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Kinetics and Mechanisms of the Gas-Phase Reactions of the Hydroxyl Radical with Organic Compounds

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Kinetics and Mechanisms of the Gas-Phase Reactions of the Hydroxyl Radical with Organic Compounds

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The literature kinetic and mechanistic data for the gas-phase reactions of the OH radical with organic compounds (through 1988) have been tabulated, reviewed and evaluated over the entire temperature ranges for which data are available.

Key words: hydroxyl radical; organic compounds; reaction kinetics; reaction mechanisms.

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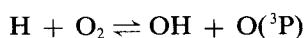
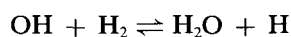
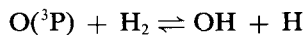
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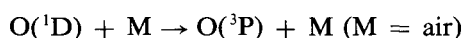
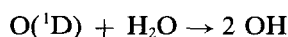
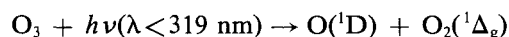
1. Introduction

The hydroxyl (OH) radical is a key reactive intermediate in both combustion¹⁻⁹ and atmospheric chemistry.¹⁰⁻¹² Thus, recent computer modeling studies of the combustion of organic compounds show that the major reaction routes of these organics are by reaction with O(³P) and H atoms and OH radicals, with the relative importance of these reaction pathways depending on the particular combustion conditions, for example, on the fuel/oxygen ratio.^{2-5,9} At combustion temperatures these reactive species are interconverted, at least in part, through the H₂-O₂ reactions.



which are common to all high temperature organic combustion systems.⁵ Measurements of OH radical concentrations, and of their temporal profiles, are now routinely carried out in flames and other combustion media.¹³⁻¹⁷

The hydroxyl radical has also been shown to play a pivotal role in the chemistry of the atmosphere,^{10,12} and apparently reliable ambient OH radical concentrations in the troposphere¹⁸⁻²⁵ and stratosphere²⁶⁻²⁸ are now available from *in situ* measurements, in addition to the global tropospheric average OH radical concentration derived from halocarbon lifetime measurements.²⁹ In the clean troposphere, hydroxyl radicals are generated through the reaction sequence,



with additional formation processes occurring in polluted urban areas.¹²

For the majority of organic compounds emitted into the troposphere from either biogenic or anthropogenic sources, reaction with the OH radical is their major, if not sole, chemical loss process.¹² Indeed, in the troposphere the chemical reactions responsible for the degradation of organic compounds comprise, in essence, a low-temperature combustion system. For these chemicals reaction with the OH radical leads to their removal from the atmosphere and limits their atmospheric concentrations, and this removal process (or the lack of it) is critical to the ongoing discussion of the effects of present and future anthropogenic halocarbons on the stratospheric ozone layer.

Clearly, OH radical kinetics and reaction mechanisms need to be known under the temperature, pressure and third-body conditions encountered in combustion sys-

tems and in the atmosphere. During the past several years major research efforts have been carried out to obtain these necessary experimental data. As an example, at room temperature reaction rate constants have been measured for over 350 organic compounds,¹² while at the higher temperatures (>1000 K) representative of combustion chemistry flash photolysis and pulsed radiolysis techniques are now providing absolute kinetic data, obtained in many cases over large temperature ranges.³⁰⁻⁴⁰ This accelerating acquisition of kinetic and mechanistic data will surely continue, especially at combustion temperatures.

However, in order to provide a consistent and integrated overview and to allow the available data base to be effectively used by other scientists (for example, chemical modelers), this data base must be reviewed and critically evaluated on an ongoing basis. This is crucial to both combustion chemistry as well as to the chemistry of the troposphere and stratosphere. In addition to providing a recommended set of kinetic data, such reviews and evaluations provide an up-to-date status of the kinetic and mechanistic information available and are the most reliable source of data for the development of techniques for rate constant and mechanism estimations. As the information base continues to grow, these ongoing evaluations become increasingly necessary, and they must be viewed as an integral part of the experimental and theoretical research efforts in combustion and atmospheric chemistry.

Unfortunately, to date this has not been the case. Thus, while the reactions of OH radicals with the inorganic reactants of atmospheric importance and certain C₁-C₃ organics (mainly the haloalkanes) are now being included in the NASA⁴¹ and CODATA/IUPAC⁴² evaluations, there is no ongoing review and evaluation of the literature kinetic and mechanistic data for the reactions of the OH radical with the other organic compounds which comprise the vast majority of combustion fuels and atmospheric emissions. Indeed, for the reactions of the OH radical with organic compounds, few reviews have been carried out during the past decade, despite the relevance of these reactions to combustion and atmospheric chemistry.

For atmospheric purposes, Atkinson *et al.*⁴³ compiled and reviewed the literature kinetic and mechanistic data (through mid-1978) for organic compounds at temperatures ≤500 K. No recommendations were given, and the emphasis was on atmospheric chemistry. In 1981, Baulch and Campbell⁴⁴ published a review covering the literature for the period 1972 through October 1979, and, because of the Atkinson *et al.* article,⁴³ dealt in most detail with inorganic compounds and those aspects of the reactions with organic compounds, such as high temperature data, which Atkinson *et al.*⁴³ did not cover. In addition, Cohen and Westberg⁴⁵ included the reactions of the OH radical with alkanes in their evaluation of the kinetics of selected reactions involved in combustion chemistry.

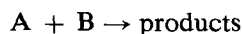
More recently, two evaluations and reviews have appeared which deal with organic compounds; one by Baulch *et al.*⁴⁶ dealing with the kinetics of the gas-phase

reactions of the OH radical with alkanes over the temperature range ~ 200 – 2000 K, covering the literature data through October 1984, and the other by Atkinson¹² dealing with the kinetics and mechanisms of the gas-phase reactions of the OH radical with organic compounds under atmospheric conditions, with the literature being covered through late 1985/early 1986. Although the review of Atkinson¹² focused on OH radical reactions under atmospheric conditions and, in general, only kinetic and mechanistic data below 500 K were reviewed, data at higher temperatures (up to ~ 1500 K) were included if these data were obtained in studies extending to temperatures below 500 K.¹² An analogous review of the gas-phase reactions of the OH radical with inorganic compounds has been carried out by Paraskevopoulos and Singleton.⁴⁷

In this article, the review of Atkinson¹² has been updated and extended to cover the entire temperature ranges for which kinetic and mechanistic data are available. The present article deals with the kinetics and mechanisms of the initial OH radical reactions with organic compounds, and the subsequent reactions of the initially-formed product species are not dealt with. In the remainder of this section, the major experimental techniques which have been used to obtain kinetic data are briefly discussed, together with the methods of presentation of the kinetic data in Sec. 2.

1.1. Experimental Techniques Used

Two general experimental approaches, namely absolute and relative rate constant measurement methods, have been used to determine rate constants for the reactions of the OH radical with organic compounds. In the absolute technique, for the bimolecular reaction,



either the pseudo-first order decay of one species is measured in the presence of a known excess concentration of the other reactant, with

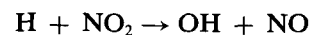
$$-\ln[A]/dt = k[B],$$

or the concentrations of both species are measured and the rate constant k derived from the equation

$$\frac{d[\text{product}]}{dt} = \frac{-d[A]}{dt} = \frac{-d[B]}{dt} = k[A][B]$$

At lower temperatures, typically $\lesssim 1000$ K, the discharge flow and flash (or laser) photolysis techniques interfaced to a variety of detection systems have been, and continue to be, widely used. To date, these detection systems for OH radical reactions have included mass spectrometry,⁴⁸ electron paramagnetic resonance,⁴⁹ laser magnetic resonance,⁵⁰ resonance absorption^{51–54} (including laser absorption⁵⁵) and resonance fluorescence^{56,57} (including laser induced fluorescence^{58,59}).

Relevant to this article was the determination by Kaufman and co-workers^{51–53} that the initially-used electric discharge in water vapor in a fast flow system^{60,61} was subject to secondary reactions regenerating OH radicals, hence yielding erroneous kinetic data. This finding^{51–53} then invalidates any data obtained in this manner, and such studies are not included in this evaluation. All more recent discharge flow studies have used the reaction of H atoms with NO₂

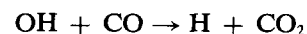


as a clean source of electronically and vibrationally ground state OH radicals.⁶² The characteristics of these discharge flow and flash (or laser) photolysis methods are discussed by Howard,⁶³ Michael and Lee,⁶⁴ Kaufman⁶⁵ and Atkinson,¹² and these articles should be consulted for more details.

At the higher temperatures characteristic of flames, OH radical concentrations have been measured by mass spectrometry,⁶⁶ laser induced fluorescence⁶⁷ and resonance absorption,⁶⁸ and have also been calculated from equilibrium considerations.⁶⁹

In the relative rate method, the rate constant of interest is determined relative to that for another reaction, normally a reaction of the OH radical with a second, or reference, species. Generally, the decay rates of two or more compounds are monitored in the presence of OH radicals, with other loss processes (chemical or physical) of these reactants being either quantitatively known or minimized.¹² Hydroxyl radicals have been generated by numerous methods, including photolysis of NO-NO₂-organic-air,⁷⁰ HONO-NO-air,^{71,72} and CH₃ONO-NO-air⁷³ mixtures, photolysis of H₂O₂,^{74,75} the dark reaction of N₂H₄ with O₃,⁷⁶ the thermal decomposition of H₂O₂⁷⁷ (at elevated temperatures) or HOONO₂,⁷⁸ and the heterogeneous reaction of H₂O₂ with NO₂.⁷⁹ Detection methods for the reactant organic and the reference species have included gas chromatography,^{70,73,75} Fourier transform infrared absorption spectroscopy^{72,76} and differential optical absorption spectroscopy.⁸⁰ The methods utilized at around room temperature for the determination of OH radical reaction rate constants using relative rate techniques have been discussed in detail by Atkinson.¹²

At elevated temperatures, relative rate constants have been derived from studies utilizing the thermal decomposition of H₂O₂ as a source of OH radicals⁷⁷ and from the effects of small amounts of added organic to the H₂-O₂ reaction system.⁸¹ In flames, numerous studies (see, for example, Refs. 82 and 83) have been carried out in which the decay rate of the organic, presumed to be due to reaction with the OH radical, was measured and the OH radical concentration calculated from the formation rate of CO₂, produced from the reaction.



In these studies the rate constants derived were thus relative to the rate constant for the reaction of OH radicals with CO.

1.2. Presentation of Kinetic Data

In Sec. 2, the kinetic data for the reactions of OH and OD radicals with the various classes of organic compounds [alkanes (including cycloalkanes), haloalkanes, alkenes (including di- and tri-alkenes and cycloalkenes), haloalkenes, alkynes, oxygen-, sulfur-, nitrogen-, phosphorus- and silicon-containing organics, aromatics, organometallics and organic radicals] are presented and discussed. As far as possible, the initial reaction mechanisms are discussed in conjunction with the compilations and evaluations of the available rate constant data. Data from relative rate constant studies have been reevaluated on the basis of the recommended rate constants for the reference reactions at the temperatures employed in the relative rate studies.

Three OH radical reactions with inorganic compounds have been used in more than one study as the reference reaction; namely the reactions of OH radicals with H₂, CO, and HONO. The rate constant for the reaction of OH radicals with H₂ has been reviewed and evaluated by Cohen and Westberg,⁴⁵ and their recommendation (also accepted by the recent evaluation of Tsang and Hampson⁸⁴) of

$$k(\text{OH} + \text{H}_2) = 1.06 \\ \times 10^{-17} T^2 e^{-1490/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 240–2400 K is utilized in this evaluation.

For the reaction of OH radicals with CO, the “low pressure” rate constant recommended in the evaluation of Baulch *et al.*⁸⁵ of

$$k(\text{OH} + \text{CO}) = 1.12 \\ \times 10^{-13} e^{0.000907T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

is employed. This low total pressure rate constant is consistent with the most recent NASA⁴¹ and CODATA/IUPAC⁴² room temperature evaluations and agrees with the recent temperature-dependent study of Ravishankara and Thompson.⁸⁶ At around room temperature this rate constant is pressure dependent for the more effective third body gases such as N₂, O₂, CF₄ and SF₆,^{87–92} and at 298 K the most recent NASA⁴¹ and IUPAC⁴² evaluations recommend that for M = O₂, N₂ and air

$$k(\text{OH} + \text{CO}) = 1.5 \\ \times 10^{-13} (1 + 0.6 P) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

where *P* is the total pressure in atmospheres. This pressure dependence is essentially independent of temperature for temperatures < 300 K,⁹² although Hynes *et al.*⁹² have observed that the pressure dependence of the rate constant for this reaction for M = air at 371 K is somewhat less than at 299 K or 262 K. Golden and co-workers⁹³ have also carried out a theoretical study of this

reaction, showing that, as expected, the pressure-dependent portion of this reaction becomes less important at elevated temperatures.

In this review article, a rate constant for the reaction of OH radicals with CO of

$$k(\text{OH} + \text{CO}) = 1.12 \times 10^{-13} e^{0.000907T} \\ \times [1 + 2.4 \times 10^{-20} [M](T/298)^{-1}] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

is used for M = O₂ and/or N₂, with the term in square brackets being an empirical relationship to take into account the pressure dependence of this rate constant over the temperature range ~290–1000 K. This expression essentially reproduces the NASA⁴¹ and IUPAC⁴² evaluations at 298 K and the data reported by Hynes *et al.*,⁹² and exhibits the behavior predicted by Golden and co-workers.⁹³ It should be noted, however, that the pressure-dependence of the rate constant at temperatures below ~298 K calculated from this equation appears to be more temperature dependent than shown by the data cited by Hynes *et al.*⁹² [This is of no real consequence to the present evaluation since the reaction of OH radicals with CO has not been used as a reference reaction in relative rate studies carried out at temperatures below ~290 K.]

As noted above, the pressure dependence of this rate constant for the reaction of OH radicals with CO is dependent on the third body M,^{87–92} with no pressure dependence being observed for M = He or Ar at around room temperature.^{88,89,91} This pressure dependence of the rate constant for the reaction of OH radicals with CO, and its dependence on the temperature and the particular third-body or third-bodies employed, introduces added uncertainties into the derivation of rate constants from relative rate studies employing CO as the reference compound. Accordingly, the rate constants derived from these relative rate studies utilizing CO as the reference compound are given a lower weight in the evaluations.

For the reaction of OH radicals with HONO, the recent data of Jenkin and Cox⁹⁴ are used, with

$$k(\text{OH} + \text{HONO}) = 1.80 \times 10^{-11} e^{-390/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

In the data tabulations in Sec. 2, the experimental techniques used are denoted by abbreviations such as (for example) DF-RF, where the first letters denote: DF, discharge flow; FP, flash photolysis; LP, laser photolysis; LH, laser heating; SH, shock heating; MPS, modulation-phase shift; PR, pulsed radiolysis; and the second set of letters denote the detection technique; MS, mass-spectroscopy (including photoionization-mass spectroscopy); EPR, electron paramagnetic resonance; KS, kinetic spectroscopy; LMR, laser magnetic resonance; RA, resonance absorption; RF, resonance fluorescence; and LIF, laser induced fluorescence. Relative rate studies are denoted by the abbreviation RR, and the reference compound and the OH radical reaction rate constant used for the reference reaction are given.

The tables list, whenever available, the rate constants obtained at the various temperatures studied. Throughout this article, $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ units are used for bimolecular reactions, and pressures are expressed in Torr (1 Torr = 133.3 Pa). The cited Arrhenius preexponential factors A and temperature dependent parameters B in the expression $k = Ae^{-B/T}$ are also listed, where B is in K. In some studies covering wide temperature ranges, the simple Arrhenius expression has, as expected, been shown not to hold, with pronounced curvature in the Arrhenius plots being observed.^{12,30,33,95} In these cases a three-parameter expression of the form

$$k = AT^n e^{-B/T} \quad (\text{I})$$

has been used (where $n = 0$ for the Arrhenius expression) and the reported values of A , B and n are tabulated. Since to date most of the available OH radical rate constant data have been obtained over relatively limited temperature ranges, the simple Arrhenius expression, although obviously too simplistic, is often adequate and convenient for expressing these experimental data over the limited temperature ranges studied.

In those cases where data are available over only limited temperature ranges (for example, at temperatures $\lesssim 500$ K) and no obvious non-Arrhenius behavior of the data is evident, recommendations are given in the form of the Arrhenius equation

$$k = Ae^{-B/T} \quad (\text{II})$$

For organic compounds for which reliable data exist covering large temperature ranges, for example, from $\lesssim 300$ to $\gtrsim 1000$ K, or for which their Arrhenius plots exhibit obvious curvature, a more realistic expression is used for the recommendations. The expression

$$k = CT^2 e^{-D/T} \quad (\text{III})$$

has been chosen in these evaluations since this has been used in the recent NASA evaluation⁴¹ and is consistent with the experimental data. Furthermore, values of $n \sim 2$ in the above three parameter expression have been derived from previous experimental studies^{30,33} and theoretical evaluations⁹⁶ of these reactions over wide temperature ranges. It should be noted, however, that Cohen and Benson^{97,98} have used transition state theory to calculate values of $n = 1.1$ – 1.8 in Eq. (I) for the reactions of the OH radical with a series of halomethanes and haloethanes, although the differences between these formulations of the three-parameter expression, i.e., with $n = 1$ or $n = 2$, are likely to be within the uncertainties of the experimental data. The expression $k = CT^n e^{-D/T}$ can be transformed into an Arrhenius expression, $k = Ae^{-B/T}$, centered at a temperature T with $A = C(eT)^n$ and $B = D + nT$.

In the rate constant data tables, the error limits cited are those reported. In many cases these are one or two least-squares standard deviations and in others they are the estimated overall error limits. While for relative rate constant studies the use of two least-squares standard deviations may be a realistic estimation of the overall error

limits with respect to the reference reaction rate constant, with additional systematic uncertainties being associated with the rate constant used for the reference reaction, the overall error limits for the absolute rate constant determinations are expected to be of the order of ~ 10 – 15% , except for some of the most recent studies for which the overall error limits may have been reduced to ~ 6 – 10% .

For the alkenes, haloalkenes, alkynes and aromatics, which react with the OH radical at around room temperature, at least partially, by initial OH radical addition to the C=C and C \equiv C bonds or to the aromatic ring(s), the measured rate constants are often in the fall-off regime between second- and third-order kinetics. For these classes of organic compounds, in general only the data obtained (or thought to have been obtained) at, or close to, the high-pressure limit are tabulated, and data which were obtained (or now realized to have been obtained) in the fall-off region are not explicitly given. However, the pressure ranges at which the high-pressure region are (effectively) attained are discussed and, where sufficient experimental data are available, the parameters in the Troe fall-off expression,^{99–101}

$$k = \left[\frac{k_0[M]}{1 + k_0[M]/k_\infty} \right] F^z$$

$$z = \left[1 + \{ \log(k_0[M]/k_\infty) \}^2 \right]^{-1}$$

where k_0 and k_∞ are the limiting low pressure third-order and high pressure second-order rate constants, respectively, are derived (mainly for M = N₂, O₂, air or Ar). [These rate constants k_0 and k_∞ are given in units of $\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ and $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively, in this article]. The broadening coefficient, F , is also temperature dependent, and can be approximately represented by^{42,100,101}

$$F = e^{-T/T^*} + e^{-4T/T^*}$$

where T^* is a constant (in K) for a given reactant. This treatment then allows the effects of fall-off behavior, especially at elevated temperatures, to be taken into account.

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2. Kinetic and Mechanistic Data

In this section, the kinetics and mechanisms of the reactions of the OH and OD radical with the various classes of organic compounds (alkanes, haloalkanes, alkenes, haloalkenes, alkynes, oxygen-, sulfur-, nitrogen-, phosphorus- and silicon-containing organics, aromatics, organometallics and organic radicals) are dealt with separately. Only the gas-phase reactions of $\text{OH}(X^2\Pi_i)_{v=0}$ radicals are dealt with in these sections, since few kinetic data exist for the reactions of vibrationally excited OH radicals,¹⁻⁶ and these measurements are mainly for vibrational quenching^{1,3-5} rather than for chemical reaction. Indeed, only for the reaction of the $\text{OH}(X^2\Pi_i)_{v=1}$ radical with CH_4 is a rate constant for chemical reaction available, with an upper limit to the rate constant of $\leq 3 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ being reported by Spencer *et al.* at $295 \pm 2 \text{ K}$.²

As far as possible, the initial reaction mechanisms are discussed together with the tabulations and evaluations of the available rate constant data. As noted above, for the relative rate studies the data have been reevaluated on the basis of the recommended rate constants for the reference reactions at the temperatures and, if necessary, the pressures employed in those relative rate studies. If such a reevaluation was not possible, then the data from these relative rate studies are not tabulated or considered in the evaluations. As also noted above, those relative rate studies employing the reaction of OH radicals with CO as the reference reaction are subject to additional uncertainties due to the dependence of the rate constant for this reference reaction on the total pressure and the diluent gas(es) present, especially at temperatures $< 500 \text{ K}$.⁷ This introduces additional uncertainties into the derivation of rate constants from relative rate studies employing CO, and accordingly, rate constants from these studies are given a lower weight in the evaluations.

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2.1. Alkanes

a. Kinetics and Mechanisms

The literature rate constant data for the reactions of the OH radical with the alkanes are given in Tables 1 (acyclic alkanes) and 2 (cycloalkanes). The available rate constants for the reactions of the OD radical with alkanes are given in Table 3. In these tables, the rate constants given are those for the overall reactions. These OH radical reactions with the alkanes and cycloalkanes proceed by H-atom abstraction from the C—H bonds,¹¹⁹⁻¹²¹



and hence in general a variety of alkyl radicals are formed with differing rate constants. Only for propane, *n*-butane and 2-methylpropane are sufficient experimental data available to allow the rate constants for the formation of the differing alkyl radicals to be derived in any direct manner.

In the evaluations of the rate constants for the individual alkanes and cycloalkanes, the previous reviews of Atkinson *et al.*¹¹⁹ and Atkinson¹²⁰ are utilized to aid in the assessment of those studies which are judged (possibly subjectively) to be free of systematic errors and are hence used for the evaluations. The kinetic data for the individual alkanes and cycloalkanes are discussed below. For methane and ethane a sufficient number of absolute rate constant data are available over a large temperature range that the recommended rate expressions can be derived solely from these absolute data, and the reliability of the relative rate studies for these alkanes can be assessed. For propane, *n*-butane, 2-methylpropane and the higher alkanes, relative rate data judged to be reliable (for example, from identical or related studies to those which agreed with the recommended absolute rate constant data for methane and ethane) were utilized together with absolute rate data in the evaluations.

(1) Methane

The available rate constant data are tabulated in Table 1. A large number of kinetic studies have been carried out for methane using both absolute and, especially at elevated temperatures, relative rate methods. In view of the large number of absolute rate data available, covering the temperature range from 240 to 1900 K, the recommended rate constant expression for methane is based solely upon the absolute rate data.

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

Alkane	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	n	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Tempera- ture range covered (K)	
Methane				17	1650–1840	RR [relative to $k(\text{CO})$ $= 1.12 \times 10^{-13} e^{0.0009077} \text{J}^a$	Westenberg and Fristrom ¹	1650–1840	
				9.8	1445	RR [relative to $k(\text{CO})$ $= 1.12 \times 10^{-13} e^{0.0009077} \text{J}^a$	Fenimore and Jones ²	1225–1800	
				10	1560				
				8.7	1580				
				10	1690				
				13	1800				
					0.171	673	RR [relative to $k(\text{CO})$ $= 1.12 \times 10^{-13} e^{0.0009077} \text{J}^a$	Hoare ³	673–923
				0.238	723				
				0.49	798				
				0.67	873				
				0.88	923				
					22	1370–1680	RR [relative to $k(\text{CO})$ $= 1.12 \times 10^{-13} e^{0.0009077} \text{J}^a$	Fristrom ⁴	1370–1680
					0.41 ± 0.21	773	RR [relative to $k(\text{CO})$ $= 2.26 \times 10^{-13} \text{J}^a$	Blundell <i>et al.</i> ⁵	
					0.175	673	RR [relative to $k(\text{CO})$ $= 1.12 \times 10^{-13} e^{0.0009077} \text{J}^a$	Hoare ⁶	673–923
					0.270	723			
					0.49	798			
					0.69	873			
					0.93	923			
					0.53	798	RR [relative to $k(\text{CO})$ $= 2.31 \times 10^{-13} \text{J}^a$	Hoare and Peacock ⁷	
					0.92 ± 0.19	773	RR [relative to $k(\text{H}_2)$ $= 9.22 \times 10^{-13} \text{J}^a$	Baldwin <i>et al.</i> ⁸	
					5.0 ± 1.7	1285	Flame - RA	Dixon-Lewis and Williams ⁹	
					0.0108 ± 0.0025	300	DF-EPR	Wilson and Westenberg ¹⁰	
					0.00880 ± 0.00033	301 ± 1	FP-KS	Greiner ¹¹	
83			2516	0.0179	298	FP-KS	Horne and Norrish ¹²	298–423	
				14 ± 3	1750–2000	RR [relative to $k(\text{CO})$ $= 1.12 \times 10^{-13} e^{0.0009077} \text{J}^a$	Wilson <i>et al.</i> ¹³	1750–2000	
				0.00848 ± 0.00071	295	FP-KS	Greiner ¹⁴	295–498	
				0.00953 ± 0.00028	295				
				0.0106 ± 0.00025	296				
				0.0103 ± 0.00053	296				
				0.00804 ± 0.00020	301				
				0.00805 ± 0.00041	301				
				0.00903 ± 0.00088	302				
				0.0154 ± 0.0006	333				
				0.0352 ± 0.0007	370				
				0.0611 ± 0.0023	424				
				0.121 ± 0.004	492				
				0.121 ± 0.003	493				
				0.120 ± 0.003	493				
				0.113 ± 0.002	497				
				0.122 ± 0.003	498				
	$5.5^{+0.8}_{-0.6}$		1898 ± 51						

TABLE 1. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with alkanes — Continued

Alkane	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	n	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
				1.0 ± 0.1	773	RR [relative to $k(\text{H}_2)$ $= 9.22 \times 10^{-13}\text{a}$]	Baldwin <i>et al.</i> ¹⁵	
				$0.18^{+0.18}_{-0.09}$	548	RR [relative to $k(\text{CO})$ $= 1.84 \times 10^{-13}\text{a}$]	Simonaitis <i>et al.</i> ¹⁶	
	50		3020	6.7	1500	Flame - MS	Peeters and Mahnen ¹⁷	1100-1900
				$0.00204 \pm 0.00036\text{b}$	240	FP-RF	Davis <i>et al.</i> ¹⁸	240-373
				$0.00508 \pm 0.00020\text{b}$	276			
				$0.00775 \pm 0.00063\text{b}$	298			
	2.36 ± 0.21		1711 ± 88	$0.0242 \pm 0.0037\text{b}$	373			
				0.00715 ± 0.00042	293	DF-RF	Margitan <i>et al.</i> ¹⁹	293-427
				0.0212 ± 0.0004	359			
				0.0306 ± 0.0001	384			
				0.0422 ± 0.0018	407			
	3.83 ± 0.20		1842 ± 20	0.0521 ± 0.0016	427			
				0.0261 ± 0.0027	381	PR-RA	Gordon and Mulac ²⁰	381-416
				0.0548 ± 0.0017	416			
				0.00651 ± 0.00027	295 ± 2	FP-RA	Overend <i>et al.</i> ²¹	
				0.0095 ± 0.0014	296	DF-LMR	Howard and Evenson ²²	
				0.0088 ± 0.0007	298	FP-RA	Zellner and Steinert ²³	298-892
				0.0148	330			
				0.020	358			
				0.028	381			
				0.061	444			
				0.070	453			
				0.113	498			
				0.174	525			
				0.257	564			
				0.251 ± 0.033	576			
				0.276 ± 0.033	584			
				0.335	622			
				0.551	629			
				0.822	671			
				0.830	680			
				1.12	738			
				1.21	756			
				1.51	776			
	$5.76^{+1.17}_{-0.98} \times 10^{-9}$	3.08	1010	2.71	892			
			1804 ± 120 (300-500 K)					
				0.0063 ± 0.0008	296 ± 2	RR [relative to $k(\text{H}_2)$ $= 6.05 \times 10^{-15}\text{a}$]	Cox <i>et al.</i> ²⁴	
				9.6	1300	RR [relative to $k(\text{H}_2)$ $= 5.69 \times 10^{-12}\text{a}$]	Bradley <i>et al.</i> ²⁵	
				3.82	1140	SH/FP-RA	Ernst <i>et al.</i> ²⁶	1140-1505
				3.82	1160			
				4.48	1165			
				3.49	1188			
				3.49	1192			
				4.82	1203			
				4.15	1220			
				3.82	1245			
				3.99	1260			

TABLE 1. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with alkanes — Continued

Alkane	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	n	B (K)	$10^{12} \times k$ (cm^3 $\text{molecule}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
				4.15	1260			
				3.49	1265			
				4.48	1270			
				4.65	1270			
				3.82	1275			
				3.99	1275			
				3.99	1303			
				4.32	1313			
				5.65	1335			
				5.31	1404			
				5.15	1410			
				4.48	1415			
				5.65	1500			
				5.31	1505			
				0.0070 ± 0.00067	296	FP-RA (of CH_3) with computer modeling	Sworski <i>et al.</i> ²⁷	
				0.00750 ± 0.00060	298	FP-RF	Tully and Ravishankara ²⁸	298–1020
				0.0473 ± 0.0045	398			
				0.081 ± 0.011	448			
				0.145 ± 0.012	511			
				0.167 ± 0.006	529			
				0.314 ± 0.040	600			
				0.275 ± 0.044	619			
				0.578 ± 0.058	696			
				0.84 ± 0.15	772			
				1.50 ± 0.15	915			
	1.32×10^{-5}	1.92	1355	2.00 ± 0.20	1020			
				0.00766 ± 0.00064	300	FP-RF	Husain <i>et al.</i> ²⁹	
				1.25 ± 0.45	830 ± 50	LH-LIF	Fairchild <i>et al.</i> ³⁰	830–1400
				1.3 ± 0.4	1030 ± 50			
				4.3 ± 1.0	1400 ± 50			
				0.00557 ± 0.00054	269	DF-RF	Jeong and Kaufman ^{31,32}	269–473
				0.00789 ± 0.00049	297			
				0.0178 ± 0.0012	339			
				0.0347 ± 0.0023	389			
				0.0549 ± 0.0035	419			
	1.28×10^{-12}	4.23	453 ± 775	0.102 ± 0.007	473			
	5.26 ± 0.88		1917 ± 60					
				0.0392 ± 0.0033	413	RR [relative to $k(\text{CO})$ $= 1.12 \times 10^{-13} e^{0.000907/T}$] ^a	Baulch <i>et al.</i> ³³	413–693
				0.0555 ± 0.0033	417			
				0.0369 ± 0.0030	422			
				0.0654 ± 0.0066	443			
				0.0792 ± 0.0073	471			
				0.0981 ± 0.0063	505			
				0.103 ± 0.018	517			
				0.0936 ± 0.0179	521			
				0.112 ± 0.006	546			
				0.165 ± 0.004	553			
				0.267 ± 0.015	603			
				0.349 ± 0.020	663			
				0.589 ± 0.060	693			
				0.00650	298	PR-RA	Jonah <i>et al.</i> ³⁴	298–1229
				0.00846	298			
				0.0189	348			
				0.0351	373			
				0.106	398			
				0.0938	415			

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

Alkane	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	n	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
				0.175	424			
				0.124	450			
				0.209	483			
				0.174	483			
				0.336	543			
				0.584	571			
				0.545	613			
				0.760	667			
				0.893	709			
				0.991	712			
				1.04	769			
				1.52	858			
				2.48	873			
				2.27	974			
				2.01	974			
				4.50	1071			
				3.22	1125			
				4.19	1125			
				4.93	1229			
				0.0085 ± 0.0006	298 ± 3	FP-RF	Madronich and Felder ³⁵	298-1512
				0.0228 ± 0.0043	362 ± 10			
				0.0463 ± 0.0034	407 ± 5			
				0.0629 ± 0.009	410 ± 14			
				0.154 ± 0.014	510 ± 10			
				0.177 ± 0.017	525 ± 10			
				0.202 ± 0.010	546 ± 5			
				0.439 ± 0.038	626 ± 16			
				0.478 ± 0.07	698 ± 22			
				1.48 ± 0.08	900 ± 12			
				2.12 ± 0.23	967 ± 35			
				2.16 ± 0.11	1005 ± 15			
				2.72 ± 0.15	1103 ± 17			
				3.34 ± 0.20	1164 ± 17			
				2.41 ± 0.22	1174 ± 22			
				3.18 ± 0.17	1176 ± 17			
				3.89 ± 0.25	1196 ± 17			
				4.26 ± 0.39	1196 ± 37			
				3.77 ± 0.32	1238 ± 18			
				3.68 ± 0.23	1244 ± 17			
				3.58 ± 0.27	1261 ± 23			
				3.80 ± 0.37	1261 ± 18			
				4.74 ± 0.20	1300 ± 18			
				4.20 ± 0.21	1307 ± 18			
				4.84 ± 0.50	1314 ± 23			
				5.32 ± 0.31	1345 ± 18			
				5.61 ± 0.34	1365 ± 19			
				6.44 ± 0.53	1396 ± 19			
				5.98 ± 0.69	1455 ± 20			
				6.52 ± 1.15	1510 ± 20			
				6.74 ± 0.35	1512 ± 20			
				3	1220	SH-RA	Cohen and Bott ³⁶	
				1.25 ± 0.6	830	LH-LIF	Smith <i>et al.</i> ³⁷	830-1412
				2.25 ± 1.0	870			
				1.55 ± 0.7	930			
				2.0 ± 1.0	966			
				2.1 ± 1.2	975			
				1.33 ± 0.5	1030			
				3.6 ± 0.9	1120			
				1.7 ± 0.7	1150			
				2.35 ± 0.7	1176			
				3.3 ± 1.0	1200			
	$2.6^{+9.7}_{-2.1} \times 10^{-5}$	1.83	1396 ± 134					

TABLE 1. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with alkanes — Continued

Alkane	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	n	B (K)	$10^{12} \times k$ (cm^3 $\text{molecule}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
				2.9 ± 0.35	1240			
				4.4 ± 0.8	1400			
				4.2 ± 0.8	1412			
Methane- ^{13}C				0.00833	c	RR [relative to $k(\text{CH}_4)$ $= 8.36 \times 10^{-15}]^d$	Rust and Stevens ³⁸	
				0.00810 ± 0.00006	297 ± 3	RR [relative to $k(\text{CH}_4)$ $= 8.18 \times 10^{-15}]^d$	Davidson <i>et al.</i> ³⁹	
Methane- d_1				0.0365 ± 0.0017	416	PR-RA	Gordon and Mulac ²⁰	
Methane- d_2				0.0299 ± 0.0017	416	PR-RA	Gordon and Mulac ²⁰	
Methane- d_3				0.0111 ± 0.0005	416	PR-RA	Gordon and Mulac ²⁰	
Methane- d_4				0.0050 ± 0.0002	416	PR-RA	Gordon and Mulac ²⁰	
Ethane				14.0	813	RR [relative to $k(\text{H}_2)$ $= 1.12 \times 10^{-12}]^a$	Baldwin and Simmons ⁴⁰	
				11.9	1420	RR [relative to $k(\text{CO})$ $= 1.12 \times 10^{-13} e^{0.0009077/T}]^a$	Fenimore and Jones ⁴¹	1420–1610
				13.4	1440			
				16.3	1600			
				16.3	1600			
				19.3	1610			
				~ 4.5	1300–1550	RR [relative to $k(\text{CO})$ $= 1.12 \times 10^{-13} e^{0.0009077/T}]^a$	Westenberg and Fristrom ⁴²	1300–1550
210^{+840}_{-170}			1812 ± 302	0.478	298	FP-KS	Horne and Norrish ¹²	298–423
				0.292 ± 0.038	302 ± 2	FP-KS	Greiner ⁴³	
				≤ 1.0	300	DF-EPR	Wilson and Westenberg ¹⁰	
				6.8	734	RR [relative to $k(\text{CH}_4)$ $= 6.95 \times 10^{-18} T^2$ $e^{-1282/T}]^d$	Hoare and Patel ⁴⁴	734–798
				7.9	773			
				10.7	798			
				5.26	773	RR [relative to $k(\text{H}_2)$ $= 9.22 \times 10^{-13}]^a$	Baldwin <i>et al.</i> ⁴⁵ Baldwin and Walker ⁴⁶	
				0.310 ± 0.007	297	FP-KS	Greiner ¹⁴	297–493
				0.340 ± 0.010	298			
				0.282 ± 0.007	299			
				0.239 ± 0.013	299			
				0.304 ± 0.035	300			
				0.224 ± 0.042	301			
				0.457 ± 0.010	335			
				0.750 ± 0.050	369			
				0.936 ± 0.058	424			
$18.6^{+3.3}_{-2.7}$			1232 ± 53	1.55 ± 0.033	493			
				0.664 ± 0.033	381	PR-RA	Gordon and Mulac ²⁰	381–416
				0.797 ± 0.050	416			
				3.74 ± 1.2	653	RR [relative to $k(\text{CH}_4)$ $= 4.16 \times 10^{-13}]^d$	Hucknall <i>et al.</i> ⁴⁷	
				0.264 ± 0.017	295 ± 2	FP-RA	Overend <i>et al.</i> ²¹	
				0.290 ± 0.060	296	DF-LMR	Howard and Evenson ⁴⁸	

TABLE 1. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with alkanes — Continued

Alkane	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	n	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
				27.8	1300	RR [relative to $k(\text{H}_2)$ $= 5.69 \times 10^{-12}]^a$	Bradley <i>et al.</i> ²⁵	
				0.26 ± 0.04	298	DF-RF	Leu ⁴⁹	
				0.112 ± 0.018	250	DF-RF	Anderson and Stephens ⁵⁰	250–364
				0.176 ± 0.022	275			
				0.257 ± 0.031	298			
				0.349 ± 0.051	322			
	16.4 ± 2.6		1245 ± 46	0.526 ± 0.080	364			
				0.231 ± 0.040	295 ± 1	DF-RF	Lee and Tang ⁵¹	
				0.080	238	LP-RF	Margitan and Watson ⁵²	
				0.259 ± 0.021	297	FP-RF	Tully <i>et al.</i> ⁵³	297–800
				0.771 ± 0.076	400			
				1.58 ± 0.10	499			
				2.61 ± 0.33	609			
				3.65 ± 0.25	697			
	1.43×10^{-2}	1.05	911	5.07 ± 0.34	800			
				0.679 ± 0.048	403	RR [relative to $k(\text{CO})$ $= 1.12 \times 10^{-13} e^{0.000907T}]^a$	Baulch <i>et al.</i> ³³	403–683
				1.21 ± 0.12	443			
				1.30 ± 0.09	493			
				2.51 ± 0.18	561			
				2.26 ± 0.25	595			
				4.47 ± 0.51	683			
				0.196 ± 0.013	248	DF-RF	Jeong <i>et al.</i> ³²	248–472
				0.228 ± 0.014	273			
				0.310 ± 0.020	294			
				0.306 ± 0.021	298			
				0.426 ± 0.027	333			
				0.403 ± 0.027	333			
				0.538 ± 0.035	375			
				0.529 ± 0.034	375			
				0.799 ± 0.054	428			
				0.770 ± 0.048	429			
				0.993 ± 0.068	464			
	3.87×10^{-9}	3.09	-171 ± 342	1.03 ± 0.067	472			
	6.11 ± 0.60		886 ± 35					
	16.1		1173	0.324	300	PR-RA	Nielsen <i>et al.</i> ⁵⁴	~300–400
				0.105 ± 0.004	240	FP-RF	Smith <i>et al.</i> ⁵⁵	240–295
				0.137 ± 0.006	251			
				0.205 ± 0.009	273			
	18.0 ± 2.5		1240 ± 110	0.263 ± 0.010	295			
				0.275	295	DF-RF	Devolder <i>et al.</i> ⁵⁶	
				0.22 ± 0.03	295	LP-LIF	Schmidt <i>et al.</i> ⁵⁷	
				0.267 ± 0.040	295 ± 2	DF-RF	Baulch <i>et al.</i> ⁵⁸	
				0.239 ± 0.010	292.5	LP-LIF	Tully <i>et al.</i> ⁵⁹	293–705
				0.407 ± 0.017	340			
				0.651 ± 0.027	396			
				1.15 ± 0.048	478			
				1.23 ± 0.051	484			
				2.01 ± 0.083	577			
				2.11 ± 0.088	586			
	8.51×10^{-6}	2.06	430	3.48 ± 0.144	705			

TABLE 1. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with alkanes — Continued

Alkane	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	n	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
Ethane- d_3 (CH_3CD_3)	8.4 ± 3.1	2.38	1050 ± 100	0.298 ± 0.021	295	PR-RA	Nielsen <i>et al.</i> ⁶⁰	
				0.127 ± 0.008	248	LP-RA	Stachnik <i>et al.</i> ⁶¹	248–297
				0.129 ± 0.009	248			
				0.251 ± 0.006	297			
				0.250 ± 0.006	297			
				0.32 ± 0.06	296	RR [relative to $k(\text{propane}) = 1.13 \times 10^{-12}$] ^d	Edney <i>et al.</i> ⁶²	
				0.277 ± 0.03	296 ± 2	DF-RF	Bourmada <i>et al.</i> ⁶³	
				0.088 ± 0.013	226	FP-RF	Wallington <i>et al.</i> ⁶⁴	226–363
				0.107 ± 0.010	241			
				0.162 ± 0.018	261			
				0.230 ± 0.026	296			
				0.487 ± 0.055	363			
				0.261 ± 0.013	296	LP-LIF	Zabarnick <i>et al.</i> ⁶⁵	
				0.142 ± 0.007	293	LP-LIF	Tully <i>et al.</i> ⁵⁹	293–705
				0.250 ± 0.011	338			
0.419 ± 0.018	396							
0.794 ± 0.033	478							
1.52 ± 0.063	586							
2.65 ± 0.110	705							
Ethane- d_6 (C_2D_6)	7.65×10^{-7}	2.38	411	0.0523 ± 0.0060	293	LP-LIF	Tully <i>et al.</i> ⁵⁹	293–705
				0.105 ± 0.007	339.5			
				0.199 ± 0.010	396			
				0.435 ± 0.020	478			
				0.965 ± 0.041	586			
				1.83 ± 0.077	705			
Propane	$12.0^{+1.5}_{-1.3}$	2.56	679 \pm 38	27.5	793	RR [relative to $k(\text{H}_2) = 1.02 \times 10^{-12}$] ^a	Baldwin ⁶⁶	
				1.37 ± 0.21	298 ± 1	FP-KS	Greiner ⁴³	
				8.23	753	RR [relative to $k(\text{H}_2) = 8.31 \times 10^{-13}$] ^a	Baker <i>et al.</i> , ⁶⁷ Baldwin and Walker ⁴⁶	
				1.21 ± 0.08	296	FP-KS	Greiner ¹⁴	296–497
				1.26 ± 0.14	298			
				1.19 ± 0.04	298			
				1.01 ± 0.03	299			
				1.10 ± 0.05	299			
				1.30 ± 0.02	299			
				1.30 ± 0.13	299			
				1.44 ± 0.04	335			
				1.91 ± 0.05	375			
				2.19 ± 0.07	423			
				2.92 ± 0.12	497			
				3.19 ± 0.15	497			
				3.15 ± 0.07	497			
				2.97 ± 0.15	497			
				3.39 ± 0.15	497			
				0.83 ± 0.17	300	DF-EPR	Bradley <i>et al.</i> ⁶⁸	
				2.1 ± 0.6	298	RR [relative to $k(\text{CO}) = 1.49 \times 10^{-13}$] ^a	Gorse and Volman ⁶⁹	

TABLE 1. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with alkanes — Continued

