–H_2O–alkane–O_2 mixtures, and the photolysis of CH_3ONO–NO–alkane–air mixtures.[3] The three methods of OH radical generation led to essentially identical results (Table 64).[3] The rate constants for propane obtained by Finlayson-Pitts *et al.*[3] are in excellent agreement with the recommended 298 K rate constant of 1.15×10^{-12} cm^3 molecule^{-1} s^{-1} (Sec. 3.1), and hence this recommendation is unchanged.

n-Pentane and n-Hexane. The relative rate constants of Donaghy *et al.*[4] (n-pentane) and McLoughlin *et al.*[5] (n-hexane) are given in Table 64. These rate constants are in good agreement (within 5% for n-pentane and 2% for n-hexane) with the recommendations given in Sec. 3.1 and by Atkinson.[8] These recommendations (Sec. 3.1 and Ref. 8) are hence unchanged.

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7.2.2. Haloalkanes

The rate constants reported since Table 37 was finalized was given in Table 65.

CH_3F. The rate constants obtained by Wallington and Hurley[1] from relative rate measurements are given in Table 65. These rate constants are in excellent agreement with that of 1.62 × 10^{-14} cm^3 molecule^{-1} s^{-1} at 296 K calculated from the recommendation of Atkinson[15] of

$$k(\mathrm{CH_3F}) = 5.51 \times 10^{-18}\, T^2\, \mathrm{e}^{-1005/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the temperature range 292–480 K. This recommendation[15] is hence unchanged.

CH_3Cl. Taylor *et al.*[2] have reinvestigated the kinetics of the OH radical reaction with CH$_3$Cl at elevated temperatures (742–955 K) to check that previous measurements[16] were not influenced by photolysis of the CH$_3$Cl reactant. This was shown to be generally the case, and the rate constants determined at 742–955 K[2] are given in Table 65. These rate constants[2] and those of Taylor *et al.*,[16] as listed by Taylor *et al.*[2] (with the rate constants of Taylor *et al.*[16] being averaged at 473 and 475 K, 524 and 525 K, 667 K, and 695 K, and the rate constant at 735 K being omitted), are used in the evaluation of the rate constant for this reaction. A unit-weighted least-squares analysis of the absolute rate constants of Howard and Evenson,[17] Perry *et al.*,[18] Davis *et al.*,[19] Paraskevopoulos *et al.*,[20] Jeong and Kaufman[21] and the absolute rate constants listed by Taylor *et al.*[2] (see above), using the expression $k = CT^2\, \mathrm{e}^{-D/T}$, yields the recommendation of

$$k(\mathrm{CH_3Cl}) = (7.33^{+1.09}_{-0.94}) \times 10^{-18}\, T^2\, \mathrm{e}^{-(809 \pm 54)/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the temperature range 250–955 K, where the indicated errors are two least-squares standard deviations, and

$$k(\mathrm{CH_3Cl}) = 4.31 \times 10^{-14}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ \text{at 298 K},$$

with an estimated overall uncertainty at 298 K of ±20%. This recommendation supersedes that of Atkinson[15] of

$$k(\mathrm{CH_3Cl}) = 3.50 \times 10^{-18}\, T^2\, \mathrm{e}^{-585/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the temperature range 250–483 K, with a 298 K rate constant of 4.36 × 10^{-14} cm^3 molecule^{-1} s^{-1}, and leads to a rate constant at 250 K 15% lower than calculated from the previous[15] recommendation.

CH_3Br. The absolute rate constants obtained by Mellouki *et al.*[3] and Zhang *et al.*[4] are given in Table 65. These rate constants are significantly lower than the previous data of Howard and Evenson[17] and Davis *et al.*[19] over a similar temperature range. A unit-weighted least-squares analysis of the rate constants of Mellouki *et al.*[3] and Zhang *et al.*,[4] using the expression $k = CT^2\, \mathrm{e}^{-D/T}$, yields the recommendation of

$$k(\mathrm{CH_3Br}) = (3.62^{+0.77}_{-0.63}) \times 10^{-18}\, T^2\, \mathrm{e}^{-(711 \pm 56)/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the temperature range 233–400 K, where the indicated errors are two least-squares standard deviations, and

$$k(\mathrm{CH_3Br}) = 2.96 \times 10^{-14}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ \text{at 298 K},$$

with an estimated overall uncertainty at 298 K of ±20%. This recommendation supersedes that of Atkinson[15] of

$$k(\mathrm{CH_3Br}) = 2.60 \times 10^{-18}\, T^2\, \mathrm{e}^{-521/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the temperature range 244–2000 K, with a 298 K rate constant of 4.02 × 10^{-14} cm^3 molecule^{-1} s^{-1}.

CH_2Cl_2. Taylor *et al.*[2] have re-investigated the kinetics of this reaction, and the rate constants obtained[2] are given in Table 65. These rate constants[2] supersede those reported previously.[16] A unit-weighted least-squares analysis of the absolute rate constants of Howard and Evenson,[17] Perry *et al.*,[18] Davis *et al.*,[19] Jeong and Kaufman[21] and Taylor *et al.*,[2] using the expression $k = CT^2\, \mathrm{e}^{-D/T}$, yields the recommendation of

$$k(\mathrm{CH_2Cl_2}) = (6.14^{+1.16}_{-0.97}) \times 10^{-18}\, T^2\, \mathrm{e}^{-(389 \pm 66)/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the temperature range 245–955 K, where the indicated errors are two least-squares standard deviations, and

$$k(\mathrm{CH_2Cl_2}) = 1.48 \times 10^{-13}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ \text{at 298 K},$$

with an estimated overall uncertainty at 298 K of ±20%. This recommendation supersedes that of Atkinson[15] of

$$k(\mathrm{CH_2Cl_2}) = 8.54 \times 10^{-18}\, T^2\, \mathrm{e}^{-500/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the temperature range 245–455 K, with a 298 K rate constant of 1.42 × 10^{-13} cm^3 molecule^{-1} s^{-1}.

CHF_2Cl. The absolute rate constants determined by Orkin and Khamaganov[5] are given in Table 65. These rate constants[5] are in good agreement (within 12% from 298–370 K and within 21% at 460 K) with the recommendation of Atkinson,[15] of

$$k(\mathrm{CHF_2Cl}) = 1.51 \times 10^{-18}\, T^2\, \mathrm{e}^{-1000/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the temperature range 250–482 K, and

$$k(\mathrm{CHF_2Cl}) = 4.68 \times 10^{-15}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ \text{at 298 K}.$$

The previous recommendation[15] is therefore unchanged.

CHF_2Br. The absolute rate constants of Orkin and Khamaganov[6] are given in Table 65. These rate constants[6] are in excellent agreement with the recommendation in Sec. 3.2 (being 1–9% higher at 314–460 K and 14% higher at 298 K) of

$$k(\mathrm{CHF_2Br}) = 1.48 \times 10^{-18}\, T^2\, \mathrm{e}^{-779/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the temperature range 233–432 K, and

$$k(\mathrm{CHF_2Br}) = 9.63 \times 10^{-15}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ \text{at 298 K.}$$

This recommendation from Sec. 3.2 is hence unchanged, although the estimated overall uncertainty at 298 K is now reduced to ±30%.

$CHCl_3$. Taylor *et al.*[2] have reinvestigated the kinetics of this reaction, and observed that at temperatures ≥400 K laser photolysis of the $CHCl_3$ reactant led to erroneously high measured rate constants unless the laser photolysis intensities were kept low. The rate constants obtained at low laser photolysis intensities, and shown to be independent of the laser photolysis intensity,[2] are given in Table 65. These rate constants supersede those of Taylor *et al.*[16] reported earlier. The rate constants of Taylor *et al.*[2] at temperatures of 360–480 K are significantly (up to a factor of ~1.7) lower than the rate constants of Jeong and Kaufman.[21] A unit-weighted least-squares analysis of the absolute rate constants of Howard and Evenson,[17] Davis *et al.*[19] and Taylor *et al.*,[2] using the expression $k = CT^2\, \mathrm{e}^{-D/T}$, leads to the recommendation of

$$k = (1.80^{+0.38}_{-0.32}) \times 10^{-18}\, T^2\, \mathrm{e}^{-(129 \pm 75)/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the temperature range 245–775 K, where the indicated errors are two least-squares standard deviations, and

$$k(\mathrm{CHCl_3}) = 1.04 \times 10^{-13}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ \text{at 298 K,}$$

with an estimated overall uncertainty at 298 K of ±20%. [Inclusion of the rate constants of Jeong and Kaufman[21] into the data set used for evaluation of this rate constant leads to $k(\mathrm{CHCl_3}) = 2.11 \times 10^{-18}\ T^2\ \mathrm{e}^{-169/T}$ cm^3 molecule^{-1} s^{-1} over the same temperature range, with a 298 K rate constant of 1.06×10^{-13} cm^3 molecule^{-1} s^{-1}].

The present recommendation supersedes the previous recommendation of Atkinson[15] of

$$k(\mathrm{CHCl_3}) = 6.30 \times 10^{-18}\, T^2\, \mathrm{e}^{-504/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the more restricted temperature range of 245–487 K, with a 298 K rate constant of 1.03×10^{-13} cm^3 molecule^{-1} s^{-1}. The present recommendation leads to significantly higher rate constants for temperatures ≤290 K than calculated from the previous recommendation.[15] In particular, the present recommendation leads to rate constants which are 20–45% higher than those measured by Davis *et al.*[19] at 245 K and Jeong and Kaufman[21] at 249 K. Clearly, further absolute rate constant studies are needed, particularly at temperatures in the range ~230–270 K, to resolve these discrepancies.[2,19,21]

CF_4, CF_3Br and CF_2BrCF_2Br. The upper limits to the rate constants reported by Ravishankara *et al.*[7] (CF_4) and Orkin and Khamaganov[6] (CF_3Br and CF_2BrCF_2Br) are given in Table 65. The upper limit to the rate constant for CF_4 reported by Ravishankara *et al.*[7] is consistent with, but a factor of 200 lower, than the recommendation of Atkinson[15] based on the data of Howard and Evenson.[17] Accordingly, a rate constant of

$$k(\mathrm{CF_4}) < 2 \times 10^{-18}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ \text{at 298 K}$$

is recommended.

The upper limits to the rate constants for CF_3Br and CF_2BrCF_2Br of Orkin and Khamaganov[6] are consistent with the upper limits recommended at 298 K in Sec. 3.2 of $<1 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} and $<1.5 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}, respectively.

CH_3CH_2Cl. The absolute rate constants determined by Markert and Nielsen[8] are given in Table 65. The 295 K rate constant reported by Markert and Nielsen[8] is identical to that reported by Markert and Nielsen[22] and used in the evaluation of the rate constant for this reaction in Sec. 3.2. However, the rate constants of Markert and Nielsen[8] at 307–360 K are 45–77% higher than calculated from the recommendation given in Sec. 3.2 of

$$k(\mathrm{CH_3CH_2Cl}) = 7.71 \times 10^{-18}\, T^2\, \mathrm{e}^{-152/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the temperature range 294–789 K, with a 298 K rate constant of 4.11×10^{-13} cm^3 molecule^{-1} s^{-1} (the 295 K rate constant of Markert and Nielsen[8,22] is only 7% higher than the recommended value). The recommendation of Sec. 3.2 is unchanged.

CH_3CH_2Br. The relative rate constant of Donaghy *et al.*[9] is given in Table 9. This 300 K rate constant of Donaghy *et al.*[9] is 25% lower than that calculated from the Arrhenius expression of Xing *et al.*[23] and Qiu *et al.*[24] (Sec. 3.2), although within the combined uncertainties cited.[9,23,24] From a unit-weighted average of the room temperature rate constants of Xing *et al.*[23] and Qiu *et al.*[24] and Donaghy *et al.*,[9] the recommendation of

$$k(\mathrm{CH_3CH_2Br}) = 2.7 \times 10^{-13}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ \text{at 298 K}$$

is obtained, with an estimated overall uncertainty at 298 K of ±40%.

CH_3CHCl_2. The absolute rate constants determined by Jiang *et al.*[10] are given in Table 65. The only previous rate constant for CH_3CHCl_2 is that measured at 296 K by Howard and Evenson,[25] and the agreement is excellent. A unit-weighted least-squares analysis of the absolute rate constants of Howard and Evenson[25] and Jiang *et al.*,[10] using the expression $k = CT^2\, \mathrm{e}^{-D/T}$, leads to the recommendation of

$$k(\mathrm{CH_3CHCl_2}) = (2.50 \pm 0.16) \times 10^{-18}\, T^2\, \mathrm{e}^{(63 \pm 27)/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the temperature range 294–800 K, where the indicated errors are two least-squares standard deviations, and

$$k(\mathrm{CH_3CHCl_2}) = 2.74 \times 10^{-13}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ \text{at 298 K,}$$

with an estimated overall uncertainty at 298 K of ±30%.

CH_3CCl_3. The absolute rate constants of Jiang *et al.*[11] are given in Table 65. These rate constants of Jiang *et al.*[11] are systematically higher than the recommendation of Sec. 3.2 based on the absolute rate constants of Finlayson-Pitts *et al.*[26] and Talukdar *et al.*[27] This discrepancy increases with temperature, with the rate constants of Jiang *et al.*[11] being 15% higher than the recommendation of Sec. 3.2 at 298 K, increasing to 34% higher at 400 K. Accordingly, the recommendation of Sec. 3.2 of

$$k(\mathrm{CH_3CCl_3}) = 2.25 \times 10^{-18}\, T^2\, \mathrm{e}^{-910/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the temperature range 243–379 K, with a 298 K rate constant of 9.43×10^{-15} cm^3 molecule^{-1} s^{-1}, is unchanged.

CH_2FCF_3. The absolute rate constants of Orkin and Khamaganov[5] are given in Table 65. These rate constants are in excellent agreement (within 14%) with the recommendation of Sec. 3.2 based on the rate constants of Martin and Parakevopoulos,[28] Liu *et al.*[29] and Gierczak *et al.*[30] Accordingly, the recommendation of Sec. 3.2 of

$$k(\mathrm{CH_2FCF_3}) = 1.61 \times 10^{-18}\, T^2\, \mathrm{e}^{-1005/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the temperature range 223–450 K, with a 298 K rate constant of 4.90×10^{-15} cm^3 molecule^{-1} s^{-1}, is unchanged.

CH_2BrCF_3. The absolute rate constants of Nelson *et al.*[12] and Orkin and Khamaganov[6] are given in Table 65. The rate constants of Nelson *et al.*[12] are uniformly lower, by ~20%, than those of Orkin and Khamaganov[6] over the temperature range common to both studies (298–353 K). A unit-weighted least-squares analysis of the absolute rate constants of Nelson *et al.*[12] and Orkin and Khamaganov,[6] using the Arrhenius expression $k = A\ \mathrm{e}^{-B/T}$, yields the recommendation of

$$k(\mathrm{CH_2BrCF_3}) = (1.44^{+1.14}_{-0.64}) \times 10^{-12}\, \mathrm{e}^{-(1337\,\pm\,192)/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the temperature range 280–460 K, where the indicated errors are two least-squares standard deviations, and

$$k(\mathrm{CH_2BrCF_3}) = 1.62 \times 10^{-14}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ \text{at 298 K},$$

with an estimated overall uncertainty at 298 K of ±40%.

$CHCl_2CHCl_2$. The absolute rate constants of Jiang *et al.*[13] are given in Table 65. These rate constants are a factor of ~2 lower than those of Xing *et al.*[23] and Qiu *et al.*[24] No recommendation is made.

$CHFBrCF_3$. The rate constants of Orkin and Khamaganov[6] are given in Table 65. These rate constants are in good agreement with the absolute rate constants of Brown *et al.*[31] A unit-weighted least-squares analysis of the rate constants of Brown *et al.*[31] and Orkin and Khamaganov,[6] using the Arrhenius expression $k = A\ \mathrm{e}^{-B/T}$, yields the recommendation of

$$k(\mathrm{CHFBrCF_3}) = (8.09^{+2.87}_{-2.12}) \times 10^{-13}\, \mathrm{e}^{-(1157\,\pm\,105)/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the temperature range 279–460 K, where the indicated errors are two least-squares standard deviations, and

$$k(\mathrm{CHFBrCF_3}) = 1.67 \times 10^{-14}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ \text{at 298 K},$$

with an overall estimated uncertainty at 298 K of ±35%.

$CHClBrCF_3$. The absolute rate constants of Orkin and Khamaganov[6] are given in Table 65. This is the first temperature-dependence study. The previous rate constant of Brown *et al.*[32,33] at 303 K is ~25% higher than that calculated from the Arrhenius expression of Orkin and Khamaganov.[6] A unit-weighted least-squares analysis of the absolute rate constants of Orkin and Khamaganov,[6] using the Arrhenius expression $k = A\ \mathrm{e}^{-B/T}$, yields the recommendation of

$$k(\mathrm{CHClBrCF_3}) = (1.20^{+0.23}_{-0.20}) \times 10^{-12}\, \mathrm{e}^{-(970\,\pm\,63)/T}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

over the temperature range 298–460 K, where the indicated errors are two least-squares standard deviations, and

$$k(\mathrm{CHClBrCF_3}) = 4.63 \times 10^{-14}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ \text{at 298 K},$$

with an estimated overall uncertainty at 298 K of ±40%.

CH_3CH_2Cl and $CH_3CHClCH_3$. The rate constants of Markert and Nielsen[8] and Donaghy *et al.*[9] are given in Table 65. For both chloropropanes, the room temperature rate constants exhibit a significant amount of scatter. Furthermore, the absolute rate constant data of Markert and Nielsen[8] are quite scattered for both compounds. Based on the relative rate constants of Donaghy *et al.*,[9] rate constants of

$$k(\mathrm{CH_3CH_2Cl}) = 1.0 \times 10^{-12}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

and

$$k(\mathrm{CH_3CHClCH_3}) = 9.0 \times 10^{-13}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

at 298 K are recommended, both with estimated overall uncertainties of ±40%.

Other Haloalkanes. For the other haloalkanes listed in Table 65, only single studies (or studies conducted by one research group) have been carried out and no recommendations are made.

Table 65. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with haloalkanes

Haloalkane	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	n	B (K)	$10^{14} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
CH_3F				1.61 ± 0.08	296 ± 2	RR [relative to k(acetylene) = 7.99×10^{-13}]^a	Wallington and Hurley[1]	
				1.51 ± 0.08	296 ± 2	RR [relative to k(methane) = 6.57×10^{-15}]^a	Wallington and Hurley[1]	
CH_3Cl				146.3 ± 4.8	742	LP-LIF	Taylor *et al.*[2]	742–955
				167.0 ± 4.6	775			
				217.0 ± 10.3	875			
				247.1 ± 11.9	925			
	2.90×10^{-2}	0.89	1447 ± 75^b	267.0 ± 31.7	955			
CH_3Br				0.98 ± 0.04	233	LP-LIF	Mellouki *et al.*[3]	233–379
				1.22 ± 0.02	243			
				1.55 ± 0.03	251			
				1.39 ± 0.06	253			
				1.43 ± 0.04	253			
				1.48 ± 0.06	253			
				1.70 ± 0.05	263			
				1.99 ± 0.04	273			
				2.08 ± 0.11	273			
				1.97 ± 0.08	273			
				2.31 ± 0.05	284			
				2.84 ± 0.06	296			
				2.82 ± 0.06	296			
				2.71 ± 0.05	296			
				3.03 ± 0.11	296			
				3.51 ± 0.06	313			
				3.80 ± 0.08	321			
				4.08 ± 0.13	322			
				4.40 ± 0.10	326			
				4.63 ± 0.10	337			
				5.75 ± 0.20	350			
				5.62 ± 0.12	352			
				6.34 ± 0.25	364			
				6.67 ± 0.40	366			
				8.00 ± 0.08	378			
	2.35		1300 ± 150	7.66 ± 0.22	379			

Table 65. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with haloalkanes – Continued

Haloalkane	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	n	B (K)	$10^{14} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
				1.17 ± 0.29	250	FP-RF	Zhang *et al.*[4]	250–400
				1.33 ± 0.19	250			
				1.68 ± 0.30	270			
				2.25 ± 0.56	283			
				2.81 ± 0.31	295			
				2.77 ± 0.74	296			
				2.96 ± 0.83	298			
				6.51 ± 0.97	340			
	5.79		1560 ± 150	12.3 ± 1.3	400			
CH_2Cl_2				14.7 ± 1.8	295	LP-LIF	Taylor *et al.*[2]	295–955
				16.1 ± 3.0	309			
				24.8 ± 2.3	335			
				24.2 ± 4.6	340			
				29.4 ± 5.6	376			
				43.9 ± 5.8	415			
				43.3 ± 4.2	425			
				61.5 ± 13.8	455			
				65.1 ± 10.6	474			
				85.8 ± 11.8	495			
				81.8 ± 10.0	535			
				101.4 ± 7.6	575			
				135.3 ± 13.0	615			
				148.1 ± 8.3	655			
				165.6 ± 11.6	695			
				184.5 ± 13.3	735			
				213.0 ± 12.8	775			
				259.0 ± 11.7	896			
	4.01×10^{-3}	1.09	771 ± 48	316.0 ± 39.2	955			
CH_2Br_2				6.0 ± 0.2	243	LP-LIF	Mellouki *et al.*[3]	243–380
				6.8 ± 0.2	253			
				7.0 ± 0.3	253			
				6.8 ± 0.4	253			
				8.4 ± 0.4	268			
				9.5 ± 0.5	283			
				10.6 ± 0.3	296			
				11.1 ± 0.4	296			
				12.0 ± 0.7	297			
				10.7 ± 0.3	298			
				11.3 ± 0.6	298			
				12.0 ± 0.2	300			
				13.5 ± 1.0	324			
				17.4 ± 1.0	350			
	1.91		840 ± 100	21.1 ± 0.7	380			