Alkane	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	n	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
				2.16 ± 0.10	381	PR-RA	Gordon and Mulac ²⁰	381–416
				1.91 ± 0.08	416			
				5.3 ± 0.8	613	RR [relative to $k(\text{ethane}) = 1.42$ $\times 10^{-17} T^2 e^{-462/T}]^d$	Hucknall <i>et al.</i> ⁴⁷	613–653
				6.5	653			
				2.02 ± 0.11	295 ± 2	FP-RA	Overend <i>et al.</i> ²¹	
				1.98 ± 0.08	329 ± 5	MPS	Harker and Burton ⁷⁰	
				1.49 ± 0.21	300 ± 1	RR [relative to $k(n\text{-butane}) = 2.56$ $\times 10^{-12}]^d$	Darnall <i>et al.</i> ⁷¹	
				2.0	300	RR [relative to $k(\text{ethene}) = 8.44$ $\times 10^{-12}]^d$	Cox <i>et al.</i> ⁷²	
				0.686 ± 0.107	253	DF-RF	Anderson and Stephens ⁵⁰	253–365
				0.879 ± 0.123	273			
				0.929 ± 0.121	297			
				1.126 ± 0.163	329			
				1.409 ± 0.195	365			
	6.21 ± 2.37		552 ± 113					
				1.21 ± 0.05	299 ± 2	RR [relative to $k(n\text{-butane}) = 2.55$ $\times 10^{-12}]^d$	Atkinson <i>et al.</i> ⁷³	
				1.05 ± 0.04	297	FP-RF	Tully <i>et al.</i> ⁵³	297–690
				1.48 ± 0.06	326			
				2.51 ± 0.20	378			
				3.37 ± 0.23	469			
				4.78 ± 0.34	554			
	1.59×10^{-3}	1.40	428	8.78 ± 0.97	690			
				1.91 ± 0.15	428	RR [relative to $k(\text{CO})$ $= 1.12 \times 10^{-13} e^{0.000907/T}]^a$	Baulch <i>et al.</i> ³³	428–696
				2.81 ± 0.23	489			
				2.84 ± 0.08	538			
				4.02 ± 0.22	589			
				4.77 ± 0.51	641			
				7.11 ± 0.68	696			
				26.2 ± 6.7	1220 ± 15	SH-RA	Bott and Cohen ⁷⁴	
				21.9 ± 6.0	1074	LH-LIF	Smith <i>et al.</i> ³⁷	
				1.0 ± 0.2	295	LP-LIF	Schmidt <i>et al.</i> ⁵⁷	
				1.20 ± 0.18	295 ± 2	DF-RF	Baulch <i>et al.</i> ⁵⁸	
				1.10 ± 0.04	293	LP-LIF	Droege and Tully ⁷⁵	293–854
				1.52 ± 0.06	342			
				1.61 ± 0.07	351.5			
				2.14 ± 0.09	401			
				2.49 ± 0.10	428			
				3.24 ± 0.13	491			
				3.36 ± 0.14	501.5			
				3.34 ± 0.14	505			
				4.84 ± 0.20	602			
				4.84 ± 0.20	603			
				7.28 ± 0.30	732			
	1.04×10^{-4}	1.72	145	9.31 ± 0.38	854			

TABLE 1. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with alkanes — Continued

Alkane	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	n	B (K)	$10^{12} \times k$ (cm^3 mole $^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Tempera- ture range covered (K)
				1.14 ± 0.15	296	RR [relative to $k(n\text{-butane}) = 2.51$ $\times 10^{-12}]^d$	Edney <i>et al.</i> ⁶²	
				1.38	300 ± 3	RR [relative to $k(n\text{-butane}) = 2.56$ $\times 10^{-12}]^d$	Behnke <i>et al.</i> ⁷⁶	
				1.27 ± 0.11	295 ± 2	PR-RA	Nielsen <i>et al.</i> ⁷⁷	
				1.27 ± 0.09	300	RR [relative to $k(\text{series of organics})]^c$	Behnke <i>et al.</i> ⁷⁸	
Propane- d_2 ($\text{CH}_3\text{CD}_2\text{CH}_3$)				0.610 ± 0.028	295	LP-LIF	Droege and Tully ⁷⁵	295–854
				0.802 ± 0.034	328.5			
				1.20 ± 0.05	376.5			
				1.72 ± 0.07	437.2			
				2.47 ± 0.10	503.5			
				3.79 ± 0.16	603			
				5.92 ± 0.24	732			
	2.02×10^{-4}	1.63	383	7.86 ± 0.32	854			
Propane- d_3 ($\text{CH}_3\text{CH}_2\text{CD}_3$)				0.984 ± 0.050	295	LP-LIF	Droege and Tully ⁷⁵	295–854
				1.28 ± 0.06	328.5			
				1.62 ± 0.07	376.5			
				2.17 ± 0.09	437.2			
				2.88 ± 0.12	503.5			
				4.19 ± 0.18	603			
				6.20 ± 0.26	728			
	2.26×10^{-5}	1.90	40	8.06 ± 0.34	854			
Propane- d_5 ($\text{CH}_3\text{CD}_2\text{CD}_3$)				0.478 ± 0.021	295	LP-LIF	Droege and Tully ⁷⁵	295–840
				0.621 ± 0.026	328.5			
				0.950 ± 0.040	376.5			
				1.38 ± 0.06	437.2			
				1.96 ± 0.08	503.5			
				3.13 ± 0.13	603			
				4.93 ± 0.20	728			
	2.59×10^{-5}	1.91	303	6.60 ± 0.27	840			
Propane- d_6 ($\text{CD}_3\text{CH}_2\text{CD}_3$)				0.826 ± 0.040	295	LP-LIF	Droege and Tully ⁷⁵	295–840
				0.999 ± 0.045	328.5			
				1.37 ± 0.06	376.5			
				1.79 ± 0.08	437.2			
				2.46 ± 0.10	503.5			
				3.55 ± 0.15	603			
				5.31 ± 0.22	728			
	1.03×10^{-5}	2.00	23	6.78 ± 0.28	840			
Propane- d_8 (C_3D_8)				0.408 ± 0.045	295	LP-LIF	Droege and Tully ⁷⁵	295–854
				0.527 ± 0.043	328.5			
				0.746 ± 0.047	376.5			
				1.09 ± 0.06	437.2			
				1.50 ± 0.07	503.5			
				2.55 ± 0.11	603			
				4.25 ± 0.18	732			
	2.36×10^{-7}	2.53	15	5.88 ± 0.25	854			
<i>n</i> -Butane				36.7	793	RR [relative to $k(\text{H}_2)$ $= 1.02 \times 10^{-12}]^a$	Baldwin and Walker ⁷⁹	
				11.0	753	RR [relative to $k(\text{H}_2)$ $= 8.31 \times 10^{-13}]^a$	Baker <i>et al.</i> , ⁶⁷ Baldwin and Walker ⁴⁶	

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

Alkane	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	n	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)					
	$14.1^{+4.1}_{-3.1}$		524 ± 93	2.56 ± 0.08	298	FP-KS	Greiner ¹⁴	298–495					
				2.59 ± 0.22	301								
				2.79 ± 0.32	336								
				2.96 ± 0.10	373								
				4.85 ± 0.18	425								
				4.12 ± 0.15	428								
				4.90 ± 0.17	495								
				4.1	298				DF-MS	Morris and Niki ⁸⁰			
				2.35 ± 0.35	298				FP-RF	Stuhl ⁸¹			
				2.9 ± 0.7	298				RR [relative to $k(\text{CO})$ $= 1.49 \times 10^{-13}]^a$	Gorse and Volman ⁶⁹			
				4.22 ± 0.17	298				PR-RA	Gordon and Mulac ²⁰	298–416		
				4.15 ± 0.17	381								
				4.98 ± 0.17	416								
	17.6		559 ± 151	9.21 ± 0.78	653	RR [relative to $k(\text{propane})$ $= 5.98 \times 10^{-12}]^d$	Hucknall <i>et al.</i> ⁴⁷						
				2.34 ± 0.15	292 ± 2	RR [relative to $k(\text{CO})$ $= 1.58 \times 10^{-13}]^a$	Campbell <i>et al.</i> ⁸²						
				2.72 ± 0.27	297.7	FP-RF	Perry <i>et al.</i> ⁸³	298–420					
				3.54 ± 0.35	351.0								
				4.69 ± 0.47	419.6	FP-RA	Paraskevopoulos and Nip ⁸⁴						
				2.67 ± 0.22	297 ± 2								
				2.52 ± 0.25	299 ± 2			RR [relative to $k(\text{propene})$ $= 2.62 \times 10^{-11}]^d$	Atkinson <i>et al.</i> ⁸⁵				
					8.17 ± 4.03		443 ± 143	1.46 ± 0.22	250	DF-RF	Anderson and Stephens ⁵⁰	250–365	
								1.63 ± 0.21	274				
								1.68 ± 0.23	297				
2.10 ± 0.34	329												
2.57 ± 0.38	365	RR [relative to $k(\text{propene})$ $= 2.68 \times 10^{-11}]^d$	Atkinson and Aschmann ⁸⁶										
2.71 ± 0.32	295 ± 1												
2.3 ± 0.3	295							LP-LIF	Schmidt <i>et al.</i> ⁵⁷				
2.42 ± 0.10	294							LP-LIF	Droege and Tully ⁸⁷	294–509			
2.95 ± 0.12	332												
3.53 ± 0.15	377												
	2.34×10^{-5}	1.95	–134	4.56 ± 0.19	439	RR [relative to $k(\text{ethene})$ $= 8.44 \times 10^{-12}]^d$	Barnes <i>et al.</i> ⁸⁸						
				5.84 ± 0.25	509								
				2.70 ± 0.34	300								
				2.53 ± 0.04	300			RR [relative to $k(n\text{-octane})$ $= 8.76 \times 10^{-12}]^d$	Behnke <i>et al.</i> ⁸⁹				
				<i>n</i> -Butane- d_{10}						0.697 ± 0.068	297 ± 2	FP-RA	Paraskevopoulos and Nip ⁸⁴

TABLE 1. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with alkanes — Continued

Alkane	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	n	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Tempera- ture range covered (K)
				0.893 ± 0.037	294	LP-LIF	Droege and Tully ⁸⁷	294-599
				1.13 ± 0.05	332			
				1.49 ± 0.06	377			
				2.07 ± 0.09	439			
				2.87 ± 0.12	509			
	2.92×10^{-6}	2.20	-33	3.98 ± 0.17	599			
2-Methylpropane				20.4	793	RR [relative to $k(\text{H}_2)$ $= 1.02 \times 10^{-12}]^a$	Baldwin and Walker ⁷⁹	
				2.13 ± 0.12	297 ± 1	FP-KS	Greiner ⁴³	
				10.5	753	RR [relative to $k(\text{H}_2)$ $= 8.31 \times 10^{-13}]^a$	Baker <i>et al.</i> , ⁶⁷ Baldwin and Walker ⁴⁶	
				2.14 ± 0.12	297	FP-KS	Greiner ¹⁴	297-498
				2.22 ± 0.05	297			
				2.67 ± 0.17	298			
				2.56 ± 0.05	304			
				2.69 ± 0.15	305			
				3.01 ± 0.07	338			
				2.87 ± 0.07	371			
				3.04 ± 0.13	374			
				3.57 ± 0.15	425			
	$8.7^{+1.8}_{-1.5}$		387 ± 63	4.25 ± 0.22	498			
				3.5 ± 0.9	298	RR [relative to $k(\text{CO})$ $= 1.49 \times 10^{-13}]^a$	Gorse and Volman ^{69,90}	
				7.65 ± 0.42	653	RR [relative to $k(\text{propane}) = 5.98$ $\times 10^{-12}]^d$	Hucknall <i>et al.</i> ⁴⁷	
				2.2	303	RR [relative to $k(\text{cis-2-butene})$ $= 5.49 \times 10^{-11}]^d$	Wu <i>et al.</i> ⁹¹	
				2.2^f	305	RR [relative to $k(\text{CO})$ $= 1.59 \times 10^{-13}]^a$	Butler <i>et al.</i> ⁹²	
				2.36 ± 0.05	300 ± 1	RR [relative to $k(n\text{-butane}) = 2.56$ $\times 10^{-12}]^d$	Darnall <i>et al.</i> ⁷¹	
				1.31 ± 0.19	251	DF-RF	Anderson and Stephens ⁵⁰	251-360
				1.46 ± 0.19	274			
				1.73 ± 0.25	299			
				1.95 ± 0.25	326			
	7.67 ± 1.12		448 ± 42	2.21 ± 0.39	360			
				2.70 ± 0.20	267	DF-RF	Trevor <i>et al.</i> ⁹³	267-324
				3.6	298			
				3.62 ± 0.40	324			
				2.24 ± 0.06	297 ± 2	RR [relative to $k(n\text{-butane}) = 2.53$ $\times 10^{-12}]^d$	Atkinson <i>et al.</i> ⁹⁴	
				1.83 ± 0.34	296	LP-LMR	Böhland <i>et al.</i> ⁹⁵	
				1.9 ± 0.3	295	LP-LIF	Schmidt <i>et al.</i> ⁵⁷	
				2.19 ± 0.11	293	LP-LIF	Tully <i>et al.</i> ⁹⁶	293-864
				2.59 ± 0.13	342			

TABLE 1. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with alkanes — Continued

Alkane	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	n	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Tempera- ture range covered (K)
				3.21 ± 0.16	403			
				3.49 ± 0.17	424			
				4.03 ± 0.20	470			
				4.58 ± 0.23	509.5			
				5.49 ± 0.27	574			
				7.40 ± 0.37	705			
	4.31×10^{-5}	1.80	-175	10.13 ± 0.51	864			
				2.35 ± 0.34	298	RR [relative to $k(n\text{-butane}) = 2.54$ $\times 10^{-12}]^d$	Edney <i>et al.</i> ⁶²	
2-Methylpropane- d_9 [[$(\text{CD}_3)_3\text{CH}$]				1.70 ± 0.09	293.5	LP-LIF	Tully <i>et al.</i> ⁹⁶	294-864
				1.91 ± 0.10	343			
				2.27 ± 0.11	403			
				2.81 ± 0.14	471			
				3.64 ± 0.18	574			
				5.28 ± 0.26	705			
	1.08×10^{-7}	2.57	-569	7.61 ± 0.38	864			
2-Methylpropane- d_1 [[$(\text{CH}_3)_3\text{CD}$]				1.36 ± 0.07	293.5	LP-LIF	Tully <i>et al.</i> ⁹⁶	294-864
				1.81 ± 0.09	344			
				2.44 ± 0.12	403			
				3.35 ± 0.17	473			
				4.84 ± 0.24	574			
				7.12 ± 0.36	705			
	1.20×10^{-4}	1.69	85	9.90 ± 0.49	864			
2-Methylpropane- d_{10} [[$(\text{CD}_3)_3\text{CD}$]				0.956 ± 0.067	293.5	LP-LIF	Tully <i>et al.</i> ⁹⁶	294-864
				1.21 ± 0.08	340.5			
				1.58 ± 0.09	403			
				2.10 ± 0.12	473			
				3.09 ± 0.15	574			
				4.92 ± 0.25	705			
	9.12×10^{-8}	2.63	-352	7.30 ± 0.37	864			
n -Pentane				15.0	753	RR [relative to $k(\text{H}_2)$ $= 8.31 \times 10^{-13}]^a$	Baldwin and Walker ⁴⁶	
				6.6	303	RR [relative to $k(\text{cis-2-butene}) = 5.49$ $\times 10^{-11}]^d$	Wu <i>et al.</i> ⁹¹	
				3.51 ± 0.13	300 ± 1	RR [relative to $k(n\text{-butane}) = 2.56$ $\times 10^{-12}]^d$	Darnall <i>et al.</i> ⁷¹	
				5.3	300	RR [relative to $k(\text{ethene})$ $= 8.44 \times 10^{-12}]^d$	Cox <i>et al.</i> ⁷²	
				4.1	300	RR [relative to $k(\text{ethene})$ $= 8.44 \times 10^{-12}]^d$	Barnes <i>et al.</i> ⁹⁷	
				4.08 ± 0.08	299 ± 2	RR [relative to $k(n\text{-butane})$ $= 2.55 \times 10^{-12}]^d$	Atkinson <i>et al.</i> ⁷³	
				4.16	300 ± 3	RR [relative to $k(n\text{-butane})$ $= 2.56 \times 10^{-12}]^d$	Behnke <i>et al.</i> ⁷⁶	

TABLE 1. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with alkanes — Continued

Alkane	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	n	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
				4.27 ± 0.16	312	RR [relative to $k(n\text{-heptane}) = 7.48 \times 10^{-12}]^d$	Nolting <i>et al.</i> ⁹⁸	
				4.12 ± 0.05	300	RR [relative to $k(n\text{-octane}) = 8.76 \times 10^{-12}]^d$	Behnke <i>et al.</i> ⁸⁹	
				2.88 ± 0.37	243	RR [relative to $k(2\text{-methylpropane}) = 1.04 \times 10^{-17} T^2 e^{277/T}]^d$	Harris and Kerr ⁹⁹	243–325
				2.95 ± 0.23	263			
				3.40 ± 0.33	273			
				4.05 ± 0.19	298			
				4.34 ± 0.40	314			
				4.77 ± 0.21	325			
				3.58 ± 0.82	247	RR [relative to $k(n\text{-butane}) = 1.51 \times 10^{-17} T^2 e^{190/T}]^d$	Harris and Kerr ⁹⁹	247–327
				3.14 ± 0.37	253			
				3.25 ± 0.28	263			
				3.37 ± 0.21	273			
				3.60 ± 0.28	275			
				3.61 ± 0.22	282			
				4.25 ± 0.15	295			
				4.22 ± 0.37	305			
				4.01 ± 0.36	314			
				4.49 ± 0.12	325			
				4.42 ± 0.35	327			
				4.09 ± 0.08	300	RR [relative to $k(\text{series of organics})]^c$	Behnke <i>et al.</i> ⁷⁸	
2-Methylbutane				2.9 ± 0.6	305 ± 2	RR [relative to $k(n\text{-butane}) = 2.62 \times 10^{-12}]^d$	Lloyd <i>et al.</i> ¹⁰⁰	
				3.54 ± 0.07	300 ± 1	RR [relative to $k(n\text{-butane}) = 2.56 \times 10^{-12}]^d$	Darnall <i>et al.</i> ⁷¹	
				3.7	300	RR [relative to $k(\text{ethene}) = 8.44 \times 10^{-12}]^d$	Cox <i>et al.</i> ⁷²	
				3.90 ± 0.11	297 ± 2	RR [relative to $k(n\text{-butane}) = 2.53 \times 10^{-12}]^d$	Atkinson <i>et al.</i> ⁹⁴	
2,2-Dimethylpropane				13.3	753	RR [relative to $k(\text{H}_2) = 8.31 \times 10^{-13}]^a$	Baker <i>et al.</i> ⁶⁷	
				0.740 ± 0.020	292	FP-KS	Greiner ¹⁴	292–493
				0.858 ± 0.038	292			
				0.875 ± 0.025	298			
				1.16 ± 0.08	335			
				1.41 ± 0.04	370			
				2.11 ± 0.10	424			
	$14.1^{+2.1}_{-1.8}$		844 ± 44	2.54 ± 0.08	493			
				8.48	753			
				0.98 ± 0.16	300 ± 1	RR [relative to $k(n\text{-butane}) = 2.56 \times 10^{-12}]^d$	Darnall <i>et al.</i> ⁷¹	

TABLE 1. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with alkanes — Continued

Alkane	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	n	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Tempera- ture range covered (K)
				0.91 ± 0.10	297 ± 2	FP-RA	Paraskevopoulos and Nip ⁸⁴	
				0.76 ± 0.05	299 ± 2	RR [relative to $k(n\text{-butane})$ $= 2.55 \times 10^{-12}]^d$	Atkinson <i>et al.</i> ¹⁰²	
				0.414 ± 0.071	249	DF-RF	Anderson and Stephens ⁵⁰	249–364
				0.460 ± 0.089	271			
				0.533 ± 0.098	296			
				0.772 ± 0.153	327			
				0.987 ± 0.231	364			
	6.0 ± 4.1		684 ± 187					
				0.909 ± 0.115	287	LP-LIF	Tully <i>et al.</i> ^{59,103}	287–901
				1.27 ± 0.14	350			
				2.08 ± 0.19	431			
				3.17 ± 0.25	518			
				4.46 ± 0.38	600			
				7.02 ± 0.67	705			
				10.1 ± 1.1	812			
				12.5 ± 1.5	901			
	8.60×10^{-9}	3.05	–340					
				0.67 ± 0.15	300	RR [relative to $k(\text{series of organics})]^e$	Behnke <i>et al.</i> ⁷⁸	
2,2-Dimethyl- propane- d_{12}				0.180 ± 0.012	290	LP-LIF	Tully <i>et al.</i> ^{59,103}	290–903
				0.375 ± 0.025	352			
				0.728 ± 0.048	430			
				1.30 ± 0.09	508.5			
				2.19 ± 0.17	598			
				3.94 ± 0.34	705			
				5.62 ± 0.55	812			
				8.09 ± 0.89	903			
	1.08×10^{-7}	2.71	307					
n -Hexane				5.5 ± 1.1	305 ± 2	RR [relative to $k(n\text{-butane}) = 2.62$ $\times 10^{-12}]^d$	Lloyd <i>et al.</i> ¹⁰⁰	
				6.0	303	RR [relative to $k(cis\text{-}2\text{-butene})$ $= 5.49 \times 10^{-11}]^d$	Wu <i>et al.</i> ⁹¹	
				5.8 ± 0.4	292	RR [relative to $k(n\text{-butane})$ $= 2.47 \times 10^{-12}]^d$	Campbell <i>et al.</i> ⁸²	
				5.63 ± 0.09	299 ± 2	RR [relative to $k(n\text{-butane}) = 2.55$ $\times 10^{-12}]^d$	Atkinson <i>et al.</i> ¹⁰²	
				5.55 ± 0.20	298 ± 2	RR [relative to $k(\text{propene})$ $= 2.63 \times 10^{-11}]^d$	Atkinson <i>et al.</i> ¹⁰⁴	
				5.31 ± 0.46	295 ± 1	RR [relative to $k(\text{propene})$ $= 2.68 \times 10^{-11}]^d$	Atkinson and Aschmann ⁸⁶	
				5.58 ± 0.55	295	RR [relative to $k(n\text{-butane})$ $= 2.50 \times 10^{-12}]^d$	Klein <i>et al.</i> ¹⁰⁵	

TABLE 1. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with alkanes — Continued

Alkane	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	n	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Tempera- ture range covered (K)
				6.6	300	RR [relative to $k(\text{toluene})$ $= 5.91 \times 10^{-12}]^d$	Klöpffer <i>et al.</i> ¹⁰⁶	
				5.91 ± 0.68	300	RR [relative to $k(\text{ethene}) = 8.44$ $\times 10^{-12}]^d$	Barnes <i>et al.</i> ⁸⁸	
				5.60	300 ± 3	RR [relative to $k(n\text{-butane})$ $= 2.56 \times 10^{-12}]^d$	Behnke <i>et al.</i> ⁷⁶	
				6.2 ± 0.6	312	RR [relative to $k(n\text{-heptane})$ $= 7.48 \times 10^{-12}]^d$	Nolting <i>et al.</i> ⁹⁸	
				5.66 ± 0.04	300	RR [relative to $k(n\text{-octane})$ $= 8.76 \times 10^{-12}]^d$	Behnke <i>et al.</i> ⁸⁹	
2-Methylpentane				4.6 ± 1.0	305 ± 2	RR [relative to $k(n\text{-butane})$ $= 2.62 \times 10^{-12}]^d$	Lloyd <i>et al.</i> ¹⁰⁰	
				5.3	300	RR [relative to $k(\text{ethene})$ $= 8.44 \times 10^{-12}]^d$	Cox <i>et al.</i> ⁷²	
				5.57 ± 0.23	297 ± 2	RR [relative to $k(n\text{-butane})$ $= 2.53 \times 10^{-12}]^d$	Atkinson <i>et al.</i> ⁹⁴	
3-Methylpentane				6.3 ± 1.3	305 ± 2	RR [relative to $k(n\text{-butane})$ $= 2.62 \times 10^{-12}]^d$	Lloyd <i>et al.</i> ¹⁰⁰	
				5.67 ± 0.11	297 ± 2	RR [relative to $k(n\text{-butane})$ $= 2.53 \times 10^{-12}]^d$	Atkinson <i>et al.</i> ⁹⁴	
2,2-Dimethyl- butane				2.61 ± 0.08	297 ± 2	RR [relative to $k(n\text{-butane})$ $= 2.53 \times 10^{-12}]^d$	Atkinson <i>et al.</i> ⁹⁴	
				1.28 ± 0.26	245	RR [relative to $k(n\text{-pentane})$ $= 2.10 \times 10^{-17} T^2 e^{2332/T}]^d$	Harris and Kerr ⁹⁹	245–328
				1.47 ± 0.19	247			
				1.44 ± 0.26	253			
				1.69 ± 0.21	263			
				1.93 ± 0.36	273			
				1.89 ± 0.30	283			
				2.22 ± 0.36	299			
				2.29 ± 0.33	303			
				2.44 ± 0.25	303			
				2.62 ± 0.26	313			
				2.95 ± 0.45	326			
				2.84 ± 0.27	328			
				2.32 ± 0.06	300	RR [relative to $k(\text{series of organics})]^e$	Behnke <i>et al.</i> ⁷⁸	
2,3-Dimethyl- butane				7.45 ± 0.22	300	FP-KS	Greiner ¹⁴	300–498
				6.71 ± 0.22	336			
				6.81 ± 0.35	372			
				7.11 ± 0.65	424			

TABLE 1. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with alkanes — Continued

Alkane	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	n	B (K)	$10^{12} \times k$ (cm^3 $\text{molecule}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
	$4.8^{+1.1}_{-0.9}$		-129 ± 67	5.94 ± 1.25	498			
				4.9 ± 1.0	305 ± 2	RR [relative to $k(2\text{-methylpropene})$ $= 4.94 \times 10^{-11}]^d$	Darnall <i>et al.</i> ¹⁰⁷	
				5.32 ± 0.28	300 ± 1	RR [relative to $k(n\text{-butane})$ $= 2.56 \times 10^{-12}]^d$	Darnall <i>et al.</i> ⁷¹	
				4.0	300	RR [relative to $k(\text{ethene}) = 8.44$ $\times 10^{-12}]^d$	Cox <i>et al.</i> ⁷²	
				6.18 ± 0.05	299 ± 2	RR [relative to $k(n\text{-butane})$ $= 2.55 \times 10^{-12}]^d$	Atkinson <i>et al.</i> ¹⁰²	
				6.95 ± 1.20	247	RR [relative to $k(n\text{-butane}) = 1.51$ $\times 10^{-17} T^2 e^{190/T}]^d$	Harris and Kerr ⁹⁹	247–327
				5.66 ± 1.21	253			
				6.02 ± 0.69	263			
				5.72 ± 0.95	273			
				5.75 ± 1.17	275			
				5.78 ± 0.36	282			
				5.90 ± 0.23	295			
				5.95 ± 0.42	305			
				4.94 ± 0.77	314			
				5.98 ± 0.12	325			
				5.75 ± 0.53	327			
<i>n</i> -Heptane				7.21 ± 0.16	299 ± 2	RR [relative to $k(n\text{-butane})$ $= 2.55 \times 10^{-12}]^d$	Atkinson <i>et al.</i> ⁷³	
				8.2	300	RR [relative to $k(\text{toluene}) = 5.91$ $\times 10^{-12}]^d$	Klöpffer <i>et al.</i> ¹⁰⁶	
				7.10	300 ± 3	RR [relative to $k(n\text{-butane})$ $= 2.56 \times 10^{-12}]^d$	Behnke <i>et al.</i> ⁷⁶	
				7.29 ± 0.08	300	RR [relative to $k(n\text{-octane})$ $= 8.76 \times 10^{-12}]^d$	Behnke <i>et al.</i> ⁸⁹	
				7.28 ± 0.08	300	RR [relative to k (series of organics)] ^c	Behnke <i>et al.</i> ⁷⁸	
2,2-Dimethyl- pentane				3.37 ± 0.03	300	RR [relative to $k(\text{series of organics})]^\text{c}$	Behnke <i>et al.</i> ⁷⁸	
2,4-Dimethyl- pentane				5.16 ± 0.11	297 ± 2	RR [relative to $k(n\text{-butane})$ $= 2.53 \times 10^{-12}]^d$	Atkinson <i>et al.</i> ⁹⁴	
2,2,3-Trimethyl- butane				5.23 ± 0.12	296	FP-KS	Greiner ¹⁴	296–497
				4.86 ± 0.12	303			
				4.50 ± 0.33	371			
				4.60 ± 0.27	373			
		$7.9^{+2.1}_{-1.6}$		115 ± 73	6.33 ± 0.19			

TABLE 1. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with alkanes — Continued

Alkane	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	n	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Tempera- ture range covered (K)
				3.7 ± 0.8	305 ± 2	RR [relative to $k(2\text{-methylpropene})$ $= 4.94 \times 10^{-11}]^d$	Darnall <i>et al.</i> ¹⁰⁷	
				10.1 ± 1.3	753	RR [relative to $k(\text{H}_2)$ $= 8.31 \times 10^{-13}]^a$	Baldwin <i>et al.</i> ¹⁰⁸	
				4.12 ± 0.08	297 ± 2	RR [relative to $k(n\text{-butane})$ $= 2.53 \times 10^{-12}]^d$	Atkinson <i>et al.</i> ⁹⁴	
				3.22 ± 0.48	263	RR [relative to $k(n\text{-pentane}) = 2.10$ $\times 10^{-17} T^2 e^{223/7T}]^d$	Harris and Kerr ⁹⁹	263–303
				4.33 ± 0.41	283			
				4.18 ± 0.25	303			
				4.02 ± 0.57	303			
				4.40 ± 0.60	243	RR [relative to $k(n\text{-hexane})$ $= 1.35 \times 10^{-11} e^{-262/7T}]^d$	Harris and Kerr ⁹⁹	243–324
				4.17 ± 0.26	244			
				4.03 ± 0.39	253			
				4.36 ± 0.54	263			
				4.23 ± 0.76	273			
				4.27 ± 0.60	282			
				4.19 ± 0.19	295			
				4.04 ± 0.20	314			
				4.11 ± 0.50	324			
				3.96 ± 0.16	324			
<i>n</i> -Octane				8.42 ± 1.25	296	FP-KS	Greiner ¹⁴	296–497
				12.0 ± 0.7	371			
				10.8 ± 0.5	371			
	$29.5^{+4.4}_{-3.8}$		364 ± 60	14.3 ± 0.4	497			
				8.89 ± 0.18	299 ± 2	RR [relative to $k(n\text{-butane})$ $= 2.55 \times 10^{-12}]^d$	Atkinson <i>et al.</i> ⁷³	
				8.63	300 ± 3	RR [relative to $k(n\text{-butane})$ $= 2.56 \times 10^{-12}]^d$	Behnke <i>et al.</i> ⁷⁶	
				8.8 ± 0.3	312	RR [relative to $k(n\text{-heptane})$ $= 7.48 \times 10^{-12}]^d$	Nolting <i>et al.</i> ⁹⁸	
2,2-Dimethyl- hexane				4.83 ± 0.04	300	RR [relative to $k(\text{series of organics})]^c$	Behnke <i>et al.</i> ⁷⁸	
2,2,4- Trimethylpentane				3.90 ± 0.15	298	FP-KS	Greiner ¹⁴	298–493
				3.55 ± 0.12	305			
				4.37 ± 0.23	339			
				5.25 ± 0.15	373			
				5.43 ± 0.13	423			
	$15.5^{+3.1}_{-2.6}$		426 ± 63	6.62 ± 0.42	493			
				3.59 ± 0.16	297 ± 2	RR [relative to $k(n\text{-butane})$ $= 2.53 \times 10^{-12}]^d$	Atkinson <i>et al.</i> ⁹⁴	
2,3,4- Trimethylpentane				9.18 ± 0.23	243	RR [relative to $k(n\text{-hexane}) = 1.35 \times$ $10^{-11} e^{-262/7T}]^d$	Harris and Kerr ⁹⁹	243–313
				9.10 ± 0.96	253			
				7.58 ± 0.45	263			
				7.81 ± 0.42	273			
				6.99 ± 0.23	295			
				6.94 ± 0.12	303			

TABLE 1. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with alkanes — Continued

Alkane	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	n	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Tempera- ture range covered (K)
				6.96 ± 0.59	313			
				7.61 ± 0.18	313			
2,2,3,3-Tetra- methylbutane				1.08 ± 0.02	294	FP-KS	Greiner ¹⁴	294–495
				1.16 ± 0.10	301			
				1.42 ± 0.04	335			
				2.04 ± 0.08	370			
				2.21 ± 0.07	424			
	$16.2^{+3.3}_{-2.7}$		802 ± 63	3.52 ± 0.12	495			
				6.65 ± 0.83	753	RR [relative to $k(\text{H}_2)$ $= 8.31 \times 10^{-13}]^a$	Baldwin <i>et al.</i> , ¹⁰⁹ Baldwin and Walker ⁴⁶	
				1.04 ± 0.08	297 ± 2	RR [relative to $k(n\text{-butane}) = 2.53$ $\times 10^{-12}]^d$	Atkinson <i>et al.</i> ⁹⁴	
				0.948 ± 0.020	290	LP-LIF	Tully <i>et al.</i> ¹⁰³	290–738
				1.48 ± 0.04	348.5			
				2.38 ± 0.03	423.5			
				3.58 ± 0.05	506			
				5.27 ± 0.09	606			
	4.75×10^{-6}	2.20	68	9.36 ± 0.35	737.5			
<i>n</i> -Nonane				10.5 ± 0.4	299 ± 2	RR [relative to $k(n\text{-butane})$ $= 2.55 \times 10^{-12}]^d$	Atkinson <i>et al.</i> ⁷³	
				10.4	300 ± 3	RR [relative to $k(n\text{-butane})$ $= 2.56 \times 10^{-12}]^d$	Behnke <i>et al.</i> ⁷⁶	
				10.1 ± 0.3	312	RR [relative to $k(n\text{-heptane})$ $= 7.48 \times 10^{-12}]^d$	Nolting <i>et al.</i> ⁹⁸	
				10.3 ± 0.2	300	RR [relative to $k(n\text{-octane})$ $= 8.76 \times 10^{-12}]^d$	Behnke <i>et al.</i> ⁸⁹	
				10.3 ± 0.2	300	RR [relative to $k(\text{series of organics})]^e$	Behnke <i>et al.</i> ⁷⁸	
2-Methyloctane				10.1 ± 0.12	300	RR [relative to $k(\text{series of organics})]^e$	Behnke <i>et al.</i> ⁷⁸	
4-Methyloctane				9.72 ± 0.12	300	RR [relative to $k(\text{series of organics})]^e$	Behnke <i>et al.</i> ⁷⁸	
2,3,5-Trimethyl- hexane				7.88 ± 0.09	300	RR [relative to $k(\text{series of organics})]^e$	Behnke <i>et al.</i> ⁷⁸	
<i>n</i> -Decane				11.3 ± 0.6	299 ± 2	RR [relative to $k(n\text{-butane})$ $= 2.55 \times 10^{-12}]^d$	Atkinson <i>et al.</i> ⁷³	
				11.6 ± 0.4	312	RR [relative to $k(n\text{-heptane})$ $= 7.48 \times 10^{-12}]^d$	Nolting <i>et al.</i> ⁹⁸	
				12.4 ± 0.2	300	RR [relative to $k(n\text{-octane})$ $= 8.76 \times 10^{-12}]^d$	Behnke <i>et al.</i> ⁸⁹	

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

Alkane	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	n	B (K)	$10^{12} \times k$ (cm^3 $\text{molecule}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Tempera- ture range covered (K)
				12.4 ± 0.3	300	RR [relative to $k(\text{series of organics})^f$	Behnke <i>et al.</i> ⁷⁸	
<i>n</i> -Undecane				13.6 ± 0.3	312	RR [relative to $k(n\text{-heptane})$ $= 7.48 \times 10^{-12}]^d$	Nolting <i>et al.</i> ⁹⁸	
				13.3 ± 0.2	300	RR [relative to $k(n\text{-octane})$ $= 8.76 \times 10^{-12}]^d$	Behnke <i>et al.</i> ⁸⁹	
<i>n</i> -Dodecane				15.0 ± 0.5	312	RR [relative to $k(n\text{-heptane})$ $= 7.48 \times 10^{-12}]^d$	Nolting <i>et al.</i> ⁹⁸	
				13.9 ± 0.2	300	RR [relative to $k(n\text{-octane})$ $= 8.76 \times 10^{-12}]^d$	Behnke <i>et al.</i> ⁸⁹	
<i>n</i> -Tridecane				17.4 ± 0.6	312	RR [relative to $k(n\text{-heptane})$ $= 7.48 \times 10^{-12}]^d$	Nolting <i>et al.</i> ⁹⁸	
				15.4 ± 0.2	300	RR [relative to $k(n\text{-octane})$ $= 8.76 \times 10^{-12}]^d$	Behnke <i>et al.</i> ⁸⁹	
<i>n</i> -Tetradecane				19.2 ± 0.7	312	RR [relative to $k(n\text{-heptane})$ $= 7.48 \times 10^{-12}]^d$	Nolting <i>et al.</i> ⁹⁸	
<i>n</i> -Pentadecane				22.2 ± 1.0	312	RR [relative to $k(n\text{-heptane})$ $= 7.48 \times 10^{-12}]^d$	Nolting <i>et al.</i> ⁹⁸	
<i>n</i> -Hexadecane				24.9 ± 1.3	312	RR [relative to $k(n\text{-heptane})$ $= 7.48 \times 10^{-12}]^d$	Nolting <i>et al.</i> ⁹⁸	

^aSee Introduction.

^bCalculated by least-squares analyses of the cited first-order OH radical decay rates against the CH_4 concentration.

^cRoom temperature, not reported.

^dFrom present recommendations, see text.

^eThe reference organics and the rate constants (in units of $10^{-12} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$) used were: *n*-butane, 2.55; *n*-hexane, 5.63; *n*-octane, 8.79; 2,2,3,3-tetramethylbutane, 1.08; 2,2,4-trimethylpentane, 3.70; and hexafluorobenzene, 0.219.⁷⁸

^fFrom the data obtained at 100 Torr total pressure. Rate constants derived from the higher pressure data decrease monotonically with increasing pressure, for unknown reasons.

TABLE 2. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with cycloalkanes

Alkane	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	n	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Tempera- ture range covered (K)		
Cyclopropane				0.08 ± 0.02	295	FP-RF	Zetzsch ¹¹⁰			
				0.062 ± 0.014	298 ± 2	FP-RA	Jolly <i>et al.</i> ¹¹¹			
Isopropyl- cyclopropane				2.84 ± 0.06	298 ± 2	RR [relative to $k(n\text{-butane})$ $= 2.54 \times 10^{-12}]^a$	Atkinson and Aschmann ¹¹²			
Cyclobutane				1.2 ± 0.3	298	RR [relative to $k(\text{CO})$ $= 1.49 \times 10^{-13}]^b$	Gorse and Volman ⁶⁹			
Cyclopentane				6.1	298	RR [relative to $k(\text{CO})$ $= 1.49 \times 10^{-13}]^b$	Volman ¹¹³			
				4.43 ± 0.27	300 ± 1	RR [relative to $k(n\text{-butane})$ $= 2.56 \times 10^{-12}]^a$	Darnall <i>et al.</i> ⁷¹			
				5.26 ± 0.07	299 ± 2	RR [relative to $k(n\text{-butane})$ $= 2.55 \times 10^{-12}]^a$	Atkinson <i>et al.</i> ¹⁰²			
				5.18 ± 0.38	298 ± 2	FP-RA	Jolly <i>et al.</i> ¹¹¹			
				5.02 ± 0.22	295	LP-LIF	Droege and Tully ¹¹⁴	295-491		
				6.12 ± 0.27	344					
				7.23 ± 0.32	402.5					
	6.04×10^{-4}	1.52	-111	9.45 ± 0.41	491					
Cyclopentane- d_{10}				1.83 ± 0.08	295	LP-LIF	Droege and Tully ¹¹⁴	295-602		
				2.46 ± 0.11	342					
				3.33 ± 0.15	401					
				4.81 ± 0.21	491					
		4.50×10^{-3}	1.21	257	6.75 ± 0.29	602				
Cyclohexane				7.95 ± 0.43	295	FP-KS	Greiner ¹⁴	295-497		
				8.40 ± 0.55	338					
				7.70 ± 0.72	338					
				11.8 ± 0.6	370					
				9.93 ± 0.23	373					
				10.4 ± 0.6	425					
				10.1 ± 0.6	425					
		$23.5^{+4.7}_{-4.0}$		319 ± 73	12.4 ± 0.4	497				
					6.7 ± 1.7	298			RR [relative to $k(\text{CO})$ $= 1.49 \times 10^{-13}]^b$	Gorse and Volman ⁶⁹
					6.6	303			RR [relative to $k(\text{cis-2-butene})$ $= 5.49 \times 10^{-11}]^a$	Wu <i>et al.</i> ⁹¹
					7.48 ± 0.05	299 ± 2			RR [relative to $k(n\text{-butane})$ $= 2.55 \times 10^{-12}]^a$	Atkinson <i>et al.</i> ¹⁰²
					7.43 ± 0.26	299 ± 2				
					7.07 ± 0.42	299 ± 2			RR [relative to $k(\text{propene})$ $= 2.62 \times 10^{-11}]^a$	Atkinson <i>et al.</i> ¹¹⁵
					7.38 ± 0.11	300 ± 3			RR [relative to $k(n\text{-butane})$ $= 2.56 \times 10^{-12}]^a$	Tuazon <i>et al.</i> ¹¹⁶

TABLE 2. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with cycloalkanes — Continued

Alkane	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	n	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Tempera- ture range covered (K)
				5.24 ± 0.36	295	PR-RA	Nielsen <i>et al.</i> ⁶⁰	
				6.22 ± 0.45	298	RR [relative to $k(n\text{-butane})$ $= 2.54 \times 10^{-12}$] ^a	Edney <i>et al.</i> ⁶²	
				8.6 ± 0.8	296 ± 2	DF-RF	Bourmada <i>et al.</i> ⁶³	
				7.14 ± 0.31	292	LP-LIF	Droege and Tully ¹¹⁴	292–491
				8.49 ± 0.37	342			
				10.1 ± 0.44	401			
	1.09×10^{-3}	1.47	–125	12.9 ± 0.56	491			
Cyclohexane- d_{12}				2.76 ± 0.12	292	LP-LIF	Droege and Tully ¹¹⁴	292–603
				3.64 ± 0.16	342			
				4.83 ± 0.21	401			
				6.94 ± 0.30	491			
	3.48×10^{-4}	1.62	56	9.78 ± 0.42	603			
Cycloheptane				13.1 ± 2.1	298 ± 2	FP-RA	Jolly <i>et al.</i> ¹¹¹	
				11.8 ± 0.2	300	RR [relative to $k(\text{series of organics})$] ^c	Behnke <i>et al.</i> ⁷⁸	
Methylcyclo- hexane				10.4 ± 0.3	297 ± 2	RR [relative to $k(n\text{-butane})$ $= 2.53 \times 10^{-12}$] ^a	Atkinson <i>et al.</i> ⁹⁴	
Cyclooctane				13.7 ± 0.3	300	RR [relative to $k(\text{series of organics})$] ^c	Behnke <i>et al.</i> ⁷⁸	
1,1,3-Trimethyl- cyclohexane				8.73 ± 0.09	300	RR [relative to $k(\text{series of organics})$] ^c	Behnke <i>et al.</i> ⁷⁸	
Bicyclo[2.2.1]- heptane				5.49 ± 0.14	299 ± 2	RR [relative to $k(\text{cyclohexane})$ $= 7.51 \times 10^{-12}$] ^a	Atkinson <i>et al.</i> ¹¹⁷	
Bicyclo[2.2.2]- octane				14.7 ± 1.0	299 ± 2	RR [relative to $k(\text{cyclohexane})$ $= 7.51 \times 10^{-12}$] ^a	Atkinson <i>et al.</i> ¹¹⁷	
Bicyclo[3.3.0]- octane				11.0 ± 0.6	299 ± 2	RR [relative to $k(\text{cyclohexane})$ $= 7.51 \times 10^{-12}$] ^a	Atkinson <i>et al.</i> ¹¹⁷	
<i>cis</i> - Bicyclo[4.3.0]- nonane				17.2 ± 1.3	299 ± 2	RR [relative to $k(\text{cyclohexane})$ $= 7.51 \times 10^{-12}$] ^a	Atkinson <i>et al.</i> ¹¹⁷	
<i>trans</i> - Bicyclo[4.3.0]- nonane				17.6 ± 1.3	299 ± 2	RR [relative to $k(\text{cyclohexane})$ $= 7.51 \times 10^{-12}$] ^a	Atkinson <i>et al.</i> ¹¹⁷	
<i>cis</i> - Bicyclo[4.4.0]- decane				19.9 ± 1.4	299 ± 2	RR [relative to $k(\text{cyclohexane})$ $= 7.51 \times 10^{-12}$] ^a	Atkinson <i>et al.</i> ¹¹⁷	
<i>trans</i> - Bicyclo[4.4.0]- decane				20.4 ± 1.3	299 ± 2	RR [relative to $k(\text{cyclohexane})$ $= 7.51 \times 10^{-12}$] ^a	Atkinson <i>et al.</i> ¹¹⁷	

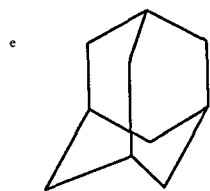
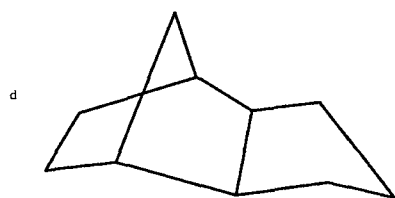
TABLE 2. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with cycloalkanes

Alkane	$10^{12} \times A$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	n	B (K)	$10^{12} \times k$ (cm^3 $\text{molecule}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference	Tempera- ture range covered (K)
Tricyclo- [5.2.1.0 ^{2,6}]- decane ^d				11.3 ± 0.4	299 ± 2	RR [relative to $k(\text{cyclohexane})$ $= 7.51 \times 10^{-12}]^a$	Atkinson <i>et al.</i> ¹¹⁷	
Tricyclo- [3.3.1.1 ^{3,7}]- decane ^c				23.1 ± 2.1	299 ± 2	RR [relative to $k(\text{cyclohexane})$ $= 7.51 \times 10^{-12}]^a$	Atkinson <i>et al.</i> ¹¹⁷	
				22.1 ± 0.3	300	RR [relative to $k(\text{series of organics})]^c$	Behnke <i>et al.</i> ⁷⁸	

^aFrom present recommendations (see text).