Table 65. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with haloalkanes – Continued

Haloalkane	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	n	B (K)	$10^{14} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
CHF_2Cl				0.49 ± 0.045	298	DF-EPR	Orkin and Khamaganov[5]	298–460
				0.72 ± 0.051	318			
				0.89 ± 0.064	330			
				1.32 ± 0.096	370			
	$0.81^{+0.15}_{-0.12}$		1516 ± 53	3.00 ± 0.22	460			
CHF_2Br				1.10 ± 0.09	298	DF-EPR	Orkin and Khamaganov[6]	298–460
				1.32 ± 0.09	314			
				1.64 ± 0.12	329			
				2.07 ± 0.15	350			
				2.62 ± 0.19	370			
				4.03 ± 0.28	410			
	$0.93^{+0.10}_{-0.09}$		1326 ± 33	5.80 ± 0.5	460			
$CHCl_3$				11.2 ± 1.0	295	LP-LIF	Taylor *et al.*[2]	295–775
				14.2 ± 2.7	327			
				17.1 ± 2.0	360			
				20.4 ± 1.2	390			
				24.2 ± 1.3	429			
				28.9 ± 4.5	452			
				29.8 ± 1.8	456			
				32.6 ± 1.8	480			
				44.0 ± 3.1	540			
				47.9 ± 3.7	600			
				65.6 ± 6.1	670			
				68.1 ± 5.0	700			
				70.2 ± 4.3	730			
	4.65×10^{-5}	1.52	261 ± 42	84.7 ± 5.0	775			
CF_4				< 0.0002	c	d	Ravishankara *et al.*[7]	
CF_3Br				< 0.04	298	DF-EPR	Orkin and Khamaganov[6]	298–460
				< 0.04	460			
CH_3CH_2Cl				43 ± 5	295	PR-RA	Markert and Nielsen[8]	295–360
				66 ± 4	307			
				83 ± 8	315			
				82 ± 16	333			
	24 ± 4		1083 ± 361	95 ± 13	360			

Table 65. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with haloalkanes – Continued

Haloalkane	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	n	B (K)	$10^{14} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
CH_3CH_2Br				23.4 ± 0.8	300	RR [relative to k(ethane) = 2.64×10^{-13}]^a	Donaghy *et al.*[9]	
CH_3CHCl_2				28.2 ± 1.4	294	LP-LIF	Jiang *et al.*[10]	294–800
				30.9 ± 2.0	321			
				35.8 ± 1.9	338			
				39.2 ± 0.6	362			
				46.5 ± 1.9	401			
				54.2 ± 1.2	441			
				64.5 ± 2.1	482			
				75.8 ± 2.2	521			
				89.1 ± 3.8	560			
				97.8 ± 2.7	602			
				114 ± 4.4	640			
				122 ± 9.4	680			
				134 ± 12.1	719			
				162 ± 18.0	760			
	2.02×10^{-8}	2.67	−378 ± 18	188 ± 7.6	800			
CH_3CCl_3				1.1 ± 0.1	298	LP-LIF	Jiang *et al.*[11]	298–761
				2.9 ± 0.6	350			
				5.0 ± 1.0	400			
				9.4 ± 0.6	457			
				10.9 ± 2.9	460			
				12.2 ± 1.2	495			
				12.7 ± 0.9	513			
				18.5 ± 1.3	527			
				20.2 ± 1.0	535			
				21.8 ± 2.8	560			
				23.5 ± 3.8	601			
				33.1 ± 8.1	642			
				36.8 ± 3.6	671			
				54.5 ± 2.0	720			
	2.78×10^{-6}	2.08	1068 ± 108	72.6 ± 3.9	761			
CH_2FCF_3				0.50 ± 0.044	298	DF-EPR	Orkin and Khamaganov[5]	298–460
				0.83 ± 0.066	330			
				1.14 ± 0.08	360			
				1.42 ± 0.11	370			
	$1.03^{+0.18}_{-0.15}$		1588 ± 52	3.31 ± 0.24	460			

Table 65. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with haloalkanes — Continued

Haloalkane	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	n	B (K)	$10^{14} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
CH_2BrCF_3				1.08 ± 0.08	280	DF-LIF	Nelson *et al.*[12]	280–353
				1.45 ± 0.13	294			
				1.99 ± 0.07	318			
				2.35 ± 0.15	328			
	1.39 ± 0.6		1350 ± 195	3.01 ± 0.10	353			
				2.05 ± 0.16	298	DF-EPR	Orkin and Khamaganov[6]	298–460
				3.06 ± 0.21	338			
				4.81 ± 0.34	389			
	$0.85^{+0.09}_{-0.08}$		1113 ± 35	7.65 ± 0.55	460			
CH_2ClCCl_3				2.0 ± 0.4^e	295	LP-LIF	Jiang *et al.*[13]	295–882
				3.1 ± 0.5^e	326			
				3.9 ± 0.8^e	335			
				5.8 ± 1.3^e	362			
				9.2 ± 1.4^e	403			
				15.3 ± 3.6^3	452			
				16.6 ± 1.7^e	460			
				24.2 ± 3.2	480			
				26.2 ± 7.2	501			
				39.9 ± 6.5	544			
				57.8 ± 11	575			
				60.4 ± 4.8	579			
				66.1 ± 3.9	623			
				85.0 ± 6.6	663			
				118 ± 34	696			
				84.6 ± 18	701			
				119 ± 33	737			
				153 ± 20	777			
				148 ± 12	783			
				171 ± 15	832			
	3.38×10^{-3}	1.21	1553 ± 92	215 ± 30	882			
$CHCl_2CHCl_2$				10.9 ± 2.7	295	LP-LIF	Jiang *et al.*[13]	295–701
				13.8 ± 2.0	316			
				15.4 ± 1.9	326			
				19.8 ± 2.6	340			
				27.1 ± 1.0	382			
				30.6 ± 2.1	402			
				32.0 ± 2.1	422			
				37.4 ± 3.4	442			
				52.2 ± 5.7	520			
				63.6 ± 6.3	562			
				80.6 ± 7.8	640			
	0.776	0.22	915 ± 62	89.6 ± 8.1	701			

Table 65. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with haloalkanes – Continued

Haloalkane	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	n	B (K)	$10^{14} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
$CHFClCF_2Cl$				1.23 ± 0.10	298	DF-EPR	Orkin and Khamaganov[5]	298–460
				1.67 ± 0.12	313			
				1.81 ± 0.13	330			
				2.19 ± 0.16	344			
				2.74 ± 0.22	360			
				2.68 ± 0.19	370			
	$0.92^{+0.25}_{-0.20}$		1281 ± 85	5.63 ± 0.41	460			
$CHFBrCF_3$				1.75 ± 0.17	298	DF-EPR	Orkin and Khamaganov[6]	298–460
				2.02 ± 0.14	314			
				2.35 ± 0.16	330			
				2.96 ± 0.27	350			
				3.61 ± 0.43	370			
				4.60 ± 0.32	410			
	$0.72^{+0.07}_{-0.06}$		1111 ± 32	6.22 ± 0.48	460			
$CHCl_2CF_2Cl$				5.30 ± 0.41	298	DF-EPR	Orkin and Khamaganov[5]	298–460
				6.75 ± 0.48	330			
				9.38 ± 0.72	370			
	$1.13^{+0.21}_{-0.16}$		918 ± 52	15.90 ± 1.10	460			
$CHClBrCF_3$				4.50 ± 0.40	298	DF-EPR	Orkin and Khamaganov[6]	298–460
				5.82 ± 0.41	317			
				7.15 ± 0.5	341			
				8.64 ± 0.6	370			
				9.53 ± 0.67	389			
				11.10 ± 0.78	410			
	$1.28^{+0.15}_{-0.12}$		995 ± 38	14.90 ± 1.4	460			
CF_2BrCF_2Br				<0.04	298	DF-EPR	Orkin and Khamaganov[6]	298–460
				<0.04	460			
$CH_3CH_2CH_2Cl$				96 ± 4	295	PR-RA	Markert and Nielsen[8]	295–353
				68 ± 7	295			
				147 ± 6	317			
				176 ± 2	328			
				116 ± 7	331			
				180 ± 20	333			
	100 ± 30		1443 ± 482	160 ± 3	353			
				111 ± 3	305	RR [relative to k(2-methylpropane) = 2.39×10^{-12}][a]	Donaghy *et al.*[9]	

Table 65. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with haloalkanes – Continued

Haloalkane	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	n	B (K)	$10^{14} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
				87.1 ± 2.5	308	RR [relative to k(n-pentane) = 4.11×10^{-12}]^a	Donaghy *et al.*[9]	
				112 ± 10	303	RR [relative to k(cyclohexane) = 7.60×10^{-12}]^a	Donaghy *et al.*[9]	
$CH_3CH_2CH_2Br$				118 ± 7	300	RR [relative to k(cyclohexane) = 7.54×10^{-12}]^a	Donaghy *et al.*[9]	
$CH_3CHClCH_3$				43 ± 4	295	PR-RA	Markert and Nielsen[8]	295–353
				104 ± 7	313			
				95 ± 3	333			
	50 ± 6		1323 ± 842	101 ± 4	353			
				92.0 ± 4.6	303	RR [relative to k(cyclohexane) = 7.60×10^{-12}]^a	Donaghy *et al.*[9]	
$CH_3CHBrCH_3$				87.6 ± 11.3	298	RR [relative to k(cyclohexane) = 7.49×10^{-12}]^a	Donaghy *et al.*[9]	
$CH_2ClCH_2CH_2Cl$				77.9 ± 3.1	305	RR [relative to k(cyclohexane) = 7.64×10^{-12}]^a	Donaghy *et al.*[9]	
CF_3CHFCF_3				0.144 ± 0.012	294	DF-LIF	Nelson *et al.*[12]	294–369
				0.165 ± 0.028	295			
				0.166 ± 0.06	297			
				0.241 ± 0.013	321			
				0.253 ± 0.011	323			
				0.323 ± 0.024	343			
				0.332 ± 0.020	343			
				0.325 ± 0.063	346			
				0.493 ± 0.061	368			
	3.7 ± 1.1		1615 ± 190	0.472 ± 0.033	369			

Table 65. Rate constants *k* and temperature-dependent parameters for the gas-phase reactions of the OH radical with haloalkanes — Continued

Haloalkane	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	n	B (K)	$10^{14} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
$CH_3CH_2CH_2CH_2Cl$				169 ± 9	295	PR-RA	Markert and Nielsen[8]	295–353
				210 ± 10	295			
				114 ± 6	295			
				128 ± 5	295			
				231 ± 7	320			
				234 ± 9	331			
	28 ± 9		842 ± 482	214 ± 6	353			
$CH_3CH_2CH_2CH_2Br$				246 ± 8	299	RR [relative to k(cyclohexane) = 7.51×10^{-12}]^a	Donaghy *et al.*[9]	
$(CH_3)_3CCl$				41.2 ± 4.5	298	RR [relative to k(cyclohexane) = 7.49×10^{-12}]^a	Donaghy *et al.*[9]	
$CHF_2CF_2CF_2CHF_2$				0.126 ± 0.050	245	FP-RF	Zhang *et al.*[14]	245–419
				0.322 ± 0.033	266			
				0.279 ± 0.024	266			
				0.418 ± 0.030	296			
				0.780 ± 0.120	335			
				1.12 ± 0.17	380			
	0.780 ± 0.340		1510 ± 260	2.53 ± 0.26	419			
$CH_3CH_2CH_2CH_2CH_2Cl$				336 ± 7	295	PR-RA	Markert and Nielsen[8]	295–353
				275 ± 8	295			
				450 ± 20	319			
				390 ± 30	331			
	17 ± 3		481 ± 361	380 ± 20	353			
$CH_3CH_2CH_2CH_2CH_2Br$				396 ± 14	304	RR [relative to k(cyclohexane) = 7.62×10^{-12}]^a	Donaghy *et al.*[9]	
$CF_3CHFCHFCF_2CF_3$				0.156 ± 0.039	250	FP-RF	Zhang *et al.*[14]	250–400
				0.194 ± 0.029	270			
				0.267 ± 0.036	270			
				0.387 ± 0.038	295			
				0.630 ± 0.097	330			
				0.887 ± 0.103	365			
	0.421 ± 0.128		1400 ± 180	1.28 ± 0.23	400			

Table 65. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with haloalkanes — Continued

Haloalkane	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	n	B (K)	$10^{14} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
$CH_3CH_2CH_2CH_2CH_2CH_2Cl$				360 ± 30	295	PR-RA	Markert and Nielsen[8]	295–353
				400 ± 30	295			
				470 ± 10	319			
				510 ± 50	333			
				470 ± 40	333			
				570 ± 40	339			
				500 ± 40	339			
				380 ± 30	339			
				520 ± 10	343			
	16 ± 2		361 ± 241	410 ± 20	353			
$CH_3CH_2CH_2CH_2CH_2CH_2Br$				585 ± 21	306	RR [relative to k(cyclohexane) = 7.67×10^{-12}][a]	Donaghy *et al.*[9]	

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[a] From present (Section 3.2) and previous[15] recommendations.

[b] Combined with the previous measurements of Taylor *et al.*[16]

[c] Not reported, expected to be room temperature.

[d] Not reported, expected to be LP-LIF.

[e] Corrected for the presence of $CHCl=CCl_2$ impurity.[13]

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7.2.3. Haloalkenes

The rate constants reported for the reactions of the OH radicals with haloalkenes since Table 39 was finalized are given in Table 66.

CHCl = CCl₂. The absolute rate constants of Jiang *et al.*,[1] measured at 740 Torr total pressure of helium diluent, are given in Table 66. At room temperature, the rate constant of Jiang *et al.*[1] is 65–70% higher than the recommendation of Atkinson,[3] although the discrepancy decreases with increasing temperature. While this effect could be due to the rate constant being pressure-dependent at total pressures up to several hundred Torr, the temperature dependence of the rate constants measured by Jiang *et al.*,[1] of $B = -1000$ K, appears anomalously high. In the absence of further confirmation of these data of Jiang *et al.*,[1] the previous recommendation[3] is unchanged.

CF₃CF = CF₂. McIlroy and Tully[2] have measured rate constants for the reaction of the OH radical with $CF_3CF{=}CF_2$ over the temperature range 293–831 K. At 293 K, the rate constant is independent of total pressure of helium over the range 75–750 Torr. The reaction is assumed to proceed by OH radical addition at temperatures $\leq$500 K.[2] Non-exponential decays of the OH radical concentration were observed[2] over the temperature range 528–641 K, indicating either thermal decomposition of the HOC_3F_6 adduct back to reactants or generation of an F atom which reacted with the H_2O present to reform OH radicals. At temperatures >736 K, the measured rate constant exceeds that for the OH radical addition pathway extrapolated from the 293–489 K temperature range, indicating a direct reaction process.[2]

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7.2.4. Alkynes

Lai *et al.*[1] have measured the forward and reverse rate constants for the reaction of the OH radical with acetylene over the temperature range 627–713 K at 414–864 Torr total pressure of He.

$$\mathrm{OH} + \mathrm{C_2H_2} \overset{M}{\rightleftharpoons} \mathrm{C_2H_2OH} \qquad (a,-a)$$

Under these temperature and pressure conditions, the rate constants k_a and k_{-a} are in the fall-off regime between second- and third-order kinetics and first- and second-order kinetics, respectively.[2] For 760 Torr of Ar diluent, Atkinson[2] used the Troe fall-off model to calculate rate constants k_a for the addition of the OH radical to C_2H_2 (H-atom abstraction is of no importance at 627–713 K) of $\sim 8 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 710 K and $\sim 1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 625 K. The rate constants k_a obtained by Lai *et al.*[1] are in accord with these calculations,[2] with $k_a = (1.1 \pm 0.2) \times 10^{-13}\, e^{(1460 \pm 500)/T}$ cm^3 molecule^{-1} s^{-1} for the restricted set of pressure and temperature conditions employed.

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Table 66. Rate constants k and temperature-dependent parameters, $k = A\ e^{-B/T}$, for the gas-phase reactions of the OH radical with haloalkenes at, or close to, the high pressure limit

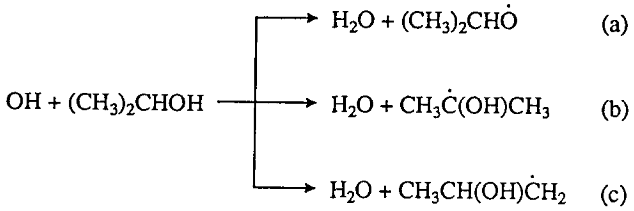
Haloalkene	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1}	at T (K)	Technique	Reference	Temperature range covered (K)
$CHCl=CCl_2$			3.97 ± 0.45	295	LP-LIF	Jiang *et al.*[1]	295–460
			3.08 ± 0.23	326			
			2.84 ± 0.29	335			
			2.17 ± 0.21	362			
			1.58 ± 0.16	403			
			1.23 ± 0.12	452			
			1.18 ± 0.11	460			
Hexafluoropropene[a] ($CF_3CF=CF_2$)			2.32 ± 0.10	293	LP-LIF	McIlroy and Tully[2]	293–831
			2.10 ± 0.09	326			
			1.87 ± 0.08	378			
			1.74 ± 0.09	438			
	0.99 ± 0.064	−245 ± 23 (293–489 K)	1.66 ± 0.08	489			
			1.16 ± 0.07	656			
			1.32 ± 0.08	713			
			1.56 ± 0.10	736			
			1.61 ± 0.10	753			
			1.72 ± 0.11	794			
			1.74 ± 0.11	831			

[a] All rate constants at 750 Torr total pressure of helium diluent.

7.2.5. Oxygen-Containing Organic Compounds

The rate constants reported since Table 41 was finalized are given in Table 67.

2-Propanol. The absolute rate constants determined by Dunlop and Tully[2] for $(CH_3)_2CHOH$, $(CH_3)_2CHOD$, $(CH_3)_2CDOH$, $(CD_3)_2CHOH$ and $(CD_3)_2CDOD$ are given in Table 67. For the reaction of ^{16}OH radicals with $(CH_3)_2CHOH$, non-exponential decays of the ^{16}OH radical were observed over the temperature range 504–600 K.[2] Above 600 K, exponential decays of the ^{16}OH radical were observed, with the rate constants being significantly lower than expected from extrapolation of the lower temperature data.[2] At 548 and 587 K, rate constants were obtained from the exponential decays of ^{18}OH radicals. These observations are expected[2,10] from the reaction sequence



with the $CH_3CH(OH)\dot{C}H_2$ radical formed in channel (c) being identical to that formed from OH radical addition to propene, and undergoing thermal decomposition at temperatures $\gtrsim 600$ K.[9]

$$CH_3CH(OH)\dot{C}H_2 \rightarrow CH_3CH{=}CH_2 + OH$$

Thus at temperatures $\lesssim 500$ K the measured rate constant for reaction with ^{16}OH radicals is $k_a + k_b + k_c$, while for temperatures > 600 K the measured rate constant for ^{16}OH radical reaction is $k_a + k_b$ (the ^{18}OH radical reaction leads to a measured rate constant for $k_a + k_b + k_c$ since ^{16}OH radicals and not ^{18}OH radicals are regenerated). Because of expected rapid exchange of the H and D atoms on the –OH or –OD groups, the rate constants for $(CH_3)_2CHOD$ and $(CH_3)_2CHOH$ are identical (note that H or D atom abstraction from the –OH or –OD groups is also of minor importance) [Table 67]. From the rate constants obtained for $(CH_3)_2CHOH$ and the partially or fully deuterated species, Dunlop and Tully[2] obtained a rate constant ratio of $k_c/(k_a + k_b + k_c)$ for $(CH_3)_2CHOH$ of

$$k_c/(k_a + k_b + k_c) = 0.698\ e^{-521/T}$$

over the temperature range 293–502 K.

The rate constants of Dunlop and Tully[2] for $(CH_3)_2CHOH$ are lower than those of Wallington and Kurylo[11] by ~10–20% over the temperature range common to both studies (293–440 K). A unit-weighted least squares analysis of the ^{16}OH and ^{18}OH radical reaction rate constants of Dunlop and Tully[2], using the expression $k = CT^2\ e^{-D/T}$, leads to the recommendation of

$$k(\text{2-propanol}) = (4.06 \pm 0.11) \times 10^{-18}\ T^2\ e^{(788 \pm 11)/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 293–587 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{2-propanol}) = 5.07 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \text{ at } 298\ \text{K},$$

with an estimated overall uncertainty at 298 K of ±20%. This recommendation supersedes that in Sec. 3.6 of

$$k(\text{2-propanol}) = 7.32 \times 10^{-18}\ T^2\ e^{620/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 240–440 K, with a 298 K rate constant of 5.21×10^{-12} cm^3 molecule^{-1} s^{-1}.

2,2-Dimethylpropan-1-ol (Neopentyl alcohol). The absolute rate constants determined by Tully[3] for the reactions of ^{16}OH and ^{18}OH radicals with $(CH_3)_3CCH_2OH$ are given in Table 67. For the ^{18}OH radical reaction, exponential ^{18}OH radical decays were observed at all temperatures,[3] while for the ^{16}OH radical reactions non-exponential ^{16}OH radical decays were observed[3] over the temperature range 437–572 K (the rate constants obtained from the initial portions of these non-exponential decays are given in Table 67). While non-exponential decays of ^{16}OH radicals were observed over a fairly limited temperature range,[3] indicating some (slow) reformation of ^{16}OH radicals,[3] the data obtained show that the previously observed reaction scheme of

$$OH + \text{alcohol} \rightarrow H_2O + OH + \text{alkene}$$

at temperatures $\gtrsim 500$ K[10] does not occur to any significant extent for neopentyl alcohol. This lack of significant regeneration of OH radicals from the OH radical reaction with neopentyl alcohol is expected, since neopentyl alcohol does not contain any abstractable β-H atoms (see above discussion for 2-pentanol).