^bSee Introduction.

^cThe reference organics and the rate constants (in units of $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) used were: *n*-butane, 2.55; *n*-hexane, 5.63; *n*-octane, 8.79; 2,2,3,3-tetramethylbutane, 1.08; 2,2,4-trimethylpentane, 3.70; and hexafluorobenzene, 0.219.⁷⁸

TABLE 3. Rate constants k for the gas-phase reactions of the OD radical with alkanes

Alkane	$10^{12} \times k$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference
Methane	0.0080 ± 0.0003	300	FP-KS	Greiner ¹¹⁸
Ethane	0.274 ± 0.027	300	FP-KS	Greiner ¹¹⁸
<i>n</i> -Butane	2.76 ± 0.22	297 ± 2	FP-RA	Paraskevopoulos and Nip ⁸⁴
<i>n</i> -Butane- d_{10}	0.804 ± 0.063	297 ± 2	FP-RA	Paraskevopoulos and Nip ⁸⁴

The absolute rate data of Wilson and Westenberg,¹⁰ Horne and Norrish,¹² Greiner¹⁴ (which supersedes the earlier room temperature study of Greiner¹¹), Peeters and Mahnen,¹⁷ Davis *et al.*,¹⁸ Margitan *et al.*,¹⁹ Zellner and Steinert,²³ Ernst *et al.*,²⁶ Tully and Ravishankara,²⁸ Jeong and Kaufman,^{31,32} Jonah *et al.*,³⁴ Madronich and Felder³⁵ and Smith *et al.*³⁷ (which supersedes the earlier preliminary data reported by Fairchild *et al.*³⁰) are plotted in Fig. 1 (the absolute room temperature rate constants of Overend *et al.*,²¹ Howard and Evenson,²² Husain *et al.*²⁹ and those obtained at elevated temperatures by Dixon-Lewis and Williams,⁹ Gordon and Mulac²⁰ and Cohen and Bott³⁶ are not included for reasons of clarity), while all of the available rate constants obtained at around 298 K are plotted in Fig. 2.

The rate constants obtained from the relative rate studies of Westenberg and Fristrom,¹ Fenimore and Jones,² Fristrom,⁴ Blundell *et al.*,⁵ Hoare⁶ (which supersedes the earlier study of Hoare³), Wilson *et al.*,¹³ Bald-

win *et al.*¹⁵ (which is judged to supersede the earlier study of Baldwin *et al.*⁸), Simonaitis *et al.*,¹⁶ Cox *et al.*,²⁴ Bradley *et al.*²⁵ and Baulch *et al.*,³³ together with the absolute rate constants determined by Dixon-Lewis and Williams,⁹ Gordon and Mulac²⁰ and Cohen and Bott,³⁶ are plotted in Fig. 3.

The rate constants obtained by Horne and Norrish¹² for methane (and also ethane, see below) are significantly higher than the other data, probably due to the occurrence of secondary reactions at the high initial OH radical concentrations used.¹⁴ Otherwise, it can be seen from Figs. 1 and 2 that the data obtained from the absolute rate constant studies^{9-11,14,17-23,26,28-32,34-37} are in general agreement, although there are certain areas of discrepancy. Thus, the room temperature rate constants (Fig. 2) range over a factor of 1.7, and at temperatures >625 K the rate constants obtained by Zellner and Steinert²³ are up to a factor of ~2 higher than those of Tully and Ravishankara,²⁸ Madronich and Felder³⁵ and

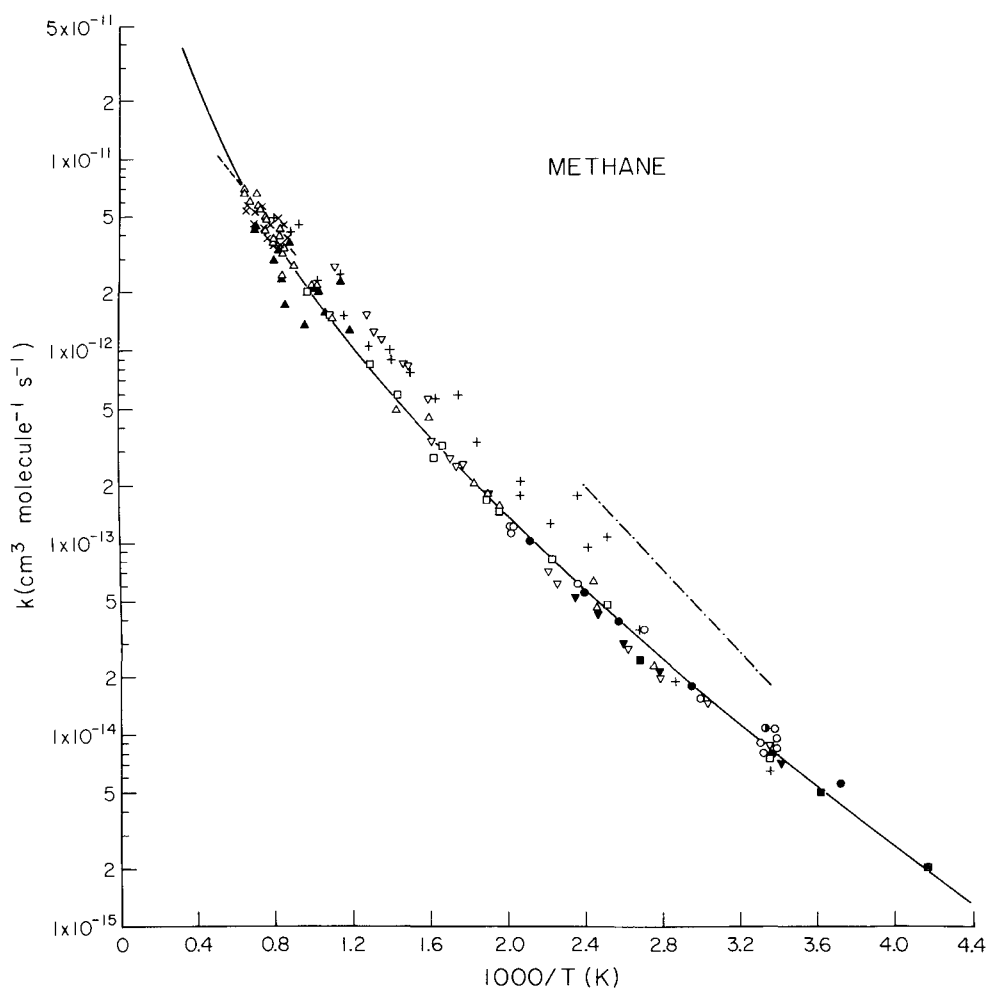


FIG. 1. Arrhenius plot of selected absolute rate constants for the reaction of the OH radical with methane. (●) Wilson and Westenberg;¹⁰ (---) Horne and Norrish;¹² (○) Greiner;¹⁴ (—) Peeters and Mahnen¹⁷; (■) Davis *et al.*;¹⁸ (▼) Margitan *et al.*;¹⁹ (▽) Zellner and Steinert;²³ (x) Ernst *et al.*;²⁶ (□) Tully and Ravishankara;²⁸ (●) Jeong and Kaufman;^{31,32} (+) Jonah *et al.*;³⁴ (Δ) Madronich and Felder;³⁵ (▲) Smith *et al.*;³⁷ (—) recommendation (see text).

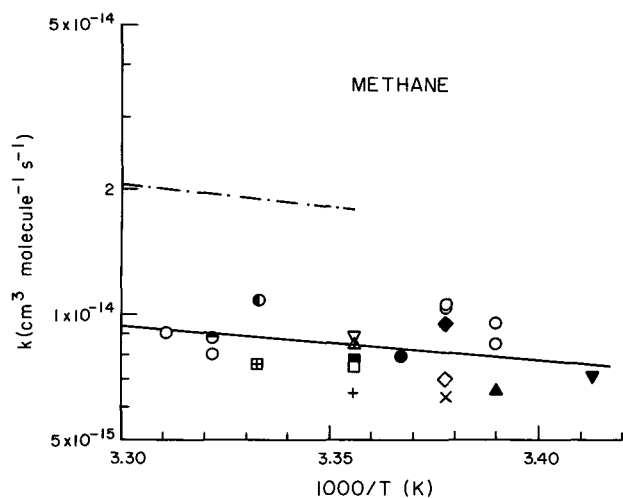


FIG. 2. Arrhenius plot of rate constants for the reaction of the OH radical with methane at around room temperature. (●) Wilson and Westenberg;¹⁰ (○) Greiner;¹¹ (---) Horne and Norrish;¹² (○) Greiner;¹⁴ (■) Davis *et al.*;¹⁸ (▼) Margitan *et al.*;¹⁹ (▲) Overend *et al.*;²¹ (◆) Howard and Evenson;²² (▽) Zellner and Steinert;²³ (x) Cox *et al.*;²⁴ (◇) Sworski *et al.*;²⁷ (□) Tully and Ravishankara;²⁸ (⊕) Husain *et al.*;²⁹ (●) Jeong and Kaufman;³¹ (+) Jonah *et al.*;³⁴ (Δ) Madronich and Felder;³⁵ (—) recommendation (see text).

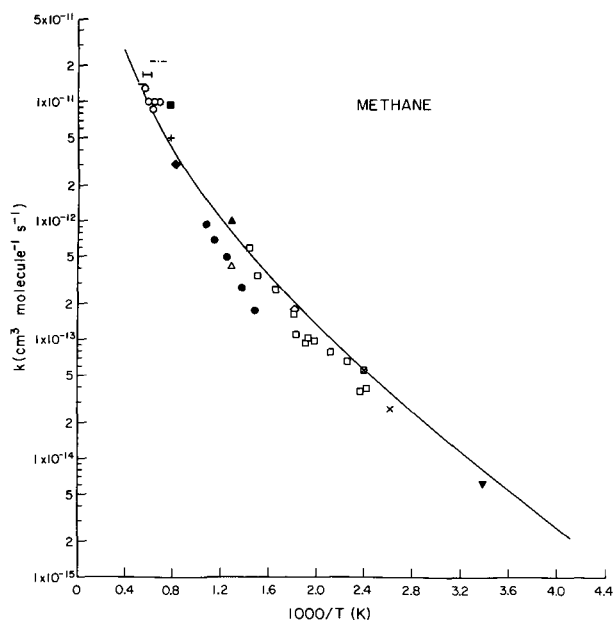


FIG. 3. Arrhenius plot of the relative and selected absolute rate constants for the reaction of the OH radical with methane. (—) Westenberg and Fristrom;¹ (○) Fenimore and Jones;² (---) Fristrom;⁴ (Δ) Blundell *et al.*;⁵ (●) Hoare;⁶ (+) Dixon-Lewis and Williams;⁹ (—) Wilson *et al.*;¹³ (▲) Baldwin *et al.*;¹⁵ (◇) Simonaitis *et al.*;¹⁶ (x) Gordon and Mulac;²⁰ (▼) Cox *et al.*;²⁴ (■) Bradley *et al.*;²⁵ (□) Baulch *et al.*;³³ (◆) Cohen and Bott;³⁶ (—) recommendation (see text).

Smith *et al.*³⁷ (although the rate constants of Smith *et al.*³⁷ exhibit a relatively high degree of scatter). These higher rate constants of Zellner and Steinert²³ at temperatures > 625 K are also probably due to the occurrence of secondary reactions, as discussed by Tully and Ravishankara.²⁸

Furthermore, the kinetic data of Jonah *et al.*,³⁴ obtained using a pulsed radiolysis-resonance absorption technique, yield a linear Arrhenius plot over the entire temperature range studied (298–1229 K). These rate constants,³⁴ while in agreement with other literature data at ~ 300 –380 K and > 600 K, are significantly higher in the intermediate temperature range of ~ 400 –600 K. Unfortunately, the reasons for these discrepancies are not presently known.

The remaining absolute rate constant data^{9–11,14,17–22,26,28–32,35–37} are in good agreement, and it is apparent from these data that the Arrhenius plot of $\ln k$ vs T^{-1} exhibits a significant degree of curvature (Fig. 1). The rate constants obtained by Gordon and Mulac²⁰ at 381 and 416 K, while in good agreement with the other literature data for methane, exhibit significant differences from the literature rate constants for certain of the other alkanes and alkenes studied (for example, for *n*-butane and propene) and are hence not used in the evaluation of the rate expression. The datum of Wilson and Westenberg¹⁰ has also been excluded from the evaluation since a stoichiometric factor was necessary to derive the rate constant for the elementary reaction from the measured rate coefficient.¹⁰ Peeters and Mahnen¹⁷ cited only an Arrhenius expression, not tabulating the individual rate constants, and hence their data could not be used in deriving the recommended rate expression.

Thus, the kinetic data of Dixon-Lewis and Williams,⁹ Greiner,¹⁴ Davis *et al.*,¹⁸ Margitan *et al.*,¹⁹ Overend *et al.*,²¹ Howard and Evenson,²² Ernst *et al.*,²⁶ Tully and Ravishankara,²⁸ Husain *et al.*,²⁹ Jeong and Kaufman,^{31,32} Madronich and Felder,³⁵ Cohen and Bott³⁶ and Smith *et al.*³⁷ 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,^{9,14,18,19,21,22,26,28,29,31,32,35–37} using the expression $k = CT^2e^{-D/T}$, yields the recommendation of

$$k(\text{methane}) = (6.95^{+0.45}_{-0.41}) \times 10^{-18} T^2 e^{-(1282 \pm 32)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 240–1512 K, where the error limits are two least-squares standard deviations, and

$$k(\text{methane}) = 8.36 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of $\pm 20\%$.

This recommendation is almost identical with that of

$$k(\text{methane}) = 6.95 \times 10^{-18} T^2 e^{-1280/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

derived by Atkinson¹²⁰ from an evaluation of the absolute rate constant data over the more restricted temperature range ≤ 1250 K, and is $\sim 10\%$ higher than that of Baulch *et al.*¹²¹ of

$$k(\text{methane}) = 2.5$$

$$\times 10^{-18} T^{2.13} e^{-1230/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over this temperature range of 240–1500 K.

As shown in Fig. 3, the rate constants derived from the relative rate studies of Westenberg and Fristrom,¹ Fenimore and Jones,² Wilson *et al.*,¹³ Baldwin *et al.*,¹⁵ Cox *et al.*²⁴ and Baulch *et al.*³³ are in reasonably good agreement with the recommended rate constant expression. This good agreement allows the related studies of these groups to be used in the evaluations of the rate constant data for those organic compounds for which less accurate absolute rate data are available or for which absolute rate data are available only for a restricted temperature range around 298 K. However, the rate constants obtained by Fristrom,⁴ Hoare and co-workers,^{3,6,7} Blundell *et al.*,⁵ Simonaitis *et al.*¹⁶ and Bradley *et al.*²⁵ show significant discrepancies with the present recommendation, and related studies by these groups are hence given less weight in the evaluations of the rate data for other organic compounds in this article.

(2) Methane-¹³C, Methane-*d*₁, Methane-*d*₂ and Methane-*d*₃

The limited data available (Table 1) show that there is no significant isotope effect for the reaction of OH radicals with ¹³CH₄, when compared to ¹²CH₄.^{38,39} The magnitude of this isotope effect is of importance with regards to the enrichment of atmospheric methane in ¹³C relative to its sources, and the most recent determination of Davidson *et al.*³⁹ of

$$k(\text{methane-}^{12}\text{C})/k(\text{methane-}^{13}\text{C})$$

$$= 1.010 \pm 0.007 \text{ at } 297 \pm 3 \text{ K}$$

is recommended.

As expected because of the increased bond dissociation energy for C–D bonds versus C–H bonds, the rate constants for the reaction of OH radicals with methane and the deuterated methanes are observed to decrease monotonically along the series CH₄ > CH₃D > CH₂D₂ > CHD₃ > CD₄, by a factor of ~ 1.8 per C–D vs. C–H bond at 416 K.²⁰

(3) Ethane

The available literature rate constants are given in Table 1, and are plotted in Arrhenius form in Figs. 4 and 5. As for methane, the rate constants obtained by Horne

and Norrish¹² are significantly higher than the more recent absolute rate data, presumably due to the occurrence of secondary reactions at the high initial OH radical concentrations used.¹⁴ The absolute rate constant studies of Greiner,¹⁴ Gordon and Mulac,²⁰ Overend *et al.*,²¹ Howard and Evenson,⁴⁸ Leu,⁴⁹ Anderson and Stephens⁵⁰ (but see below), Lee and Tang,⁵¹ Martigan and Watson,⁵² Tully *et al.*,^{53,59} Jeong *et al.*³² (at temperatures ≥ 273 K, see below), Nielsen *et al.*,^{54,60} Smith *et al.*,⁵⁵ Devolder *et al.*,⁵⁶ Schmidt *et al.*,⁵⁷ Baulch *et al.*,⁵⁸ Stachnik *et al.*,⁶¹ Bourmada *et al.*,⁶³ Wallington *et al.*⁶⁴ and Zabarnick *et al.*⁶⁵ are in generally good agreement. Many of these rate constant determinations were carried out to assess the reliabilities of experimental systems for the determination of OH radical reaction rate constants for other reactant molecules.^{49,51,52,55,56,61,64,65}

However, somewhat disturbing is the marked disagreement at temperatures $\lesssim 250$ K between the rate constant determined by Jeong *et al.*³² and those of Margitan and Watson,⁵² Anderson and Stephens⁵⁰ (though it should be noted that for *n*-butane, 2-methylpropane, 2,2-dimethylpropane and, to a lesser extent, propane, the rate constants determined by Anderson and Stephens⁵⁰ are significantly lower than other literature data), Smith *et al.*,⁵⁵ Stachnik *et al.*⁶¹ and Wallington *et al.*⁶⁴ This discrepancy at low temperatures (i.e., $\lesssim 270$ K) may suggest that erroneously high rate constants were measured in this temperature regime for methane, ethane and a series of haloalkanes by Jeong and Kaufman³¹ and Jeong *et al.*,³² thus leading to an exaggerated curvature in their Arrhenius plots (see also the section below dealing with the reactions of OH radicals with the haloalkanes). Clearly, further experimental data are needed for the reaction of OH radicals with ethane at temperatures ≤ 275 K.

Since the rate constants obtained by Gordon and Mulac,²⁰ Anderson and Stephens,⁵⁰ Lee and Tang,⁵¹ and Nielsen *et al.*^{54,60} for certain other organic reactants do not agree with the recommendations (see below), the data from these studies have not been used in the present evaluation. Furthermore, due to a lack of experimental details, the rate constant of Schmidt *et al.*⁵⁷ has also been omitted from the data set used in the evaluation. Thus, the absolute kinetic data of Greiner,¹⁴ Overend *et al.*,²¹ Howard and Evenson,⁴⁸ Leu,⁴⁹ Margitan and Watson,⁵² Tully *et al.*,^{53,59} Jeong *et al.*,³² Smith *et al.*,⁵⁵ Devolder *et al.*,⁵⁶ Baulch *et al.*,⁵⁸ Stachnik *et al.*,⁶¹ Bourmada *et al.*,⁶³ Wallington *et al.*⁶⁴ and Zabarnick *et al.*⁶⁵ have been utilized. A unit-weighted least-squares fit of these data, using the expression $k = CT^2 e^{-D/T}$, yields the recommendation of

$$k(\text{ethane}) = (1.42_{-0.18}^{+0.21})$$

$$\times 10^{-17} T^2 e^{-(462 \pm 43)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

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

$k(\text{ethane}) = 2.68 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K,

with an estimated overall uncertainty at 298 K of $\pm 20\%$. This recommendation is essentially identical to that of Atkinson¹²⁰ of

$k(\text{ethane}) = 1.37 \times 10^{-17} T^2 e^{-444/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

over the temperature range 238–800 K, but is significantly different, especially at ≈ 1000 K, from that recommended by Baulch *et al.*¹²¹ of

$k(\text{ethane}) = 2.3 \times 10^{-11} e^{-1340/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

The rate constants obtained by Fenimore and Jones,⁴¹ Westenberg and Fristrom,⁴² Hoare and Patel⁴⁴ and Bradley *et al.*²⁵ from relative rate studies exhibit a significant degree of scatter about the recommended rate expression (Fig. 4), with the rate constant derived from the study of Bradley *et al.*²⁵ being significantly dependent on which reference reaction of OH radicals (with H₂ or CO) is utilized. However, the relative rate data of Baldwin *et al.*,^{45,46} Hucknall *et al.*,⁴⁷ Baulch *et al.*³³ and Edney *et al.*⁶² are in good agreement with the recommendation, suggesting that the related studies of Baldwin and co-workers⁴⁶ and Edney *et al.*⁶² for more complex organic compounds can be used with some confidence in the rate constant evaluations.

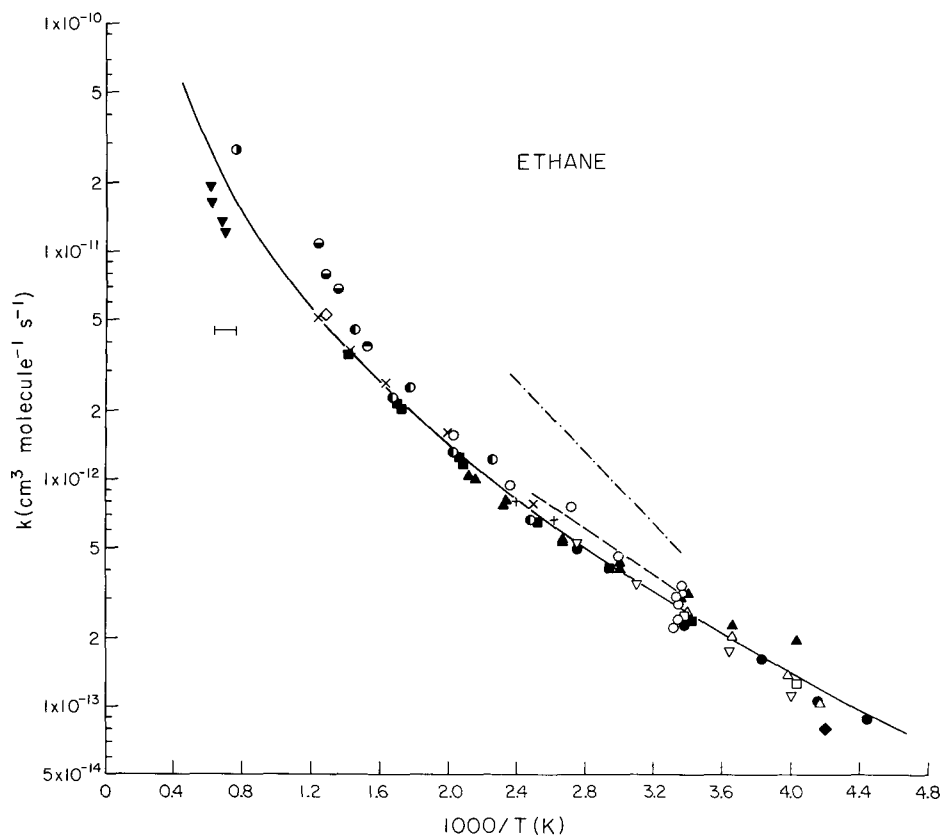


FIG. 4. Arrhenius plot of rate constants for the reaction of the OH radical with ethane. (\blacktriangledown) Fenimore and Jones;⁴¹ (\perp) Westenberg and Fristrom;⁴² (---) Horne and Norrish;¹² (\bullet) Hoare and Patel;⁴⁴ (\diamond) Baldwin *et al.*;^{45,46} (\circ) Greiner;¹⁴ (+) Gordon and Mulac;²⁰ (\ominus) Hucknall *et al.*;⁴⁷ (\odot) Bradley *et al.*;²⁵ (∇) Anderson and Stephens;⁵⁰ (\blacklozenge) Margitan and Watson;⁵² (\times) Tully *et al.*;⁵³ (\oplus) Baulch *et al.*;³³ (\blacktriangle) Jeong *et al.*;³² (---) Nielsen *et al.*;⁵⁴ (Δ) Smith *et al.*;⁵⁵ (\blacksquare) Tully *et al.*;⁵⁹ (\square) Stachnik *et al.*;⁶¹ (\bullet) Wallington *et al.*;⁶⁴ (—) recommendation (see text).

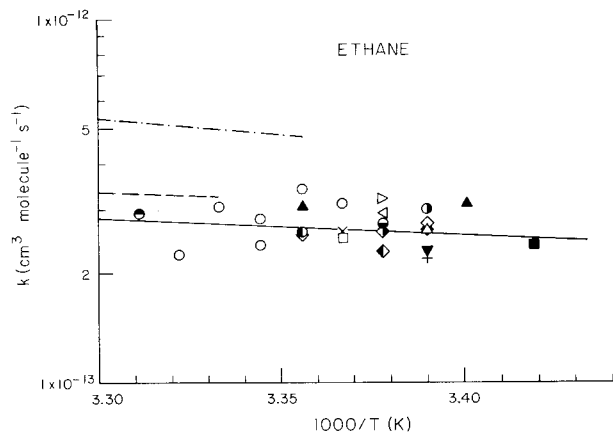


FIG. 5. Arrhenius plot of the rate constants for the reaction of the OH radical with ethane at around room temperature. (---) Horne and Norrish;¹² (●) Greiner;⁴³ (○) Greiner;¹⁴ (◆) Overend *et al.*,²¹ Smith *et al.*,⁵⁵ Baulch *et al.*,⁵⁸ (<) Howard and Evenson;⁴⁸ (⊙) Leu;⁴⁹ (∇) Anderson and Stephens;⁵⁰ (▼) Lee and Tang;⁵¹ (x) Tully *et al.*,⁵³ (▲) Jeong *et al.*,³² (—) Nielsen *et al.*,⁵⁴ (◇) Devolder *et al.*,⁵⁶ (+) Schmidt *et al.*,⁵⁷ (■) Tully *et al.*,⁵⁹ (⊕) Nielsen *et al.*,⁶⁰ (□) Stachnik *et al.*,⁶¹ (▷) Edney *et al.*,⁶² (⊗) Bourmada *et al.*,⁶³ (◇) Wallington *et al.*,⁶⁴ (◇) Zabarnick *et al.*,⁶⁵ (—) recommendation (see text).

(4) Ethane-*d*₃ (CH₃CD₃) and Ethane-*d*₆

Rate constants for CH₃CD₃ and C₂D₆ (as well as C₂H₆) have been determined by Tully *et al.*⁵⁹ using a laser photolysis-laser induced fluorescence technique (Table 1). From these data, Tully *et al.*⁵⁹ observed that the rate constants for the -CH₃ and/or -CD₃ groups [$k(-\text{CH}_3)$ and $k(-\text{CD}_3)$, respectively] could be treated as being independent of the neighboring -CH₃ or -CD₃ group, and hence that for CH₃CD₃ the rate constant is given to a very good approximation by,

$$k(\text{CH}_3\text{CD}_3) = k(-\text{CH}_3) + k(-\text{CD}_3)$$

with a deuterium isotope effect of⁵⁹

$$k(-\text{CH}_3)/k(-\text{CD}_3) = (1.01 \pm 0.06) e^{(456 \pm 26)/T}$$

(5) Propane

The available kinetic data for propane, propane-*d*₈ and a series of partially deuterated propanes are given in Table 1, and the rate constants for propane of Baker *et al.*,^{46,67} Greiner,¹⁴ Bradley *et al.*,⁶⁸ Gorse and Volman,⁶⁹ Gordon and Mulac,²⁰ Hucknall *et al.*,⁴⁷ Overend *et al.*,²¹ Harker and Burton,⁷⁰ Cox *et al.*,⁷² Anderson and Stephens,⁵⁰ Atkinson *et al.*,⁷³ Baulch *et al.*,^{33,58} Bott and Cohen,⁷⁴ Smith *et al.*,³⁷ Schmidt *et al.*,⁵⁷ Droege and Tully⁷⁵ and Behnke *et al.*⁷⁶ are plotted in Arrhenius form in Fig. 6. For reasons which are not understood, a signif-

icant amount of scatter in these rate constants is observed (up to a factor of >2 at room temperature). The absolute rate constants determined by Anderson and Stephens⁵⁰ at ≥ 298 K are consistently lower, by $\sim 20\%$, than those of Greiner¹⁴ and Droege and Tully.⁷⁵ (This most recent study of Droege and Tully⁷⁵ supersedes the earlier work of Tully *et al.*,⁵³ which is believed to be in error due to a temperature calibration error⁷⁵). Additionally, the rate constants at around room temperature of Bradley *et al.*,⁶⁸ Gorse and Volman,⁶⁹ Overend *et al.*,²¹ Harker and Burton⁷⁰ and Cox *et al.*⁷² disagree with the remaining absolute rate constant data by significant factors.

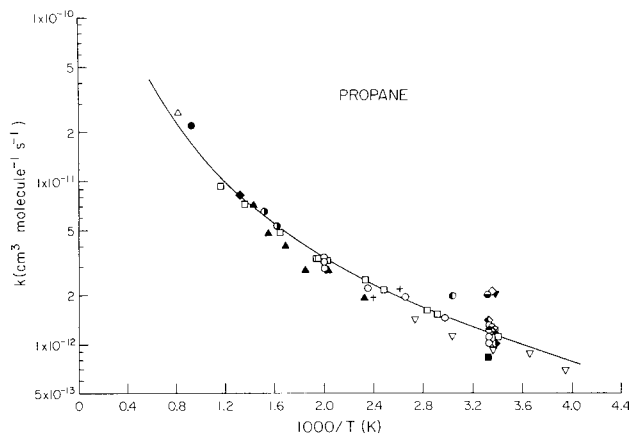


FIG. 6. Arrhenius plot of the rate constants for the reaction of the OH radical with propane. (◆) Baker *et al.*,^{46,67} (○) Greiner,¹⁴ (■) Bradley *et al.*,⁶⁸ (◇) Gorse and Volman,⁶⁹ (+) Gordon and Mulac,²⁰ (⊙) Hucknall *et al.*,⁴⁷ (▼) Overend *et al.*,²¹ (⊕) Harker and Burton,⁷⁰ (⊗) Cox *et al.*,⁷² (∇) Anderson and Stephens,⁵⁰ (⊕) Atkinson *et al.*,⁷³ (▲) Baulch *et al.*,³³ (Δ) Bott and Cohen,⁷⁴ (●) Smith *et al.*,³⁷ (x) Baulch *et al.*,⁵⁸ (◇) Schmidt *et al.*,⁵⁷ (□) Droege and Tully,⁷⁵ (◇) Behnke *et al.*,⁷⁶ (—) recommendation (see text).

The absolute rate constants of Greiner,¹⁴ Bott and Cohen,⁷⁴ Smith *et al.*,³⁷ Baulch *et al.*,⁵⁸ and Droege and Tully⁷⁵ and the relative rate constants of Baker *et al.*,^{46,67} and Atkinson *et al.*⁷³ (which supersedes the study of Darnall *et al.*⁷¹) are utilized for the evaluation of the overall rate constant for this reaction. Using the expression $k = CT^2 e^{-D/T}$, a unit-weighted least-squares analysis of these data yields the recommendation of

$$k(\text{propane}) = (1.50^{+0.17}_{-0.16}) \times 10^{-17} T^2 e^{-(44 \pm 42)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

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

$$k(\text{propane}) = 1.15$$

$$\times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated uncertainty at 298 K of $\pm 30\%$. Over the temperature range ~ 290 – 1200 K this recommendation is similar to those of

$$k(\text{propane}) = 1.27 \times 10^{-17} T^2 e^{14/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

recommended by Atkinson¹²⁰ and

$$k(\text{propane}) = 1.8 \times 10^{-20} T^{2.93} e^{390/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

recommended by Baulch *et al.*¹²¹

As for methane and ethane, the relative rate constant data of Baulch *et al.*³³ are in reasonably good agreement with this recommendation. Furthermore, the rate constants derived from the recent relative rate studies of Edney *et al.*⁶² and Behnke *et al.*⁷⁸ [which is relative to a series of organic compounds and cannot be readily reevaluated using the present recommendations (though the rate constants used⁷⁸ for the alkane reference compounds are within 2% of the present recommendations)] are in good agreement with the present recommendation.

Knox *et al.*¹²² carried out competitive oxidations of ethane and propane over the temperature range 547–768 K, and determined that the relative disappearance rates of ethane and propane were essentially independent of temperature over this range, with a value of 0.44 ± 0.03 . It is likely that the major loss process for these alkanes in the experimental system used was by reaction with the OH radical,⁶ and this relative rate constant of

$$k(\text{ethane})/k(\text{propane}) = 0.44 \pm 0.03$$

is in reasonable agreement with that of 0.44 at 547 K, increasing to 0.55 at 768 K, calculated from the present recommendations for ethane and propane.

Since propane contains non-equivalent C–H bonds, the overall rate constant is the sum of the contributions from the two primary $-\text{CH}_3$ groups and the secondary $-\text{CH}_2-$ group, with

$$k = 2k(-\text{CH}_3) + k(-\text{CH}_2-) = k_{\text{primary}} + k_{\text{secondary}}.$$

Using the absolute rate constants determined for C_3H_8 , $\text{CH}_3\text{CD}_2\text{CH}_3$, $\text{CH}_3\text{CH}_2\text{CD}_3$, $\text{CH}_3\text{CD}_2\text{CD}_3$, $\text{CD}_3\text{CH}_2\text{CD}_3$ and C_3D_8 , Droege and Tully⁷⁵ showed that the $-\text{CH}_3$, $-\text{CD}_3$, $-\text{CH}_2-$ and $-\text{CD}_2-$ groups could be treated as having group rate constants which were independent of the H/D isotopic nature of the neighboring group(s). Utilizing the deuterium isotope ratio of $k(-\text{CH}_3)/k(-\text{CD}_3)$ obtained from their related kinetic study of the

OH radical reactions with C_2H_6 , CH_3CD_3 and C_2D_6 ,⁵⁹ Droege and Tully⁷⁵ obtained

$$2k(-\text{CH}_3) = 1.75$$

$$\times 10^{-14} T^{0.97} e^{-798/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

$$k(-\text{CH}_2-) = 7.76$$

$$\times 10^{-17} T^{1.61} e^{18/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

and

$$k(-\text{CH}_2-)/k(-\text{CD}_2-) = (1.13 \pm 0.19) e^{(262 \pm 78)/T}$$

Thus, from these data,⁷⁵

$$\frac{k(-\text{CH}_2-)}{2k(-\text{CH}_3)} = \frac{k_{\text{secondary}}}{k_{\text{primary}}} = 0.00443 T^{0.64} e^{816/T}$$

for propane, and hence $k_{\text{secondary}}/k_{\text{primary}} = 0.91$ at 753 K. This ratio derived from kinetic measurements is in reasonable agreement with that of 1.2 ± 0.1 obtained by Baker *et al.*¹²³ from a product study at 753 K.

Over the temperature range 250–1000 K, this ratio of $k_{\text{secondary}}/k_{\text{primary}}$ for propane of $0.00443 T^{0.64} e^{816/T}$ can be well approximated by the Arrhenius expression of

$$k_{\text{secondary}}/k_{\text{primary}} = 0.39 e^{560/T},$$

centered at 400 K. This $k_{\text{secondary}}/k_{\text{primary}}$ ratio can then be combined with the recommended expression for the overall rate constant of $(k_{\text{primary}} + k_{\text{secondary}})$ to yield the individual OH radical reaction rate constants for H-atom abstraction from the primary and secondary C–H bonds in propane at any temperature in the range ~ 290 – 850 K.

(6) *n*-Butane and *n*-Butane-*d*₁₀

The available kinetic data for *n*-butane are given in Table 1, and the rate constants of Baker *et al.*,^{46,67} Greiner,¹⁴ Morris and Niki,⁸⁰ Stuhl,⁸¹ Gorse and Volman,⁶⁹ Gordon and Mulac,²⁰ Hucknall *et al.*,⁴⁷ Campbell *et al.*,⁸² Perry *et al.*,⁸³ Paraskevopoulos and Nip,⁸⁴ Atkinson *et al.*,⁸⁵ Anderson and Stephens,⁵⁰ Atkinson and Aschmann,⁸⁶ Schmidt *et al.*,⁵⁷ Droege and Tully,⁸⁷ Barnes *et al.*⁸⁸ and Behnke *et al.*⁸⁹ are plotted in Fig. 7. Unfortunately, the degree of scatter of these reported data is almost a factor of 2.5 at room temperature. The absolute rate constant data of Gordon and Mulac²⁰ (which also show significant discrepancies with more recent data for propene), Anderson and Stephens⁵⁰ (which are also significantly lower than other reported data for 2-methylpropane and 2,2-dimethylpropane), Schmidt *et al.*⁵⁷ and Morris and Niki,⁸⁰ together with the relative

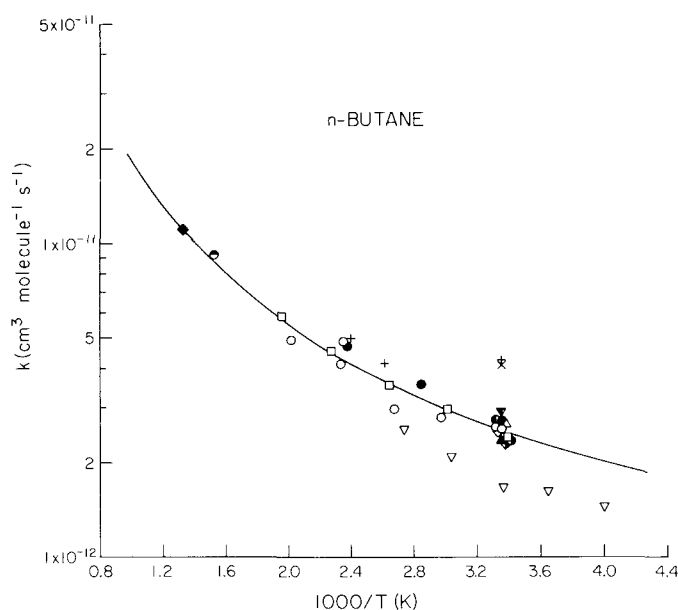


FIG. 7. Arrhenius plot of the rate constants for the reaction of the OH radical with *n*-butane. (◆) Baker *et al.*,^{46,67} (○) Greiner,¹⁴ (x) Morris and Niki,⁸⁰ (▲) Stuhl,⁸¹ (▼) Gorse and Volman,⁶⁹ (+) Gordon and Mulac,²⁰ (●) Hucknall *et al.*,⁴⁷ (⊙) Campbell *et al.*,⁸² (●) Perry *et al.*,⁸³ (Δ) Paraskevopoulos and Nip,⁸⁴ Atkinson and Aschmann,⁸⁶ (◇) Atkinson *et al.*,⁸⁵ Behnke *et al.*,⁸⁹ (▽) Anderson and Stephens,⁵⁰ (⊠) Schmidt *et al.*,⁵⁷ (□) Droege and Tully,⁸⁷ (⊙) Barnes *et al.*,⁸⁸ (—) recommendation (see text).

rate constants of Gorse and Volman,⁶⁹ Hucknall *et al.*⁴⁷ and Campbell *et al.*,⁸² have not been used in the evaluation. Furthermore, due to the availability of apparently reliable absolute rate constant data and the frequent use of *n*-butane as a reference compound in relative rate studies, the room temperature rate constants of Atkinson *et al.*,⁸⁵ Atkinson and Aschmann,⁸⁶ Barnes *et al.*⁸⁸ and Behnke *et al.*⁸⁹ derived from relative rate studies were also not utilized to derive the recommended rate expression.

Thus, a unit-weighted least-squares analysis of the absolute rate constants of Greiner,¹⁴ Stuhl,⁸¹ Perry *et al.*,⁸³ Paraskevopoulos and Nip⁸⁴ and Droege and Tully⁸⁷ and the relative rate constant of Baker *et al.*,^{46,67} using the expression $k = CT^2e^{-D/T}$, yields the recommendation of

$$k(n\text{-butane}) = (1.51^{+0.30}_{-0.25}) \times 10^{-17} T^2 e^{(190 \pm 64)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

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

$$k(n\text{-butane}) = 2.54$$

$$\times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of $\pm 20\%$. This recommendation is almost identical to the three-parameter expression of

$$k(n\text{-butane}) = 1.49 \times 10^{-17} T^2 e^{196/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

obtained by Atkinson¹²⁰ (and is very similar over the temperature range ~ 290 –510 K to the Arrhenius expression of

$$k(n\text{-butane}) = 1.55 \times 10^{-11} e^{-540/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

recommended by Atkinson¹²⁰) and over the range 298–1000 K agrees to within 40% with that of

$$k(n\text{-butane}) = 1.7 \times 10^{-15} T^{1.3} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

recommended by Baulch *et al.*¹²¹

The absolute rate constant of Schmidt *et al.*⁵⁷ is in good agreement with the recommendation, as are the rate constants obtained from the relative rate studies of Hucknall *et al.*,⁴⁷ Campbell *et al.*,⁸² Atkinson *et al.*,⁸⁵ Atkinson and Aschmann,⁸⁶ Barnes *et al.*⁸⁸ and Behnke *et al.*⁸⁹ The rate constants reported by Morris and Niki,⁸⁰ Gordon and Mulac,²⁰ and Anderson and Stephens⁵⁰ exhibit significant discrepancies with the recommended rate expression.

For *n*-butane- d_{10} , the room temperature rate constant determined by Paraskevopoulos and Nip⁸⁴ is $\sim 20\%$ lower than the more recent measurements of Droege and Tully.⁸⁷ From their experimental data for *n*-butane and *n*-butane- d_{10} ,⁸⁷ the deuterium isotope ratio obtained for ethane⁵⁹ and the rate constant ratio for H-atom abstraction from the primary and secondary C–H bonds in *n*-butane of

$$k_{\text{primary}}/k_{\text{secondary}} = k(-\text{CH}_3)/k(-\text{CH}_2-) = 1.035 e^{-536/T}$$

estimated by Atkinson,¹²⁴ Droege and Tully⁸⁷ derived the rate constants for H-atom abstraction from the $-\text{CH}_3$ and $-\text{CH}_2-$ groups in *n*-butane of

$$k_{\text{primary}} = 2k(-\text{CH}_3) = 6.86 \times 10^{-17} T^{1.73} e^{-379/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

$$k_{\text{secondary}} = 2k(-\text{CH}_2-) = 1.20 \times 10^{-16} T^{1.64} e^{124/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

and

$$k(-\text{CH}_2-)/k(-\text{CD}_2-) = (1.31 \pm 0.12) e^{(196 \pm 32)/T}$$

At 753 K, the ratio of $k_{\text{secondary}}/k_{\text{primary}} = 1.88$ calculated from the above expressions for k_{primary} and $k_{\text{secondary}}$ is, as it

should be, similar to that of 1.97 estimated by Atkinson,¹²⁴ and is in reasonably good agreement with the ratio of $k_{\text{secondary}}/k_{\text{primary}} = 2.2$ determined by Baker *et al.*¹²⁵ from a product study.