Di-isopropyl ether. The absolute and relative rate constants of McLaughlin *et al.*[4] and Wallington *et al.*[5,6] are given in Table 67. The room temperature absolute and relative rate constants of McLoughlin *et al.*[4] and Wallington *et al.*[5,6] are in excellent agreement with those of Nelson *et al.*[12] given in Table 41 of Sec. 3.6. Over the temperature range employed by Wallington *et al.*,[5] the rate constants were well fit by an Arrhenius expression and no evidence for curvature in the Arrhenius plot was observed.[5] Accordingly, a unit-weighted least-squares analysis of the absolute rate constants of Nelson *et al.*[12] and Wallington *et al.*[5] and the relative rate constants of Nelson *et al.*,[12] McLoughlin *et al.*,[4] and Wallington *et al.*,[5,6] using the Arrhenius expression $k = A\ e^{-B/T}$, yields the recommendation of

$$k(\text{di-isopropyl ether}) = (2.20^{+1.08}_{-0.73}) \times 10^{-12}\ e^{(457 \pm 120)/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 240–400 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{di-isopropyl ether}) = 1.02 \times 10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \text{ at } 298\ \text{K},$$

with an estimated overall uncertainty at 298 K of ±25%.

Ethyl tert-butyl ether. The relative rate constants of Wallington *et al.*[5,6] given in Table 67 are in excellent agreement with the recommended rate constant from Sec. 3.6 of

$$k(\text{ethyl } t\text{-butyl ether}) = 8.84 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \text{ at } 298\ \text{K}.$$

This recommendation is hence unchanged, although the estimated overall uncertainties are reduced to ±30%.

Methyl t-amyl ether. The absolute and relative rate constants of Wallington *et al.*[6] are given in Table 67. These room temperature rate constants[6] are ~30% lower than the previously reported absolute room temperature rate constant of Wallington *et al.*,[13] and reanalysis[6] of the ether sample used by Wallington *et al.*[13] showed the presence of a reactive alkene impurity. An Arrhenius plot of the absolute rate constants of Wallington *et al.*[6] showed no evidence of curvature.[6] Hence, a unit-weighted least-squares of the absolute and relative rate constants of Wallington *et al.*,[6] using the Arrhenius expression $k = A\ e^{-B/T}$, yields the recommendation of

$$k(\text{methyl } t\text{-amyl ether}) = (6.49^{+1.45}_{-1.18}) \times 10^{-12}\ e^{(48 \pm 61)/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 240–400 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{methyl } t\text{-amyl ether}) = 5.52 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \text{ at } 298\ \text{K},$$

with an estimated overall uncertainty at 298 K of ±35%.

n-Propyl acetate and n-butyl acetate. The relative rate constants of Williams *et al.*[8] are given in Table 67. For *n*-propyl acetate, the rate constants of Williams *et al.*[8] are in good agreement with the previous recommendation of Atkinson[9] of

$$k(n\text{-propyl acetate}) = 3.4 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \text{ at } 298\ \text{K},$$

which is therefore unchanged.

For *n*-butyl acetate, the rate constants of Williams *et al.*[8] are ~35% higher than the previous absolute rate constants of Hartmann *et al.*[14] and Wallington *et al.*[15] A unit-weighted average of the absolute and relative room temperature rate constants of Hartmann *et al.*,[14] Wallington *et al.*[15] and Williams *et al.*[8] leads to the recommendation of

$$k(n\text{-butyl acetate}) = 4.9 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \text{ at } 298\ \text{K},$$

with an estimated overall uncertainty of ±50%. This recommendation supersedes that of Atkinson[9] of

$$k(n\text{-butyl acetate}) = 4.2 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \text{ at } 298\ \text{K}.$$

1-Acetoxy-2-ethoxyethane. The relative rate constants of Williams *et al.*[8] given in Table 67 are in good agreement with the room temperature rate constant of Hartmann *et al.*,[14] of $(1.3 \pm 0.2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K. Accordingly, a unit-weighted average of the room temperature rate constants of Hartmann *et al.*[14] and Williams *et al.*[8] leads to the recommendation of

$$k(\text{1-acetoxy-2-ethoxyethane}) = 1.14 \times 10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \text{ at } 298\ \text{K},$$

with an estimated overall uncertainty of ±40%.

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Table 67. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with oxygen-containing organic compounds

Oxygenate	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	n	B (K)	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
Aldehydes								
Formyl fluoride [HC(O)F]				<0.0041	296 ± 2	RR [relative to $k(CH_3F) = 1.62 \times 10^{-14}$][a]	Wallington and Hurley[1]	
Alcohols								
2-Propanol [$(CH_3)_2CHOH$]				5.10 ± 0.21	293	LP-LIF	Dunlop and Tully[2]	293–745
				4.89 ± 0.20	326			
				4.68 ± 0.20	378			
				4.73 ± 0.22	438			
				4.86 ± 0.24	502			
				5.16 ± 0.27[b]	548			
	1.044×10^{-5}	1.86	736 (293–587 K)	5.37 ± 0.47[b]	587			
				3.93 ± 0.29	624			
				3.96 ± 0.27	643			
				4.06 ± 0.26	653			
				4.42 ± 0.38	745			
2-Propanol-d_1 [$(CH_3)_2CHOD$]				5.13 ± 0.22	293	LP-LIF	Dunlop and Tully[2]	293–502
				4.88 ± 0.20	326			
				4.68 ± 0.20	378			
				4.82 ± 0.23	438			
				4.86 ± 0.25	502			
2-Propanol-d_1 [$(CH_3)_2CDOH$]				3.23 ± 0.13	293	LP-LIF	Dunlop and Tully[2]	293–502
				3.13 ± 0.13	326			
				3.21 ± 0.14	378			
				3.38 ± 0.16	438			
				3.58 ± 0.19	502			
2-Propanol-d_6 [$(CD_3)_2CHOH$]				4.68 ± 0.20	293	LP-LIF	Dunlop and Tully[2]	293–502
				4.37 ± 0.18	326			
				4.12 ± 0.17	378			
				4.04 ± 0.18	438			
				4.13 ± 0.20	502			
2-Propanol-d_8 [$(CD_3)_2CDOD$]				2.71 ± 0.11	293	LP-LIF	Dunlop and Tully[2]	293–587
				2.60 ± 0.11	326			
				2.64 ± 0.11	378			
				2.76 ± 0.13	438			

Table 67. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with oxygen-containing organic compounds – Continued

Oxygenate	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1}) n	B (K)	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
			2.89 ± 0.14	502			
			3.30 ± 0.21^b	587			
2,2-Dimethylpropan-1-ol [$(CH_3)_3CCH_2OH$]			5.53 ± 0.24	293	LP-LIF	Tully[3]	293–764
			5.41 ± 0.24	327			
			5.41 ± 0.25	377.5			
			5.66 ± 0.35^c	437.5			
			5.62 ± 0.27^b	438.5			
			5.78 ± 0.37^c	456			
			5.73 ± 0.27^b	456			
			6.11 ± 0.38^c	478			
			5.90 ± 0.30^b	489			
			6.08 ± 0.38^c	501			
			6.25 ± 0.40^c	521.5			
			6.42 ± 0.40^c	546			
			6.52 ± 0.34^b	547			
			6.89 ± 0.37^c	572			
			7.42 ± 0.41	596			
			6.97 ± 0.39^b	596			
			7.47 ± 0.42	601			
			7.83 ± 0.48	619.5			
			8.82 ± 0.58	645			
			9.08 ± 0.57	673			
			10.4 ± 0.67	715.5			
			11.6 ± 0.75	763.5			
Ethers							
Di-isopropyl ether [$(CH_3)_2CHOCH(CH_3)_2$]			10.6 ± 0.5	300 ± 3	RR [relative to k(diethyl ether) = 1.31 × 10^{-11}]^a	McLoughlin *et al.*[4]	
			12.9 ± 1.4	240	FP-RF	Wallington *et al.*[5]	240–400
			12.4 ± 1.7	270			
			10.6 ± 0.9	296			
			10.8 ± 0.9	296			
			8.67 ± 1.16	330			
			6.51 ± 1.02	365			
	$2.2^{+1.4}_{-0.8}$	−445 ± 145	6.98 ± 1.38	400			
			9.81 ± 0.23	295 ± 2	RR [relative to k(cyclohexane) = 7.43 × 10^{-12}]^a	Wallington *et al.*[5]	

Table 67. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with oxygen-containing organic compounds – Continued

Oxygenate	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1}) n	B (K)	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
			10.7 ± 0.6	295 ± 2	RR [relative to k(methyl t-amyl ether) = 5.52 x 10^{-12}]^a	Wallington *et al.*[5,6]	
Ethyl t-butyl ether [$CH_3CH_2OC(CH_3)_3$]			8.67 ± 0.43	295 ± 2	RR [relative to k(methyl t-amyl ether) = 5.52 x 10^{-12}]^a	Wallington *et al.*[6]	
			8.62 ± 0.30	295 ± 2	RR [relative to k(cyclohexane) = 7.43 × 10^{-12}]^a	Wallington *et al.*[5]	
Methyl t-amyl ether [$CH_3OC(CH_3)_2CH_2CH_3$]			5.12 ± 0.48	240	FP-RF	Wallington *et al.*[6]	240–400
			5.76 ± 0.43	270			
			5.68 ± 0.36	296			
			5.66 ± 0.38	330			
			5.45 ± 0.48	365			
	6.32 ± 0.72	40 ± 70	5.85 ± 0.62	400			
			5.33 ± 0.24	295 ± 2	RR [relative to k(cyclohexane) = 7.43 × 10^{-12}]^a	Wallington *et al.*[6]	
$CH_3OCH_2CH_2Cl$			4.69 ± 0.28	300 ± 3	RR [relative to k(diethyl ether) = 1.31 × 10^{-11}]^a	McLoughlin *et al.*[4]	
$CH_3OCH_2CHCl_2$			2.27 ± 0.11	300 ± 3	RR [relative to k(diethyl ether) = 1.31 × 10^{-11}]^a	McLoughlin *et al.*[4]	
$CH_3OCH_2CH_2Br$			6.64 ± 0.23	300 ± 3	RR [relative to k(diethyl ether) = 1.31 × 10^{-11}]^a	McLoughlin *et al.*[4]	
$CH_3CHFOCF_2CH_2Cl$			<0.3	300 ± 3	RR [relative to k(diethyl ether) = 1.31 × 10^{-11}]^a	McLoughlin *et al.*[4]	
$CHF_2OCHClCF_3$			<0.3	300 ± 3	RR [relative to k(diethyl ether) = 1.31 × 10^{-11}]^a	McLoughlin *et al.*[4]	