As expected, these individual rate constants for H-atom abstraction from the primary and secondary C–H bonds in *n*-butane are totally consistent with the ratio of

$$\frac{k_{\text{secondary}}}{k_{\text{primary}}} = \frac{k(-\text{CH}_2-)}{k(-\text{CH}_3)} = 0.966 e^{536/T}$$

estimated by Atkinson¹²⁴ for the temperature range 250–1000 K. Use of this expression, together with the recommendation for the overall OH radical reaction rate constant with *n*-butane, allows the individual rate constants for H-atom abstraction from the $-\text{CH}_3$ and $-\text{CH}_2-$ groups in *n*-butane to be calculated.

(7) 2-Methylpropane and 2-Methylpropane- d_1 , - d_9 and - d_{10}

The available kinetic data are given in Table 1, and the rate constants of Baker *et al.*,^{46,67} Greiner,¹⁴ Hucknall *et al.*,⁴⁷ Wu *et al.*,⁹¹ Anderson and Stephens,⁵⁰ Trevor *et al.*,⁹³ Atkinson *et al.*,⁹⁴ Böhland *et al.*,⁹⁵ Schmidt *et al.*,⁵⁷ Tully *et al.*⁹⁶ and Edney *et al.*⁶² for 2-methylpropane are plotted in Fig. 8. The relative rate constant of Butler *et al.*⁹² is only of an approximate nature, and those of Baldwin and Walker,⁷⁹ Greiner,⁴³ and Darnall *et al.*⁷¹ have been superseded by the more recent studies of these groups.^{14,46,94} Significant discrepancies still exist, however, with the data of Anderson and Stephens⁵⁰ being a factor of ~ 1.5 lower, and those of Trevor *et al.*⁹³ being a factor of ~ 1.5 higher, than the data of Greiner,¹⁴ Atkinson *et al.*⁹⁴ and Tully *et al.*⁹⁶

In accordance with the criteria used to evaluate the rate constants for methane, ethane, propane and *n*-butane, the data of Baker *et al.*,^{46,67} Greiner,¹⁴ Atkinson *et al.*⁹⁴ and Tully *et al.*⁹⁶ have been used to derive the recommended rate expression. The Arrhenius plot (Fig. 8) exhibits curvature, and a unit-weighted least-squares fit of these data,^{14,46,94,96} using the expression $k = CT^2 e^{-D/T}$, yields the recommended expression of

$$k(\text{2-methylpropane}) = (1.04_{-0.13}^{+0.15}) \times 10^{-17} T^2 e^{(277 \pm 49)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 293–864 K, where the indicated error limits are two least-squares standard deviations, and

$$k(\text{2-methylpropane}) = 2.34 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty at 298 K of $\pm 25\%$. This recommended expression is essentially identical to that of

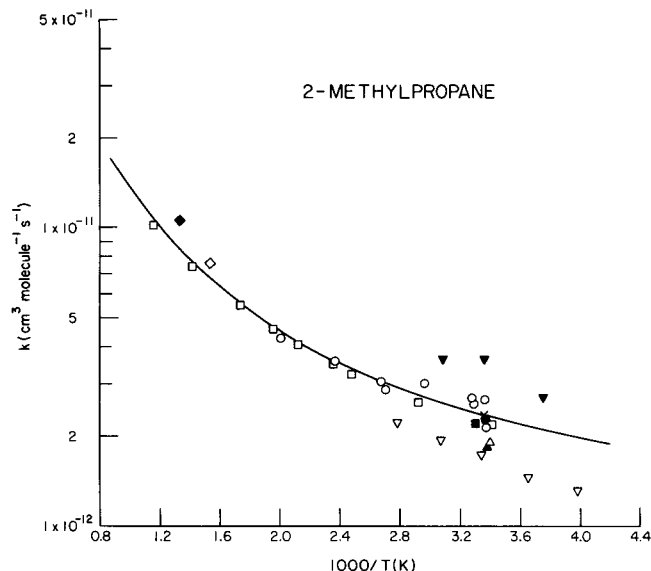


FIG. 8. Arrhenius plot of rate constants for the reaction of the OH radical with 2-methylpropane. (◆) Baker *et al.*;^{46,67} (○) Greiner;¹⁴ (◇) Hucknall *et al.*;⁴⁷ (■) Wu *et al.*;⁹¹ (▽) Anderson and Stephens;⁵⁰ (▼) Trevor *et al.*;⁹³ (●) Atkinson *et al.*;⁹⁴ (▲) Böhland *et al.*;⁹⁵ (△) Schmidt *et al.*;⁵⁷ (□) Tully *et al.*;⁹⁶ (x) Edney *et al.*;⁶² (—) recommendation (see text).

$$k(\text{2-methylpropane}) = 9.58$$

$$\times 10^{-18} T^2 e^{305/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

recommended by Atkinson¹²⁰ over this same temperature range, and agrees well with that of Baulch *et al.*¹²¹ of

$$k(\text{2-methylpropane}) = 3.2$$

$$\times 10^{-21} T^{3.1} e^{860/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 298–1000 K, but diverges rapidly at temperatures below 298 K.

The room temperature absolute rate constants of Böhland *et al.*,⁹⁵ Schmidt *et al.*⁵⁷ and the rate constants derived from the relative rate studies of Hucknall *et al.*,⁴⁷ and Edney *et al.*⁶² are in reasonable^{57,95} or good^{47,62} agreement with the present recommendation.

From the study of Falconer *et al.*¹²⁶ of the competitive oxidations of a series of alkanes, and assuming that the major loss process for these alkanes was by reaction with the OH radical, a rate constant ratio of

$$k(\text{propane})/k(\text{2-methylpropane}) = 0.67$$

was obtained over the temperature range 583–693 K. This rate constant ratio is in reasonable agreement with that derived from the present recommendations of 0.83 at 583 K, increasing to 0.91 at 693 K.

Tully *et al.*⁹⁶ also determined rate constants for the reactions of the OH radical with (CH₃)₃CD, (CD₃)₃CH and (CD₃)₃CD. As expected, at a given temperature the rate constants for these partially or fully deuterated 2-methylpropanes are significantly lower than that for (CH₃)₃CH. These rate constant data were shown to be accurately expressed by

$$k = k_{\text{primary}} + k_{\text{tertiary}}$$

where k_{primary} and k_{tertiary} are the rate constants for H-atom abstraction from the primary C–H or C–D bonds [= $3k(-\text{CH}_3)$ or $3k(-\text{CD}_3)$] and the tertiary C–H or C–D bonds [= $k(>\text{CH}-)$ or $k(>\text{CD}-)$], respectively.⁹⁶ Values of

$$3k(-\text{CH}_3) = 3.81$$

$$\times 10^{-16} T^{1.53} e^{-391/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

$$3k(-\text{CD}_3) = 4.13$$

$$\times 10^{-20} T^{2.79} e^{-218/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

$$k(>\text{CH}-) = 9.52$$

$$\times 10^{-14} T^{0.51} e^{-32/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

and

$$k(>\text{CD}-) = 1.05 \times 10^{-15} T^{1.16} e^{15/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

were obtained.⁹⁶ For (CH₃)₃CH, a ratio of the rate constants for H-atom abstraction from the primary and tertiary C–H bonds of

$$\frac{k_{\text{tertiary}}}{k_{\text{primary}}} = \frac{k(>\text{CH}-)}{3k(-\text{CH}_3)} = 250 T^{-1.02} e^{359/T}$$

was obtained, and over the temperature range 250–1000 K this is reasonably well approximated by the Arrhenius expression of

$$k_{\text{tertiary}}/k_{\text{primary}} = 0.200 e^{767/T},$$

centered at 400 K. Use of this ratio of $k_{\text{tertiary}}/k_{\text{primary}}$, together with the recommended overall rate constant expression, allows the individual rate constants for H-atom abstraction from the primary and tertiary C–H bonds in 2-methylpropane to be calculated over the temperature range ~290–860 K.

(8) *n*-Pentane

The available rate constant data are given in Table 1, and the rate constants obtained by Baldwin and Walker,⁴⁶ Wu *et al.*,⁹¹ Cox *et al.*,⁷² Barnes *et al.*,⁹⁷ Atkinson *et al.*,⁷³ (which supersedes the earlier study of Darnall *et al.*⁷¹), Behnke *et al.*,^{76,89} Nolting *et al.*⁹⁸ and Harris and Kerr⁹⁹ are plotted in Fig. 9. All of these rate constants

were obtained from relative rate studies, with those of Wu *et al.*⁹¹ and Cox *et al.*⁷² being subject to significant uncertainties. At room temperature the relative rate constants of Barnes *et al.*,⁹⁷ Atkinson *et al.*,⁷³ Behnke *et al.*,^{76,78,89} Nolting *et al.*⁹⁸ and Harris and Kerr⁹⁹ are in excellent agreement. Furthermore, the rate constants derived by Harris and Kerr⁹⁹ relative to those for the reactions of OH radicals with *n*-butane and 2-methylpropane are in good agreement, showing that the rate constants for *n*-butane, *n*-pentane and 2-methylpropane are self-consistent.

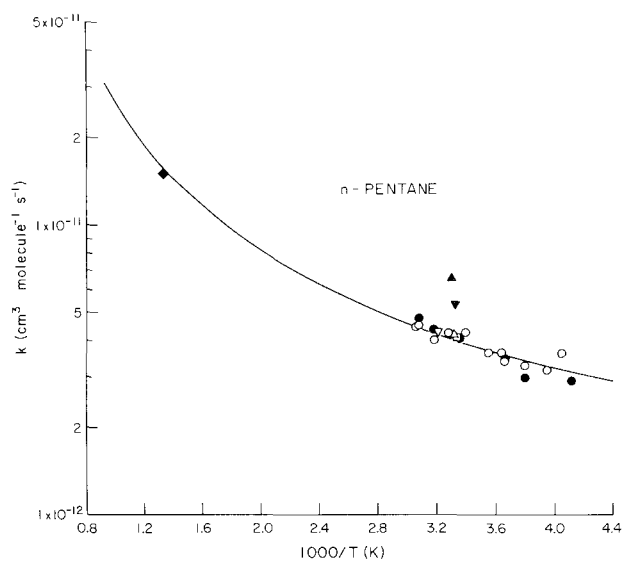


FIG. 9. Arrhenius plot of rate constants for the reaction of the OH radical with *n*-pentane. (◆) Baldwin and Walker;⁴⁶ (▲) Wu *et al.*;⁹¹ (▼) Cox *et al.*;⁷² (□) Barnes *et al.*⁹⁷ and Atkinson *et al.*;⁷³ (Δ) Behnke *et al.*;^{76,89} (▽) Nolting *et al.*;⁹⁸ (○) Harris and Kerr,⁹⁹ relative to *n*-butane; (●) Harris and Kerr,⁹⁹ relative to 2-methylpropane; (—) recommendation (see text).

The rate constants of Baldwin and Walker,⁴⁶ Atkinson *et al.*,⁷³ Behnke *et al.*,^{76,89} Nolting *et al.*⁹⁸ and Harris and Kerr⁹⁹ have been used in the rate constant evaluation. A unit-weighted least-squares analysis of these data, using the equation $k = CT^2 e^{-D/T}$, yields the recommendation of

$$k(n\text{-pentane}) = (2.10_{-0.33}^{+0.39}) \times 10^{-17} T^2 e^{(223 \pm 49)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

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

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

at 298 K, with an estimated overall uncertainty at 298 K of $\pm 25\%$. Over the temperature range 250–1000 K, the rate constants given by this recommended rate expression are in good agreement (within 5%) with those calculated using the estimation method of Atkinson,^{124,127} indicating that the above recommendation is self-consistent with those for the other alkanes. This point is discussed in more detail below.

(9) 2-Methylbutane

Rate constants for 2-methylbutane are only available at around room temperature (Table 1), and all are derived from relative rate studies.^{71,72,94,100} The agreement is reasonable, and a rate constant of

$$k(2\text{-methylbutane}) = 3.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K is recommended from the most recent study of Atkinson *et al.*,⁹⁴ with an estimated overall uncertainty of $\pm 40\%$.

(10) 2,2-Dimethylpropane and 2,2-Dimethylpropane-*d*₁₂

The available data are given in Table 1, and those of Greiner,¹⁴ Baker *et al.*,^{46,101} Paraskevopoulos and Nip,⁸⁴ Atkinson *et al.*,¹⁰² Anderson and Stephens,⁵⁰ and Tully *et al.*⁵⁹ (which supersede the data reported earlier by Tully *et al.*¹⁰³) for 2,2-dimethylpropane are plotted in Fig. 10. The rate constant of Darnall *et al.*⁷¹ has not been included since this work has been superseded by the more recent study of Atkinson *et al.*¹⁰² using a more reliable and precise technique. Consistent with the data for propane, *n*-butane and 2-methylpropane, the rate constants obtained by Anderson and Stephens⁵⁰ for 2,2-dimethylpropane are $\sim 30\%$ lower than those of Greiner,¹⁴ Paraskevopoulos and Nip,⁸⁴ Atkinson *et al.*,¹⁰² and Tully *et al.*,⁵⁹ all of which are in excellent agreement.

The rate constant for this reaction is evaluated from the data of Greiner,¹⁴ Baldwin and Walker,⁴⁶ Paraskevopoulos and Nip,⁸⁴ Atkinson *et al.*¹⁰² and Tully *et al.*⁵⁹ The Arrhenius expression clearly exhibits significant curvature (Fig. 10), and a unit-weighted least-squares analysis of these data,^{14,46,59,84,102} using the expression $k = CT^2e^{-D/T}$, yields the recommendation of

$$k(2,2\text{-dimethylpropane}) = (1.79^{+0.24}_{-0.21}) \times 10^{-17} T^2 e^{-(187 \pm 47)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 287–901 K, where the indicated errors are two least-squares standard deviations, and

$$k(2,2\text{-dimethylpropane}) = 8.49$$

$$\times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of $\pm 20\%$. This recommended expression is virtually identical to that of

$$k(2,2\text{-dimethylpropane}) = 1.75$$

$$\times 10^{-17} T^2 e^{-179/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

recommended by Atkinson¹²⁰ over this same temperature range and is in good agreement (within $\sim 20\%$ over the temperature range 290–750 K) with that of

$$k(2,2\text{-dimethylpropane}) = 7.5$$

$$\times 10^{-18} T^{2.08} e^{-70/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

recommended by Baulch *et al.*¹²¹

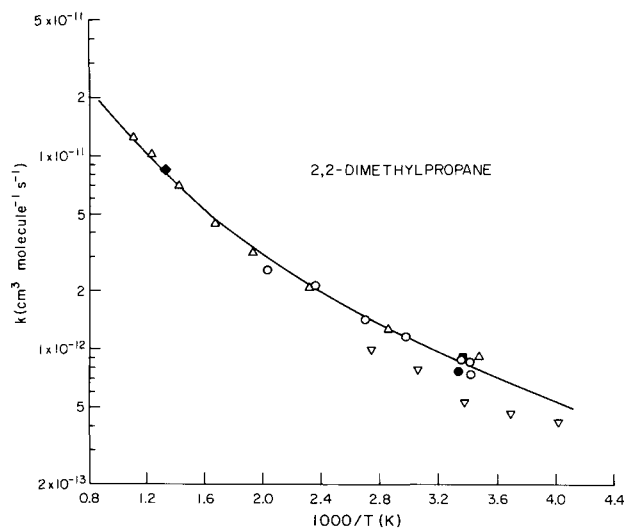


FIG. 10. Arrhenius plot of rate constants for the reaction of the OH radical with 2,2-dimethylpropane. (○) Greiner,¹⁴ (◆) Baker *et al.*,^{46,101} (■) Paraskevopoulos and Nip,⁸⁴ (●) Atkinson *et al.*,¹⁰² (▽) Anderson and Stephens,⁵⁰ (Δ) Tully *et al.*,⁵⁹ (—) recommendation (see text).

From the study of Falconer *et al.*¹²⁶ of the competitive oxidations of a series of alkanes, and assuming that the major loss process for these alkanes was by reaction with the OH radical, rate constant ratios of

$$k(\text{ethane})/k(2,2\text{-dimethylpropane}) = 0.14 e^{805/T}$$

over the temperature range 601–768 K and

$$k(2,2\text{-dimethylpropane})/k(2\text{-methylpropane})$$

$$= 0.26 e^{503/T}$$

over the temperature range 599–765 K were obtained.¹²⁶

These rate constant ratios of

$$k(\text{ethane})/k(2,2\text{-dimethylpropane}) = 0.53 \text{ to } 0.40$$

and

$$k(2,2\text{-dimethylpropane})/k(2\text{-methylpropane})$$

$$= 0.50 \text{ to } 0.60$$

over the temperature ranges studied are in reasonably good agreement with the values of 0.50 to 0.55 and 0.79 to 0.94, respectively, calculated from the above rate constant recommendations.

As expected from the higher bond dissociation energy for C–D versus C–H bonds, the rate constants for the reaction of the OH radical with 2,2-dimethylpropane-*d*₁₂ are significantly lower than those for 2,2-dimethylpropane.⁵⁹ The deuterium isotope ratio of

$$k(-\text{CH}_3)/k(-\text{CD}_3) = (0.94 \pm 0.09) e^{(472 \pm 46)/T}$$

is very similar to that for ethane.⁵⁹

(11) *n*-Hexane

Rate constants for *n*-hexane are available only at around room temperature (Table 1), and all have been derived from relative rate studies. These room temperature rate constants^{76,82,86,88,89,91,98,100,102,104–106} are in reasonably good agreement. The data of Atkinson and co-workers^{86,102,104} and Zetzsch and co-workers^{76,89,98} have been used to derive the 298 K rate constant, using a temperature dependence of $B = 262$ K (calculated from the estimation method of Atkinson^{124,127} for the temperature range 250–333 K) to normalize these rate constants to 298 K. This procedure yields the recommended rate constant of

$$k(n\text{-hexane}) = 5.61 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty of $\pm 25\%$.

This rate constant is in good agreement with the recent relative rate data of Klein *et al.*¹⁰⁵ and Barnes *et al.*⁸⁸ and with the less precise relative rate data of Lloyd *et al.*¹⁰⁰ and Wu *et al.*⁹¹ Combining this 298 K rate constant

with the temperature dependence calculated from the estimation method of Atkinson^{124,127} leads to the Arrhenius expression of

$$k(n\text{-hexane}) = 1.35 \times 10^{-11} e^{-262/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

which is applicable only over the restricted temperature range of ~ 250 – 335 K. Over a larger temperature range non-Arrhenius behavior is expected, consistent with the rate constants calculated by the estimation methods of Atkinson,^{124,127} Walker¹²⁸ and Cohen.¹²⁹ The above Arrhenius expression has been used in this evaluation to place the relative rate data of Harris and Kerr⁹⁹ for 2,2,3-trimethylbutane and 2,3,4-trimethylpentane on an absolute basis.

(12) 2-Methylpentane and 3-Methylpentane

Rate constants for 2- and 3-methylpentane, all derived from relative rate studies,^{72,94,100} are available only at room temperature (Table 1). Based upon the data of Atkinson *et al.*,⁹⁴ rate constants of

$$k(2\text{-methylpentane}) = 5.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

and

$$k(3\text{-methylpentane}) = 5.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

are recommended at 298 K, with estimated overall uncertainty limits of $\pm 30\%$.

(13) 2,2-Dimethylbutane

Rate constants for the reaction of the OH radical with 2,2-dimethylbutane have been obtained by Atkinson *et al.*,⁹⁴ Harris and Kerr⁹⁹ and Behnke *et al.*⁷⁸ from relative rate studies carried out at 297 ± 2 K, 245–328 K and 300 K, respectively. The rate constants derived from these studies are given in Table 1 and those of Atkinson *et al.*⁹⁴ and Harris and Kerr⁹⁹ are plotted in Fig. 11 (the rate constant of Behnke *et al.*⁷⁸ cannot be readily reevaluated to be consistent with the present recommendations for the reference organics used, although it is not expected to change by more than 1–2%). A unit-weighted least-squares analysis of these data,^{94,99} using the Arrhenius equation, yields the recommended expression of

$$k(2,2\text{-dimethylbutane}) = (2.84_{-0.80}^{+1.11})$$

$$\times 10^{-11} e^{-(747 \pm 94)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

applicable only over the temperature range 245–328 K, where the indicated errors are two least-squares standard deviations, and

$k(2,2\text{-dimethylbutane}) = 2.32$

$\times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K,

with an estimated overall uncertainty at 298 K of $\pm 30\%$. The rate constant reported by Behnke *et al.*⁷⁸ at 300 K is in excellent agreement with this recommendation.

The temperature dependence of this rate constant appears to be somewhat high, based upon the data for other alkanes and the temperature dependence calculated from the estimation technique of Atkinson^{124,127} of $B = 475 \text{ K}$ over this same temperature range of 250–333 K. Hence, the temperature dependence obtained from the experimental data is not recommended for use outside of the range $\sim 240\text{--}330 \text{ K}$.

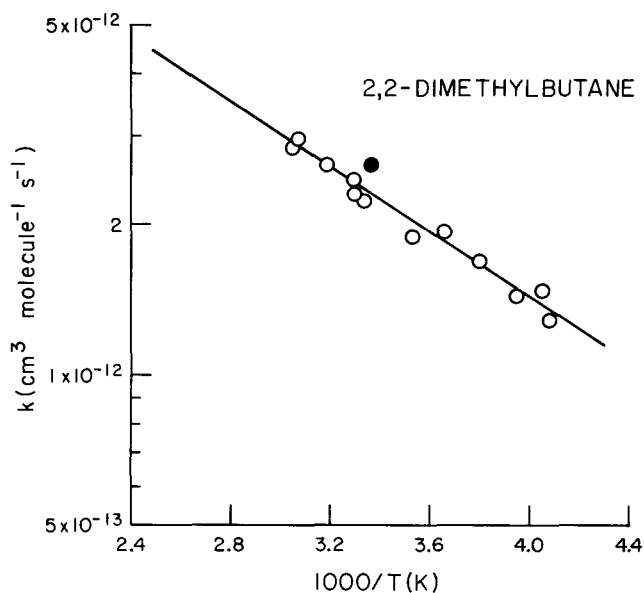


FIG. 11. Arrhenius plot of rate constants for the reaction of the OH radical with 2,2-dimethylbutane. (●) Atkinson *et al.*;⁹⁴ (○) Harris and Kerr;⁹⁹ (—) recommendation (see text).

(14) 2,3-Dimethylbutane

The available rate constant data of Greiner,¹⁴ Darnall *et al.*,^{71,107} Cox *et al.*,⁷² Atkinson *et al.*¹⁰² and Harris and Kerr⁹⁹ are given in Table 1 and those of Greiner,¹⁴ Darnall *et al.*,^{71,107} Cox *et al.*,⁷² Atkinson *et al.*¹⁰² (which supersedes the earlier study of Darnall *et al.*⁷¹) and Harris and Kerr⁹⁹ are plotted in Arrhenius form in Fig. 12. The sole absolute rate constant study is that of Greiner.¹⁴ The room temperature rate constant determined by Greiner¹⁴ is $\sim 20\%$ higher than those derived by Atkinson *et al.*¹⁰² and Harris and Kerr,⁹⁹ which are the most recent and precise of the relative rate studies.

The rate constants determined by Greiner,¹⁴ Atkinson *et al.*¹⁰² and Harris and Kerr⁹⁹ are independent of temperature, within one least-squares standard deviation, and it is recommended for the temperature range 247–498 K that

$k(2,3\text{-dimethylbutane}) = 6.2$

$\times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$,

independent of temperature, with an estimated uncertainty at 298 K of $\pm 25\%$. This recommendation is identical to that of Atkinson,¹²⁰ although the present recommendation covers a wider temperature range (247–498 K versus 299–498 K).

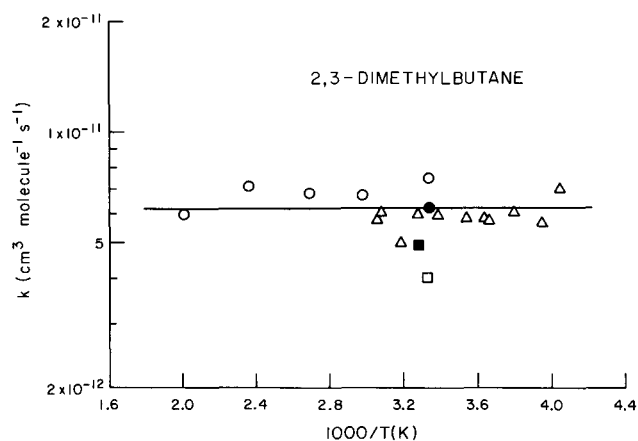


FIG. 12. Arrhenius plot of rate constants for the reaction of the OH radical with 2,3-dimethylbutane. (○) Greiner;¹⁴ (■) Darnall *et al.*;¹⁰⁷ (□) Cox *et al.*;⁷² (●) Atkinson *et al.*;¹⁰² (Δ) Harris and Kerr;⁹⁹ (—) recommendation (see text).

(15) *n*-Heptane

The available rate constants for the reaction of the OH radical with *n*-heptane are all from relative rate studies^{73,76,78,89,106} carried out at room temperature. Based upon the studies of Atkinson *et al.*⁷³ and Behnke *et al.*^{76,89} (the study of Klöpffer *et al.*¹⁰⁶ not being used in the evaluation due to a lack of details), a rate constant of

$k(n\text{-heptane}) = 7.20 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

is recommended at 300 K. This recommendation is in excellent agreement with the rate constant reported from the relative rate study of Behnke *et al.*,⁷⁸ within the uncertainties due to experimental errors and reevaluation to be consistent with the present recommendations for the reference organics used.

The estimation method of Atkinson^{124,127} predicts that over the temperature range 290–320 K the temperature dependence of this reaction rate constant is $B \approx 300$ K, and using this temperature dependence leads to the recommendation of

$$k(n\text{-heptane}) = 7.15 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty of $\pm 25\%$. At 312 K, the temperature at which the Nolting *et al.*⁹⁸ relative rate study was carried out, a rate constant of $7.48 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is then calculated and used to place their relative rate data⁹⁸ on an absolute basis.

(16) 2,2,3-Trimethylbutane

The available rate constants of Greiner,¹⁴ Darnall *et al.*,¹⁰⁷ Baldwin *et al.*,¹⁰⁸ Atkinson *et al.*⁹⁴ and Harris and Kerr⁹⁹ are given in Table 1 and are plotted in Arrhenius form in Fig. 13. There is seen to be a significant degree of scatter in the reported data for temperatures < 305 K. A unit-weighted least-squares analysis of the rate constant data of Greiner,¹⁴ Baldwin *et al.*,¹⁰⁸ Atkinson *et al.*⁹⁴ and Harris and Kerr,⁹⁹ using the expression $k = CT^2e^{-D/T}$, leads to the recommendation of

$$k(2,2,3\text{-trimethylbutane}) = (9.04^{+2.08}_{-1.70}) \times 10^{-18} T^2 e^{(495 \pm 63)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

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

$$k(2,2,3\text{-trimethylbutane}) = 4.23$$

$$\times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of $\pm 30\%$. In the absence of further experimental data at or below 250 K, the above expression should be used with caution at temperatures below ~ 275 K.

(17) *n*-Octane

The available kinetic data of Greiner,¹⁴ Atkinson *et al.*,⁷³ Behnke *et al.*⁷⁶ and Nolting *et al.*⁹⁸ are given in Table 1 and are plotted in Arrhenius form in Fig. 14. These data are in excellent agreement. Since there is no evidence of curvature in the Arrhenius plot (Fig. 14), a unit-weighted least-squares analysis of the data of Greiner,¹⁴ Atkinson *et al.*⁷³ and Behnke *et al.*⁷⁶ [the rate constant of Nolting *et al.*⁹⁸ at 312 K is relative to the less-well studied reaction of the OH radical with *n*-heptane (see above), and is hence not used in the evaluation] yields the recommended Arrhenius expression of

$$k(n\text{-octane}) = (3.15^{+0.74}_{-0.60}) \times 10^{-11} e^{-(384 \pm 72)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 296–497 K, where the indicated error limits are two least-squares standard deviations, and

$$k(n\text{-octane}) = 8.68$$

$$\times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of $\pm 20\%$.

This recommendation is essentially identical to that of

$$k(n\text{-octane}) = 3.12 \times 10^{-11} e^{-380/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

of Atkinson¹²⁰ over the same temperature range. Although, as seen from Fig. 14, the Arrhenius expression provides a satisfactory fit over this restricted temperature range, this is not expected to be the case over a wider temperature range extending to higher or lower temperatures, and this point is discussed below.

(18) 2,2,4-Trimethylpentane

The available rate constants^{14,94} are given in Table 1 and are plotted in Arrhenius form in Fig. 14. The relative rate measurement of Atkinson *et al.*⁹⁴ at room temperature is in excellent agreement with that determined by Greiner¹⁴ using flash photolysis-kinetic spectroscopy.

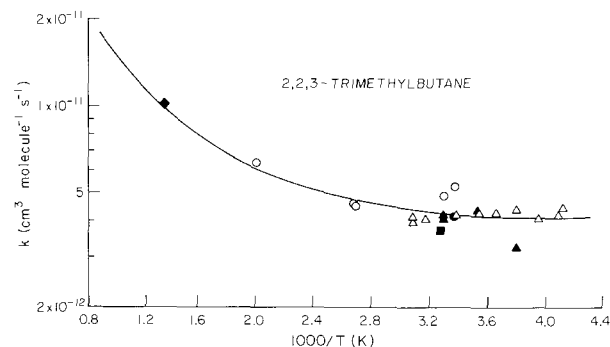


FIG. 13. Arrhenius plot of rate constants for the reaction of the OH radical with 2,2,3-trimethylbutane. (○) Greiner;¹⁴ (■) Darnall *et al.*;¹⁰⁷ (◆) Baldwin *et al.*;¹⁰⁸ (●) Atkinson *et al.*;⁹⁴ (▲) Harris and Kerr,⁹⁹ relative to *n*-pentane; (Δ) Harris and Kerr,⁹⁹ relative to *n*-hexane; (—) recommendation (see text).

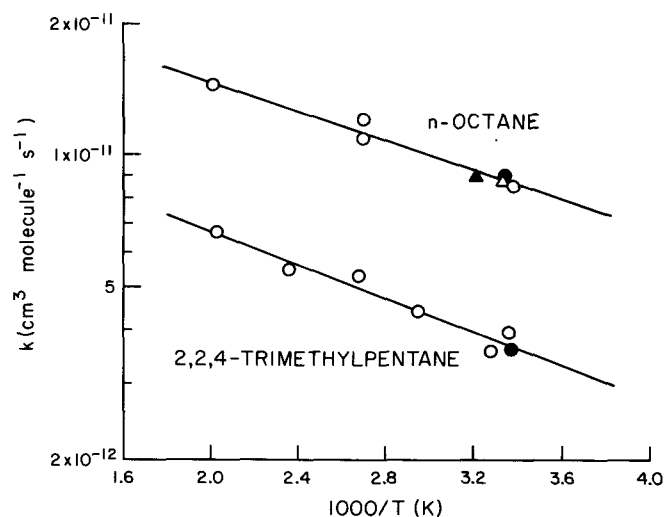


FIG. 14. Arrhenius plots of rate constants for the reactions of the OH radical with *n*-octane and 2,2,4-trimethylpentane. (○) Greiner;¹⁴ (●) Atkinson *et al.*⁷³ (*n*-octane), Atkinson *et al.*⁹⁴ (2,2,4-trimethylpentane); (Δ) Behnke *et al.*;⁷⁶ (▲) Nolting *et al.*;⁹⁸ (—) recommendations (see text).

A unit-weighted least-squares analysis of these data^{14,94} yields the recommended Arrhenius expression of

$$k(2,2,4\text{-trimethylpentane}) = (1.61^{+0.44}_{-0.35}) \times 10^{-11} e^{-(440 \pm 84)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 297–493 K, where the indicated error limits are two least-squares standard deviations, and

$$k(2,2,4\text{-trimethylpentane}) = 3.68 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K},$$

with an estimated overall uncertainty at 298 K of $\pm 20\%$. This expression is virtually identical to that recommended by Atkinson¹²⁰ of

$$k(2,2,4\text{-trimethylpentane}) = 1.62 \times 10^{-11} e^{-443/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the same temperature range (the slight difference arising from reevaluating the relative rate constant of Atkinson *et al.*⁹⁴).

(19) 2,2,3,3-Tetramethylbutane

The available rate constant data of Greiner,¹⁴ Baldwin *et al.*,^{46,109} Atkinson *et al.*⁹⁴ and Tully *et al.*¹⁰³ are given in

Table 1 and are plotted in Arrhenius form in Fig. 15. Again, the agreement between these kinetic studies is generally excellent. The Arrhenius plot (Fig. 15) clearly exhibits curvature and hence a unit-weighted least-squares analysis of these data of Greiner,¹⁴ Baldwin *et al.*,⁴⁶ Atkinson *et al.*⁹⁴ and Tully *et al.*,¹⁰³ using the expression $k = CT^2 e^{-D/T}$, yields the recommendation of

$$k(2,2,3,3\text{-tetramethylbutane}) = (1.63^{+0.34}_{-0.28}) \times 10^{-17} T^2 e^{-(86 \pm 72)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 290–753 K, where the indicated error limits are two least-squares standard deviations, and

$$k(2,2,3,3\text{-tetramethylbutane}) = 1.08 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K},$$

with an estimated overall uncertainty at 298 K of $\pm 20\%$. This recommendation agrees to within 10% over this temperature range with that of Atkinson¹²⁰ of

$$k(2,2,3,3\text{-tetramethylbutane}) = 1.87 \times 10^{-17} T^2 e^{-133/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

derived over the temperature range 290–738 K.

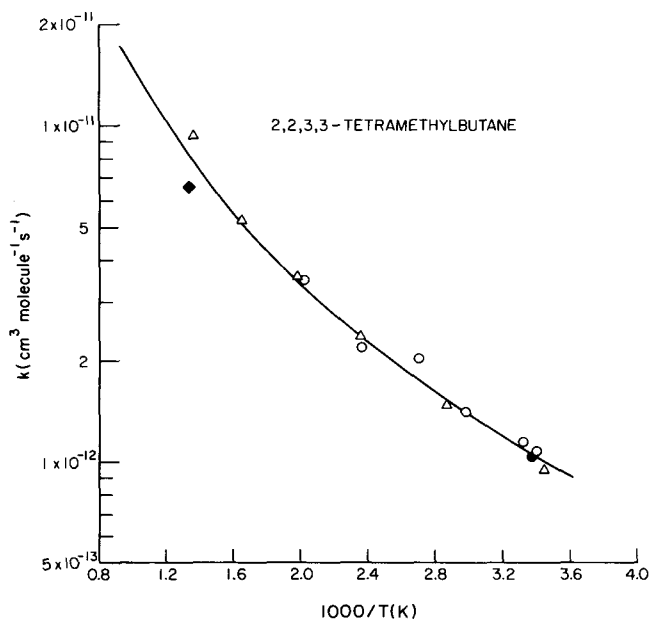


FIG. 15. Arrhenius plot of rate constants for the reaction of the OH radical with 2,2,3,3-tetramethylbutane. (○) Greiner;¹⁴ (◆) Baldwin *et al.*;^{46,109} (●) Atkinson *et al.*;⁹⁴ (Δ) Tully *et al.*;¹⁰³ (—) recommendation (see text).

(20) *n*-Nonane through *n*-Tridecane

For these *n*-alkanes, the only rate constant data available are from the relative rate studies of Zetzsch and co-workers^{76,78,89,98} and, for *n*-nonane and *n*-decane, of Atkinson *et al.*,⁷³ all carried out at around room temperature. The agreement between these studies is good. For these alkanes, the temperature dependence of the rate constant around 300 K is calculated to be approximately equivalent to $B = 225$ K,^{124,127} and hence the rate constants at 312 K should be $\sim 3\%$ higher than those at 299–300 K. From the data of Behnke *et al.*,^{76,89} Nolting *et al.*⁹⁸ and Atkinson *et al.*,⁷³ the recommended rate constants at 298 K are:

$$k(n\text{-nonane}) = 1.02 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

$$k(n\text{-decane}) = 1.16 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

$$k(n\text{-undecane}) = 1.32 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

$$k(n\text{-dodecane}) = 1.42 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

and

$$k(n\text{-tridecane}) = 1.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

all with estimated overall uncertainties at 298 K of $\pm 25\%$.

(21) Cyclopentane

The rate constant data of Volman,¹¹³ Darnall *et al.*,⁷¹ Atkinson *et al.*¹⁰² (which supersedes the earlier rate constant of Darnall *et al.*⁷¹), Jolly *et al.*¹¹¹ and Droege and Tully¹¹⁴ are given in Table 2 and are plotted in Arrhenius form in Fig. 16. No details are available concerning the rate constant obtained by Volman¹¹³ from a relative rate study and, as noted above, the study of Darnall *et al.*⁷¹ has been superseded by the more recent kinetic investigation of Atkinson *et al.*¹⁰² At room temperature the absolute rate constants of Jolly *et al.*¹¹¹ and Droege and Tully¹¹⁴ and the relative rate measurement of Atkinson *et al.*¹⁰² are in excellent agreement. A unit-weighted least-squares analysis of these data,^{102,111,114} using the equation $k = CT^2e^{-D/T}$, leads to the recommendation of

$$k(\text{cyclopentane}) = (2.13_{-0.14}^{+0.16}) \times 10^{-17} T^2 e^{(299 \pm 24)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 295–491 K, where the indicated error limits are two least-squares standard deviations, and

$$k(\text{cyclopentane}) = 5.16 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty at 298 K of $\pm 20\%$.

Droege and Tully¹¹⁴ also determined rate constants for cyclopentane-*d*₁₀ (Table 2) and, from their data for cyclopentane and cyclopentane-*d*₁₀, obtained the deuterium isotope ratio of

$$\frac{k(\text{cyclopentane})}{k(\text{cyclopentane-}d_{10})} = \frac{k(-\text{CH}_2-)}{k(-\text{CD}_2-)} = (1.16 \pm 0.10) e^{(254 \pm 15)/T}.$$

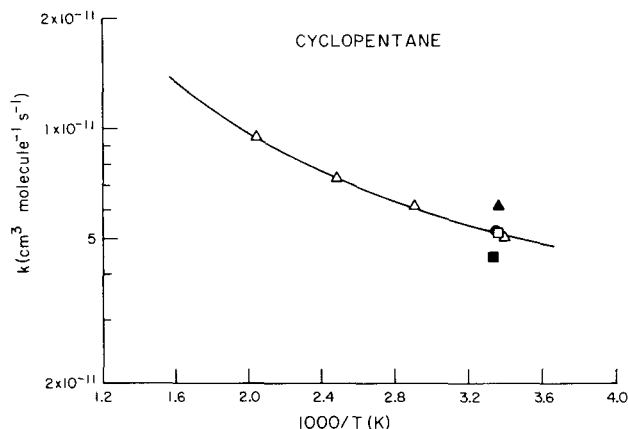


FIG. 16. Arrhenius plot of rate constants for the reaction of the OH radical with cyclopentane. (▲) Volman;¹¹³ (■) Darnall *et al.*;⁷¹ (●) Atkinson *et al.*;¹⁰² (□) Jolly *et al.*;¹¹¹ (Δ) Droege and Tully;¹¹⁴ (—) recommendation (see text).

(22) Cyclohexane

The available rate constant data of Greiner,¹⁴ Gorse and Volman,⁶⁹ Wu *et al.*,⁹¹ Atkinson *et al.*,^{102,115} Tuazon *et al.*,¹¹⁶ Nielsen *et al.*,⁶⁰ Edney *et al.*,⁶² Bourmada *et al.*⁶³ and Droege and Tully¹¹⁴ are given in Table 2 and are plotted in Arrhenius form in Fig. 17. There is an appreciable degree of scatter in the rate constants determined at around room temperature. The relative rate constants of Gorse and Volman⁶⁹ and Wu *et al.*⁹¹ are subject to large uncertainties (of the order of $\pm 20\text{--}25\%$) and the absolute rate constant reported by Nielsen *et al.*⁶⁰ is significantly lower than the other room temperature data. Hence, the rate constants of Greiner,¹⁴ Atkinson *et al.*,^{102,115} Tuazon *et al.*,¹¹⁶ Edney *et al.*,⁶² Bourmada *et al.*⁶³ and Droege and Tully¹¹⁴ have been used in the evaluation of this rate constant. A unit-weighted least-squares analysis of these rate constants, using the equation $k = CT^2e^{-D/T}$, yields the recommendation of

$$k(\text{cyclohexane}) = (2.66_{-0.65}^{+0.85}) \times 10^{-17} T^2 e^{(344 \pm 95)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 292–497 K, where the indicated error limits are two least-squares standard deviations, and

$$k(\text{cyclohexane}) = 7.49$$

$$\times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of $\pm 25\%$.

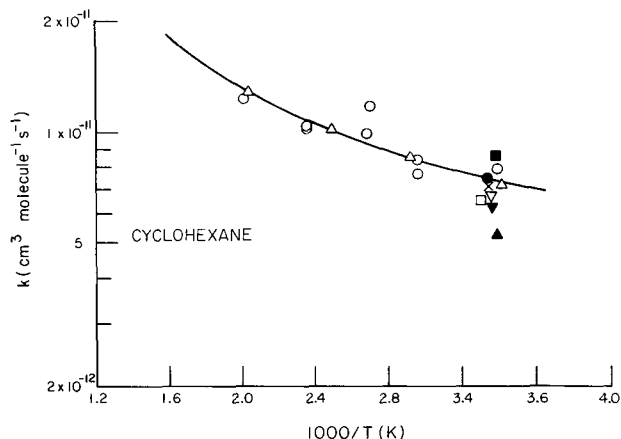


FIG. 17. Arrhenius plot of rate constants for the reaction of the OH radical with cyclohexane. (○) Greiner;¹⁴ (∇) Gorse and Volman;⁶⁹ (□) Wu *et al.*;⁹¹ (●) Atkinson *et al.*¹⁰² and Tuazon *et al.*;¹¹⁶ (x) Atkinson *et al.*;¹¹⁵ (▲) Nielsen *et al.*;⁶⁰ (▼) Edney *et al.*;⁶² (■) Bourmada *et al.*;⁶³ (Δ) Droege and Tully;¹¹⁴ (—) recommendation (see text).

This recommendation yields similar rate constants over the temperature range 290–500 K to those calculated from the Arrhenius expression of

$$k(\text{cyclohexane}) = 2.73$$

$$\times 10^{-11} e^{-390/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

recommended by Atkinson,¹²⁰ although it yields significantly different rate constants at temperatures above 500 K and below 290 K.

From their rate constants for cyclohexane and cyclohexane-*d*₁₂, Droege and Tully¹¹⁴ derived the deuterium isotope effect of

$$\frac{k(\text{cyclohexane})}{k(\text{cyclohexane-}d_{12})} = \frac{k(-\text{CH}_2-)}{k(-\text{CD}_2-)} \\ = (1.16 \pm 0.06) e^{(237 \pm 9)/T}.$$

(23) Other Acyclic and Cycloalkanes

For the remaining acyclic alkanes and cycloalkanes for which rate constants are available (Tables 1 and 2), data are available only at room temperature or from only one study. No specific recommendations are made for these alkanes based upon the experimental data, although it should be noted that the data of Jolly *et al.*¹¹¹ and Behnke *et al.*⁷⁸ for cycloheptane are in good agreement, and those of Atkinson *et al.*¹¹⁷ and Behnke *et al.*⁷⁸ for tricyclo[3.3.1.1^{3,7}]decane (adamantane) are in excellent agreement.