Table 67. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with oxygen-containing organic compounds – Continued

Oxygenate	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	n	B (K)	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
CHF_2OCF_2CHFCl				< 0.3	300 ± 3	RR [relative to k(diethyl ether) = 1.31×10^{-11}]^a	McLoughlin *et al.*[4]	
CH_3OCF_3				0.0214 ± 0.0015	296	FP-RF	Zhang *et al.*[7]	
CHF_2OCF_3				0.00338 ± 0.00041 0.00356 ± 0.00062	296 296	FP-RF	Zhang *et al.*[7]	
CHF_2OCHF_2				0.0253 ± 0.0024 0.0241 ± 0.0016	296 296	FP-RF	Zhang *et al.*[7]	
$CH_3OCH_2CF_3$				0.624 ± 0.067	296	FP-RF	Zhang *et al.*[7]	
$CHF_2OCH_2CF_3$				0.0125 ± 0.0009 0.0120 ± 0.0016	296 296	FP-RF	Zhang *et al.*[7]	
cyclo-CF_2CHFCF_2O-				0.00251 ± 0.00035 0.00240 ± 0.00030	296 296	FP-RF	Zhang *et al.*[7]	
cyclo-$(CF_2)_3O$-				< 0.0002	296	FP-RF	Zhang *et al.*[7]	
Esters								
n-Propyl acetate [$CH_3C(O)OCH_2CH_2CH_3$]				3.45 ± 0.88	297 ± 2	RR [relative to k(propene) = 2.65×10^{-11}]^a	Williams *et al.*[8]	
				3.56 ± 0.85	297 ± 2	RR [relative to k(*n*-butane) = 2.53×10^{-12}]^a	Williams *et al.*[8]	
n-Butyl acetate [$CH_3C(O)OCH_2CH_2CH_2CH_3$]				5.75 ± 0.96	297 ± 2	RR [relative to k(propene) = 2.65×10^{-11}]^a	Williams *et al.*[8]	
				5.53 ± 0.86	297 ± 2	RR [relative to k(*n*-butane) = 2.53×10^{-12}]^a	Williams *et al.*[8]	
n-Pentyl acetate [$CH_3C(O)OCH_2CH_2CH_2CH_2CH_3$]				7.58 ± 0.48	297 ± 2	RR [relative to k(propene) = 2.65×10^{-11}]^a	Williams *et al.*[8]	

Table 67. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with oxygen-containing organic compounds – Continued

Oxygenate	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1}) n	B (K)	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
			7.51 ± 0.56	297 ± 2	RR [relative to k(n-butane) = 2.53×10^{-12}][a]	Williams *et al.*[8]	
1-Acetoxy-2-ethoxyethane [$CH_3C(O)OCH_2CH_2OCH_2CH_3$]			10.7 ± 1.4	297 ± 2	RR [relative to k(propene) = 2.65×10^{-11}][a]	Williams *et al.*[8]	
			10.6 ± 0.7	297 ± 2	RR [relative to k(n-butane) = 2.53×10^{-12}][a]	Williams *et al.*[8]	
2-Ethoxyethyl isobutyrate [$(CH_3)_2CHC(O)OCH_2CH_2OCH_2CH_3$]			13.6 ± 2.4	297 ± 2	RR [relative to k(propene) = 2.65×10^{-11}][a]	Williams *et al.*[8]	
			13.0 ± 1.1	297 ± 2	RR [relative to k(n-butane) = 2.53×10^{-12}][a]	Williams *et al.*[8]	
			13.7 ± 1.7	297 ± 2	RR [relative to k(*trans*-2-butene) = 6.44×10^{-11}][a]	Williams *et al.*[8]	
2-Ethoxyethyl methacrylate [$CH_2=C(CH_3)C(O)OCH_2CH_2OCH_2CH_3$]			27.4 ± 2.1	297 ± 2	RR [relative to k(propene) = 2.65×10^{-11}][a]	Williams *et al.*[8]	
			28.2 ± 3.5	297 ± 2	RR [relative to k(*trans*-2-butene) = 6.44×10^{-11}][a]	Williams *et al.*[8]	
4-Penten-1-yl acetate [$CH_3C(O)OCH_2CH_2CH_2CH=CH_2$]			43.7 ± 3.9	297 ± 2	RR [relative to k(propene) = 2.65×10^{-11}][a]	Williams *et al.*[8]	
			43.1 ± 2.9	297 ± 2	RR [relative to k(*trans*-2-butene) = 6.44×10^{-11}][a]	Williams *et al.*[8]	
Ethyl 3-ethoxy-2-propenoate [$CH_3CH_2OCH=CHC(O)OCH_2CH_3$]			33.2 ± 1.3	297 ± 2	RR [relative to k(*trans*-2-butene) = 6.44×10^{-11}][a]	Williams *et al.*[8]	

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[a] From present or previous[9] recommendations.

[b] Reaction of ^{18}OH radical.

[c] Non-exponential ^{16}OH radical decays observed. Rate constant obtained from the initial portion of the decay curve.

7.2.6. Aromatic Compounds

The rate constants reported for the gas-phase reactions of OH radicals with aromatic compounds since Table 47 was finalized are given in Table 68.

Toluene. The rate constant obtained by Finlayson-Pitts *et al.*,[1] using a relative rate method and ozone as a dark source of OH radicals,[1] of $(6.00 \pm 0.29) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K (Table 68), is in excellent agreement with the recommendation of Atkinson[3] of

$$k(\text{toluene}) = 5.96 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K},$$

which is therefore unchanged.

Hexafluorobenzene. The absolute rate constants determined by McIlroy and Tully[2] over the temperature 244–830 K are given in Table 68. No evidence for OH radical reformation was observed[2] at elevated temperatures, consistent with either a larger C–OH bond dissociation energy in the HO–C_6F_6 adduct than in the hydroxycyclohexadienyl radical[3] or with an exothermic reaction pathway to products other than the reactants.[2]

The room temperature rate constant of McIlroy and Tully[2] is in reasonable or good agreement, respectively, with the previous absolute rate constants of Ravishankara *et al.*[4] and Wallington *et al.*[5] The rate constants of Wallington *et al.*[5] over the temperature range 234–438 K are in reasonable agreement with those of McIlroy and Tully,[2] although the data of Wallington *et al.*[5] lead to a significantly lower Arrhenius activation energy B of $B = 610 \pm 80$ K.

A unit-weighted least-squares analysis of the absolute rate constants of Ravishankara *et al.*,[4] Wallington *et al.*[5] and McIlroy and Tully,[2] using the Arrhenius expression $k = A\ e^{-B/T}$, leads to the recommendation of

$$k(\text{hexafluorobenzene}) = (3.88^{+0.98}_{-0.79}) \times 10^{-12}\ e^{-(931 \pm 78)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 234–830 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{hexafluorobenzene}) = 1.71 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K},$$

with an estimated overall uncertainty at 298 K of ±30%.

This recommendation supersedes that of Atkinson[3] of

$$k(\text{hexafluorobenzene}) = 1.46 \times 10^{-12}\ e^{-638/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 234–438 K, with a 298 K rate constant of 1.72×10^{-13} cm^3 molecule^{-1} s^{-1}.

References

[1] B. J. Finlayson-Pitts, S. K. Hernandez, and H. N. Berko, J. Phys. Chem. **97**, 1172 (1993).
[2] A. McIlroy and F. P. Tully, J. Phys. Chem. **97**, 610 (1993).
[3] R. Atkinson, J. Phys. Chem. Ref. Data Monograph 1, 1 (1989).
[4] 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).
[5] T. J. Wallington, D. M. Neuman, and M. J. Kurylo, Int. J. Chem. Kinet. **19**, 725 (1987).

7.2.7. Organic Radicals

Rate constants reported for the gas-phase reactions of the OH radical with organic radicals since Table 49 was finalized are given in Table 69.

CH_3. The absolute room temperature rate constants of Hughes *et al.*[1] and Fagerström *et al.*[2] are given in Table 69. Hughes *et al.*[1] observed no pressure dependence of the rate constant over the total pressure range 7.4–700 Torr of helium diluent, while Fagerström *et al.*[2] observed the rate constant to increase from $(9.6 \pm 0.5) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 64 Torr total pressure of SF_6 to $(1.30 \pm 0.12) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 750 torr total pressure of SF_6. The absolute room temperature rate constants from these two studies[1,2] and those of Anastasi *et al.*[4] and Osner *et al.*[5] exhibit discrepancies of a factor of ~2. The recommendation of Sec. 3.13 of

$$k_\infty(CH_3) = 1.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K},$$

applicable to total pressures of air ≳100 Torr and with an estimated overall uncertainty of a factor of 2, is unchanged.

References

[1] K. J. Hughes, A. R. Pereira, and M. J. Pilling, Ber. Bunsenges. Phys. Chem. **96**, 1352 (1992).
[2] K. Fagerström, A. Lund, G. Mahmoud, J. T. Jodkowski, and E. Ratajczak, Chem. Phys. Lett. **204**, 226 (1993).
[3] K. Fagerström, A. Lund, G. Mahmoud, J. T. Jodkowski, and E. Ratajczak, Chem. Phys. Lett. **208**, 321 (1993).
[4] C. Anastasi, S. Beverton, T. Ellermann, and P. Pagsberg, J. Chem. Soc. Faraday Trans. **87**, 2325 (1991).
[5] H. Osner, N. D. Stothard, R. Humpfer, and H. H. Grotheer, J. Phys. Chem. **96**, 5359 (1992).

Table 68. Rate constants k and temperature-dependent parameters, $k = A\ e^{-B/T}$, for the gas-phase reactions of the OH radical with aromatic compounds

Aromatic	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
Toluene			6.00 ± 0.29	298	RR [relative to k(n-hexane) = 5.61×10^{-12}][a]	Finlayson-Pitts *et al.*[1]	
Hexafluorobenzene (C_6F_6)			0.0790 ± 0.0042	244	LP-LIF	McIlroy and Tully[2]	244–830
			0.109 ± 0.006	260			
			0.136 ± 0.008	275			
			0.152 ± 0.009	294			
			0.215 ± 0.012	327			
			0.300 ± 0.018	377			
			0.413 ± 0.028	420			
			0.532 ± 0.031	467			
			0.703 ± 0.050	529			
			0.838 ± 0.048	586			
			1.05 ± 0.069	637			
			1.30 ± 0.15	709			
	4.78 ± 0.90	1005 ± 116	1.31 ± 0.10	830			

[a] From previous recommendation.[3]

TABLE 69. Rate constants k for the gas-phase reactions of the OH radical with organic radicals at, or close to, the high-pressure limit

Radical	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference
CH_3	76 ± 8	290	LP-RA	Hughes *et al.*[1]
	144 ± 15[a]	298	PR-RA	Fagerström *et al.*[2]
C_2H_5	118 ± 17[b]	298	PR-RA	Fagerström *et al.*[3]

[a] Extrapolated high-pressure limit[2]; see text.
[b] Independent of total pressure of SF_6 diluent over the range 188–750 Torr.