In the above evaluation and recommendation of OH radical reaction rate constants for the alkanes, data are available in many cases over only restricted temperature ranges (for example, ~ 300 – 500 K) and then often only for the overall reaction. For the majority of alkanes, the C–H bonds are non-equivalent, and hence multiple reaction pathways are operative leading to a variety of alkyl radicals. While the experimental data generally do not distinguish between these initial OH radical reaction routes, estimation methods are now available^{124,127–129} which do allow the overall reaction rate constants and the distribution of alkyl radicals formed to be estimated, apparently with reasonable accuracy.

In the recent estimation technique of Atkinson,^{124,127} H-atom abstraction from C–H bonds is dealt with in terms of H-atom abstraction from $-\text{CH}_3$, $-\text{CH}_2-$ and $>\text{CH}-$ groups, with:

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

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

and

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

where

k_{prim}° , k_{sec}° and k_{tert}° are the group rate constants for H-atom abstraction from primary, secondary and tertiary groups, respectively, for a standard substituent, and $F(\text{X})$, $F(\text{Y})$ and $F(\text{Z})$ are the factors for substituent groups X, Y and Z, respectively. The standard substituent is taken to be $-\text{CH}_3$, with $F(-\text{CH}_3) = 1.00$ at all temperatures. From the previous review and evaluation of Atkinson,¹²⁰ the following parameters were obtained:^{124,127}

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

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

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

and

$$F(-\text{CH}_2-) = F(>\text{CH}-) = F(>\text{C}<) = e^{76/T},$$

applicable for the temperature range ~ 250 – 1000 K. For three- to seven-membered cyclic rings, the factors F_{ring} of $F_3 = e^{-1214/T}$, $F_4 = e^{-451/T}$, $F_5 = e^{-66/T}$ and $F_6 = F_7 = 1.00$ were derived (these ring strain factors are applicable only to the C–H bonds involved in the ring structure, and not to substituent side-chains).¹¹² Figures 18–20 show the fits of the rate constants calculated in this manner with the recommended rate constants for those alkanes (apart from methane and ethane) for which recommendations have been made as a function of temperature. The fits are seen to be generally excellent over the temperature ranges for which experimental data and recommendations are available (~ 250 – 1000 K). Thus, this estimation method can be used to provide the rate constants and/or temperature dependencies of the rate constants for these alkanes for which either no data are available or only room temperature rate constants are available.

In addition, this estimation technique allows the distribution of alkyl radicals formed in these OH radical reactions to be calculated at temperatures in the range ~ 250 – 1000 K. Thus, the calculated distributions of the individual reaction pathways for H-atom abstraction from the primary, secondary and tertiary C–H bonds for propane, *n*-butane and 2-methylpropane agree well with those derived from the kinetic studies of Tully and co-workers.^{75,87,96}

Based upon the kinetic studies of Tully and co-workers for the reactions of OH radicals with ethane,⁵⁹ propane,⁷⁵ *n*-butane,⁸⁷ 2-methylpropane,⁹⁶ 2,2-dimethylpropane,⁵⁹ cyclopentane¹¹⁴ and cyclohexane,¹¹⁴ the deuterium isotope effects for H- or D-atom abstraction from primary, secondary and tertiary C–H or C–D bonds depend predominantly on whether the C–H or C–D bond is primary, secondary or tertiary, and not on the neighboring groups. Based upon the experimental data of Tully and co-workers,^{59,75,87,96,114} the ratios $k(\text{abstraction from C–H bonds})/k(\text{abstraction from C–D bonds}) = k^{\text{H}}/k^{\text{D}}$ of

$$k^{\text{H}}/k^{\text{D}} = e^{460/T} \text{ for primary bonds,}$$

$$k^{\text{H}}/k^{\text{D}} = e^{290/T} \text{ for secondary bonds}$$

and

$$k^{\text{H}}/k^{\text{D}} \approx e^{190/T} \text{ for tertiary bonds,}$$

are applicable over the temperature range ~ 290 – 800 K. These deuterium isotope ratios can be combined with the $-\text{CH}_3$, $-\text{CH}_2-$ and $>\text{CH}-$ group rate constants discussed above to allow the OH radical reaction rate constants to be calculated for fully or partially deuterated alkanes for which no experimental data are available.

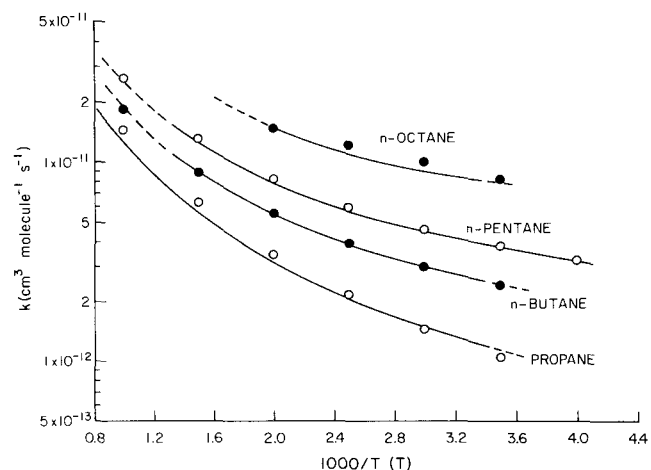


FIG. 18. Arrhenius plot of rate constants for the reactions of the OH radical with propane, *n*-butane, *n*-pentane, and *n*-octane. (○, ●) Recommended rate constants; (—, — —) calculated from the estimation technique of Atkinson^{124,127} (solid lines define the temperature ranges encompassed by the recommendations).

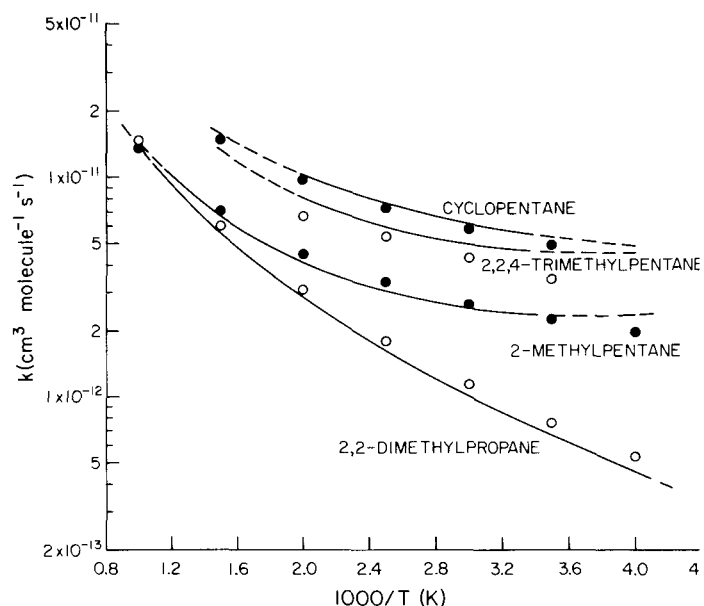


FIG. 19. Arrhenius plots of rate constants for the reactions of the OH radical with 2,2-dimethylpropane, 2-methylpentane, 2,2,4-trimethylpentane and cyclopentane. (○, ●) Recommended rate constants; (—, — —) calculated from the estimation technique of Atkinson^{124,127} (solid lines define the temperature ranges encompassed by the recommendations).

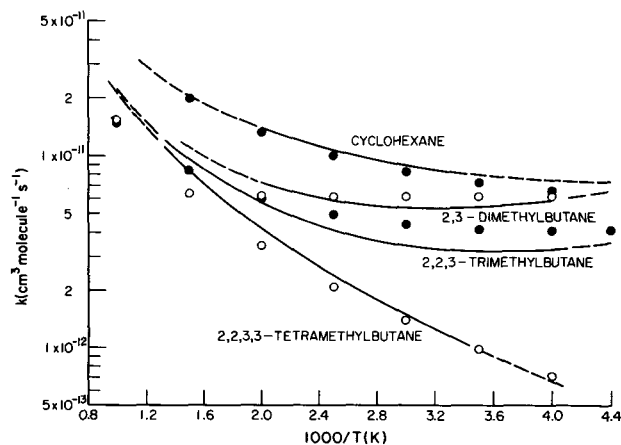


FIG. 20. Arrhenius plots of rate constants for the reactions of the OH radical with 2,3-dimethylbutane, 2,2,3-trimethylbutane, 2,2,3,3-tetramethylbutane and cyclohexane. (○, ●) Recommended rate constants; (—, — — —) calculated from the estimation technique of Atkinson^{124,127} (solid lines define the temperature ranges encompassed by the recommendations).

(24) Reactions of OD Radicals with Alkanes

To date, kinetic data are available (Table 3) for only four alkanes, and then only at room temperature. By comparison with the data given in Table 1, it is evident that the rate constants at room temperature for the reactions of the OD radical with methane, ethane and *n*-butane are essentially identical to those for the reactions of the OH radical with these alkanes. This is to be expected, since the thermochemistries of these OD radical reactions are essentially identical to those for the corresponding OH radical reactions.¹³⁰ Moreover, as with the OH radical reactions, the rate constant for the reaction of OD radicals with *n*-butane-*d*₁₀⁸⁴ is lower by a factor of ~3 than that for the reaction of OD radicals with *n*-butane, and is essentially identical to that for the reaction of OH radicals with *n*-butane-*d*₁₀. This is again expected on thermochemical grounds, since the abstraction of D-atoms from C—D bonds by OH or OD radicals are less exothermic by ~0.9 kcal mole⁻¹ than are the corresponding abstractions of H-atoms from C—H bonds.¹³⁰

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2.2. Haloalkanes

a. Kinetics

The available rate constant data are listed in Table 4. The relative rate constants reported by Butler *et al.*³⁴ are not included, since these were derived from a complex expression which cannot be reevaluated using the more recent rate constants for the reference reactions. It should also be noted that the rate constants derived from the study of Cox *et al.*⁷ have a stated accuracy of approximately a factor of two, due to uncertainties in the number of molecules of NO oxidized per OH radical reacted.⁷ It can then be seen that essentially all of the data listed in Table 4 for the C₁ and C₂ haloalkanes have been determined from absolute rate constant studies.

As discussed below for the individual haloalkanes, apart from CH₃CCl₃ for which significant discrepancies appear to have arisen in all but the most recent studies^{4,28,29} due to problems associated with the presence of reactive impurities, these absolute rate data are in general agreement, with the exception of the rate constants determined from the studies of Clyne and Holt¹⁴ and Nielsen *et al.*¹¹ As noted in previous evaluations,³⁵⁻³⁷ for several of the haloalkanes studied by Clyne and Holt¹⁴ the room temperature rate constants and Arrhenius activation energies are significantly higher than the other absolute literature values. Furthermore, in many cases the derived Arrhenius preexponential factors¹⁴ (Table 4) appear to be unreasonably high. Thus, these data of Clyne and Holt¹⁴ have not been used in the evaluations of the recommended rate expressions for the haloalkanes.

It is apparent that for most of these haloalkanes the Arrhenius plots exhibit distinct curvature. In accordance with the recent evaluations of Atkinson³⁶ and DeMore *et al.*,³⁷ in most cases least-squares analyses of the rate constant data for these haloalkanes have been carried out

using the expression $k = CT^2e^{-D/T}$, and the recommendations are generally in this form. The use of this expression yields good fits to the experimental data over the temperature ranges studied (i.e., ~240–500 K), although Cohen and Benson^{38,39} used transition state calculations to obtain values of n in the three parameter equation $k = AT^n e^{-B/T}$ of ~1.1–1.8 for a series of halomethanes and haloethanes.

The kinetic data for the individual haloalkanes are discussed below.

(1) CH₃F

The available rate constants¹⁻⁵ are listed in Table 4 and plotted in Arrhenius form in Fig. 21. These rate constants of Howard and Evenson,¹ Nip *et al.*,² Jeong and Kaufman^{3,4} and Bera and Hanrahan⁵ are in reasonably good agreement at room temperature. However, since secondary reactions of the OH radical with CH₂F radicals and other radical species were expected⁵ to occur in the pulsed radiolysis study of Bera and Hanrahan,⁵ the rate constant determined by Bera and Hanrahan⁵ was not used in the rate constant evaluation. (This was also the case for the CH₂F₂ reaction.) A unit-weighted least-squares analysis of the data of Howard and Evenson,¹ Nip *et al.*² and Jeong and Kaufman^{3,4} yields the recommended expression of

$$k(\text{CH}_3\text{F}) = (5.51^{+3.36}_{-2.09}) \times 10^{-18} T^2 e^{-(1005 \pm 168)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 292–480 K, where the indicated error limits are two least-squares standard deviations, and

$$k(\text{CH}_3\text{F}) = 1.68 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of $\pm 30\%$. This recommendation is identical to that of Atkinson.³⁶

(2) CH₃Cl

The available rate constants of Wilson *et al.*,⁶ Howard and Evenson,¹ Cox *et al.*⁷ (which, as noted above, is uncertain by a factor of ~2), Perry *et al.*,⁸ Davis *et al.*,⁹ Paraskevopoulos *et al.*,¹⁰ Jeong and Kaufman,³ Nielsen *et al.*¹¹ and Taylor *et al.*¹² are given in Table 4 and are plotted in Arrhenius form in Fig. 22. It can be seen that the room temperature rate constants of Howard and Evenson,¹ Perry *et al.*,⁸ Davis *et al.*,⁹ Paraskevopoulos *et al.*,¹⁰ Jeong and Kaufman³ and Taylor *et al.*¹² are in good agreement. The rate constants obtained by Nielsen *et al.*¹¹ over the temperature range ~300–400 K are uniformly higher by a factor of ~1.7 than those of Howard and Evenson,¹ Perry *et al.*,⁸ Davis *et al.*,⁹ Paraskevopoulos *et al.*,¹⁰ Jeong and Kaufman³ and Taylor *et al.*,¹² probably due to fragmentation of the CH₃Cl reactant by the

radiation beam, leading to enhanced OH radical reaction.¹¹ Furthermore, the rate constants reported from the recent laser photolysis-laser induced fluorescence study of Taylor *et al.*¹² are significantly higher than those of Perry *et al.*⁸ and Jeong and Kaufman³ at temperatures ~420–485 K. Incorporation of these data of Taylor *et al.*¹² into the evaluation leads to a rate expression which predicts rate constants at ~250 K which are ~30% lower than the measured rate constants of Davis *et al.*⁹ and Jeong and Kaufman.³ Accordingly, the rate constant data of Taylor *et al.*¹² have not been used in the evaluation of the rate constant for this reaction.

A unit-weighted least-squares analysis of the rate constant data of Howard and Evenson,¹ Perry *et al.*,⁸ Davis *et al.*,⁹ Paraskevopoulos *et al.*¹⁰ and Jeong and Kaufman,³ using the expression $k = CT^2e^{-D/T}$, yields the recommendation of

$$k(\text{CH}_3\text{Cl}) = (3.50^{+0.71}_{-0.58}) \times 10^{-18} T^2 e^{-(885 \pm 59)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 250–483 K, where the indicated error limits are two least-squares standard deviations, and

$$k(\text{CH}_3\text{Cl}) = 4.36 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of $\pm 20\%$. This recommendation is identical to that of Atkinson³⁶ and essentially identical to that recommended in the recent NASA evaluation.³⁷

The rate constants calculated from the recommended expression at 1850–2100 K are in good agreement with those derived from the relative rate study of Wilson *et al.*,⁶ and this observation allows the recommended expression to be used with some degree of confidence up to ~2000 K. The rate constant of Wilson¹³ for CH_3Br obtained from a related relative rate study can then be used, in conjunction with the absolute rate constants determined over the temperature range 244–350 K, for the evaluation of the OH radical reaction with CH_3Br (see below).

TABLE 4. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with haloalkanes

Haloalkane	$10^{12} \times A$ ($\text{cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$)	n	B (K)	$10^{14} \times k$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) at T (K)	Technique	Reference	Temperature range covered (K)		
CH ₃ F				1.6 ± 0.35	296 \pm 2	DF-LMR	Howard and Evenson ¹		
				2.17 ± 0.18	297 \pm 2	FP-RA	Nip <i>et al.</i> ²		
				1.40 ± 0.09	292	DF-RF	Jeong and Kaufman ^{3,4}		
				2.50 ± 0.18	330				
				3.86 ± 0.33	356				
				4.76 ± 0.31	368				
				5.48 ± 0.66	385				
				8.56 ± 0.66	416				
		7.96×10^{-13}	4.32	277 ± 730	13.1 ± 1.1	455			
		8.11 ± 1.35		1887 ± 60	17.1 ± 1.1	480			
				1.71 ± 0.24	308	PR-RA	Bera and Hanrahan ⁵		
CH ₃ Cl				1200	1850–2100	RR [relative to $k(\text{CO}) = 1.12 \times 10^{-13} e^{0.000907/T}$] ^a	Wilson <i>et al.</i> ⁶	1850–2100	
				3.6 ± 0.8	296 \pm 2	DF-LMR	Howard and Evenson ¹		
				10.2	298	RR [relative to $k(\text{methane}) = 8.36 \times 10^{-15}$] ^b	Cox <i>et al.</i> ⁷		
				4.4 ± 0.5	298.4	FP-RF	Perry <i>et al.</i> ⁸	298–423	
				8.1 ± 0.8	349.3				
	4.1			1359 ± 151	16.8 ± 1.7	422.6			
					2.38 ± 0.14	250	FP-RF	Davis <i>et al.</i> ⁹	250–350
					3.26 ± 0.06	273			

TABLE 4. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with haloalkanes — Continued

Haloalkane	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	n	B (K)	$10^{14} \times k$ (cm^3 $\text{molecule}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Tempera- ture range covered (K)
	1.84 ± 0.18		1098 ± 35	4.29 ± 0.21	298			
				8.28 ± 0.28	350			
				4.10 ± 0.68	297	FP-RA	Paraskevopoulos <i>et al.</i> ¹⁰	
				2.03 ± 0.15	247	DF-RF	Jeong and Kaufman ^{3,4}	247–483
				3.95 ± 0.26	293			
				6.68 ± 0.46	332			
				8.74 ± 0.58	363			
				12.8 ± 0.9	401			
				16.3 ± 1.3	426			
	2.21×10^{-9}	3.08	232 ± 423	25.4 ± 2.0	483			
	3.04 ± 0.43		1263 ± 45					
	5.31		1263	7.14	300	PR-RA	Nielsen <i>et al.</i> ¹¹	300–400
				4.9 ± 0.6	295	LP-LIF	Taylor <i>et al.</i> ¹²	295–800
				7.0 ± 0.6	335			
				10.3 ± 1.9	375			
				10.1 ± 1.1	378			
				20.1 ± 1.9	428			
				29.3 ± 6.6	473			
				31.8 ± 3.5	475			
				53.3 ± 4.7	524			
				48.2 ± 1.4	525			
				71.0 ± 3.7	575			
				80.8 ± 3.4	615			
				103 ± 3.5	655			
				109 ± 9.7	667			
				111 ± 9.6	667			
				130 ± 12.0	695			
				137 ± 10.9	695			
				168 ± 20.1	735			
	8.38×10^{-4}	1.38	1202 ± 72	185 ± 6.8	800			
CH ₃ Br				760	1800–2000	RR [relative to $k(\text{CH}_4) = 6.95$ $\times 10^{-18} T^2 e^{-1282/T}$] ^b	Wilson ¹³	1800–2000
				3.5 ± 0.8	296 ± 2	DF-LMR	Howard and Evenson ¹	
				2.01 ± 0.12	244	FP-RF	Davis <i>et al.</i> ⁹	244–350
				3.16 ± 0.15	273			
				4.14 ± 0.43	298			
	0.793 ± 0.079		889 ± 58	6.08 ± 0.4	350			
CH ₂ F ₂				0.78 ± 0.12	296 ± 2	DF-LMR	Howard and Evenson ¹	
				0.58 ± 0.03	293	DF-RF	Clyne and Holt ¹⁴	293–429
				1.61 ± 0.50	327			
				2.41 ± 0.35	368			
	$7.4^{+7.4}_{-3.7}$		2100 ± 200	6.03 ± 0.40	429			
				1.17 ± 0.14	297 ± 2	FP-RA	Nip <i>et al.</i> ²	
				0.429 ± 0.038	250	DF-RF	Jeong and Kaufman ^{3,4}	250–492
				1.12 ± 0.075	298			
				2.10 ± 0.14	336			
				4.34 ± 0.27	384			
				7.27 ± 0.46	432			
				9.51 ± 0.66	464			
	2.52×10^{-9}	3.09	679 ± 458	14.1 ± 1.2	492			
	4.37 ± 0.58		1766 ± 50					

TABLE 4. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with haloalkanes — Continued

Haloalkane	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$) ^{<i>n</i>}	<i>B</i> (K)	$10^{14} \times k$ (cm^3 molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference	Tempera- ture range covered (K)
			0.88 ± 0.14	308	PR-RA	Bera and Hanrahan ⁵	
CH ₂ FCI			3.7 ± 0.6	296 ± 2	DF-LMR	Howard and Evenson ¹	
			1.65 ± 0.36	245	FP-RF	Watson <i>et al.</i> ¹⁵	245–375
			4.21 ± 0.41	298			
	2.84 ± 0.3	1259 ± 50	9.80 ± 0.34	375			
			2.8 ± 0.5	273	FP-RA	Handwerk and Zellner ¹⁶	273–373
			3.5 ± 0.7	293			
	3.1 ± 0.9	1320 ± 100	11 ± 2	373			
			4.45 ± 0.66	297	FP-RA	Paraskevopoulos <i>et al.</i> ¹⁰	
			2.76 ± 0.18	250	DF-RF	Jeong and Kaufman ^{3,4}	250–486
			4.94 ± 0.30	295			
			6.60 ± 0.40	323			
			8.85 ± 0.55	348			
			14.0 ± 0.9	399			
			17.2 ± 1.1	438			
	1.57×10^{-7}	2.41	307 ± 382	25.4 ± 1.7	486		
2.37 ± 0.29		1137 ± 40					
CH ₂ Cl ₂			15.5 ± 3.4	296 ± 2	DF-LMR	Howard and Evenson ¹	
			12.4	298	RR [relative to k (methane) $= 8.36 \times 10^{-15}$] ^b	Cox <i>et al.</i> ⁷	
			14.5 ± 2.0	298.5	FP-RF	Perry <i>et al.</i> ⁸	
			4.75 ± 0.57	245	FP-RF	Davis <i>et al.</i> ⁹	245–375
			11.6 ± 0.5	298			
	4.27 ± 0.63	1094 ± 81	22.3 ± 0.5	375			
			9.59 ± 0.69	251	DF-RF	Jeong and Kaufman ^{3,4}	251–455
			15.3 ± 0.95	292			
			20.8 ± 1.4	323			
			27.6 ± 1.9	342			
			35.2 ± 2.4	384			
			45.0 ± 2.9	415			
	1.61×10^{-7}	2.54	186 ± 493	60.9 ± 3.8	455		
	5.57 ± 0.77		1042 ± 45				
	6.81	1117	14.6	300	PR-RA	Nielsen <i>et al.</i> ¹¹	300–400
			17.6 ± 2.0	298	LP-LIF	Taylor <i>et al.</i> ¹²	298–775
			18.7 ± 4.7	299			
			24.8 ± 2.3	335			
			29.4 ± 2.8	376			
			43.3 ± 4.2	425			
			61.5 ± 6.9	455			
		72.1 ± 18.0	474				
		85.8 ± 5.9	495				
		97.8 ± 9.1	535				
		119 ± 7.3	575				
		151 ± 13.4	615				
		155 ± 10.9	615				
		163 ± 8.7	655				
		170 ± 7.5	655				
		202 ± 10.7	695				
		224 ± 11.7	735				
1.52×10^{-4}	1.58	622 ± 60	257 ± 10.8	775			

TABLE 4. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with haloalkanes — Continued

Haloalkane	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	n	B (K)	$10^{14} \times k$ (cm^3 $\text{molecule}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Tempera- ture range covered (K)	
CHF ₃				$0.02^{+0.02}_{-0.015}$	296 ± 2	DF-LMR	Howard and Evenson ¹		
				183	1300	RR [relative to $k(\text{H}_2) = 5.69 \times 10^{-12}]^a$	Bradley <i>et al.</i> ¹⁷		
				55	1255	SH/FP-RA	Ernst <i>et al.</i> ¹⁸	1255–1445	
				60	1320				
				66	1320				
				83	1345				
				70	1395				
				55	1400				
				93	1445				
					0.13 ± 0.04	296	DF-RF	Clyne and Holt ¹⁴	296–430
					0.14 ± 0.06	430			
					0.035 ± 0.017	297 ± 2	FP-RA	Nip <i>et al.</i> ²	
					0.169 ± 0.011	387	DF-RF	Jeong and Kaufman ^{3,4}	387–480
					0.237 ± 0.017	410			
					0.331 ± 0.027	428			
					0.448 ± 0.029	447			
					0.564 ± 0.036	465			
		2.98 ± 1.07		2909 ± 156	0.719 ± 0.045	480			
					0.23 ± 0.04	308	PR-RA	Bera and Hanrahan ⁵	
CHF ₂ Cl				0.475 ± 0.048	296.9	FP-RF	Atkinson <i>et al.</i> ¹⁹	297–434	
				1.15 ± 0.12	348.0				
		1.21		1636 ± 151	2.71 ± 0.27	433.7			
					0.34 ± 0.07	296 ± 2	DF-LMR	Howard and Evenson ¹	
					0.170 ± 0.040	250	FP-RF	Watson <i>et al.</i> ¹⁵	250–350
					0.277 ± 0.038	273			
					0.48 ± 0.046	298			
		0.925 ± 0.10		1575 ± 71	1.01 ± 0.08	350			
					0.177 ± 0.002	253	DF-RF	Chang and Kaufman ²⁰	253–427
					0.425 ± 0.028	296			
					1.20 ± 0.03	358			
		1.20 ± 0.16		1657 ± 39	2.49 ± 0.10	427			
					0.20	263	FP-RA	Handwerk and Zellner ¹⁶	263–373
					0.27	273			
					0.51	283			
					0.46 ± 0.08	293			
		2.1 ± 0.6		1780 ± 150	1.7 ± 0.3	373			
					0.33 ± 0.07	294	DF-RF	Clyne and Holt ¹⁴	294–426
					0.77 ± 0.12	321			
				1.28 ± 0.11	343				
				1.97 ± 0.07	376				
				2.77 ± 0.17	391				
	$9.5^{+1.7}_{-1.4}$		2300 ± 200	3.90 ± 0.07	426				
				0.458 ± 0.058	297	FP-RA	Paraskevopoulos <i>et al.</i> ¹⁰		
				0.483 ± 0.032	293	DF-RF	Jeong and Kaufman ^{3,4}	293–482	
				0.768 ± 0.048	327				
				1.08 ± 0.075	360				
				1.79 ± 0.14	391				
				2.75 ± 0.18	436				

TABLE 4. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with haloalkanes — Continued

Haloalkane	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	n	B (K)	$10^{14} \times k$ (cm^3 $\text{molecule}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
	5.03×10^{-16}	5.11	-252 ± 780	4.39 ± 0.27	482			
	1.27 ± 0.21		1661 ± 60					
CHFC _l ₂				2.6 ± 0.4	296 ± 2	DF-LMR	Howard and Evenson ¹	
				2.7 ± 0.3	298.4	FP-RF	Perry <i>et al.</i> ⁸	298–422
				4.8 ± 0.5	349.5			
	1.75		1253 ± 151	9.1 ± 0.9	421.7			
				1.12 ± 0.12	245	FP-RF	Watson <i>et al.</i> ¹⁵	245–375
				2.09 ± 0.18	273			
				2.88 ± 0.24	298			
	1.87 ± 0.2		1245 ± 26	6.68 ± 0.82	375			
				1.28 ± 0.25	241	DF-RF	Chang and Kaufman ²⁰	241–396
				1.73 ± 0.13	250			
				2.70 ± 0.20	288			
				3.04 ± 0.11	296			
				7.17 ± 0.16	380			
	1.16 ± 0.17		1073 ± 40	7.52 ± 0.29	396			
				3.54 ± 0.26	293	DF-RF	Clyne and Holt ¹⁴	293–413
				6.57 ± 0.22	330			
				9.77 ± 0.38	373			
	$4.8_{-0.8}^{+1.0}$		1400 ± 100	15.2 ± 1.0	413			
				3.39 ± 0.86	297	FP-RA	Paraskevopoulos <i>et al.</i> ¹⁰	
				1.88 ± 0.14	250	DF-RF	Jeong and Kaufman ^{3,4}	250–483
				3.37 ± 0.22	295			
				4.25 ± 0.27	315			
				5.85 ± 0.36	354			
				7.86 ± 0.48	392			
				10.5 ± 0.65	433			
	1.97×10^{-6}	1.94	382 ± 413	14.8 ± 1.0	483			
	1.19 ± 0.15		1052 ± 45					
	1.83		1787	0.515	300	PR-RA	Nielsen <i>et al.</i> ¹¹	300–400
CHCl ₃				10.1 ± 1.5	296 ± 2	DF-LMR	Howard and Evenson ¹	
				20.0	298	RR [relative to $k(\text{methane})$ $= 8.36 \times 10^{-15}]^b$	Cox <i>et al.</i> ⁷	
				4.39 ± 0.28	245	FP-RF	Davis <i>et al.</i> ⁹	245–375
				11.4 ± 0.7	298			
	4.69 ± 0.71		1134 ± 108	21.8 ± 1.4	375			
				5.51 ± 0.41	249	DF-RF	Jeong and Kaufman ^{3,4}	249–487
				10.1 ± 0.65	298			
				16.0 ± 1.0	339			
				23.2 ± 1.6	370			
				30.8 ± 2.0	411			
				44.8 ± 2.7	466			
	6.91×10^{-8}	2.65	262 ± 398	55.0 ± 3.9	487			
	5.63 ± 0.68		1183 ± 45					
				29	300	RR [relative to $k(\text{toluene})$ $= 5.91 \times 10^{-12}]^b$	Klöpffer <i>et al.</i> ²¹	
				10.3 ± 1.5	295	LP-LIF	Taylor <i>et al.</i> ¹²	295–775
				11.0 ± 1.9	295			

TABLE 4. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with haloalkanes — Continued

Haloalkane	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	n	B (K)	$10^{14} \times k$ (cm^3 $\text{molecule}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
				15.5 ± 4.1	339			
				22.1 ± 2.4	383			
				32.8 ± 3.2	430			
				48.2 ± 6.4	476			
				82.8 ± 6.8	571			
				95.7 ± 10.1	626			
				108 ± 8.1	627			
				118 ± 7.9	680			
				166 ± 15.1	735			
				187 ± 11.1	772			
	1.92×10^{-8}	2.78	95 ± 60	188 ± 28.2	775			
CF ₄				<0.04	296 ± 2	DF-LMR	Howard and Evenson ¹	
				<0.1	293	DF-RF	Clyne and Holt ²²	
CF ₃ Cl				<0.07	296 ± 2	DF-LMR	Howard and Evenson ¹	
CF ₃ Br				≤0.1	298	DF-EPR	Le Bras and Combourieu ²³	
CF ₃ I				12 ± 2	295	FP-RA	Garraway and Donovan ²⁴	
CF ₂ Cl ₂				<0.1	297.3	FP-RF	Atkinson <i>et al.</i> ¹⁹	297–424
				<0.1	342.9			
				<0.1	423.8			
				<0.04	296 ± 2	DF-LMR	Howard and Evenson ¹	
				<0.012	298	RR [relative to $k(\text{methane})$ $= 8.36 \times 10^{-15}]^b$	Cox <i>et al.</i> ⁷	
				<0.06	478	DF-RF	Chang and Kaufman ²⁵	298–478
				<0.1	293	DF-RF	Clyne and Holt ²²	
CF ₂ ClBr				<0.1	293	DF-RF	Clyne and Holt ²²	
CFCl ₃				<0.1	296.8	FP-RF	Atkinson <i>et al.</i> ¹⁹	297–424
				<0.1	347.7			
				<0.1	423.8			
				<0.05	296 ± 2	DF-LMR	Howard and Evenson ¹	
				<0.005	298	RR [relative to $k(\text{methane})$ $= 8.36 \times 10^{-15}]^b$	Cox <i>et al.</i> ⁷	
				<0.05	480	DF-RF	Chang and Kaufman ²⁵	381–480
				<0.1	293	DF-RF	Clyne and Holt ²²	
CCl ₄				<0.4	296 ± 2	DF-LMR	Howard and Evenson ¹	
				<0.012	298	RR [relative to $k(\text{methane})$ $= 8.36 \times 10^{-15}]^b$	Cox <i>et al.</i> ⁷	
				<0.1	293	DF-RF	Clyne and Holt ²²	
CH ₃ CH ₂ F				23.2 ± 3.7	297 ± 2	FP-RA	Nip <i>et al.</i> ²	
CH ₃ CH ₂ Cl				39.0 ± 7.0	296	DF-LMR	Howard and Evenson ²⁶	

TABLE 4. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with haloalkanes -- Continued

Haloalkane	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$) n	B (K)	$10^{14} \times k$ (cm^3 $\text{molecule}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
CH_3CHF_2	$3.0^{+1.0}_{-0.8}$	1200 ± 100	39.4 ± 5.3	297	FP-RA	Paraskevopoulos <i>et al.</i> ¹⁰	
			3.1 ± 0.7	296	DF-LMR	Howard and Evenson ²⁶	
			3.5 ± 0.5	293	FP-RA	Handwerk and Zellner ¹⁶	
			4.66 ± 0.16	293	DF-RF	Clyne and Holt ¹⁴	293-417
			7.16 ± 0.26	323			
			10.1 ± 0.8	363			
$\text{CH}_2\text{FCH}_2\text{F}$			16.4 ± 0.5	417			
			3.70 ± 0.37	297 ± 2	FP-RA	Nip <i>et al.</i> ²	
$\text{CH}_2\text{FCH}_2\text{F}$			11.2 ± 1.2	298	FP-RA	Martin and Paraskevopoulos ²⁷	
CH_3CHCl_2			26.0 ± 6.0	296	DF-LMR	Howard and Evenson ²⁶	
$\text{CH}_2\text{ClCH}_2\text{Cl}$			22.0 ± 5.0	296	DF-LMR	Howard and Evenson ²⁶	
$\text{CH}_2\text{BrCH}_2\text{Br}$			25.0 ± 5.5	296	DF-LMR	Howard and Evenson ²⁶	
CH_3CF_3	69^{+105}_{-42}	3200 ± 500	<0.1	293	DF-RF	Clyne and Holt ¹⁴	293-425
			0.47 ± 0.15	333			
			1.29 ± 0.35	378			
			3.84 ± 1.23	425			
			0.171 ± 0.044	298	FP-RA	Martin and Paraskevopoulos ²⁷	
CH_2FCHF_2	$1.5^{+0.5}_{-0.4}$	1000 ± 100	4.98 ± 0.82	293	DF-RF	Clyne and Holt ¹⁴	293-441
			4.68 ± 0.40	294			
			6.74 ± 0.43	335			
			9.09 ± 0.42	383			
			18.9 ± 0.6	441			
$\text{CH}_3\text{CF}_2\text{Cl}$			1.83 ± 0.18	298	FP-RA	Martin and Paraskevopoulos ²⁷	
			0.283 ± 0.042	296	DF-LMR	Howard and Evenson ²⁶	
$\text{CH}_3\text{CF}_2\text{Cl}$	1.15 ± 0.15	1748 ± 30	0.46	298	RR [relative to $k(\text{methane}) = 8.36 \times 10^{-15}]^b$	Cox <i>et al.</i> ⁷	
			0.192 ± 0.048	273	FP-RF	Watson <i>et al.</i> ¹⁵	273-375
			0.322 ± 0.048	298			
			1.09 ± 0.14	375			
			0.37 ± 0.07	293	FP-RA	Handwerk and Zellner ¹⁶	293-373
$\text{CH}_3\text{CF}_2\text{Cl}$	$3.3^{+4.3}_{-1.9}$	1800 ± 300	1.4 ± 0.3	373			
			0.84 ± 0.18	293	DF-RF	Clyne and Holt ¹⁴	293-417
			0.60 ± 0.07	293			
			1.20 ± 0.11	323			
			1.44 ± 0.37	363			
			3.09 ± 0.15	380			
			4.06 ± 0.27	417			
CH_3CCl_3			0.463 ± 0.173	297	FP-RA	Paraskevopoulos <i>et al.</i> ¹⁰	
			1.5 ± 0.3	296	DF-LMR	Howard and Evenson ²⁶	
			3.36	298	RR [relative to $k(\text{methane}) = 8.36 \times 10^{-15}]^b$	Cox <i>et al.</i> ⁷	

TABLE 4. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with haloalkanes — Continued

Haloalkane	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	n	B (K)	$10^{14} \times k$ (cm^3 $\text{molecule}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
	3.72 ± 0.4		1627 ± 50	0.712 ± 0.094	260	FP-RF	Watson <i>et al.</i> ¹⁵	260–375
				1.59 ± 0.16	298			
				4.85 ± 0.58	375			
	1.95 ± 0.24		1331 ± 37	1.55 ± 0.22	275	DF-RF	Chang and Kaufman ²⁰	275–405
				2.19 ± 0.26	298			
				3.03 ± 0.30	320			
				4.94 ± 0.48	355			
				6.87 ± 0.40	405			
	$2.4^{+0.9}_{-0.7}$		1394 ± 113	1.81 ± 0.16	293	DF-RF	Clyne and Holt ²²	293–430
				2.78 ± 0.74	310			
				4.59 ± 0.56	338			
				5.73 ± 0.51	371			
				7.29 ± 0.44	399			
				8.63 ± 0.40	430			
	5.95×10^{-8}	2.65	858 ± 866	0.83 ± 0.07	278	DF-RF	Jeong and Kaufman ²⁸ ; Jeong <i>et al.</i> ⁴	278–457
				1.06 ± 0.11	293			
				2.93 ± 0.19	352			
				5.52 ± 0.41	400			
				10.2 ± 0.65	457			
5.04 ± 0.96	1797 ± 65							
	5.4 ± 1.8		1810 ± 100 (253–363 K)	0.318 ± 0.095	222	FP-RF	Kurylo <i>et al.</i> ²⁹	222–363
				0.447 ± 0.135	253			
				0.540 ± 0.145	263			
				1.08 ± 0.20	296			
				3.85 ± 0.75	363			
				0.87	298 ± 3	RR [relative to $k(\text{CH}_3\text{Cl})$ $= 4.36 \times 10^{-14}]^b$	Nelson <i>et al.</i> ³⁰	
$\text{CH}_2\text{ClCHCl}_2$				28.4 ± 2.1	277	DF-RF	Jeong and Kaufman ²⁸ ; Jeong <i>et al.</i> ⁴	277–461
				31.8 ± 2.0	295			
				37.6 ± 2.3	322			
				43.6 ± 2.8	346			
				46.8 ± 2.9	386			
				49.2 ± 3.1	400			
				52.7 ± 3.5	424			
				57.6 ± 3.7	461			
6.76×10^3	-1.21	906 ± 674						
1.65 ± 0.27		483 ± 55						
CH_2FCF_3				0.55 ± 0.07	294	DF-RF	Clyne and Holt ¹⁴	294–429
				1.32 ± 0.10	327			
				1.64 ± 0.31	344			
				1.92 ± 0.08	358			
				3.83 ± 0.49	393			
				4.20 ± 0.47	424			
				3.64 ± 0.38	429			
				0.515 ± 0.058	298	FP-RA	Martin and Paraskevopoulos ²⁷	
				0.393 ± 0.024	249	DF-RF	Jeong <i>et al.</i> ⁴	249–473
				0.441 ± 0.040	250			
				0.552 ± 0.035	268			
				0.773 ± 0.071	291			
				0.823 ± 0.055	295			
				0.844 ± 0.073	298			
				1.54 ± 0.12	342			
2.54 ± 0.17	380							

TABLE 4. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with haloalkanes — Continued

Haloalkane	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	n	B (K)	$10^{14} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
				3.94 ± 0.26	430			
				4.56 ± 0.29	447			
	1.22×10^{-13}	4.36	-45 ± 388	6.44 ± 0.40	473			
	1.10 ± 0.11		1424 ± 35					
CHF_2CHF_2				0.53 ± 0.15	294	DF-RF	Clyne and Holt ¹⁴	294-434
				1.88 ± 0.27	333			
				2.12 ± 0.41	389			
N	$2.8^{+6.5}_{-2.0}$		1800 ± 400	4.82 ± 0.36	434			
CH_2ClCF_3				1.05 ± 0.23	296	DF-LMR	Howard and Evenson ²⁶	
				1.1 ± 0.2	263	FP-RA	Handwerk and Zellner ¹⁶	263-373
				1.2 ± 0.2	268			
				1.2 ± 0.2	273			
				1.5 ± 0.3	283			
				1.5 ± 0.3	293			
				2.8	337			
	1.1 ± 0.3		1260 ± 60	3.6 ± 0.8	373			
				1.03 ± 0.30	294	DF-RF	Clyne and Holt ¹⁴	294-427
				3.83 ± 0.57	322			
				3.86 ± 0.31	344			
				6.94 ± 0.33	358			
				6.58 ± 0.25	385			
				13.0 ± 1.2	407			
	39^{+46}_{-21}		2300 ± 300	15.4 ± 1.3	427			
$\text{CH}_2\text{ClCF}_2\text{Cl}$				0.839 ± 0.037	250	FP-RF	Watson <i>et al.</i> ³¹	250-350
				1.9 ± 0.2	298			
	1.87 ± 0.27		1351 ± 78	3.95 ± 0.10	350			
	$\left[3^{+6}_{-1} \right]$		$\left[1578^{+400}_{-230} \right]^c$					
				1.42 ± 0.11	249	DF-RF	Jeong <i>et al.</i> ⁴	249-473
				1.60 ± 0.10	253			
				1.91 ± 0.16	267			
				2.72 ± 0.18	295			
				2.42 ± 0.16	297			
				4.31 ± 0.28	333			
				5.95 ± 0.37	365			
				8.06 ± 0.51	383			
				10.4 ± 0.65	418			
	5.54×10^{-14}	4.58	-252 ± 377	16.0 ± 1.15	473			
	2.02 ± 0.24		1263 ± 35					
CHF_2CF_3				0.50 ± 0.22	294	DF-RF	Clyne and Holt ¹⁴	294-441
				0.49 ± 0.14	294			
				0.62 ± 0.18	336			
				1.13 ± 0.33	378			
	$0.17^{+0.10}_{-0.06}$		1100 ± 100	1.58 ± 0.29	441			
				0.249 ± 0.028	298	FP-RA	Martin and Paraskevopoulos ²⁷	
CHFClCF_3				1.24 ± 0.19	296	DF-LMR	Howard and Evenson ²⁶	
				0.433 ± 0.019	250	FP-RF	Watson <i>et al.</i> ³¹	250-375
				0.94 ± 0.03	301			
	0.613 ± 0.04		1244 ± 90	2.28 ± 0.16	375			
CHCl_2CF_3				2.84 ± 0.43	296	DF-LMR	Howard and Evenson ²⁶	
				1.62 ± 0.05	245	FP-RF	Watson <i>et al.</i> ³¹	245-375

TABLE 4. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with haloalkanes — Continued

Haloalkane	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$) n	B (K)	$10^{14} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
	1.24 ± 0.3	1056 ± 70	3.6 ± 0.4	298			
	$[1.4 \pm 0.4$	$1102^{+157}_{-106}]^c$	7.2 ± 0.35	375			
			3.86 ± 0.19	293	DF-RF	Clyne and Holt ¹⁴	293–429
			5.86 ± 0.15	329			
			8.01 ± 0.33	366			
	1.12 ± 0.05	1000 ± 100	11.1 ± 0.4	429			
$\text{CF}_2\text{ClCF}_2\text{Cl}$			<0.05	296	DF-LMR	Howard and Evenson ²⁶	
$\text{CF}_2\text{ClCFCl}_2$			<0.03	296	DF-LMR	Howard and Evenson ²⁶	
			<0.03	298	FP-RF	Watson <i>et al.</i> ¹⁵	
$\text{CH}_2\text{ClCHClCH}_3$			≤ 44	~ 296	RR [relative to k (dimethyl ether) = 2.96×10^{-12}] ^b	Tuazon <i>et al.</i> ³²	
$\text{CH}_2\text{BrCHBrCH}_2\text{Cl}$			43.5 ± 5.0	296 ± 2	RR [relative to k (dimethyl ether) = 2.96×10^{-12}] ^b	Tuazon <i>et al.</i> ³³	

^aSee Introduction.