7.3. Kinetics and Mechanisms of the Gas-Phase Reactions of the NO_3 Radical with Organic Compounds

7.3.1. Alkanes

Since Table 50 was finalized, Langer *et al.*[1] have used a discharge flow system with optical absorption detection of NO_3 radicals at 662 nm to obtain a rate constant of $(2.8 \pm 0.3) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 296 ± 2 K for the reaction of the NO_3 radical with *n*-hexane. Due to the expected occurrence of secondary reactions leading to a stoichiometry of ~2 for disappearance of NO_3 radicals,[1] this rate constant is an upper limit and is consistent with the discussion given in Sec. 4.1.

Reference

[1] S. Langer, E. Ljungström and I. Wängberg, J. Chem. Soc. Faraday Trans. **89**, 425 (1993).

7.3.2. Alkenes

The rate constants reported since Table 52 was finalized are given in Table 70. For 1,3-butadiene, isoprene and 2,3-dimethyl-1,3-butadiene, the absolute rate constants of Ellermann *et al.*[1] are higher than the recommendations of Atkinson[2] at 298 K of

$$k(\text{1,3-butadiene}) = 1.0 \times 10^{-13}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1},$$

$$k(\text{2-methyl-1,3-butadiene}) = 6.78 \times 10^{-13}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1},$$

and

$$k(\text{2,3-dimethyl-1,3-butadiene}) = 2.1 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1},$$

with estimated overall uncertainties of factors of 3 (1,3-butadiene) and 2 (2-methyl-1,3-butadiene and 2,3-dimethyl-1,3-butadiene). The recommendations of Atkinson[2] are unchanged (see also Sec. 4.3 for isoprene).

The absolute rate constant for 1,3-cyclohexadiene of $(1.2 \pm 0.2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 295 K is in excellent agreement with the recommendation of Atkinson[2] of

$$k(\text{1,3-cyclohexadiene}) = 1.16 \times 10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

which is therefore unchanged.

References

[1] T. Ellermann, O. J. Nielsen, and H. Skov, Chem. Phys. Lett. **200**, 224 (1992).
[2] R. Atkinson, J. Phys. Chem. Ref. Data **20**, 459 (1991).

7.3.3. Oxygen-Containing Organic Compounds

The rate constants reported since Table 55 was finalized are given in Table 71. The duplicate sets of experiments at 296 ± 2 K for several of the esters studied are for ester samples obtained from different commercial sources.[1] Because of the slowness of these reactions, the rate constants given in Table 71 should be considered to be upper limits to the elementary rate constants.[1]

References

[1] S. Langer, E. Ljungström and I. Wängberg, J. Chem. Soc. Faraday Trans. **89**, 425 (1993).

7.3.4. Aromatic Compounds

The rate constants reported since Table 57 was finalized are given in Table 72, where the rate constants k_{abs}, k_a, k_b, k_c and k_d are those for the reactions (abs), (a), (b), (c) and (d), respectively.

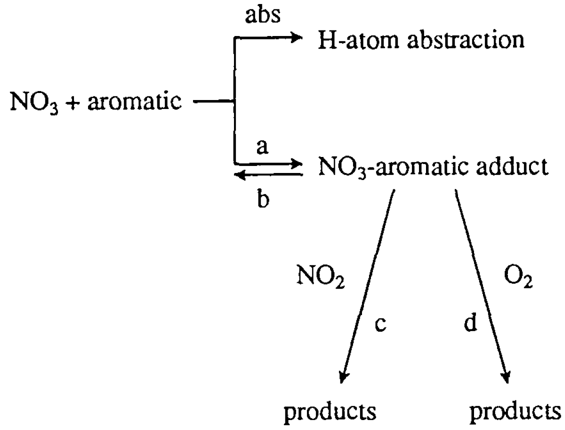

Table 70. Rate constants k for the gas-phase reactions of the NO_3 radical with alkenes

Alkene	k(cm^3 $molecule^{-1}$ s^{-1})	at T (K)	Technique	Reference
1,3-Butadiene	$(1.8 \pm 0.4) \times 10^{-13}$	295	PR-A	Ellermann *et al.*[1]
2-Methyl-1,3-butadiene (isoprene)	$(1.07 \pm 0.20) \times 10^{-12}$	295	PR-A	Ellermann *et al.*[1]
2,3-Dimethyl-1,3-butadiene	$(2.7 \pm 0.2) \times 10^{-12}$	295	PR-A	Ellermann *et al.*[1]
cis-1,3-Pentadiene	$(1.4 \pm 0.1) \times 10^{-12}$	295	PR-A	Ellermann *et al.*[1]
trans-1,3-Pentadiene	$(1.6 \pm 0.1) \times 10^{-12}$	295	PR-A	Ellermann *et al.*[1]
1,3-Cyclohexadiene	$(1.2 \pm 0.2) \times 10^{-11}$	295	PR-A	Ellermann *et al.*[1]
trans,*trans*-2,4-Hexadiene	$(1.6 \pm 0.3) \times 10^{-11}$	295	PR-A	Ellermann *et al.*[1]

These rate constant data are from the relative rate constant study of Kwok *et al.*[1] Of particular interest is the determination of the rate constant $k_a = 6.8 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} at 297 K for the addition reaction of the NO_3 radical with dibenzo-*p*-dioxin. Assuming that the rate constant k_c for the reaction of NO_2 with the NO_3-dibenzo-*p*-dioxin adduct is similar to those determined by Knispel *et al.*[3] for the reactions of NO_2 with the OH-benzene, OH-toluene and OH-phenol adducts, of $\sim 3 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, than a rate constant for the thermal decomposition of NO_3-dibenzo-*p*-dioxin back to reactants of $k_b \sim 520$ s^{-1} at 297 ± 2 K was obtained.[1] Furthermore, with the same assumption, $k_d < 1.2 \times 10^{-17}$ cm^3 $molecule^{-1}$ s^{-1} at 297 ± 2 K, approximately an order of magnitude (or greater) less than the room temperature rate constants determined by Knispel *et al.*[3] for the corresponding reactions of OH-benzene and OH-toluene adducts with O_2.

References

[1] E. S. C. Kwok, R. Atkinson, and J. Arey, Int. J. Chem. Kinet., in press (1994).

[2] R. Atkinson, J. Phys. Chem. Ref. Data **20**, 459 (1991).

[3] R. Knispel, R. Koch, M. Siese, and C. Zetzsch, Ber. Bunsenges. Phys. Chem. **94**, 1375 (1990).

7.4. Kinetics and Mechanisms of the Gas-Phase Reactions of Ozone with Organic Compounds

The kinetic and mechanistic data reported since Sec. 5 was finalized are presented and briefly discussed in the sections below.

7.4.1. Alkenes

The rate constants reported since Table 58 was finalized are given in Table 73. In addition to the rate constants given in Table 73, Munshi *et al.*[3] have reported lower limits to the (unspecified) room temperature rate constants for α-pinene, β-pinene, limonene and α-phellandrene of (in cm^3 $molecule^{-1}$ s^{-1} units) $>8.0 \times 10^{-17}$, $>9.6 \times 10^{-18}$, $>5.0 \times 10^{-18}$ and $>4.1 \times 10^{-17}$, respectively.

2-Methyl-1,3-butadiene (isoprene). The absolute rate constant of Grosjean *et al.*[1] is given in Table 73. This rate constant of Grosjean *et al.*[1] is in reasonable agreement with that of 1.15×10^{-17} cm^3 $molecule^{-1}$ s^{-1} calculated from the recommendation of Sec. 5.2 of

$$k(\text{2-methyl-1,3-butadiene}) = 7.86 \times 10^{-15}\, e^{-1913/T}\ cm^3\ molecule^{-1}\ s^{-1}$$

over the temperature range 240–324 K, which is unchanged.

Cycloheptene. The rate constant of Greene and Atkinson[2] supersedes that of Atkinson *et al.*[4] (and is 30% lower), and is in good agreement with the relative rate constant of Nolting *et al.*[5] of $(2.70 \pm 0.15) \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1} at 297 ± 2 K. A unit-weighted average of the relative rate constants of Nolting *et al.*[5] and Greene and Atkinson[2] leads to the recommendation of

$$k(\text{cycloheptene}) = 2.48 \times 10^{-16}\ cm^3\ molecule^{-1}\ s^{-1} \text{ at } 298\ K,$$

with an estimated overall uncertainty of ±40%.

Other Alkenes. The rate constants measured by Greene and Atkinson[2] using a relative rate method are given in Table 73. These rate constants of Greene and Atkinson[2] supersede those of Atkinson *et al.*[4,6]

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7.4.2. Oxygen-Containing Organic Compounds

The rate constants reported since Table 60 was finalized are given in Table 74 (those of Hatakeyama *et al.*[3] and Munshi *et al.*[4] were inadvertently omitted from Sec. 5.4).

Table 71. Rate constants k and temperature-dependent parameters, $k = A\ e^{-B/T}$, for the gas-phase reactions of the NO_3 radical with oxygen-containing compounds

Organic	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	k (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
Methyl formate			$(3 \pm 1) \times 10^{-18}$	296 ± 2	DF-A	Langer *et al.*[1]	
[$HC(O)OCH_3$]			$(4.1 \pm 0.6) \times 10^{-18}$	296 ± 2			
Methyl acetate			$(7 \pm 2) \times 10^{-18}$	296 ± 2	DF-A	Langer *et al.*[1]	
[$CH_3C(O)OCH_3$]			$(7.2 \pm 0.4) \times 10^{-17}$	296 ± 2			
Methyl propionate [$CH_3CH_2C(O)OCH_3$]			$(3.3 \pm 0.8) \times 10^{-17}$	296 ± 2	DF-A	Langer *et al.*[1]	
Methyl butyrate [$CH_3CH_2CH_2C(O)OCH_3$]			$(4.8 \pm 0.5) \times 10^{-17}$	296 ± 2	DF-A	Langer *et al.*[1]	
Ethyl formate			$(1.7 \pm 0.3) \times 10^{-17}$	296 ± 2	DF-A	Langer *et al.*[1]	
[$HC(O)CH_2CH_3$]			$(2.2 \pm 0.4) \times 10^{-17}$	296 ± 2			
Ethyl acetate			$(5 \pm 3) \times 10^{-18}$	273	DF-A	Langer *et al.*[1]	273-373
[$CH_3C(O)OCH_2CH_3$]			$(1.4 \pm 0.3) \times 10^{-17}$	296 ± 2			
			$(1.1 \pm 0.2) \times 10^{-17}$	296 ± 2			
			$(1.6 \pm 0.4) \times 10^{-17}$	313			
			$(1.8 \pm 0.5) \times 10^{-17}$	328			
			$(4.2 \pm 0.4) \times 10^{-17}$	353			
	0.133	2795 ± 962	$(1.05 \pm 0.07) \times 10^{-16}$	373			
Ethyl propionate			$(3.3 \pm 0.4) \times 10^{-17}$	296 ± 2	DF-A	Langer *et al.*[1]	
[$CH_3CH_2C(O)OCH_2CH_3$]			$(3.8 \pm 0.1) \times 10^{-17}$	296 ± 2			
Propyl formate [$HC(O)OCH_2CH_2CH_3$]			$(5.4 \pm 0.9) \times 10^{-17}$	296 ± 2	DF-A	Langer *et al.*[1]	
Propyl acetate [$CH_3C(O)OCH_2CH_2CH_3$]			$(5 \pm 2) \times 10^{-17}$	296 ± 2	DF-A	Langer *et al.*[1]	

Methacrolein and Methyl Vinyl Ketone. The absolute rate constants of Grosjean *et al.*[1] are given in Table 74. These rate constants are in good agreement, to within 6% for methacrolein and 17% for methyl vinyl ketone, with the rate constants calculated from the recommendations given in Sec. 5.4 of

$$k(\text{methacrolein}) = 1.36 \times 10^{-15}\, e^{-2112/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

and

$$k(\text{methyl vinyl ketone}) = 7.51 \times 10^{-16}\, e^{-1521/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1},$$

both over the temperature range 240–324 K. These previous recommendations are unchanged.

2-Cyclohexen-1-one. The upper limit to the rate constant obtained by Greene and Atkinson[2] from a relative rate study is consistent with the absolute rate constant of Atkinson *et al.*[6]

3-Penten-2-one. The relative rate constant of Greene and Atkinson[2] supersedes the previous absolute rate constant of Atkinson *et al.*[6]

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7.4.3. Nitrogen-Containing Organic Compounds

Blatchley *et al.*[1] have used a static system with ultraviolet absorption spectroscopy to investigate the kinetics of the gas-phase reaction of pyridine, 2-, 3- and 4-methylpyridine, and 2,5- and 2,6-dimethylpyridine with O_3. Due to spectroscopic interferences between O_3 and the pyridine and/or pyridine reaction products, only semi-quantitative data were obtained, indicating that these reactions were slow, with room temperature rate constants of $\sim(5–50) \times 10^{-21}$ cm^3 molecule^{-1} s^{-1} being reported.

Munshi *et al.*[2] used a flow technique with ultraviolet absorption spectroscopy to measure rate constants at room temperature (unspecified) for the gas phase reactions of O_3 with acrylonitrile ($CH_2=CHCN$) and methacrylonitrile ($CH_2=C(CH_3)CN$) of 1.38×10^{-19} cm^3 molecule^{-1} s^{-1} and 3.52×10^{-19} cm^3 molecule^{-1} s^{-1}, respectively. Decidedly non-unit stoichiometry was observed for the O_3 reaction with acrylonitrile[2] ($\Delta O_3/\Delta$acrylonitrile = 0.33), and the rate constant obtained[2] is marginally inconsistent with the upper limit of k(acrylonitrile) $< 1 \times 10^{-19}$ cm^3 molecule^{-1} s^{-1} determined by Atkinson *et al.*[3] at 296 ± 2 K.

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[2] H. B. Munshi, K. V. S. R. Rao, and R. M. Iyer, Atmos. Environ. **23**, 1971 (1989).

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Table 72. Rate constants k_{abs} and k_a and rate constant ratios k_ak_c/k_b and k_ak_d/k_b for the gas-phase reactions of the NO_3 radical with aromatic compounds at 297 ± 2 K[1]

Aromatic	k_a (cm^3 molecule^{-1} s^{-1})[a]	k_{abs} (cm^3 molecule^{-1} s^{-1})[a]	k_ak_c/k_b (cm^6 molecule^{-2} s^{-1})[a]	k_ak_d/k_b (cm^6 molecule^{-2} s^{-1})[a]
Methoxybenzene		$<1.6 \times 10^{-15}$	$<7 \times 10^{-30}$	
1,2-Dimethoxybenzene		$(9.8 \pm 4.8) \times 10^{-15}$	$(1.02 \pm 0.18) \times 10^{-28}$	
1,3-Dimethoxybenzene		$(1.02 \pm 0.35) \times 10^{-14}$	$(3.3 \pm 0.6) \times 10^{-29}$	
1,4-Dimethoxybenzene		$(8.8 \pm 0.6) \times 10^{-15}$	$(1.34 \pm 0.03) \times 10^{-28}$	
Dibenzofuran		$<1.6 \times 10^{-15}$	$<7 \times 10^{-30}$	
Dibenzo-*p*-dioxin	6.8×10^{-14} [b]	$<8 \times 10^{-15}$	3.9×10^{-27} [b]	$<1.6 \times 10^{-33}$

[a] Relative to k(1-butene) $= 1.19 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}.[2]

[b] Estimated overall uncertainty of a factor of ~2.

Table 73. Rate constants k for the gas-phase reaction of O_3 with alkenes

Alkene	k (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference
2-Methyl-1,3-butadiene (isoprene)	$(8.95 \pm 0.25) \times 10^{-18}$	293 ± 2	S-UV	Grosjean *et al.*[1]
1,3-Cyclohexadiene	$(1.22 \pm 0.05) \times 10^{-15}$	296 ± 2	RR [relative to k(2,3-dimethyl-2-butene) = 1.12×10^{-15}][a]	Greene and Atkinson[2]
Cycloheptene	$(2.26 \pm 0.04) \times 10^{-16}$	296 ± 2	RR [relative to k(*cis*-2-butene) = 1.22×10^{-16}][a]	Greene and Atkinson[2]
1,3-Cycloheptadiene	$(1.54 \pm 0.03) \times 10^{-16}$	296 ± 2	RR [relative to k(*cis*-2-butene) = 1.22×10^{-16}][a]	Greene and Atkinson[2]
Bicyclo[2.2.1]-2-heptene	$(1.55 \pm 0.05) \times 10^{-15}$	296 ± 2	RR [relative to k(2,3-dimethyl-2-butene) = 1.12×10^{-15}][a]	Greene and Atkinson[2]
Bicyclo[2.2.1]-2,5-heptadiene	$(3.55 \pm 0.07) \times 10^{-15}$	296 ± 2	RR [relative to k(2,3-dimethyl-2-butene) = 1.12×10^{-15}][a]	Greene and Atkinson[2]
Bicyclo[2.2.2]-2-octene	$(7.09 \pm 0.10) \times 10^{-17}$	296 ± 2	RR [relative to k(*cis*-2-butene) = 1.22×10^{-16}][a]	Greene and Atkinson[2]

[a] From previous recommendations.

Table 74. Rate constants k for the gas-phase reactions of O_3 with oxygen-containing organic compounds

Organic	k (cm^3 $molecule^{-1}$ s^{-1})	at T (K)	Technique	Reference
Methacrolein [$CH_2=C(CH_3)CHO$]	$(1.02 \pm 0.05) \times 10^{-18}$	291 ± 2	S-UV	Grosjean *et al.*[1]
Methyl vinyl ketone [$CH_3C(O)CH=CH_2$]	$(4.72 \pm 0.09) \times 10^{-18}$	291 ± 2	S-UV	Grosjean *et al.*[1]
3-Penten-2-one [$CH_3C(O)CH=CHCH_3$]	$(3.50 \pm 0.16) \times 10^{-17}$	296 ± 2	RR [relative to k(propene) = 9.68×10^{-18}][a]	Greene and Atkinson[2]
2-Cyclohexene-1-one	$<1.9 \times 10^{-18}$	296 ± 2	RR [relative to k(propene) = 9.68×10^{-18}][a]	Greene and Atkinson[2]
Ketene [$CH_2=C=O$]	$<1 \times 10^{-21}$	b	S-IR	Hatakeyama *et al.*[3]
Methylketene [$CH_3CH=C=O$]	$<7 \times 10^{-19}$	303 ± 1	S-IR	Hatakeyama *et al.*[3]
Ethylketene [$CH_3CH_2CH=C=O$]	$<1 \times 10^{-18}$	303 ± 1	S-IR	Hatakeyama *et al.*[3]
Dimethylketene [$(CH_3)_2C=C=O$]	$<4 \times 10^{-17}$	303 ± 1	S-IR	Hatakeyama *et al.*[3]
Methyl acrylate [$CH_2=CHC(O)OCH_3$]	2.91×10^{-18}	b	F-UV	Munshi *et al.*[4]
Ethyl acrylate [$CH_2=CHC(O)OCH_2CH_3$]	5.70×10^{-18}	b	F-UV	Munshi *et al.*[4]
1,2-Epoxy-2-methyl-3-butene	$(2.49 \pm 0.15) \times 10^{-18}$	296 ± 2	RR [relative to k(propene) = 9.68×10^{-18}][a]	Atkinson *et al.*[5]

[a] From previous recommendations.
[b] Room temperature, not specified.

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The American Chemical Society was founded in 1876 as a scientific and educational society, and in 1937 was granted a national charter by an act of Congress. Its objectives include the advancement of chemistry, the promotion of research in science and industry, improvement of qualifications and usefulness of chemists, increased diffusion of chemical knowledge, and the promotion of scientific interest and inquiry.

ACS publishes 26 magazines, journals, and other scientific periodicals in addition to its participation in publication of the *Journal of Physical and Chemical Reference Data*. It also publishes books and other nonperiodical reports and operates the Chemical Abstracts Service, the key to the world's chemical literature. It pursues its objectives through its services to chemists and chemical engineers and to education, industry, and government.

Inquiries regarding ACS participation in JPCRD should be directed to this division.

National Institute of Standards and Technology

U.S. Department of Commerce
Gaithersburg, MD 20899-0001

U.S. Department of Commerce	Ronald H. Brown, Secretary
Technology Administration	Mary L. Good, Under Secretary for Technology
National Institute of Standards and Technology	Arati Prabhakar, Director

The National Institute of Standards and Technology (NIST), formerly the National Bureau of Standards, was established by an act of Congress 3 March 1901. NIST works to strengthen U.S. industry's international competitiveness, advance science and engineering, and improve public health, safety, and the environment. With an annual budget of more than $350 million and about 3100 staff members, NIST conducts science and engineering research in commercially important fields such as advanced materials, information systems, biotechnology, optoelectronics, computer-integrated manufacturing, and sensor technology.

NIST's laboratory research is designed to support development of critical emerging technologies and the new measurement methods and standards necessary to make them commercially viable. The ability of U.S.-based industries to exploit these new technologies determines in large part the health of the U.S. economy.

Several new NIST programs are designed to help spur innovation at U.S. businesses through seed money for development of generic technologies; grants to states for support of technology transfer programs; and financial and technical assistance to help small and mid-sized companies adopt more efficient manufacturing methods.

Throughout its history, NIST has helped industry to develop high-quality products and processes by supplying standard reference materials and data; by continuously improving technologies for precision measurements of mass, time, length, voltage, radiation, and other units; and through active participation in voluntary standards-setting bodies.