^bFrom the present recommendations.

^cArrhenius expression estimated after allowance for possible contributions to the observed OH radical decay rates from the measured impurity levels present (see text).

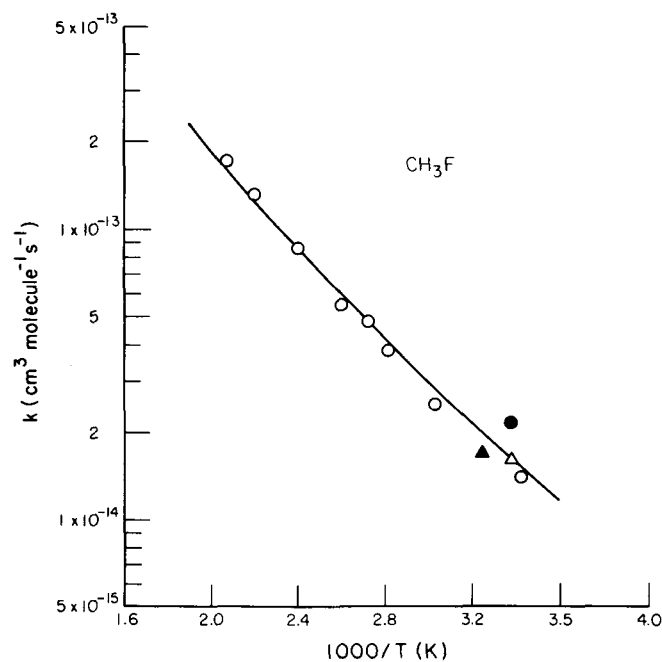


FIG. 21. Arrhenius plot of rate constants for the reaction of the OH radical with CH_3F . (Δ) Howard and Evenson;¹ (\bullet) Nip *et al.*;² (\circ) Jeong and Kaufman;^{3,4} (\blacktriangle) Bera and Hanrahan;⁵ (—) recommendation (see text).

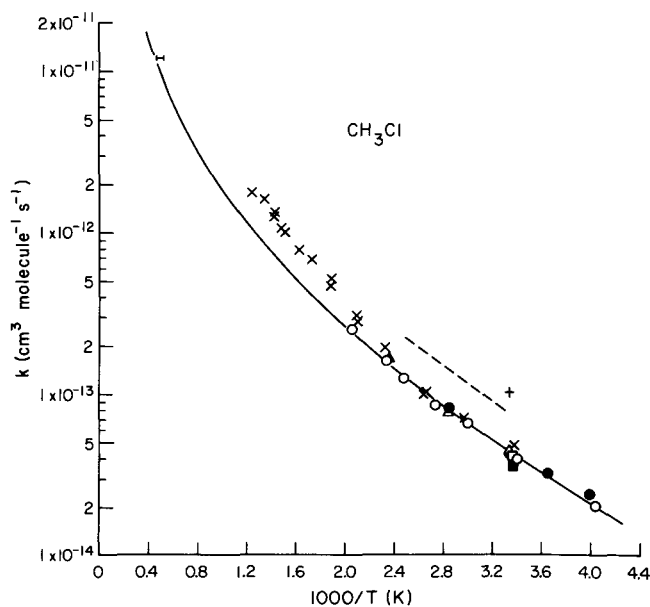


FIG. 22. Arrhenius plot of rate constants for the reaction of the OH radical with CH_3Cl . (\times) Wilson *et al.*;⁶ (\blacksquare) Howard and Evenson;¹ ($+$) Cox *et al.*;⁷ (Δ) Perry *et al.*;⁸ (\bullet) Davis *et al.*;⁹ (\square) Paraskevopoulos *et al.*;¹⁰ (\circ) Jeong and Kaufman;³ (---) Nielsen *et al.*;¹¹ (\times) Taylor *et al.*;¹² (—) recommendation (see text).

(3) CH₃Br

The available rate constants of Wilson,¹³ Howard and Evenson¹ and Davis *et al.*⁹ are listed in Table 4 and are plotted in Arrhenius form in Fig. 23. The two absolute studies carried out^{1,9} are in good agreement at room temperature. The Arrhenius plot of these absolute data^{1,9} does not show any evidence of curvature over the relatively small temperature range (244–350 K) studied (Fig. 23), and a unit-weighted least-squares analysis of these data^{1,9} yields the Arrhenius expression of

$$k(\text{CH}_3\text{Br}) = (7.40^{+5.32}_{-3.10}) \times 10^{-13} e^{-(875 \pm 155)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 244–350 K, where the indicated error limits are two least-squares standard deviations, and

$$k(\text{CH}_3\text{Br}) = 3.93 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of $\pm 20\%$. This is identical to the recommendation of Atkinson,³⁶ and is plotted in Fig. 23 as the dashed line.

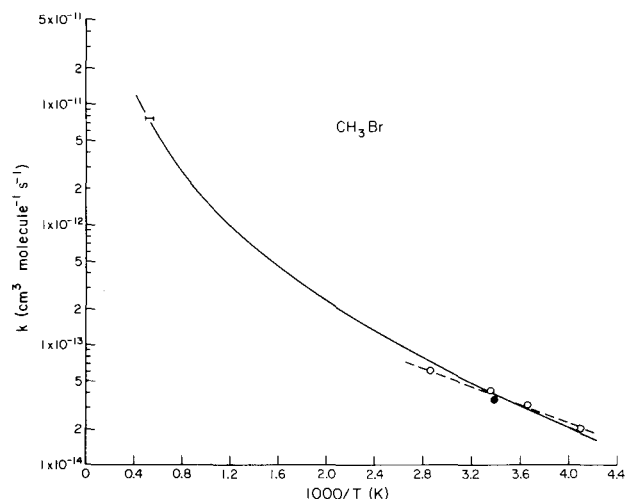


FIG. 23. Arrhenius plot of rate constants for the reaction of the OH radical with CH₃Br (□) Wilson;¹³ (●) Howard and Evenson;¹ (○) Davis *et al.*⁹ (— — —) Arrhenius expression derived from the data of Howard and Evenson¹ and Davis *et al.*⁹; (—) recommendation (see text).

As discussed above, the rate constant obtained from the relative rate study of Wilson¹³ at 1800–2000 K can be utilized to derive a recommendation applicable up to

~2000 K. Thus, using the expression $k = CT^2e^{-D/T}$, a unit-weighted least-squares analysis of the data of Wilson,¹³ Howard and Evenson¹ and Davis *et al.*⁹ yields the recommendation of

$$k(\text{CH}_3\text{Br}) = (2.60^{+0.86}_{-0.65}) \times 10^{-18} T^2 e^{-(521 \pm 89)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 244–2000 K, where the indicated error limits are two least-squares standard deviations, and

$$k(\text{CH}_3\text{Br}) = 4.02 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of $\pm 20\%$. Over the temperature range ~240–350 K this expression yields similar rate constants to the recent NASA recommendation³⁷ of

$$k(\text{CH}_3\text{Br}) = 1.17 \times 10^{-18} T^2 e^{-295/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

derived from the data of Howard and Evenson¹ and Davis *et al.*⁹

(4) CH₂F₂

The available rate constants of Howard and Evenson,¹ Clyne and Holt,¹⁴ Nip *et al.*,² Jeong and Kaufman³ and Bera and Hanrahan⁵ are given in Table 4 and are plotted in Arrhenius form in Fig. 24. In this case the rate constants of Clyne and Holt¹⁴ are in reasonably good agreement with those of Howard and Evenson,¹ Nip *et al.*² and Jeong and Kaufman,³ although their room temperature rate constant¹⁴ is the lowest of those measured. In accordance with the discussion above, a unit-weighted least-squares analysis of the data of Howard and Evenson,¹ Nip *et al.*² and Jeong and Kaufman,³ using the expression $k = CT^2e^{-D/T}$, yields the recommendation of

$$k(\text{CH}_2\text{F}_2) = (5.06^{+2.66}_{-1.74}) \times 10^{-18} T^2 e^{-(1107 \pm 142)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 250–492 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{CH}_2\text{F}_2) = 1.09 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of $\pm 30\%$. This recommendation is identical to that of Atkinson,³⁶ being based upon the same data set.

(5) CH₂FCl

The available rate constants of Howard and Evenson,¹ Watson *et al.*,¹⁵ Handwerk and Zellner,¹⁶ Paraskevopoulos *et al.*¹⁰ and Jeong and Kaufman³ are given in Table 4

and are plotted in Arrhenius form in Fig. 25. These rate constants are in reasonably good agreement, although there is a significant discrepancy between the rate constants obtained by Watson *et al.*¹⁵ and Jeong and Kaufman³ at ~250 K. Although it is not obvious from Fig. 25 whether or not the Arrhenius plot exhibits curvature, a unit-weighted least-squares analysis of these data^{1,3,10,15,16} has been carried out, using the equation $k = CT^2e^{-D/T}$, to yield the recommendation of

$$k(\text{CH}_2\text{FCl}) = (3.77^{+1.66}_{-1.16}) \times 10^{-18} T^2 e^{-(604 \pm 115)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 245–486 K, where the indicated error limits are two least-squares standard deviations, and

$$k(\text{CH}_2\text{FCl}) = 4.41 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of $\pm 20\%$. This recommendation is identical to those of Atkinson³⁶ and DeMore *et al.*³⁷

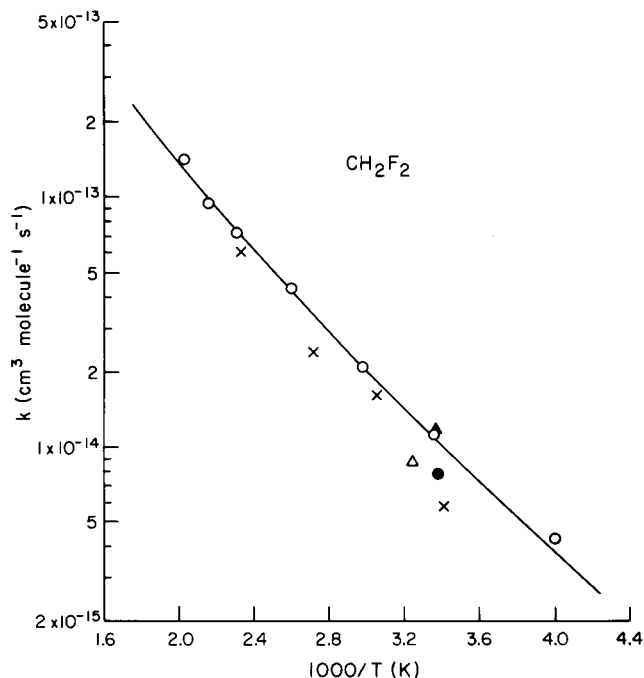


FIG. 24. Arrhenius plot of rate constants for the reaction of the OH radical with CH_2F_2 . (●) Howard and Evenson;¹ (x) Clyne and Holt;¹⁴ (▲) Nip *et al.*;² (○) Jeong and Kaufman;³ (Δ) Bera and Hanrahan;⁵ (—) recommendation (see text).

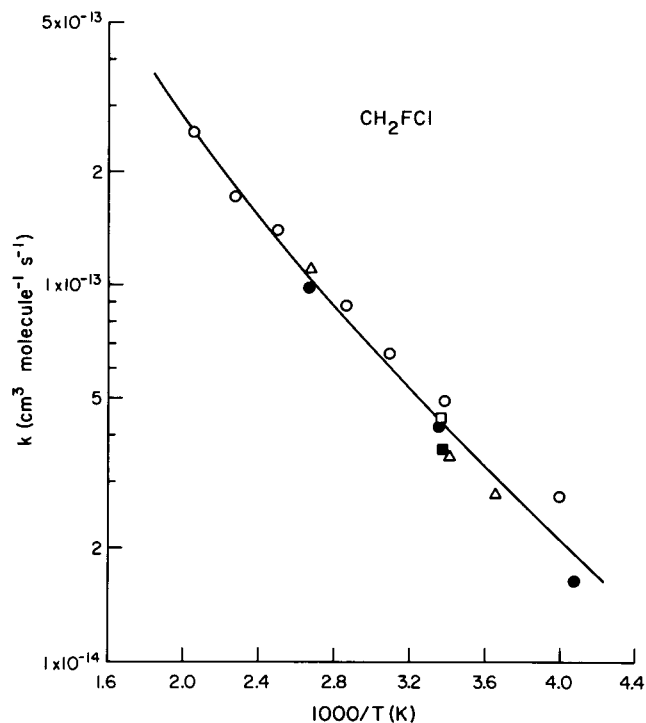


FIG. 25. Arrhenius plot of rate constants for the reaction of the OH radical with CH_2FCl . (■) Howard and Evenson;¹ (●) Watson *et al.*;¹⁵ (Δ) Handwerk and Zellner;¹⁶ (□) Paraskevopoulos *et al.*;¹⁰ (○) Jeong and Kaufman;³ (—) recommendation (see text).

(6) CH_2Cl_2

The available kinetic data of Howard and Evenson,¹ Cox *et al.*,⁷ Perry *et al.*,⁸ Davis *et al.*,⁹ Jeong and Kaufman,³ Nielsen *et al.*¹¹ and Taylor *et al.*¹² are given in Table 4 and are plotted in Arrhenius form in Fig. 26. While the room temperature rate constants of Howard and Evenson,¹ Perry *et al.*⁸ and Jeong and Kaufman³ are in excellent agreement, the rate constants obtained by Davis *et al.*⁹ are uniformly lower than those of Jeong and Kaufman³ by ~20–40% over the temperature range common to both studies. In view of the situation concerning the data of Taylor *et al.*¹² for CH_3Cl discussed above, their data¹² have not been used in the evaluation of the rate constant for CH_2Cl_2 . A unit-weighted least-squares analysis of the data of Howard and Evenson,¹ Perry *et al.*,⁸ Davis *et al.*⁹ and Jeong and Kaufman,³ using the equation $k = CT^2e^{-D/T}$, yields the recommendation of

$$k(\text{CH}_2\text{Cl}_2) = (8.54^{+8.18}_{-4.19}) \times 10^{-18} T^2 e^{-(500 \pm 212)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 245–455 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{CH}_2\text{Cl}_2) = 1.42 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K},$$

with an estimated overall uncertainty at 298 K of $\pm 25\%$. The rate constants measured by Taylor *et al.*,¹² especially for temperatures ≥ 350 K, are in excellent agreement with this recommended rate expression (Fig. 26). This recommendation is identical to that of Atkinson³⁶ and very similar to the recent NASA evaluation,³⁷ but with slightly higher estimated uncertainty limits at 298 K. The Arrhenius expression of Nielsen *et al.*¹¹ is in good agreement with the present recommendation over the temperature range ~ 300 –400 K studied.¹¹

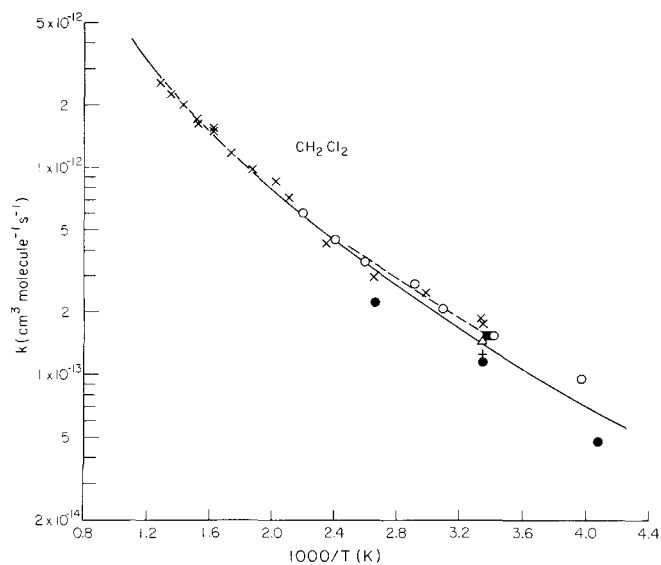


FIG. 26. Arrhenius plot of rate constants for the reaction of the OH radical with CH_2Cl_2 . (■) Howard and Evenson;¹ (+) Cox *et al.*;⁷ (Δ) Perry *et al.*;⁸ (●) Davis *et al.*;⁹ (○) Jeong and Kaufman;³ (— — —) Nielsen *et al.*;¹¹ (x) Taylor *et al.*;¹² (—) recommendation (see text).

(7) CHF_3

The available rate constants of Howard and Evenson,¹ Bradley *et al.*,¹⁷ Ernst *et al.*,¹⁸ Clyne and Holt,¹⁴ Nip *et al.*,² Jeong and Kaufman^{3,4} and Bera and Hanrahan⁵ are given in Table 4 and are plotted in Arrhenius form in Fig. 27. The reaction of the OH radical with CHF_3 is very slow at room temperature, and the rate constants determined by Howard and Evenson¹ and Nip *et al.*² are subject to large uncertainties. This appears to be also true for the rate constants reported by Clyne and Holt,¹⁴

since their data show no significant effect of temperature and differ by factors of >2 from the other literature data. The rate constant measured by Bera and Hanrahan⁵ is clearly in error, possibly due to the presence of reactive impurities.⁵

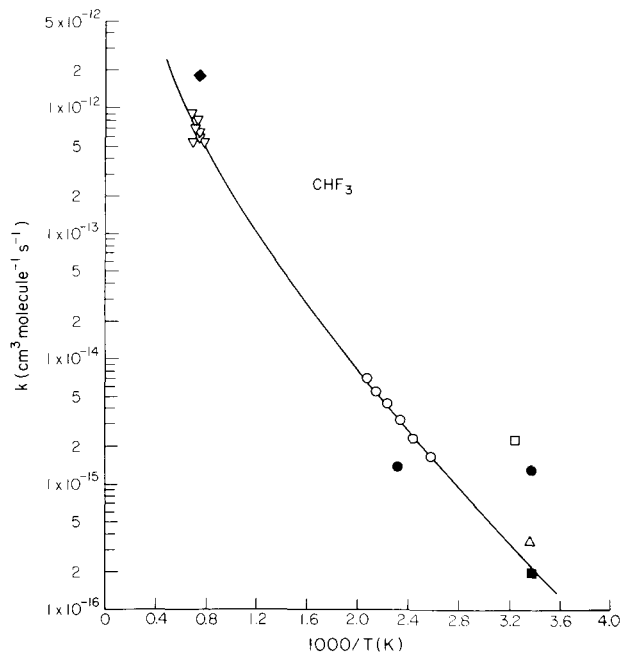


FIG. 27. Arrhenius plot of rate constants for the reaction of the OH radical with CHF_3 . (■) Howard and Evenson;¹ (◆) Bradley *et al.*;¹⁷ (▽) Ernst *et al.*;¹⁸ (●) Clyne and Holt;¹⁴ (Δ) Nip *et al.*;² (○) Jeong and Kaufman;^{3,4} (□) Bera and Hanrahan;⁵ (—) recommendation (see text).

In view of the significant uncertainties associated with the rate constants measured by Howard and Evenson,¹ Nip *et al.*² and Bradley *et al.*¹⁷ (due to the large differences in the rate constant derived depending on whether H_2 or CO is used as the reference compound in their relative rate study),¹⁷ a unit-weighted least-squares analysis of the data of Ernst *et al.*¹⁸ and Jeong and Kaufman^{3,4} was carried out, using the equation $k = CT^2e^{-D/T}$, to yield the recommendation of

$$k(\text{CHF}_3) = (1.49^{+0.25}_{-0.21}) \times 10^{-18} T^2 e^{-(1887 \pm 92)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 387–1445 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{CHF}_3) = 2.4 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K},$$

with an estimated overall uncertainty at 298 K of $\pm 50\%$.

This recommended expression yields a rate constant at 296 K in agreement, within the experimental error limits, with those measured by Howard and Evenson¹ and Nip *et al.*² Since this recommendation is based upon data obtained at temperatures ≥ 387 K, it should be used with caution for temperatures $\lesssim 300$ K. This recommendation is similar to that of

$$k(\text{CHF}_3) = 2.17 \times 10^{-18} T^2 e^{-2048/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

of Atkinson,³⁶ derived from the data of Jeong and Kaufman^{3,4} over the temperature range 387–480 K (due to a typographical error, the value of C was incorrectly cited³⁶ as $2.1 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).

(8) CHF₂Cl

The available rate constants^{1,3,10,14–16,19,20} are given in Table 4 and are plotted in Arrhenius form in Fig. 28. It can be seen that the rate constants of Atkinson *et al.*,¹⁹ Howard and Evenson,¹ Watson *et al.*,¹⁵ Chang and Kaufman,²⁰ Handwerk and Zellner,¹⁶ Paraskevopoulos *et al.*¹⁰ and Jeong and Kaufman³ are in good agreement. While the rate constants measured by Clyne and Holt¹⁴ agree well with those studies at ~ 294 – 321 K, their rate constants at higher temperatures are increasingly higher than the consensus values from these other studies. A unit-weighted least-squares analysis of the rate constant data of Atkinson *et al.*,¹⁹ Howard and Evenson,¹ Watson *et al.*,¹⁵ Chang and Kaufman,²⁰ Handwerk and Zellner,¹⁶ Paraskevopoulos *et al.*¹⁰ and Jeong and Kaufman,³ using the equation $k = CT^2 e^{-D/T}$, yields the recommendation of

$$k(\text{CHF}_2\text{Cl}) = (1.51_{-0.39}^{+0.52}) \times 10^{-18} T^2 e^{-(1000 \pm 94)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 250–482 K, where the indicated error limits are two least-squares standard deviations, and

$$k(\text{CHF}_2\text{Cl}) = 4.68 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of $\pm 20\%$. This recommendation is identical to those of Atkinson³⁶ and DeMore *et al.*³⁷

(9) CHFCl₂

The available rate constants^{1,3,8,10,11,14,15,20} are given in Table 4 and are plotted in Arrhenius form in Fig. 29.

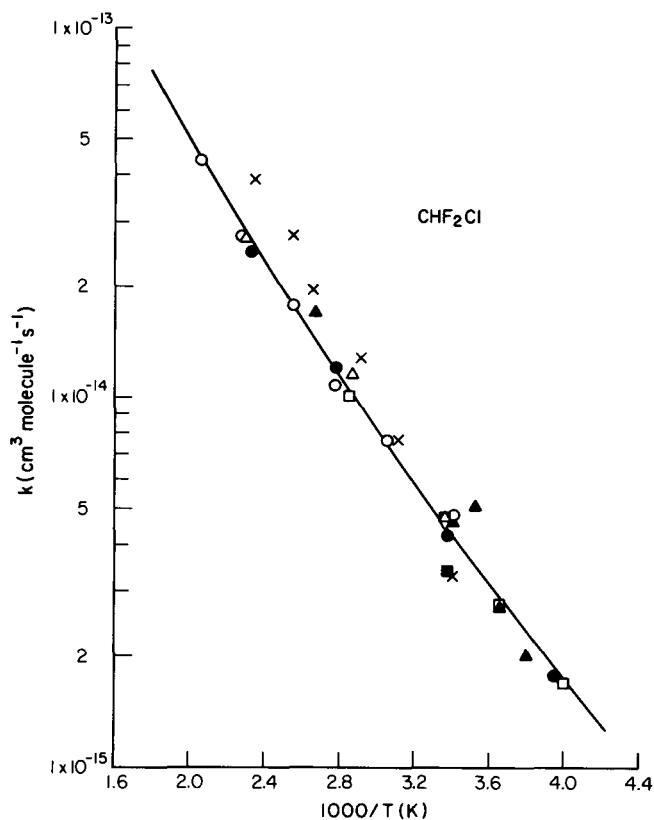


FIG. 28. Arrhenius plot of rate constants for the reaction of the OH radical with CHF₂Cl. (Δ) Atkinson *et al.*,¹⁹ (\blacksquare) Howard and Evenson,¹ (\square) Watson *et al.*,¹⁵ (\bullet) Chang and Kaufman,²⁰ (\blacktriangle) Handwerk and Zellner,¹⁶ (\times) Clyne and Holt,¹⁴ (∇) Paraskevopoulos *et al.*,¹⁰ (\circ) Jeong and Kaufman,³ (—) recommendation (see text).

Analogous to CHF₂Cl, the rate constants measured by Clyne and Holt¹⁴ at elevated temperatures are significantly higher than those of Howard and Evenson,¹ Perry *et al.*,⁸ Watson *et al.*,¹⁵ Chang and Kaufman,²⁰ Paraskevopoulos *et al.*¹⁰ and Jeong and Kaufman,³ all of which are in reasonably good agreement. The data reported for this reaction by Nielsen *et al.*¹¹ are lower than those from the other studies by a factor of ~ 5 , suggesting that the reactant studied was CHF₂Cl, and not CHFCl₂ as reported. A unit-weighted least-squares analysis of the data of Howard and Evenson,¹ Perry *et al.*,⁸ Watson *et al.*,¹⁵ Chang and Kaufman,²⁰ Paraskevopoulos *et al.*¹⁰ and Jeong and Kaufman,³ using the equation $k = CT^2 e^{-D/T}$, yields the recommendation of

$$k(\text{CHFCl}_2) = (1.70_{-0.37}^{+0.47}) \times 10^{-18} T^2 e^{-(479 \pm 76)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 241–483 K, where the indicated error limits are two least-squares standard deviations, and

$$k(\text{CHFCl}_2) = 3.03 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of $\pm 20\%$. This recommendation is identical to that of Atkinson³⁶ and essentially identical to that of the recent NASA evaluation.³⁷

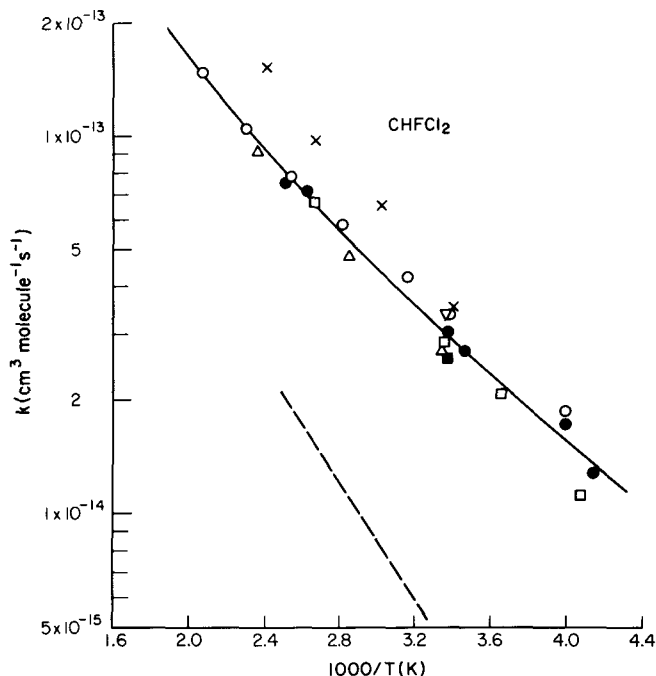


FIG. 29. Arrhenius plot of rate constants for the reaction of the OH radical with CHFCl_2 . (■) Howard and Evenson;¹ (Δ) Perry *et al.*;⁸ (□) Watson *et al.*;¹⁵ (●) Chang and Kaufman;²⁰ (x) Clyne and Holt;¹⁴ (∇) Paraskevopoulos *et al.*;¹⁰ (○) Jeong and Kaufman;³ (---) Nielsen *et al.*;¹¹ (—) recommendation (see text).

(10) CHCl_3

The available kinetic data of Howard and Evenson,¹ Cox *et al.*,⁷ Davis *et al.*,⁹ Jeong and Kaufman,³ Klöpffer *et al.*²¹ and Taylor *et al.*¹² are given in Table 4 and those of Howard and Evenson,¹ Cox *et al.*,⁷ Davis *et al.*,⁹ Jeong and Kaufman³ and Taylor *et al.*¹² are plotted in Arrhenius form in Fig. 30. It can be seen that the rate constants of Howard and Evenson,¹ Davis *et al.*,⁹ Jeong and Kaufman³ and Taylor *et al.*¹² are in excellent agreement. However, consistent with the evaluations for the reactions of the OH radical with CH_3Cl and CH_2Cl_2 , the rate constants of Taylor *et al.*¹² were not used in the derivation of the recommended rate expression for CHCl_3 . Thus, a unit-weighted least-squares analysis of the data of Howard and Evenson,¹ Davis *et al.*,⁹ and Jeong and Kaufman,³ using the equation $k = CT^2e^{-D/T}$, yields the recommendation of

$$k(\text{CHCl}_3) = (6.30_{-1.00}^{+1.18}) \times 10^{-18} T^2 e^{-(504 \pm 56)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 245–487 K, where the indicated error limits are two least-squares standard deviations, and

$$k(\text{CHCl}_3) = 1.03 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of $\pm 20\%$.

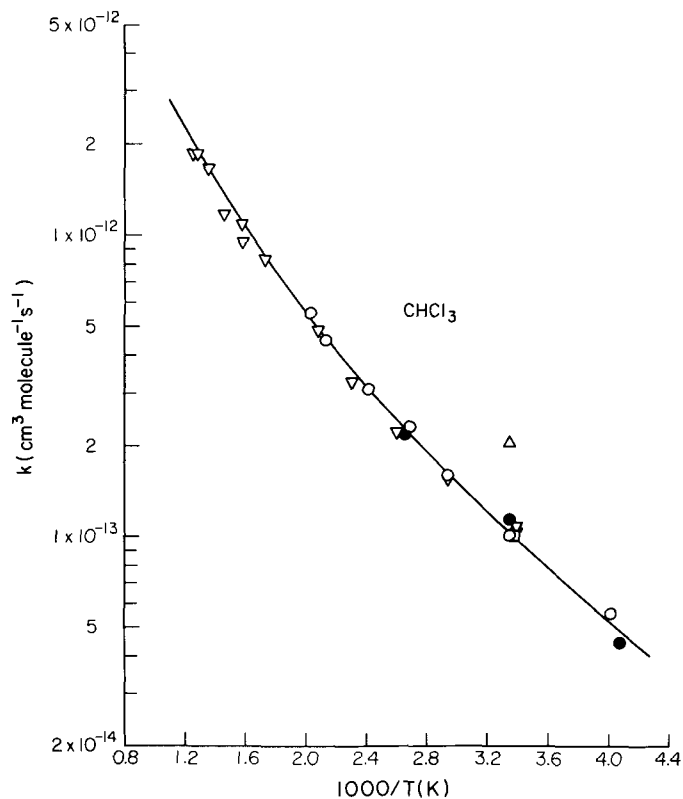


FIG. 30. Arrhenius plot of rate constants for the reaction of the OH radical with CHCl_3 . (□) Howard and Evenson;¹ (Δ) Cox *et al.*;⁷ (●) Davis *et al.*;⁹ (○) Jeong and Kaufman;³ (∇) Taylor *et al.*;¹² (—) recommendation (see text).

This recommendation is identical to those of Atkinson³⁶ and DeMore *et al.*³⁷

(11) CF_4 , CF_3Cl , CF_3Br , CF_2Cl_2 , CF_2ClBr , CFCl_3 and CCl_4

For these halomethanes, no reaction with the OH radical has been observed. Based upon the measured room temperature upper limits to the rate constants (Table 4), the following recommendations are made for 298 K

$$\begin{aligned}
 k(\text{CF}_4) &< 4 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \\
 k(\text{CF}_3\text{Cl}) &< 7 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \\
 k(\text{CF}_3\text{Br}) &< 1 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \\
 k(\text{CF}_2\text{ClBr}) &< 1 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \\
 \text{and } k(\text{CCl}_4) &< 5 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}
 \end{aligned}$$

These room temperature upper limits to the rate constants for CF_4 , CF_3Cl , CF_3Br and CF_2ClBr are based upon the data of Howard and Evenson¹ (CF_4 and CF_3Cl), Le Bras and Combourieu²³ (CF_3Br) and Clyne and Holt²² (CF_2ClBr). For CCl_4 the upper limit reported by Cox *et al.*⁷ has been used, increased by a factor of 4 to take into account uncertainties in the number of NO to NO_2 conversions occurring in their relative rate study. The rate constants for these reactions at 298 K are likely to be orders of magnitude lower than the upper limits given here.

For CF_2Cl_2 and CFCl_3 , upper limits to the rate constants for the OH radical reactions have been determined at temperatures >298 K by Chang and Kaufman²⁵ and Atkinson *et al.*¹⁹ Based upon the upper limits to the rate constants measured by Chang and Kaufman²⁵ at 478–480 K and the rate expressions $k = Ae^{-B/T}$ or $k = CT^2e^{-D/T}$, with $A \geq 1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ or $C \geq 1 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (consistent with the recommendations for the halomethanes containing H-atoms), then at 298 K the following recommendations are made

$$\begin{aligned}
 k(\text{CF}_2\text{Cl}_2) &< 1 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \\
 \text{and} \\
 k(\text{CFCl}_3) &< 1 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}
 \end{aligned}$$

These upper limits to the 298 K reaction rate constants are somewhat more conservative than the recent NASA recommendations³⁷ of upper limits to the rate constants of $<6 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for CF_2Cl_2 and $<5 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for CFCl_3 .

(12) $\text{CH}_3\text{CH}_2\text{Cl}$

The rate constants obtained by Howard and Evenson²⁶ and Paraskevopoulos *et al.*¹⁰ at room temperature (Table 4) are in excellent agreement, and it is recommended that

$$\begin{aligned}
 k(\text{CH}_3\text{CH}_2\text{Cl}) &= 3.9 \\
 &\times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K},
 \end{aligned}$$

with an estimated uncertainty of $\pm 35\%$. No temperature dependence is available.

(13) CH_3CHF_2

Rate constants have been determined for the reaction of OH radicals with CH_3CHF_2 by Howard and Even-

son,²⁶ Handwerk and Zellner,¹⁶ Clyne and Holt¹⁴ and Nip *et al.*² The rate constants of Howard and Evenson,²⁶ Handwerk and Zellner¹⁶ and Nip *et al.*² are in reasonable agreement, but are significantly lower than the room temperature rate constant of Clyne and Holt.¹⁴ Since the data of Clyne and Holt¹⁴ are neglected in these evaluations of the OH radical reactions with the haloalkanes, a unit-weighted average of the room temperature rate constants of Howard and Evenson,²⁶ Handwerk and Zellner¹⁶ and Nip *et al.*² yields the recommendation of

$$\begin{aligned}
 k(\text{CH}_3\text{CHF}_2) &= 3.4 \\
 &\times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } \sim 295 \text{ K},
 \end{aligned}$$

with an estimated overall uncertainty of $\pm 30\%$. This room temperature recommendation is identical to those of Atkinson³⁶ and DeMore *et al.*³⁷

(14) $\text{CH}_3\text{CF}_2\text{Cl}$

The available rate constants of Howard and Evenson,²⁶ Cox *et al.*,⁷ Watson *et al.*,¹⁵ Handwerk and Zellner,¹⁶ Clyne and Holt¹⁴ and Paraskevopoulos *et al.*¹⁰ are given in Table 4 and are plotted in Arrhenius form in Fig. 31. It is evident that the rate constants of Howard and Evenson,²⁶ Watson *et al.*,¹⁵ Handwerk and Zellner¹⁶ and Paraskevopoulos *et al.*¹⁰ are in reasonably good agreement, although significantly lower than those measured by Clyne and Holt.¹⁴ A unit-weighted least-squares analysis of these data of Howard and Evenson,²⁶ Watson *et al.*,¹⁵ Handwerk and Zellner¹⁶ and Paraskevopoulos *et al.*¹⁰ using the equation $k = CT^2e^{-D/T}$, yields the recommendation of

$$\begin{aligned}
 k(\text{CH}_3\text{CF}_2\text{Cl}) &= (2.05^{+5.76}_{-1.52}) \\
 &\times 10^{-18} T^2 e^{-(1171 \pm 413)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}
 \end{aligned}$$

over the temperature range 273–375 K, where the indicated errors are two least-squares standard deviations, and

$$\begin{aligned}
 k(\text{CH}_3\text{CF}_2\text{Cl}) &= 3.58 \\
 &\times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K},
 \end{aligned}$$

with an estimated overall uncertainty at 298 K of $\pm 50\%$. This recommendation is identical to that of Atkinson,³⁶ obtained using the same data set.

(15) CH_2Cl_2

The available kinetic data^{4,7,15,20,22,26,28–30} are given in Table 4. As discussed previously,^{28,29,36} it now appears that the earlier rate constants determined by Howard and Evenson,²⁶ Watson *et al.*,¹⁵ Chang and Kaufman²⁰

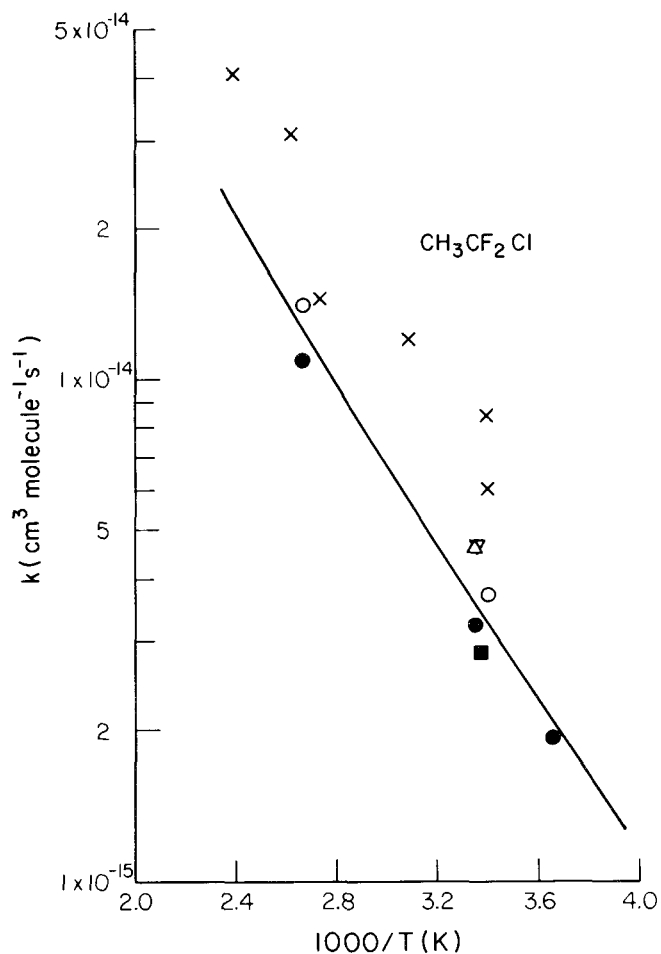


FIG. 31. Arrhenius plot of rate constants for the reaction of the OH radical with $\text{CH}_3\text{CF}_2\text{Cl}$. (■) Howard and Evenson;²⁶ (Δ) Cox *et al.*;⁷ (●) Watson *et al.*;¹⁵ (○) Handwerk and Zellner;¹⁶ (x) Clyne and Holt;¹⁴ (∇) Paraskevopoulos *et al.*;¹⁰ (—) recommendation (see text).

and Clyne and Holt,²² which yielded a room temperature rate constant of $\sim(1.5\text{--}2.2) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and a temperature dependence of $B \sim 1300\text{--}1600 \text{ K}$, were erroneously high due to contamination by small amounts of highly reactive (relative to CH_3CCl_3) $\text{CH}_2=\text{CCl}_2$ impurity. The most recent studies of Kaufman and co-workers^{4,28} and Kurylo *et al.*,²⁹ in which the CH_3CCl_3 samples were extensively purified, are in excellent agreement and yield significantly lower rate constants than did these previous studies. The room temperature rate constant derived from the relative rate study of Nelson *et al.*³⁰ is in good agreement with these absolute rate constants of Jeong and Kaufman^{4,28} and Kurylo *et al.*,²⁹ and these data are plotted in Arrhenius form in Fig. 32. The rate constant measured by Kurylo *et al.*²⁹ at 222 K, which is significantly higher than expected

by extrapolation of the higher temperature data,^{4,28,29} may still have been affected by $\text{CH}_2=\text{CCl}_2$ impurity problems.²⁹

Thus, only the absolute rate constant data of Jeong and Kaufman^{4,28} and those of Kurylo *et al.*²⁹ at $\geq 253 \text{ K}$ are used in the evaluation. A unit-weighted least-squares analysis of these data,^{4,28,29} using the equation $k = CT^2e^{-D/T}$, yields the recommendation of

$$k(\text{CH}_3\text{CCl}_3) = (5.92^{+1.29}_{-1.05}) \times 10^{-18} T^2 e^{-(1129 \pm 62)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 253–457 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{CH}_3\text{CCl}_3) = 1.19 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K},$$

with an estimated overall uncertainty at 298 K of $\pm 30\%$. This recommendation is identical to that of Atkinson³⁶ and similar to the recent NASA evaluation,³⁷ which, although using the same data set, utilized the simple Arrhenius expression rather than a three-parameter equation.

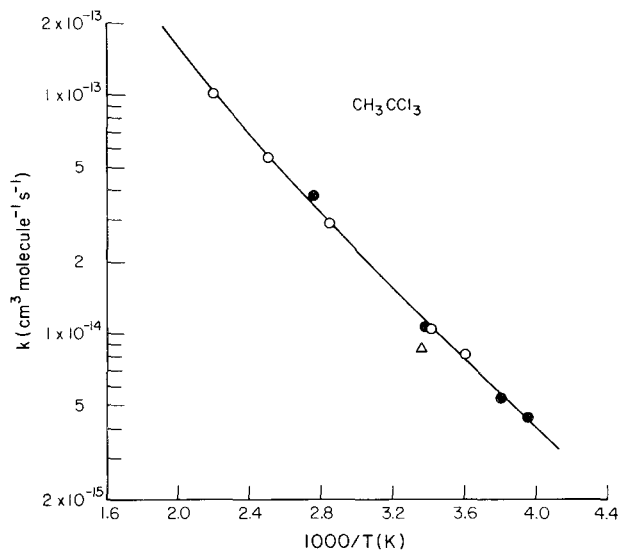


FIG. 32. Arrhenius plot of rate constants for the reaction of the OH radical with CH_3CCl_3 . (○) Jeong *et al.*;^{4,28} (●) Kurylo *et al.*²⁹ ($T \geq 253 \text{ K}$); (Δ) Nelson *et al.*;³⁰ (—) recommendation (see text).

(16) CH_2FCF_3

The available kinetic data of Clyne and Holt,¹⁴ Martin and Paraskevopoulos²⁷ and Jeong *et al.*⁴ are given in Table 4 and are plotted in Arrhenius form in Fig. 33.

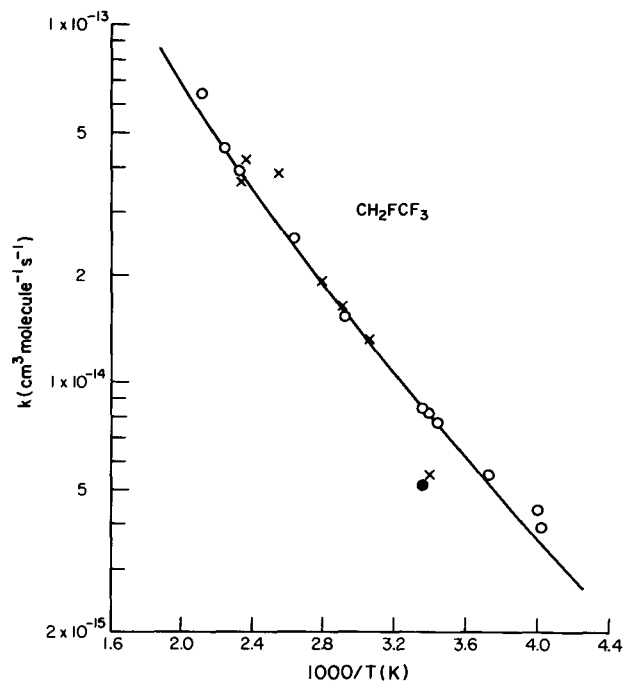


FIG. 33. Arrhenius plot of rate constants for the reaction of the OH radical with CH_2FCF_3 . (x) Clyne and Holt;¹⁴ (●) Martin and Paraskevopoulos;²⁷ (○) Jeong *et al.*;⁴ (—) recommendation (see text).

The rate constant of Martin and Paraskevopoulos²⁷ at 298 K is significantly lower than that of Jeong *et al.*⁴ (although it is in agreement with that of Clyne and Holt¹⁴). However, in view of the criteria for evaluating these reactions, the rate constants determined by Clyne and Holt¹⁴ were not used in the evaluation. A unit-weighted least-squares analysis of the data of Martin and Paraskevopoulos²⁷ and Jeong *et al.*⁴ using the expression $k = CT^2e^{-D/T}$, yields the recommendation of

$$k(\text{CH}_2\text{FCF}_3) = (1.27^{+0.87}_{-0.52}) \times 10^{-18} T^2 e^{-(769 \pm 163)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 249–473 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{CH}_2\text{FCF}_3) = 8.54 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated uncertainty at 298 K of +30%, –50%. This recommendation is identical to that of Atkinson,³⁶ and similar to that of NASA³⁷ which used the Arrhenius expression.

(17) CH_2ClCF_3

The available rate constants of Howard and Evenson,²⁶ Handwerk and Zellner¹⁶ and Clyne and Holt¹⁴ are given in Table 4 and are plotted in Arrhenius form in Fig. 34. Again, the rate constants of Clyne and Holt¹⁴ exhibit a much higher temperature dependence than do those of Handwerk and Zellner.¹⁶

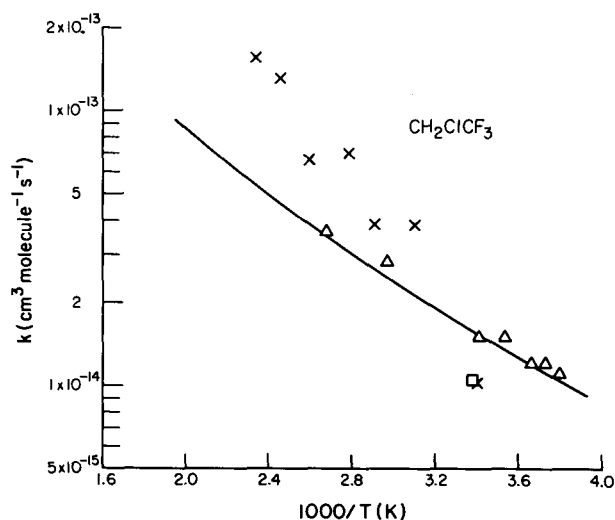


FIG. 34. Arrhenius plot of rate constants for the reaction of the OH radical with CH_2ClCF_3 . (□) Howard and Evenson;²⁶ (Δ) Handwerk and Zellner;¹⁶ (x) Clyne and Holt;¹⁴ (—) recommendation (see text).

A unit-weighted least-squares analysis of the rate constant data of Howard and Evenson²⁶ and Handwerk and Zellner,¹⁶ using the equation $k = CT^2e^{-D/T}$, yields the recommendation of

$$k(\text{CH}_2\text{ClCF}_3) = (8.50^{+20.75}_{-6.03}) \times 10^{-19} T^2 e^{-(458 \pm 362)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 263–373 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{CH}_2\text{ClCF}_3) = 1.62$$

$$\times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated uncertainty at 298 K of \pm a factor of 2. This recommendation is identical to that of Atkinson.³⁶

(18) $\text{CH}_2\text{ClCF}_2\text{Cl}$

The available rate constants of Watson *et al.*³¹ and Jeong *et al.*⁴ are given in Table 4 and are plotted in Arrhenius form in Fig. 35.

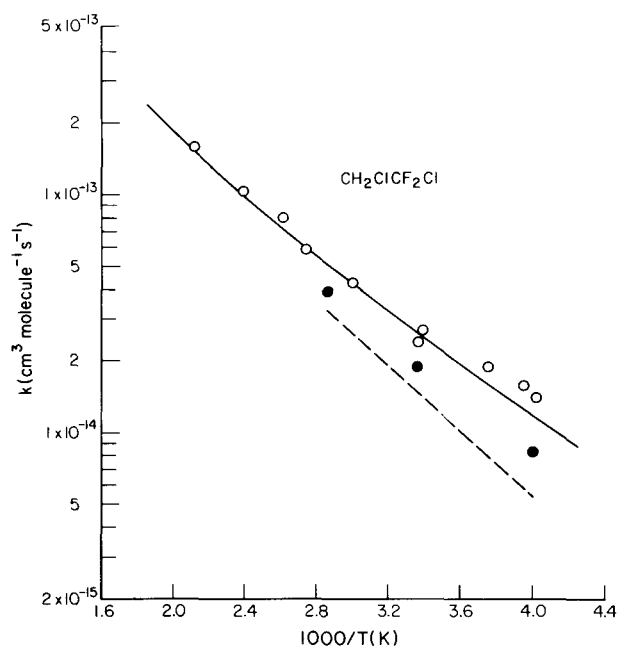


FIG. 35. Arrhenius plot of rate constants for the reaction of the OH radical with $\text{CH}_2\text{ClCF}_2\text{Cl}$. (●) Watson *et al.*,³¹ measured rate constants; (— — —) Watson *et al.*,³¹ corrected for measured impurities (see text); (○) Jeong *et al.*,⁴ (——) recommendation (see text).

It can be seen that the measured rate constants of Watson *et al.*³¹ are consistently lower than those of Jeong *et al.*,⁴ especially at lower temperatures. Furthermore, Watson *et al.*,³¹ from an analysis of the purity of the $\text{CH}_2\text{ClCF}_2\text{Cl}$ sample used which showed the presence of $\sim 0.045\%$ of haloethenes, concluded that the true rate constants for this reaction were lower than those measured. Their estimated Arrhenius expression,³¹ after correction for the presence of these impurities, is given in Table 4 and is shown in Fig. 35 as the dashed line. However, the $\text{CH}_2\text{ClCF}_2\text{Cl}$ sample used by Jeong *et al.*⁴ was stated to have a purity level of $>99.999\%$, and hence their data should have been essentially free from any complications arising from the presence of reactive im-

purities. It should be noted that, analogous to the situation for methane and ethane, the rate constants measured by Jeong *et al.*⁴ at temperatures $\lesssim 275 \text{ K}$ may have been systematically high.

In the absence of further experimental data, a unit-weighted least-squares analysis of the measured rate constants of Watson *et al.*³¹ and Jeong *et al.*⁴ has been carried out, using the equation $k = CT^2e^{-D/T}$, to yield the recommendation of

$$k(\text{CH}_2\text{ClCF}_2\text{Cl}) = (2.80^{+2.29}_{-1.26})$$

$$\times 10^{-18} T^2 e^{-(672 \pm 183)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 249–473 K, where the indicated errors are two least-squares standard deviations (which are associated only with the measured rate constants and do not include the corrected values of Watson *et al.*³¹), and

$$k(\text{CH}_2\text{ClCF}_2\text{Cl}) = 2.61 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty at 298 K of $+30\%$, -60% .

The NASA evaluation³⁷ uses the corrected Arrhenius expression of Watson *et al.*³¹ (which is encompassed by the uncertainties associated with the above recommended 298 K rate constant). Clearly, further kinetic studies employing carefully purified $\text{CH}_2\text{ClCF}_2\text{Cl}$ are necessary.

(19) CHFClCF_3

The rate constants of Howard and Evenson²⁶ and Watson *et al.*³¹ are given in Table 4 and are plotted in Arrhenius form in Fig. 36. These two studies are in good agreement and no curvature in the Arrhenius plot is evident. Accordingly, a unit-weighted least-squares analysis of these data yields the recommended Arrhenius expression of

$$k(\text{CHFClCF}_3) = (6.38^{+18.20}_{-4.73})$$

$$\times 10^{-13} e^{-(1233 \pm 400)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 250–375 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{CHFClCF}_3) = 1.02 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated uncertainty at 298 K of $\pm 30\%$. Using the expression $k = CT^2e^{-D/T}$, a unit-weighted least-squares analysis of these data^{26,31} yields

$$k(\text{CHFClCF}_3) = (9.12^{+29.27}_{-6.96})$$

$$\times 10^{-19} T^2 e^{-(624 \pm 416)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

where the indicated errors are two least-squares standard deviations, and

$$k(\text{CHFClCF}_3) = 1.00$$

$$\times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

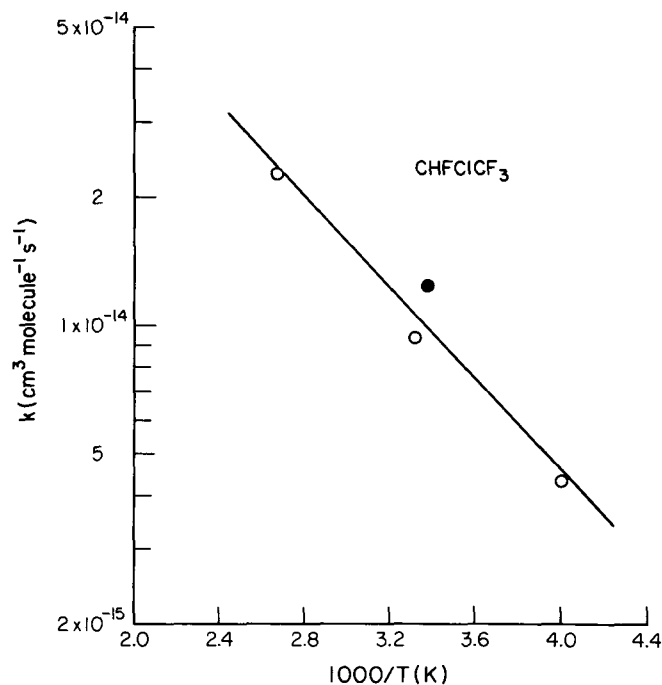


FIG. 36. Arrhenius plot of rate constants for the reaction of the OH radical with CHFClCF_3 . (●) Howard and Evenson,²⁶ (○) Watson *et al.*,³¹ (—) recommendation (see text).

In view of the small temperature range covered (250–375 K) and the fact that these two expressions yield essentially identical (within 2%) rate constants over this range, the use of the simple Arrhenius expression (the recommended line in Fig. 36) is recommended over this temperature range.

(20) CHCl_2CF_3

The rate constants of Howard and Evenson,²⁶ Watson *et al.*³¹ and Clyne and Holt¹⁴ are given in Table 4 and are plotted in Arrhenius form in Fig. 37. Watson *et al.*³¹ estimated that contributions of C_4 haloalkene impurities could have led to their observed rate constants being somewhat high, and estimated the corrected Arrhenius expression given in Table 4 and shown as the dashed line in Fig. 37. These estimated rate constants of Watson *et al.*,³¹ taking into account the presence of reactive impurities, are only slightly different from their measured rate constants (which exhibit no unambiguous evidence for

curvature in the Arrhenius plot). A unit-weighted least-squares analysis of the measured rate constants of Howard and Evenson²⁶ and Watson *et al.*³¹ has been carried out to yield the Arrhenius expression of

$$k(\text{CHCl}_2\text{CF}_3) = (1.16^{+1.44}_{-0.65})$$

$$\times 10^{-12} \text{ e}^{-(1056 \pm 237)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 245–375 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{CHCl}_2\text{CF}_3) = 3.35$$

$$\times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated uncertainty at 298 K of +20%, –40%.

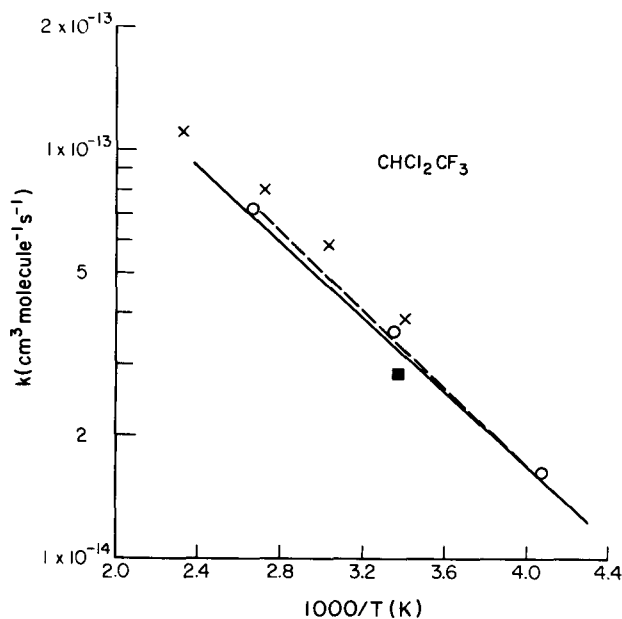


FIG. 37. Arrhenius plot of rate constants for the reaction of the OH radical with CHCl_2CF_3 . (■) Howard and Evenson,²⁶ (○) Watson *et al.*,³¹ measured rate constants; (---) Watson *et al.*,³¹ corrected for measured impurities (see text); (x) Clyne and Holt,¹⁴ (—) recommendation (see text).

Using the expression $k = CT^2 e^{-D/T}$, a least-squares analysis of these data^{26,31} leads to

$$k(\text{CHCl}_2\text{CF}_3) = (1.70^{+1.87}_{-0.89})$$

$$\times 10^{-18} T^2 \text{ e}^{-(455 \pm 217)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

where the indicated errors are two least-squares standard deviations, and

$$k(\text{CHCl}_2\text{CF}_3) = 3.28$$

$$\times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

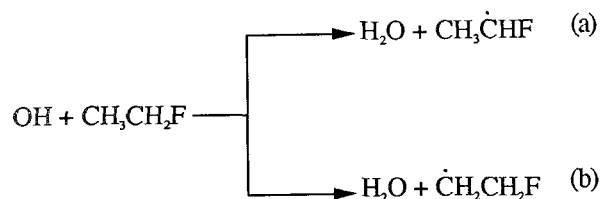
Over the temperature range 245–375 K, these two expressions yield essentially identical rate constants, and the recommended Arrhenius expression is shown in Fig. 37.

(21) Other Haloalkanes

For the remaining haloalkanes listed in Table 4, only single reliable studies have been carried out (thus, although two experimental studies were carried out for CH_3CF_3 , CH_2FCHF_2 and CHF_2CF_3 , the rate constant data of Clyne and Holt¹⁴ are discounted). In the absence of further experimental data, the results of these studies (other than that of Clyne and Holt¹⁴) should be used, with correspondingly wide uncertainty limits.

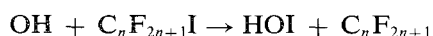
b. Mechanism

Analogous to the alkanes, for the haloalkanes with F, Cl and Br substituents these reactions proceed via H-atom abstraction. For the reaction of the OH radical with $\text{CH}_3\text{CH}_2\text{F}$ at 297 K, Singleton *et al.*⁴⁰ determined a rate constant ratio



of $k_a/(k_a + k_b) = 0.85 \pm 0.03$.

However, Garraway and Donovan²⁴ have reported a room temperature rate constant of $1.2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the reaction of the OH radical with CF_3I , and also reported that reaction occurs for other iodine-substituted non-hydrogen containing alkanes such as $\text{C}_2\text{F}_5\text{I}$ and $\text{C}_3\text{F}_7\text{I}$. If these observations are correct, then these reactions must then occur via I-atom abstraction to yield HOI and the corresponding $\text{C}_n\text{F}_{2n+1}$ radical.



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2.3. Alkenes

a. Kinetics

The OH radical reaction rate constants obtained at, or close to, the limiting high-pressure second-order kinetic regime or at ~ 760 Torr of diluent gas are listed in Tables 5 (acyclic monoalkenes), 6 (acyclic di- and tri-alkenes), and 7 (cyclic mono-, di- and tri-alkenes). The rate constants for the OD radical reactions with monocyclic alkenes are given in Table 8. The data reported by Cox⁶¹ from the photolysis of HONO-alkene-air mixtures at 300 K and atmospheric pressure of air have not been included, since the stoichiometric factors were not specified. However, based upon our present knowledge of the rate constants for the reactions of the OH radical with the reference compounds NO, NO₂ and HONO⁶² and the reaction stoichiometries⁶³ for these OH-alkene reactions, these data⁶¹ are reasonably consistent with the elementary rate constants recommended below. Simonaitis and Heicklen⁶⁴ also obtained rate constants for propene at 373 and 473 K relative to those for the reaction of OH radicals with CO at total pressures of ~ 400 – 800 Torr (mainly H₂O). Rate constant ratios of

$$k(\text{OH} + \text{propene})/k(\text{OH} + \text{CO}) = 75 \pm 8 \text{ at } 373 \text{ K}$$

and 55 ± 6 at 473 K were determined.⁶⁴ As discussed previously,⁶⁵ while subject to significant uncertainties, mainly concerning the rate constant of the reference reaction under the experimental conditions employed, these data⁶⁴ are generally consistent with the present recommendation.

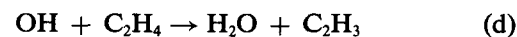
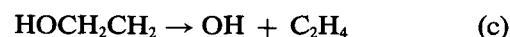
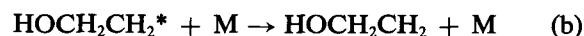
In addition, a set of rate constants at 301 ± 1 K for 2-methyl-1,3-butadiene and a series of monoterpenes can be derived from the experimental NO-photooxidation data of Grimsrud *et al.*⁶⁶ These data⁶⁶ must be viewed as semi-quantitative only,^{28,55} since their use assumes that the OH radical concentrations were identical in the separate NO_x-organic-air irradiations carried out and that the contributions of any O₃ reactions to the monoterpene reaction rates were negligible.

As noted above, in most cases the rate constants listed in Tables 5–8 are at, or close to, the high-pressure second-order limit. However, the rate constants determined for the C₃ and C₄ alkenes using discharge flow techniques at total pressures of ~ 1 Torr may still be in the fall-off regime between second- and third-order kinetics. These data are not used in the evaluation of the recommended rate constants. For ethene and propene the most reliable rate constant data in the fall-off region are indicated and used to derive the fall-off parameters in the Troe fall-off expression.

(1) Ethene and Ethene-*d*₄

As discussed below, the available experimental data and theoretical expectations show that three reasonably distinct temperature regimes are observed for the

reactions of the OH (or OD) radical with ethene and ethene-*d*₄. Taking the OH radical reaction with ethene as an example, these temperature regimes are characterized by the following reaction pathways: (a, –a and b) OH radical addition to ethene to form the species HOCH₂CH₂* (where * denotes an initially energy-rich radical), followed by stabilization and/or decomposition of this adduct radical; (c) at temperatures above ~ 450 – 550 K the thermalized HOCH₂CH₂ radical undergoes decomposition back to the OH radical and C₂H₄ reactants sufficiently rapidly that, unless the HOCH₂CH₂ radical is removed by reaction on a shorter time-scale, OH radical addition to ethene is neither observed nor of any importance; and (d) at temperatures above ~ 600 – 700 K, where the effective rate constant for OH radical addition to ethene is decreasing rapidly due to the decomposition of the thermalized HOCH₂CH₂ radical and/or fall-off effects, H-atom abstraction from ethene becomes the sole reaction pathway observed:



The bimolecular rate constants obtained for the reactions of the OH radical with ethene and ethene-*d*₄, with the rate constants at temperatures < 650 K being supposedly at or close to the high pressure second-order limit, are given in Table 5, and these rate constants are plotted in Arrhenius form in Figs. 38 (ethene) and 39 (ethene-*d*₄), respectively. The analogous rate constants for the reactions of the OD radical with ethene and ethene-*d*₄ are given in Table 8.

Ethene. Figure 38 shows that for the reaction of OH radicals with ethene, at elevated temperatures (> 700 K) the relative rate data of Westenberg and Fristrom,¹ Baldwin *et al.*,² Hoare and Patel³ and Bradley *et al.*⁶ exhibit significant differences from the more recent absolute rate constant data of Smith,¹⁵ Tully,¹⁶ and Liu *et al.*,^{17,18} indicating that these earlier relative rate studies^{1–3,6} were subject to unrecognized complexities and/or systematic errors.

Extrapolation of the elevated temperature (> 650 K) kinetic data of Smith,¹⁵ Tully¹⁶ and Liu *et al.*^{17,18} to room temperature leads to the conclusion that any H-atom abstraction process is totally negligible. This expectation, based upon the extrapolation of elevated temperature data, is totally consistent with (a) the thermochemistry of the H-atom abstraction reaction,⁶² (b) the room temperature kinetic study of Howard⁶⁷ over the total pressure range 0.7–7 Torr of helium which showed that the rate constant extrapolates to essentially zero at zero pressure, and (c) the discharge flow-mass spectrometric study of Bartels *et al.*⁶⁸ which showed that the H-atom abstraction rate constant accounts for $< 2.5\%$ of the

overall reaction rate constant at ~ 2 Torr total pressure and 295 K.

In addition to the rate constants given in Table 5, Wilson and Westenberg,⁶⁹ Greiner,⁷⁰ Morris *et al.*²¹, Smith and Zellner,⁷¹ Bradley *et al.*,²² Stuhl,²³ Pastrana and Carr,²⁵ Davis *et al.*,⁷² Atkinson *et al.*,⁷ Overend and Paraskevopoulos,⁸ Howard,⁶⁷ Farquharson and Smith,⁷³ Tully,^{10,19} Zellner and Lorenz¹¹ and Klein *et al.*¹³ measured rate constants at temperatures ≈ 525 K which are in the fall-off region (although this fact was not always known or appreciated^{22,23,69-71}).

The experimental data obtained at temperatures ≈ 525 K can be used to derive the limiting low pressure

third-order and high pressure second-order rate constants k_0 and k_∞ , respectively. Use of the Troe fall-off equation,^{74,75}

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

where $[M]$ is the concentration of the diluent gas and F is the broadening factor, then allows the bimolecular OH radical addition rate constants k to be calculated as a function of temperature and pressure.

TABLE 5. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with acyclic monoalkenes at, or close to, the high pressure limit

Alkene	$10^{12} \times A$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{molecule}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
Ethene			9	1250–1400	RR [relative to $k(\text{CO}) = 1.12 \times 10^{-13} e^{0.000907T}$] ^a	Westenberg and Fristrom ¹	1250–1400
			7.5	813	RR [relative to $k(\text{H}_2) = 1.12 \times 10^{-12}$] ^a	Baldwin <i>et al.</i> ²	
			4.8	734	RR [relative to $k(\text{CH}_4) = 6.95 \times 10^{-18} T^2 e^{-1282/T}$] ^b	Hoare and Patel ³	734–798
			4.1	748			
			3.9	773			
			3.8	798			
			6.23 \pm 0.33	381	PR-RA	Gordon and Mulac ⁴	381–416
			7.31 \pm 0.33	416			
			7.55 \pm 1.51	305 \pm 2	RR [relative to $k(n\text{-butane}) = 2.62 \times 10^{-12}$] ^b	Lloyd <i>et al.</i> ⁵	
			22.5	1300	RR [relative to $k(\text{H}_2) = 5.69 \times 10^{-12}$] ^a	Bradley <i>et al.</i> ⁶	
			7.85 \pm 0.79	299.2	FP-RF	Atkinson <i>et al.</i> ⁷	299–425
			6.76 \pm 0.68	351.3			
	2.18	-388 ± 151	5.35 \pm 0.54	425.1			
			10.0 \pm 1.7	296	FP-RA	Overend and Paraskevopoulos ⁸	
			8.38 \pm 0.38	299 \pm 2	RR [relative to $k(n\text{-butane}) = 2.55 \times 10^{-12}$] ^b	Atkinson <i>et al.</i> ⁹	
			8.47 \pm 0.24	291	LP-LIF	Tully ¹⁰	291–591
			6.15 \pm 0.35	361.5			
		4.55 \pm 0.27 ^c	438				
		3.08 \pm 0.13 ^c	515				
		1.3 ^c	591				
		8.8 \pm 2.0 ^d	296	LP-RF	Zellner and Lorenz ¹¹	296–524	
3.3 \pm 1.4	-320 ± 150	5.5 ^{+3.3d} _{-1.7}	524				
		8.66 \pm 0.38	295 \pm 1	RR [relative to $k(\text{propene}) = 2.68 \times 10^{-11}$] ^b	Atkinson and Aschmann ¹²		

TABLE 5. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with acyclic monoalkenes at, or close to, the high pressure limit — Continued

Alkene	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
			8.4 ± 0.6^d	295	RR [relative to $k(n\text{-hexane})$ $= 5.55 \times 10^{-12}]^b$	Klein <i>et al.</i> ¹³	
			7.3 ± 1.0	295	LP-LIF	Schmidt <i>et al.</i> ¹⁴	
			2.5 ± 0.5	1220	LH-LIF	Smith ¹⁵	
			0.319 ± 0.030	651	LP-LIF	Tully ¹⁶	651-901
			0.438 ± 0.029	694			
			0.477 ± 0.030	701			
			0.615 ± 0.047	746			
			0.672 ± 0.042	757			
			0.725 ± 0.059	779			
			0.803 ± 0.057	800			
			0.899 ± 0.055	829			
			0.971 ± 0.073	849			
			1.20 ± 0.12	898			
	33.6 ± 6.4	2997 ± 144	1.16 ± 0.10	901			
			6.78	343	PR-RA	Liu <i>et al.</i> ^{17,18}	343-1173
			6.02	373			
			5.20	403			
			5.04	423			
			4.24	483			
			4.12	523			
	1.66	-479 (343-563 K)	4.01	563			
			3.14	603			
			2.06	653			
			1.58	703			
			1.29	730			
			1.47	748			
			1.70	773			
			1.65	794			
			1.51	800			
			1.85	855			
			2.32	873			
			2.15	901			
			2.30	943			
			2.60	973			
			2.51	990			
			2.92	1042			
			3.53	1087			
			3.20	1099			
			3.46	1136			
			4.28	1163			
			4.03	1173			
			7.91	295	LP-LIF	Tully ¹⁹	295-420
			8.07	295			
			6.60	350			
			5.23	420			
Ethene- d_4			8.78 ± 0.52	298 ± 2	RR [relative to $k(\text{ethene}) =$ $8.52 \times 10^{-12}]^b$	Niki <i>et al.</i> ²⁰	
			0.132 ± 0.017	651	LP-LIF	Tully ¹⁶	651-901
			0.209 ± 0.018	694			
			0.211 ± 0.013	701			
			0.297 ± 0.018	746			
			0.335 ± 0.026	757			

TABLE 5. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with acyclic monoalkenes at, or close to, the high pressure limit — Continued

Alkene	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Tempera- ture range covered (K)
			0.403 ± 0.027	779			
			0.426 ± 0.030	800			
			0.492 ± 0.034	829			
			0.571 ± 0.029	849			
			0.614 ± 0.054	871			
	58.5 ± 15.4	3934 ± 205	0.771 ± 0.087	901			
			6.85	333	PR-RA	Liu <i>et al.</i> ¹⁸	333–1123
			4.29	473			
			3.59	603			
			1.53	653			
			1.09	703			
			0.79	723			
			1.13	773			
			1.29	798			
			1.50	873			
			1.62	923			
			1.85	973			
			1.95	1023			
			2.10	1073			
			2.36	1123			
			8.49	295	LP-LIF	Tully ¹⁹	295–420
			8.49	295			
			7.00	350			
			5.84	420			
Propene			17 ± 4	300	DF-MS	Morris <i>et al.</i> ²¹	
			5.0 ± 1.7	300	DF-EPR	Bradley <i>et al.</i> ²²	
			14.5 ± 2.2	298	FP-RF	Stuhl ²³	
			13.3 ± 3.4	298	RR [relative to $k(\text{CO}) = 1.49$ $\times 10^{-13}]^a$	Gorse and Volman ²⁴	
			14.3 ± 0.7	381	PR-RA	Gordon and Mulac ⁴	381–416
			20.0 ± 1.0	416			
			5 ± 1	300	DF-RA	Pastrana and Carr ²⁵	
			25.1 ± 2.5	297.6	FP-RF	Atkinson and Pitts ²⁶	298–424
			20.4 ± 2.1	345.5			
			16.4 ± 1.6	390.3			
	4.1	-544 ± 151	14.7 ± 1.5	423.6			
			25.4 ± 5.1	305 ± 2	RR [relative to $k(n\text{-butane}) =$ $2.62 \times 10^{-12}]^b$	Lloyd <i>et al.</i> ⁵	
			22.0	303	RR [relative to $k(\text{cis-2-butene}) =$ $5.49 \times 10^{-11}]^b$	Wu <i>et al.</i> ²⁷	
			24.2 ± 3.6	305 ± 2	RR [relative to $k(2\text{-methylpropene})$ $= 4.94 \times 10^{-11}]^b$	Winer <i>et al.</i> ²⁸	
			24.2 ± 4.9	305 ± 2	RR [relative to $k(2\text{-methylpropene})$ $= 4.94 \times 10^{-11}]^b$	Winer <i>et al.</i> ²⁹	

TABLE 5. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with acyclic monoalkenes at, or close to, the high pressure limit — Continued

Alkene	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Tempera- ture range covered (K)
Propene- d_6	4.58 ± 0.46	-524 ± 38 (293–467 K)	26.0 ± 1.6	298	FP-RF	Ravishankara <i>et al.</i> ³⁰	
			24.6 ± 2.8	297 ± 2	FP-RA	Nip and Paraskevopoulos ³¹	
			25.3	300	RR [relative to $k(\text{ethene}) =$ $8.44 \times 10^{-12}]^b$	Cox <i>et al.</i> ³²	
			26.2	300	RR [relative to $k(\text{ethene}) =$ $8.44 \times 10^{-12}]^b$	Barnes <i>et al.</i> ³³	
			19 ± 3	298	DF-RF	Smith ³⁴	
			30 ± 5^d	297	LP-RF	Zellner and Lorenz ¹¹	
			46	673	RR [relative to $k(2,2,3,3\text{-tetramethyl-}$ $\text{butane}) = 1.63 \times$ $10^{-17} T^2 e^{-86/7T}]^b$	Baldwin <i>et al.</i> ³⁵	673–773
			42	713			
			47	743			
			55	773			
			8	1200	LH-LIF	Smith ³⁶	
			29.5 ± 2.0^d	295	RR [relative to $k(n\text{-hexane}) =$ $5.55 \times 10^{-12}]^b$	Klein <i>et al.</i> ¹³	
			22 ± 4	295	LP-LIF	Schmidt <i>et al.</i> ¹⁴	
			27.1 ± 0.3	293	LP-LIF	Tully and Goldsmith ³⁷	293–896
			21.7 ± 0.2	338.5			
			17.5 ± 0.2	400			
			15.9 ± 0.2	422			
			14.9 ± 0.3	440.5			
			13.9 ± 0.2	467			
			3.79 ± 0.17	701			
3.60 ± 0.11	705						
4.57 ± 0.12	781						
4.74 ± 0.08	785						
5.44 ± 0.11	857						
33.1 ± 7.6	1541 ± 178 (701–896 K)	5.95 ± 0.16	896				
Propene- d_6	4.58 ± 0.46	-524 ± 38 (293–467 K)	4.5 ± 0.7	960	LH-LIF	Smith <i>et al.</i> ³⁸	960–1210
			5.8 ± 1.1	1090			
			7.0 ± 1.0	1180			
			8.9 ± 1.2	1210			
			27.9 ± 2.6	300	RR [relative to $k(\text{ethene}) =$ $8.44 \times 10^{-12}]^b$	Barnes <i>et al.</i> ³⁹	
			21 ± 2	298	FP-RF	Wallington ⁴⁰	
			27.0 ± 0.7	296 ± 2	RR [relative to $k(\text{cyclohexane}) =$ $7.45 \times 10^{-12}]^b$	Atkinson and Aschmann ⁴¹	
			18.7	298	DF-MS	Morris and Niki ⁴²	
			16.8	298	FP-RF	Stuhl ²³	

TABLE 5. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with acyclic monoalkenes at, or close to, the high pressure limit — Continued

Alkene	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Tempera- ture range covered (K)
			27.9 ± 0.2	293	LP-LIF	Tully and Goldsmith ³⁷	293–896
			22.3 ± 0.3	338			
			18.4 ± 0.3	392			
	4.79 ± 0.51	-518 ± 39 (293–481 K)	15.7 ± 0.2	440.5			
			13.7 ± 0.1	481			
			2.65 ± 0.10	701			
			2.35 ± 0.09	705			
			3.21 ± 0.16	781			
			3.29 ± 0.15	785			
	18.7 ± 9.7	1403 ± 404 (701–896 K)	3.56 ± 0.13	857			
			3.85 ± 0.12	896			
1-Butene			40.8	298	DF-MS	Morris and Niki ⁴²	
			15 ± 1	300	DF-RA	Pastrana and Carr ²⁵	
			35.3 ± 3.6	297.7	FP-RF	Atkinson and Pitts ²⁶	298–424
	7.6	-468 ± 151	30.0 ± 3.0	344.1			
			22.2 ± 2.2	423.7			
			28.5	303	RR [relative to $k(\text{cis-2-butene}) =$ 5.49×10^{-11}] ^b	Wu <i>et al.</i> ²⁷	
			29.5 ± 2.0	298	FP-RF	Ravishankara <i>et al.</i> ³⁰	
			33.4 ± 2.5	297 ± 2	FP-RA	Nip and Paraskevopoulos ³¹	
			32.1	300	RR [relative to $k(\text{ethene}) =$ 8.44×10^{-12}] ^b	Barnes <i>et al.</i> ³³	
			30 ± 4	298	DF-MS	Biermann <i>et al.</i> ⁴³	
			31.3 ± 0.8	298 ± 2	RR [relative to $k(\text{propene}) =$ 2.63×10^{-11}] ^b	Ohta ⁴⁴	
			31.9 ± 1.6	295 ± 1	RR [relative to $k(\text{propene}) =$ 2.68×10^{-11}] ^b	Atkinson and Aschmann ¹²	
			19.7 ± 4.2	1225	LH-LIF	Smith ¹⁵	
			6.60 ± 0.44	650	LP-LIF	Tully ¹⁶	650–833
			7.55 ± 0.49	691			
			8.22 ± 0.52	732			
			8.92 ± 0.64	778			
	37.4 ± 6.3	1116 ± 122	9.67 ± 0.68	833			
1-Butene- d_8			4.32 ± 0.27	650	LP-LIF	Tully ¹⁶	650–833
			4.86 ± 0.30	691			
			5.42 ± 0.34	732			
			6.13 ± 0.45	778			
	35.6 ± 2.5	1374 ± 49	6.85 ± 0.50	833			
2-Methyl- propene			64.6	298	DF-MS	Morris and Niki ⁴²	
			50.7 ± 5.1	297.2	FP-RF	Atkinson and Pitts ²⁶	297–424
			39.0 ± 3.9	345.5			
	9.2	-503 ± 151	30.5 ± 3.1	423.9			

TABLE 5. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with acyclic monoalkenes at, or close to, the high pressure limit — Continued

Alkene	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Tempera- ture range covered (K)
<i>cis</i> -2-Butene			50.5	303	RR [relative to $k(\textit{cis}-2-butene) =5.49 \times 10^{-11}]b$	Wu <i>et al.</i> ²⁷	
			61.6	300	RR [relative to $k(\text{ethene}) =$ 8.44×10^{-12}] ^b	Barnes <i>et al.</i> ³³	
			54.7 ± 0.9	298 ± 2	RR [relative to $k(\text{2-methyl-2-butene}) =$ 8.69×10^{-11}] ^b	Ohta ⁴⁴	
			52.3 ± 2.4	295 ± 1	RR [relative to $k(\text{propene}) =$ 2.68×10^{-11}] ^b	Atkinson and Aschmann ¹²	
			29.6 ± 6.8	1259	LH-LIF	Smith ¹⁵	
			61.2	298	DF-MS	Morris and Niki ⁴²	
			53.7 ± 5.4	297.6	FP-RF	Atkinson and Pitts ²⁶	298–425
		10.4	-488 ± 151	43.0 ± 4.3			
				32.9 ± 3.3	424.9		
				57.1 ± 11.5	305 ± 2	RR [relative to $k(\textit{n}-butane) =2.62 \times 10^{-12}]b$	Lloyd <i>et al.</i> ⁵
<i>trans</i> -2-Butene			60.3 ± 9.0	305 ± 2	RR [relative to $k(\text{2-methylpropene}) =$ 4.94×10^{-11}] ^b	Winer <i>et al.</i> ²⁸	
			42.6 ± 2.5	298	FP-RF	Ravishankara <i>et al.</i> ³⁰	
			54.7 ± 1.8	298 ± 2	RR [relative to $k(\text{2-methyl-2-butene}) =$ 8.69×10^{-11}] ^b	Ohta ⁴⁴	
			57.1 ± 1.4	295 ± 1	RR [relative to $k(\text{propene}) =$ 2.68×10^{-11}] ^b	Atkinson and Aschmann ¹²	
			71.4	298	DF-MS	Morris and Niki ⁴²	
			12 ± 10	300	DF-RA	Pastrana and Carr ²⁵	
			69.9 ± 7.0	297.8	FP-RF	Atkinson and Pitts ²⁶	298–425
		11.2	-549 ± 151	57.0 ± 5.7	346.1		
				40.3 ± 4.1	425.0		
				71.4	303	RR [relative to $k(\textit{cis}-2-butene) =5.49 \times 10^{-11}]b$	Wu <i>et al.</i> ²⁷
			59.6 ± 3.1	297 ± 2	RR [relative to $k(\textit{cis}-1,3-pentadiene)= 1.01 \times 10^{-10}]c$	Ohta ⁴⁵	
			65.1 ± 1.4	295 ± 1	RR [relative to $k(\text{propene}) =$ 2.68×10^{-11}] ^b	Atkinson and Aschmann ¹²	

TABLE 5. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with acyclic monoalkenes at, or close to, the high pressure limit — Continued

Alkene	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
			73 ± 13	297	RR [relative to $k(\text{propene}) = 2.65 \times 10^{-11}$] ^b	Edney <i>et al.</i> ⁴⁶	
			27.0 ± 3.6	1275	LH-LIF	Smith ¹⁵	
			72.1 ± 3.8	298 ± 3	RR [relative to $k(\text{propene}) = 2.63 \times 10^{-11}$] ^b	Rogers ⁴⁷	
1-Pentene			42.5	298	DF-MS	Morris and Niki ⁴²	
			30.7	303	RR [relative to $k(\text{cis-2-butene}) = 5.49 \times 10^{-11}$] ^b	Wu <i>et al.</i> ²⁷	
			39.7 ± 3.8	297 ± 2	FP-RA	Nip and Paraskevopoulos ³¹	
			29 ± 4	298	DF-MS	Biermann <i>et al.</i> ⁴³	
			28.7 ± 1.3	298	FP-RF	Biermann <i>et al.</i> ⁴³	
			31.9 ± 1.4	295 ± 1	RR [relative to $k(\text{propene}) = 2.68 \times 10^{-11}$] ^b	Atkinson and Aschmann ¹²	
<i>cis</i> -2-Pentene			65.9	303	RR [relative to $k(\text{cis-2-butene}) = 5.49 \times 10^{-11}$] ^b	Wu <i>et al.</i> ²⁷	
			65.4 ± 1.7	298 ± 2	RR [relative to $k(\text{cis-2-butene}) = 5.64 \times 10^{-11}$] ^b	Ohta ⁴⁴	
<i>trans</i> -2-Pentene			66.9 ± 2.1	297 ± 2	RR [relative to $k(\text{1,3-butadiene}) = 6.69 \times 10^{-11}$] ^b	Ohta ⁴⁵	
2-Pentene (<i>cis</i> , <i>trans</i> mixture)			90.1	298	DF-MS	Morris and Niki ⁴²	
2-Methyl-1-butene			90.1	298	DF-MS	Morris and Niki ⁴²	
			60.4	303	RR [relative to $k(\text{cis-2-butene}) = 5.49 \times 10^{-11}$] ^b	Wu <i>et al.</i> ²⁷	
			60.7 ± 1.1	298 ± 2	RR [relative to $k(\text{2-methylpropene}) = 5.14 \times 10^{-11}$] ^b	Ohta ⁴⁴	
3-Methyl-1-butene	5.23	-533 ± 151	31.0 ± 3.1 24.0 ± 2.4 18.4 ± 1.9	299.2 349.9 423.2	FP-RF	Atkinson <i>et al.</i> ⁴⁸	299–423
			32.4 ± 1.1	295 ± 1	RR [relative to $k(\text{propene}) = 2.68 \times 10^{-11}$] ^b	Atkinson and Aschmann ¹²	
2-Methyl-2-butene			119	298	DF-MS	Morris and Niki ⁴²	
			78 ± 8	297.7	FP-RF	Atkinson <i>et al.</i> ⁴⁹	298–425

TABLE 5. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with acyclic monoalkenes at, or close to, the high pressure limit — Continued

Alkene	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
			77 ± 8	298.0			
			67 ± 7	345.2			
			62 ± 9	421.6			
	36	-226 ± 201	62 ± 9	424.5			
			87.3 ± 8.8	299.5	FP-RF	Atkinson and Pitts ⁵⁰	299–426
			65.4 ± 6.6	356.2			
	19.1	-450 ± 151	56.0 ± 5.6	426.1			
			92 ± 7	300 ± 1	RR [relative to $k(\text{cis-2-butene}) = 5.58 \times 10^{-11}$] ^b	Atkinson <i>et al.</i> ⁵¹	
			89.9 ± 3.4	299 ± 2	RR [relative to $k(\text{propene}) = 2.62 \times 10^{-11}$] ^b	Atkinson <i>et al.</i> ⁹	
			85.0 ± 2.7	297 ± 2	RR [relative to $k(1,3\text{-butadiene}) = 6.69 \times 10^{-11}$] ^b	Ohta ⁴⁵	
			88.4 ± 3.5	295 ± 1	RR [relative to $k(\text{propene}) = 2.68 \times 10^{-11}$] ^b	Atkinson and Aschmann ¹²	
1-Hexene			32.9	303	RR [relative to $k(\text{cis-2-butene}) = 5.49 \times 10^{-11}$] ^b	Wu <i>et al.</i> ²⁷	
			37.5 ± 1.1	295 ± 1	RR [relative to $k(\text{propene}) = 2.68 \times 10^{-11}$] ^b	Atkinson and Aschmann ¹²	
2-Methyl-1-pentene			62.6 ± 0.9	298 ± 2	RR [relative to $k(2\text{-methyl-2-butene}) = 8.69 \times 10^{-11}$] ^b	Ohta ⁴⁴	
2-Methyl-2-pentene			87.8 ± 1.8	298 ± 2	RR [relative to $k(2\text{-methyl-2-butene}) = 8.69 \times 10^{-11}$] ^b	Ohta ⁴⁴	
			90.3 ± 1.4	298 ± 2	RR [relative to $k(\text{cis-2-pentene}) = 6.54 \times 10^{-11}$] ^f	Ohta ⁴⁴	
<i>trans</i> -4-Methyl-2-pentene			60.5 ± 0.7	298 ± 2	RR [relative to $k(\text{trans-2-pentene}) = 6.65 \times 10^{-11}$] ^g	Ohta ⁴⁴	
3,3-Dimethyl-1-butene			28.5	303	RR [relative to $k(\text{cis-2-butene}) = 5.49 \times 10^{-11}$] ^b	Wu <i>et al.</i> ²⁷	
2,3-Dimethyl-2-butene			153	298	DF-MS	Morris and Niki ⁴²	
			110 ± 22	298	FP-RF	Perry ⁵²	
			56.9 ± 1.3	298	FP-RF	Ravishankara <i>et al.</i> ³⁰	
			129 ± 9	300 ± 1	RR [relative to $k(\text{cis-2-butene}) = 5.58 \times 10^{-11}$] ^b	Atkinson <i>et al.</i> ⁵¹	

TABLE 5. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with acyclic monoalkenes at, or close to, the high pressure limit — Continued

Alkene	$10^{12} \times A$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{molecule}^{-1} \text{ s}^{-1}$) at T (K)	Technique	Reference	Temperature range covered (K)
			112 ± 6	299 ± 2	RR [relative to $k(\text{propene}) =$ $2.62 \times 10^{-11}]^b$	Atkinson <i>et al.</i> ⁹
			115 ± 5	298 ± 2	RR [relative to $k(2\text{-methyl-1,3-butadiene})$ $= 1.01 \times 10^{-10}]^b$	Atkinson <i>et al.</i> ⁵³
			110 ± 3	294 ± 2	RR [relative to $k(2\text{-methyl-1,3-butadiene})$ $= 1.02 \times 10^{-10}]^b$	Atkinson <i>et al.</i> ⁵⁴
			112 ± 5	295 ± 1	RR [relative to $k(\text{propene}) =$ $2.68 \times 10^{-11}]^b$	Atkinson and Aschmann ¹²
			103 ± 1	298 ± 2	RR [relative to $k(2\text{-methyl-2-butene})$ $= 8.69 \times 10^{-11}]^b$	Ohta ⁴⁴
			111 ± 3	294 ± 1	RR [relative to $k(2\text{-methyl-1,3-butadiene})$ $= 1.02 \times 10^{-10}]^b$	Atkinson <i>et al.</i> ⁵⁵
			37.0 ± 5.6	1237	LH-LIF	Smith ¹⁵
			111 ± 8	296 ± 2	RR [relative to $k(2\text{-methyl-1,3-butadiene})$ $= 1.01 \times 10^{-10}]^b$	Atkinson <i>et al.</i> ⁵⁶
			111 ± 3	296 ± 2	RR [relative to $k(2\text{-methyl-1,3-butadiene})$ $= 1.01 \times 10^{-10}]^b$	Atkinson and Aschmann ⁵⁷
1-Heptene			36.1 ± 7.2	305 ± 2	RR [relative to $k(2\text{-methylpropene}) =$ $4.94 \times 10^{-11}]^b$	Darnall <i>et al.</i> ⁵⁸
			40.5 ± 1.6	295 ± 1	RR [relative to $k(\text{propene}) =$ $2.68 \times 10^{-11}]^b$	Atkinson and Aschmann ¹²
2,3-Dimethyl- 2-pentene			98.2 ± 0.9	298 ± 2	RR [relative to $k(2\text{-methyl-2-butene})$ $= 8.69 \times 10^{-11}]^b$	Ohta ⁴⁴
			108 ± 2	298 ± 2	RR [relative to $k(2,3\text{-dimethyl-2-butene})$ $= 1.10 \times 10^{-10}]^b$	Ohta ⁴⁴
<i>trans</i> -4,4- Dimethyl- 2-pentene			54.5 ± 0.7	298 ± 2	RR [relative to $k(\text{trans-2-pentene})$ $= 6.65 \times 10^{-11}]^g$	Ohta ⁴⁴

^aSee Introduction.^bFrom present recommendations (see text).^cNon-exponential OH radical decays observed.^dExtrapolated to high-pressure limit using the Troe fall-off expression.^eFrom the rate constant determined by Ohta⁴⁵ (Table 6).^fFrom the rate constant determined by Ohta.⁴⁴^gFrom the rate constant determined by Ohta,⁴⁵ using an assumed temperature dependence of $B = -500$ K.

TABLE 6. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with acyclic di- and trialkenes at, or close to, the high pressure limit

Alkene	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Tempera- ture range covered (K)
Propadiene			4.5 ± 2.5^a	300	DF-EPR	Bradley <i>et al.</i> ²²	
			9.30 ± 0.93	299.0	FP-RF	Atkinson <i>et al.</i> ⁴⁸	299–421
			8.70 ± 0.87	349.7			
	5.59	-153 ± 151	8.02 ± 0.80	420.8			
			10.0 ± 1.4	297 ± 2	RR [relative to $k(1,3\text{-butadiene}) =$ $6.69 \times 10^{-11}]^b$	Ohta ⁴⁵	
			9.84 ± 0.97	295 ± 1	RR [relative to $k(\text{propene}) =$ $2.68 \times 10^{-11}]^b$	Atkinson and Aschmann ¹²	
			9.0 ± 1.0	305	PR-RA	Liu <i>et al.</i> ⁵⁹	305–1173
			8.7 ± 0.9	373			
			8.2 ± 0.8	398			
			8.8 ± 0.9	478			
			8.0 ± 0.9	543			
	6.7 ± 0.9	-100 ± 50 (305–613 K)	7.8 ± 0.8	613			
			7.2 ± 0.7	673			
		7.3 ± 0.7	773				
		7.6 ± 0.8	808				
		7.9 ± 0.8	853				
		8.2 ± 0.8	873				
		7.8 ± 0.8	888				
		6.7 ± 0.7	973				
		6.5 ± 0.7	1073				
		5.6 ± 0.6	1173				
1,2-Butadiene			26.1 ± 2.1	297 ± 2	RR [relative to $k(1,3\text{-butadiene}) =$ $6.69 \times 10^{-11}]^b$	Ohta ⁴⁵	
1,3-Butadiene			67.6 ± 13.6	305 ± 2	RR [relative to $k(n\text{-butane}) =$ $2.62 \times 10^{-12}]^b$	Lloyd <i>et al.</i> ⁵	
			68.5 ± 6.9	299.5	FP-RF	Atkinson <i>et al.</i> ⁴⁸	299–424
			57.2 ± 5.7	347.2			
	14.5	-468 ± 151	43.3 ± 4.4	424.0			
			65.0	300	RR [relative to $k(\text{ethene}) =$ $8.44 \times 10^{-12}]^b$	Barnes <i>et al.</i> ³³	
			61.6 ± 1.5	297 ± 2	RR [relative to $k(\text{propene}) =$ $2.65 \times 10^{-11}]^b$	Ohta ⁴⁵	
			68.8 ± 2.2	297 ± 2	RR [relative to $k(2\text{-methyl-2-butene}) =$ $8.74 \times 10^{-11}]^b$	Ohta ⁴⁵	
			67.8 ± 2.2	295 ± 1	RR [relative to $k(\text{propene}) =$ $2.68 \times 10^{-11}]^b$	Atkinson and Aschmann ¹²	
			61 ± 6	313	PR-RA	Liu <i>et al.</i> ⁵⁹	313–1203
			50 ± 5	333			
		51 ± 5	338				
		46 ± 5	373				

TABLE 6. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with acyclic di- and trialkenes at, or close to, the high pressure limit — Continued

Alkene	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
			41 ± 4	393			
			47 ± 5	408			
			42 ± 4	438			
			35 ± 4	483			
			29 ± 3	563			
	14 ± 1	-440 ± 40 (313–623 K)	30 ± 3	623			
			30 ± 3	673			
			24 ± 3	723			
			20 ± 2	773			
			17 ± 2	873			
			15 ± 2	923			
			11 ± 1	1023			
			10 ± 1	1053			
			6.5 ± 0.6	1153			
			6.9 ± 0.7	1173			
			7.7 ± 0.8	1203			
1,2-Pentadiene			35.5 ± 1.4	297 ± 2	RR [relative to $k(1,3\text{-butadiene}) =$ $6.69 \times 10^{-11}]^b$	Ohta ⁴⁵	
<i>cis</i> -1,3-Pentadiene			101 ± 4	297 ± 2	RR [relative to $k(1,3\text{-butadiene}) =$ $6.69 \times 10^{-11}]^b$	Ohta ⁴⁵	
1,4-Pentadiene			53.3 ± 1.4	297 ± 2	RR [relative to $k(\text{propene}) =$ $2.65 \times 10^{-11}]^b$	Ohta ⁴⁵	
3-Methyl-1,2-butadiene			56.9 ± 2.1	297 ± 2	RR [relative to $k(1,3\text{-butadiene}) =$ $6.69 \times 10^{-11}]^b$	Ohta ⁴⁵	
2-Methyl-1,3-butadiene			78.1	300	RR [relative to $k(\text{ethene}) =$ $8.44 \times 10^{-12}]^b$	Cox <i>et al.</i> ³²	
			99.8 ± 4.5	299 ± 2	RR [relative to $k(\text{propene}) =$ $2.62 \times 10^{-11}]^b$	Atkinson <i>et al.</i> ⁹	
			92.6 ± 15	299	FP-RF	Kleindienst <i>et al.</i> ⁶⁰	299–422
	23.6	-409 ± 28	76.4 ± 12	349			
			62.1 ± 8.2	422			
			99.0 ± 2.7	297 ± 2	RR [relative to $k(1,3\text{-butadiene}) =$ $6.69 \times 10^{-11}]^b$	Ohta ⁴⁵	
			102 ± 4	295 ± 1	RR [relative to $k(\text{propene}) =$ $2.68 \times 10^{-11}]^b$	Atkinson and Aschmann ¹²	
			101 ± 2	297	RR [relative to $k(\text{propene}) =$ $2.65 \times 10^{-11}]^b$	Edney <i>et al.</i> ⁴⁶	
<i>trans</i> -1,3-Hexadiene			112 ± 4	297 ± 2	RR [relative to $k(1,3\text{-butadiene}) =$ $6.69 \times 10^{-11}]^b$	Ohta ⁴⁵	

TABLE 6. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with acyclic di- and trialkenes at, or close to, the high pressure limit — Continued

Alkene	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Tempera- ture range covered (K)
<i>trans</i> -1,4-Hexadiene			90.3 ± 5.4	297 ± 2	RR [relative to $k(1,3\text{-butadiene}) = 6.69 \times 10^{-11}$] ^b	Ohta ⁴⁵	
			90.9 ± 4.3	297 ± 2	RR [relative to $k(\text{propene}) = 2.65 \times 10^{-11}$] ^b	Ohta ⁴⁵	
1,5-Hexadiene			62.2 ± 1.4	297 ± 2	RR [relative to $k(1,3\text{-butadiene}) = 6.69 \times 10^{-11}$] ^b	Ohta ⁴⁵	
			61.7 ± 3.5	297 ± 2	RR [relative to $k(\text{propene}) = 2.65 \times 10^{-11}$] ^b	Ohta ⁴⁵	
2,4-Hexadiene (<i>cis</i> + <i>trans</i> mixture)			134 ± 6	297 ± 2	RR [relative to $k(1,3\text{-butadiene}) = 6.69 \times 10^{-11}$] ^b	Ohta ⁴⁵	
2-Methyl-1,4-pentadiene			78.8 ± 8.1	297 ± 2	RR [relative to $k(\textit{cis}\text{-}1,3\text{-pentadiene}) = 1.01 \times 10^{-10}$] ^c	Ohta ⁴⁵	
3-Methyl-1,3-pentadiene			136 ± 9	297 ± 2	RR [relative to $k(\textit{cis}\text{-}1,3\text{-pentadiene}) = 1.01 \times 10^{-10}$] ^c	Ohta ⁴⁵	
4-Methyl-1,3-pentadiene			131 ± 5	297 ± 2	RR [relative to $k(\textit{cis}\text{-}1,3\text{-pentadiene}) = 1.01 \times 10^{-10}$] ^c	Ohta ⁴⁵	
2,3-Dimethyl-1,3-butadiene			122 ± 6	297 ± 2	RR [relative to $k(1,3\text{-butadiene}) = 6.69 \times 10^{-11}$] ^b	Ohta ⁴⁵	
2-Methyl-1,5-hexadiene			96.1 ± 4.4	297 ± 2	RR [relative to $k(1,5\text{-hexadiene}) = 6.20 \times 10^{-11}$] ^c	Ohta ⁴⁵	
2,5-Dimethyl-1,5-hexadiene			120 ± 2	297 ± 2	RR [relative to $k(1,5\text{-hexadiene}) = 6.20 \times 10^{-11}$] ^c	Ohta ⁴⁵	
2,5-Dimethyl-2,4-hexadiene			210 ± 10	297 ± 2	RR [relative to $k(2\text{-methyl-}1,5\text{-hexadiene}) = 9.61 \times 10^{-11}$] ^c	Ohta ⁴⁵	
<i>cis</i> -1,3,5-Hexatriene			110 ± 8	294 ± 2	RR [relative to $k(2\text{-methyl-}1,3\text{-butadiene}) = 1.02 \times 10^{-10}$] ^b	Atkinson <i>et al.</i> ⁵⁴	
<i>trans</i> -1,3,5-Hexatriene			111 ± 18	294 ± 2	RR [relative to $k(2\text{-methyl-}1,3\text{-butadiene}) = 1.02 \times 10^{-10}$] ^b	Atkinson <i>et al.</i> ⁵⁴	
3-Methylene-7-methyl-1,6-octadiene (Myrcene)			215 ± 16	294 ± 1	RR [relative to $k(2,3\text{-dimethyl-}2\text{-butene}) = 1.13 \times 10^{-10}$] ^b	Atkinson <i>et al.</i> ⁵⁵	

TABLE 6. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with acyclic di- and trialkenes at, or close to, the high pressure limit — Continued

Alkene	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{molecule}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
3,7-Dimethyl-1,3,6-octatriene (<i>cis</i> -, <i>trans</i> -Ocimene)			252 ± 20^d	294 ± 1	RR [relative to k (2,3-dimethyl-2-butene) = 1.13×10^{-10}]b	Atkinson <i>et al.</i> ⁵⁵	

^aMay not be the high pressure limit.^bFrom the present recommendations (see text).^cFrom the rate constants determined by Ohta.⁴⁵^d*cis*- and *trans*-Isomers have identical rate constants within $\pm 20\%$.⁵⁵TABLE 7. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with cyclic mono-, di- and trialkenes

Alkene	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{molecule}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
Cyclopentene			67.3 ± 2.5	298 ± 2	RR [relative to k (2-methyl-1,3-butadiene) = 1.01×10^{-10}]a	Atkinson <i>et al.</i> ⁵³	
			50.2 ± 4.0	298 ± 3	RR [relative to k (<i>trans</i> -2-butene) = 6.40×10^{-11}]a	Rogers ⁴⁷	
			63.6 ± 1.7	298 ± 3	RR [relative to k (cyclohexene) = 6.77×10^{-11}]a	Rogers ⁴⁷	
Cyclohexene			65.9	303	RR [relative to k (<i>cis</i> -2-butene) = 5.49×10^{-11}]a	Wu <i>et al.</i> ²⁷	
			75.6 ± 15.2	305 ± 2	RR [relative to k (2-methylpropene) = 4.94×10^{-11}]a	Darnall <i>et al.</i> ⁵⁸	
			65.4	300	RR [relative to k (ethene) = 8.44×10^{-12}]a	Cox <i>et al.</i> ³²	
			67.5	300	RR [relative to k (ethene) = 8.44×10^{-12}]a	Barnes <i>et al.</i> ³³	
			64.5 ± 2.5	297 ± 2	RR [relative to k (1,5-hexadiene) = 6.20×10^{-11}]b	Ohta ⁴⁵	
			67.7 ± 1.8	298 ± 2	RR [relative to k (2-methyl-1,3-butadiene) = 1.01×10^{-10}]a	Atkinson <i>et al.</i> ⁵³	

TABLE 7. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with cyclic mono-, di- and trialkenes — Continued

Alkene	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{molecule}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Tempera- ture range covered (K)
			54.3 ± 2.4	298 ± 3	RR [relative to $k(\text{trans-2-butene}) =$ $6.40 \times 10^{-11}]^a$	Rogers ⁴⁷	
1,3-Cyclo- hexadiene			164 ± 6	298 ± 2	RR [relative to $k(2\text{-methyl-1,3-buta-}$ $\text{diene}) = 1.01 \times 10^{-10}]^a$	Atkinson <i>et al.</i> ⁵³	
1,4-Cyclo- hexadiene			99.2 ± 3.1	297 ± 2	RR [relative to $k(1,5\text{-hexadiene}) =$ $6.20 \times 10^{-11}]^b$	Ohta ⁴⁵	
			99.8 ± 4.1	298 ± 2	RR [relative to $k(2\text{-methyl-1,3-buta-}$ $\text{diene}) = 1.01 \times 10^{-10}]^a$	Atkinson <i>et al.</i> ⁵³	
Cycloheptene			74.4 ± 2.4	298 ± 2	RR [relative to $k(2\text{-methyl-1,3-buta-}$ $\text{diene}) = 1.01 \times 10^{-10}]^a$	Atkinson <i>et al.</i> ⁵³	
1,3-Cyclo- heptadiene			139 ± 5	294 ± 2	RR [relative to $k(2\text{-methyl-1,3-buta-}$ $\text{diene}) = 1.02 \times 10^{-10}]^a$	Atkinson <i>et al.</i> ⁵⁴	
1,3,5-Cyclo- heptatriene			96.9 ± 2.5	294 ± 2	RR [relative to $k(2\text{-methyl-1,3-buta-}$ $\text{diene}) = 1.02 \times 10^{-10}]^a$	Atkinson <i>et al.</i> ⁵⁴	
1-Methyl- cyclohexene			94.4 ± 18.9	305 ± 2	RR [relative to $k(2\text{-methylpropene})$ $= 4.94 \times 10^{-11}]^a$	Darnall <i>et al.</i> ⁵⁸	
Bicyclo[2.2.1]- 2-heptene			49.3 ± 4.1	298 ± 2	RR [relative to $k(2\text{-methyl-}$ $1,3\text{-butadiene})$ $= 1.01 \times 10^{-10}]^a$	Atkinson <i>et al.</i> ⁵³	
Bicyclo[2.2.1]- 2,5-heptadiene			120 ± 11	298 ± 2	RR [relative to $k(2\text{-methyl-}$ $1,3\text{-butadiene})$ $= 1.01 \times 10^{-10}]^a$	Atkinson <i>et al.</i> ⁵³	
Bicyclo[2.2.2]- 2-octene			40.8 ± 2.0	298 ± 2	RR [relative to $k(2\text{-methyl-}$ $1,3\text{-butadiene})$ $= 1.01 \times 10^{-10}]^a$	Atkinson <i>et al.</i> ⁵³	
α -Pinene ^c			56.3 ± 8.5	305 ± 2	RR [relative to $k(2\text{-methylpropene})$ $= 4.94 \times 10^{-11}]^a$	Winer <i>et al.</i> ²⁸	
			60.1 ± 8.2	298	FP-RF	Kleindienst <i>et al.</i> ⁶⁰	298-422
			51.0 ± 6.9	349			
	13.7	-446 ± 75	38.8 ± 5.7	422			
			55.0 ± 3.2	294 ± 1	RR [relative to $k(2,3\text{-dimethyl-}$ $2\text{-butene}) =$ $1.13 \times 10^{-10}]^a$	Atkinson <i>et al.</i> ⁵⁵	
β -Pinene ^c			65.7 ± 9.9	305 ± 2	RR [relative to $k(2\text{-methylpropene})$ $= 4.94 \times 10^{-11}]^a$	Winer <i>et al.</i> ²⁸	

TABLE 7. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with cyclic mono-, di- and trialkenes — Continued

Alkene	$10^{12} \times A$ ($\text{cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference	Tempera- ture range covered (K)
			77.6 ± 11	297	FP-RF	Kleindienst <i>et al.</i> ⁶⁰	297–423
			67.8 ± 11	350			
	23.6	-358 ± 58	54.2 ± 10	423			
			80.2 ± 5.2	294 ± 1	RR [relative to $k(2,3\text{-dimethyl-}2\text{-butene}) =$ $1.13 \times 10^{-10}\text{a}$	Atkinson <i>et al.</i> ⁵⁵	
<i>d</i> -Limonene ^c			146 ± 22	305 ± 2	RR [relative to $k(2\text{-methylpropene}) =$ $4.94 \times 10^{-11}\text{a}$	Winer <i>et al.</i> ²⁸	
			171 ± 5	294 ± 1	RR [relative to $k(2,3\text{-dimethyl-}2\text{-butene}) =$ $1.13 \times 10^{-10}\text{a}$	Atkinson <i>et al.</i> ⁵⁵	
Δ^3 -Carene ^c			87.8 ± 4.3	294 ± 1	RR [relative to $k(2,3\text{-dimethyl-}2\text{-butene}) =$ $1.13 \times 10^{-10}\text{a}$	Atkinson <i>et al.</i> ⁵⁵	
γ -Terpinene ^c			177 ± 19	294 ± 1	RR [relative to $k(2,3\text{-dimethyl-}2\text{-butene}) =$ $1.13 \times 10^{-10}\text{a}$	Atkinson <i>et al.</i> ⁵⁵	
α -Phellandrene ^c			313 ± 72	294 ± 1	RR [relative to $k(2,3\text{-dimethyl-}2\text{-butene}) =$ $1.13 \times 10^{-10}\text{a}$	Atkinson <i>et al.</i> ⁵⁵	
α -Terpinene ^c			363 ± 40	294 ± 1	RR [relative to $k(2,3\text{-dimethyl-}2\text{-butene}) =$ $1.13 \times 10^{-10}\text{a}$	Atkinson <i>et al.</i> ⁵⁵	

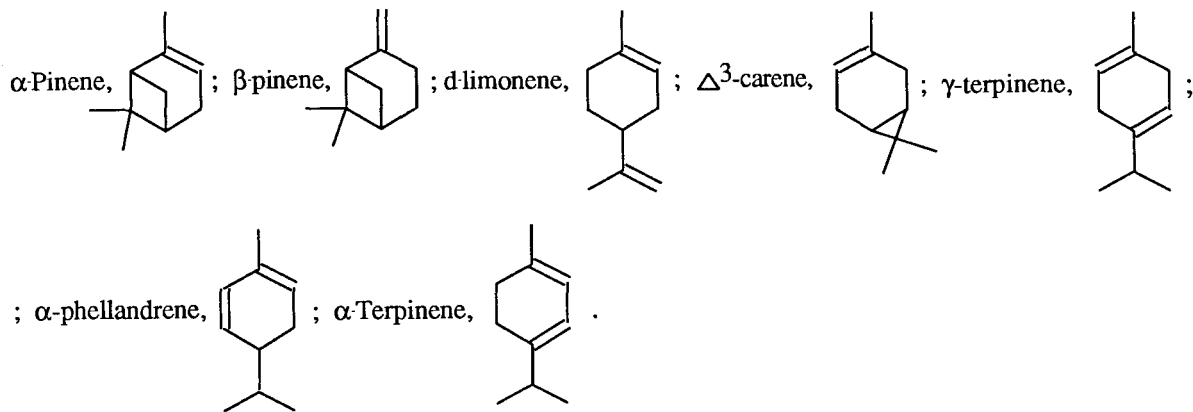
^aFrom the present recommendations (see text).^bFrom the rate constant determined by Ohta.⁴⁵^cStructures:

TABLE 8. Rate constants for the gas-phase reactions of the OD radical with acyclic monoalkenes at one atmosphere total pressure of argon diluent

Alkene	$10^{12} \times k$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
Ethene	6.14	343	PR-RA	Liu <i>et al.</i> ^{17,18}	343–1173
	4.75	373			
	4.34	403			
	3.52	483			
	3.23	563			
	2.94	603			
	1.79	653			
	1.32	703			
	1.26	748			
	1.53	773			
	1.88	873			
	2.23	973			
	2.62	1073			
3.52	1173				
Ethene- d_4	4.91	383	PR-RA	Liu <i>et al.</i> ¹⁸	383–1173
	4.28	393			
	4.23	448			
	3.20	523			
	3.10	603			
	1.47	653			
	0.84	708			
	0.88	748			
	1.08	801			
	1.13	873			
	1.30	973			
	1.86	1023			
	2.34	1173			

The broadening parameter F has been calculated to be 0.70 at 298 K,¹³ and this value has been used, with the temperature dependence of F being given by,

$$F = e^{-T/T^*} + e^{-4T^*/T}$$

with $T^* = 840$ K. There are only a limited number of studies which provide reliable data concerning the third-order rate constant k_0 ^{11,13,19} and, based upon these studies of Zellner and Lorenz,¹¹ Klein *et al.*¹³ and Tully,¹⁹ and the discussion of Klein *et al.*,¹³ the following values of k_0 for ethene are obtained at 298 K

$$k_0(\text{M} = \text{N}_2, \text{O}_2) = 1.0 \times 10^{-28} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

$$k_0(\text{M} = \text{Ar}) = 6.0 \times 10^{-29} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

and

$$k_0(\text{M} = \text{He}) = 3.0 \times 10^{-29} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

The data of Tully¹⁹ for $\text{M} = \text{He}$ at 295, 350 and 420 K allow a temperature dependence of these low pressure rate constants of T^{-3} to be estimated, leading to

$$k_0(\text{M} = \text{N}_2, \text{O}_2) = 1.0$$

$$\times 10^{-28} (T/298)^{-3} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

$$k_0(\text{M} = \text{Ar}) = 6.0$$

$$\times 10^{-29} (T/298)^{-3} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

and

$$k_0(\text{M} = \text{He}) = 3.0$$

$$\times 10^{-29} (T/298)^{-3} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

The absolute rate constants determined by Atkinson *et al.*,⁷ Tully^{10,19} and Liu *et al.*^{17,18} over the temperature range 291–425 K which are given in Table 5 are reasonably close to the high pressure limit, and are in good agreement (Fig. 38). A least-squares analysis of the rate constants given in Table 5 from these studies^{7,10,17–19} leads to the Arrhenius expression of

$$k(\text{ethene}) = (1.85^{+0.24}_{-0.22})$$

$$\times 10^{-12} e^{(438 \pm 43)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

which is applicable only for the temperature range 290–425 K and a total pressure of ~ 760 Torr of argon diluent.

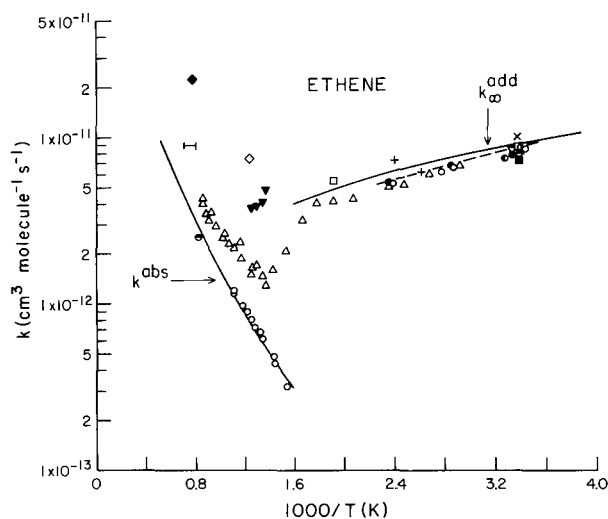


FIG. 38. Arrhenius plot of rate constants at, or close to, the high-pressure limit for the reaction of the OH radical with ethene. (—) Westenberg and Fristrom;¹ (\diamond) Baldwin *et al.*;² (∇) Hoare and Patel;³ (+) Gordon and Mulac;⁴ (\bullet) Lloyd *et al.*;⁵ (\blacklozenge) Bradley *et al.*;⁶ (\bullet) Atkinson *et al.*;⁷ (\times) Overend and Paraskevopoulos;⁸ (∇) Atkinson *et al.*;⁹ (\circ) Tully *et al.*;^{10,16,19} (\square) Zellner and Lorenz;¹¹ (\bullet) Atkinson and Aschmann;¹² (\blacktriangle) Klein *et al.*;¹³ (\blacksquare) Schmidt *et al.*;¹⁴ (\bullet) Smith;¹⁵ (Δ) Liu *et al.*;^{17,18} (— —) recommended Arrhenius expression applicable to 760 Torr total pressure of N₂ or air; (—) recommendations for k_{∞}^{add} and k^{abs} (see text).

From precise relative rate constant determinations carried out at ~ 740 Torr total pressure of air, Atkinson *et al.*⁹ derived a value of

$$k(\text{ethene}) = (8.38 \pm 0.38) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 299 ± 2 K relative to the present recommendation for *n*-butane, while Atkinson and Aschmann¹² derived a value of

$$k(\text{ethene}) = 8.66$$

$$\times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 295 \pm 1 \text{ K,}$$

relative to the atmospheric pressure of air recommendation for propene (see the discussion below concerning propene). Since this rate constant for propene was derived from a least-squares analysis of the relative rate constants for a series of alkenes and dialkenes at atmospheric pressure of air with the corresponding “high-pressure” absolute rate constant data, this rate constant of Atkinson and Aschmann¹² for ethene at 295 K has

been combined with the above temperature dependence to recommend that

$$k(\text{ethene; 760 Torr of air}) = (1.96_{-0.24}^{+0.26}) \times 10^{-12} e^{(438 \pm 43)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the restricted temperature range of 291–425 K, where the indicated error limits are equivalent to two least-squares standard deviations, and

$$k(\text{ethene}) = 8.52 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}$$

and ~ 760 Torr total pressure of air, with an estimated uncertainty at 298 K of $\pm 15\%$. This expression is plotted in Fig. 38 as the dashed line and is used in this article to reevaluate those relative rate studies carried out at atmospheric pressure of air and utilizing ethene as the reference organic.

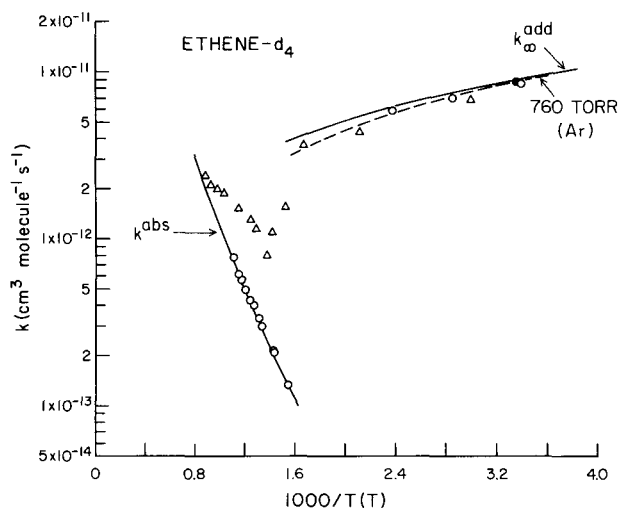


FIG. 39. Arrhenius plot of rate constants at, or close to, the high-pressure limit for the reaction of the OH radical with ethene-*d*₄. (\bullet) Niki *et al.*;²⁰ (\circ) Tully;^{16,19} (Δ) Liu *et al.*;¹⁸ (— —, —) recommendations (see text).

Using the above Arrhenius expressions applicable to ~ 760 Torr total pressure of argon and air diluents and an assessment of the degree of fall-off (calculated from the Troe fall-off equation), a limiting high-pressure second-order rate constant of

$$k_{\infty}(\text{ethene}) = 9.0 \times 10^{-12} (T/298)^{-1.1} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

is obtained. Use of these above values of k_o , k_∞ and F reproduce to within better than 5% the Arrhenius expressions given above which are applicable to 760 Torr total pressure of argon and air. This recommended expression for k_∞ is plotted in Fig. 38 and Fig. 40, which also shows the absolute rate constant data of Atkinson *et al.*,⁷ Overend and Paraskevopoulos,⁸ Tully,^{10,16,19} Zellner and Lorenz,¹¹ Schmidt *et al.*,¹⁴ Smith¹⁵ and Liu *et al.*^{17,18} Also shown in Fig. 40 are the calculated rate constants at 760 and 100 Torr total pressure of argon diluent. The absolute rate constants of Atkinson *et al.*,⁷ Tully^{10,19} and Liu *et al.*^{17,18} obtained at temperatures ≈ 525 K are in good agreement with these calculations (Fig. 40).

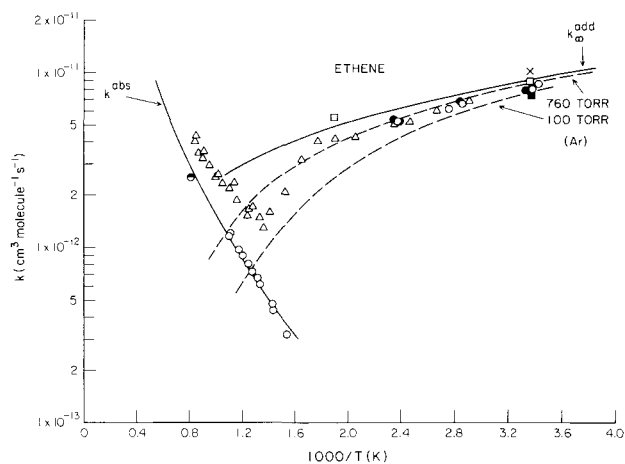


FIG. 40. Arrhenius plot of absolute rate constants obtained at, or close to, the high-pressure limit for the reaction of the OH radical with ethene. (●) Atkinson *et al.*,⁷ (x) Overend and Paraskevopoulos,⁸ (○) Tully,^{10,16,19} (□) Zellner and Lorenz,¹¹ (■) Schmidt *et al.*,¹⁴ (⊙) Smith,¹⁵ (Δ) Liu *et al.*,^{17,18} (— — —, —) recommendations (see text).

These calculations show that at 298 K the high pressure limit is not attained at 760 Torr total pressure of air, with the measured rate constant being $\sim 5\%$ below k_∞ under these conditions. At higher temperatures, rate data measured at 760 Torr total pressure of air, argon or helium move progressively into the fall-off region. At temperatures ≈ 550 K, thermal decomposition of the HOCH₂CH₂ adduct also becomes important. The formation of the thermalized HOCH₂CH₂ radical from the reaction of OH radicals with ethene is calculated to be 32.1 kcal mol⁻¹ exothermic⁷⁶ and hence the thermal dissociation of the thermalized HOCH₂CH₂ radical to reactants is expected⁷⁶ to have a high-pressure rate constant of

$$k_\infty(\text{HOCH}_2\text{CH}_2 \rightarrow \text{OH} + \text{C}_2\text{H}_4) \sim 3 \times 10^{13} e^{-15000/T} \text{ s}^{-1}$$

[The thermal decomposition rates of the higher OH-

alkene adducts are expected to be similar to that for the HOCH₂CH₂ radical; these thermal decompositions may be in the fall-off regime at the temperatures and pressures encountered.]

Thus, the decomposition rate of the thermalized HOCH₂CH₂ radical is calculated to be $\sim 400 \text{ s}^{-1}$ at 600 K (typical of the OH radical decay rates measured in the LP-LIF experiments of Tully¹⁶) and $\sim 15000 \text{ s}^{-1}$ at 700 K (the upper range of the OH radical decay rates utilized in the PR-RA experiments of Liu *et al.*^{17,18}). Thus, from ~ 550 K upwards, depending upon the experimental technique used, the thermal decomposition of the HOCH₂CH₂ radical will lead to a rapid decrease in the measured OH radical reaction rate constant with increasing temperature. Note, however, that the temperature range at which this effect occurs is dependent upon the experimental technique, being ~ 100 K higher for the PR-RA technique of Liu *et al.*^{17,18} than for the LF-LIF method of Tully.¹⁶

Since the temperature range in which this thermal decomposition of the OH-ethene adduct becomes important is also that in which the OH radical addition reaction rate constant is highly dependent upon the total pressure and the identity of the diluent gas (and in which the H-atom abstraction reaction is becoming significant), this temperature region from ~ 550 K to ~ 750 K is one in which the measured rate constants are dependent on the measurement method time scale, the total pressure and the identity of the diluent gas.

At temperatures ≈ 600 K the only absolute rate constants available are those of Smith,¹⁵ Tully¹⁶ and Liu *et al.*,^{17,18} with the rate constants of Liu *et al.*^{17,18} being significantly higher than those of Smith¹⁵ and Tully.¹⁶ At least part of this difference in the measured rate constants may be due to the above mentioned effects of total pressure, diluent gas and measurement technique. Thus, the measurements of Liu *et al.*^{17,18} were carried out with a short measurement time scale (OH radical decay rates up to $\sim 15000 \text{ s}^{-1}$) at 760 Torr total pressure of argon. In contrast, the data of Tully¹⁶ were obtained using longer measurement time scales (OH radical decay rates of up to $\sim 750 \text{ s}^{-1}$) with helium as the diluent gas at total pressures of ~ 300 – 600 Torr. Thus, the study of Tully¹⁶ was carried out at an effective pressure which was a factor of ~ 3 lower, and hence more into the fall-off region, than that employed in the study of Liu *et al.*^{17,18} In addition, thermal decomposition of the HOCH₂CH₂ radical was more important in the study of Tully¹⁶ due to the longer measurement time scales employed. Thus, the conditions of the study of Tully¹⁶ were effective in suppressing the OH radical addition pathway and in isolating the H-atom abstraction route, while in the study of Liu *et al.*^{17,18} the OH radical addition process may have contributed to the measured rate constant at temperatures ≈ 750 K, leading to measured rate constants which were higher than those of the H-atom abstraction pathway up to higher temperatures than anticipated. Indeed, the rate data of Smith¹⁵ and Tully¹⁶ and of Liu *et al.*^{17,18} do converge somewhat as the temperature approaches 1200 K.

Accordingly, the rate constants measured at temperatures ≥ 650 K by Smith¹⁵ and Tully¹⁶ are taken to be those due to the H-atom abstraction pathway, and a least-squares analysis of the data from these two studies,^{15,16} using the expression $k^{\text{abs}} = CT^2e^{-D/T}$, yields the recommendation of

$$k^{\text{abs}}(\text{ethene}) = (4.87^{+1.79}_{-1.31}) \times 10^{-18} T^2 e^{-(1125 \pm 247)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 651–1220 K, where the indicated error limits are two least-squares standard deviations. This recommended expression is plotted in Fig. 38 and Fig. 40. Extrapolation to 298 K yields an H-atom abstraction rate constant of

$$k^{\text{abs}} \sim 1 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \sim 0.1\%$$

of the observed 298 K high pressure rate constant k_{∞} .

Interestingly, this rate constant for H-atom abstraction from ethene is very similar to the recommended rate constant for the reaction of the OH radical with methane of

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

$$[k^{\text{abs}}(\text{ethene})/k(\text{methane}) = 0.70 e^{157/T}],$$

totally consistent with the similar C–H bond energies in ethene (105.6 kcal mol⁻¹) and methane (104.8 kcal mol⁻¹).⁶²

Ethene-d₄. The available rate constants measured at or close to the high pressure second-order limit at temperatures $\lesssim 525$ K^{18–20} show that the rate constant k_{∞} for ethene-d₄ is essentially identical to that for ethene, as expected for an addition process. Accordingly, the value of k_{∞} derived above for ethene is also appropriate for ethene-d₄,

$$k_{\infty}(\text{ethene-d}_4) = 9.0 \times 10^{-12} (T/298)^{-1.1} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The rate constants measured in the fall-off region by Tully¹⁹ at 295, 350 and 420 K for M = He and at 295 K for M = Ar show that at any given temperature the limiting low pressure third-order rate constant k_0 is greater for ethene-d₄ than for ethene, as expected from the increased density of states in the HOCD₂CD₂ radical compared to the HOCH₂CH₂ radical.^{74,75} A rate constant ratio of

$$k_0(\text{ethene-d}_4)/k_0(\text{ethene}) = 3$$

can be derived from the rate constant data of Tully.¹⁹ Thus,

$$k_0^{\text{He}}(\text{ethene-d}_4) = 9.0 \times 10^{-29} (T/298)^{-3} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1},$$

$$k_0^{\text{Ar}}(\text{ethene-d}_4) = 1.8 \times 10^{-28} (T/298)^{-3} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1},$$

and

$$k_0^{\text{N}_2\text{O}_2}(\text{ethene-d}_4) = 3.0 \times 10^{-28} (T/298)^{-3} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}.$$

The rate constant calculated for the reaction of the OH radical with ethene-d₄ at 760 Torr total pressure of argon is plotted in Fig. 39 as the dashed line. In contrast to the analogous situation for acetylene and acetylene-d₂ (see Sec. 2.5), the rate constants for the reactions of the OH radical with both ethene and ethene-d₄ at ~ 760 Torr total pressure of argon and $\lesssim 525$ K are sufficiently close to the high-pressure limit that the measured rate constants are essentially indistinguishable from k_{∞} within the measurement uncertainties.

Analogous to the case for ethene, at temperatures ≥ 650 –750 K the measured rate constants are those for the D-atom abstraction process. By similar arguments to the ethene reaction, a least-squares analysis of the rate constant data of Tully,¹⁶ using the equation $k = CT^2e^{-D/T}$, yields the recommendation of

$$k^{\text{abs}}(\text{ethene-d}_4) = (1.42^{+0.45}_{-0.34}) \times 10^{-17} T^2 e^{-(2448 \pm 210)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 651–901 K, where the indicated errors are two least-squares standard deviations. Kinetic data are required at temperatures > 900 K to ascertain whether the above three-parameter equation overestimates the D-atom abstraction rate constants above ~ 900 K.

The OD radical reactions with ethene and ethene-d₄ have been studied by Liu *et al.*,^{17,18} and the rate constants measured at 760 Torr total pressure of argon diluent for these OD radical reactions (Table 8) are similar to those for the corresponding OH radical reactions, as expected. However, the rate constants over the temperature region $\lesssim 563$ K, which are those for OD radical addition to ethene and ethene-d₄, are uniformly $\sim 20\%$ lower than those for the corresponding OH radical reactions.

(2) Propene and Propene-d₆

Totally analogous to the situation for ethene, the kinetic data for the reaction of OH radicals with propene exhibit three distinct temperature regions. Below ~ 470 K the measured bimolecular rate constants are pressure dependent,^{11,13,37} although this pressure dependence is much less marked than that for ethene, and the

rate constants decrease with increasing temperature. At room temperature the measured rate constants are essentially independent of the total pressure and the identity of the diluent gas above ~ 25 Torr.^{11,13,26,30} Furthermore, in this temperature region the rate constants for propene and propene- d_6 are essentially identical.³⁷ Above ~ 700 K the rate constants increase rapidly with temperature, and are independent of the pressure of the diluent gas,³⁷ with a significant deuterium isotope effect being observed.³⁷ In the intermediate temperature range of ~ 500 – 700 K non-exponential OH radical decays have been observed.³⁷

As for the OH radical reaction with ethene, these data are totally consistent with the occurrence of OH radical addition and H-atom abstraction pathways, with the addition process totally dominating at temperatures $\lesssim 470$ K. Above this temperature, thermal decomposition of the OH–C₃H₆ adduct occurs and the OH radical addition pathway becomes rapidly less important with increasing temperature. Above ~ 700 K, the measured rate constants, at least using absolute rate techniques, appear to be those for the H-atom abstraction reaction³⁷ (for the OH radical reaction with propene- d_6 , OD radical formation arising from the OH radical addition channel was also observed at 602 K³⁷).

The available rate constants, other than that of Cox⁶¹ (as noted above), are listed in Table 5, with those at temperatures < 470 K being at, or close to, the high pressure limit. The rate constants obtained from the absolute rate studies of Gordon and Mulac,⁴ Atkinson and Pitts,²⁶ Ravishankara *et al.*,³⁰ Nip and Paraskevopoulos,³¹ Zellner and Lorenz,¹¹ Schmidt *et al.*,¹⁴ Tully and Goldsmith³⁷ and Smith *et al.*³⁸ (which supersedes the preliminary rate constant reported earlier by Smith³⁶) and from the relative rate studies of Winer *et al.*,^{28,29} Baldwin *et al.*,³⁵ Klein *et al.*,¹³ Barnes *et al.*³⁹ and Atkinson and Aschmann⁴¹ (with the rate constants at temperatures < 470 K being at, or close to, the high-pressure limit) are plotted in Arrhenius form in Fig. 41.

The absolute rate constants obtained by Atkinson and Pitts,²⁶ Ravishankara *et al.*,³⁰ Nip and Paraskevopoulos³¹ and Tully and Goldsmith³⁷ at ≤ 467 K are in excellent agreement, and a unit-weighted least-squares analysis of these data yields the Arrhenius expression of

$$k(\text{propene}, T \leq 467 \text{ K}) = (4.72_{-0.57}^{+0.64}) \times 10^{-12} e^{(504 \pm 45)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 293–467 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{propene}) = 2.56 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K and ~ 25 – 400 Torr total pressure of helium, argon or hydrogen diluent. The room temperature rate constants obtained by Lloyd *et al.*,⁵ Wu *et al.*,²⁷ Winer *et al.*,^{28,29} Cox *et al.*,³² Barnes *et al.*,^{33,39} Klein *et al.*¹³ and Atkinson and Aschmann⁴¹ from relative rate studies are

in good agreement with this expression, as are the absolute rate data of Zellner and Lorenz,¹¹ Schmidt *et al.*¹⁴ and Wallington.⁴⁰ However, there are significant discrepancies with the rate constants reported by Morris *et al.*,²¹ Bradley *et al.*,²² Stuhl,²³ Gorse and Volman,²⁴ Gordon and Mulac,⁴ Pastrana and Carr²⁵ and Smith,³⁴ with those of Morris *et al.*,²¹ Bradley *et al.*,²² Pastrana and Carr²⁵ and Smith³⁴ being in the fall-off region at the low total pressures (~ 1 Torr) employed¹³ (although discrepancies still occur when the fall-off behavior is taken into account¹³). The room temperature rate constant determined by Stuhl²³ was probably low because of wall losses of propene in the static system used.

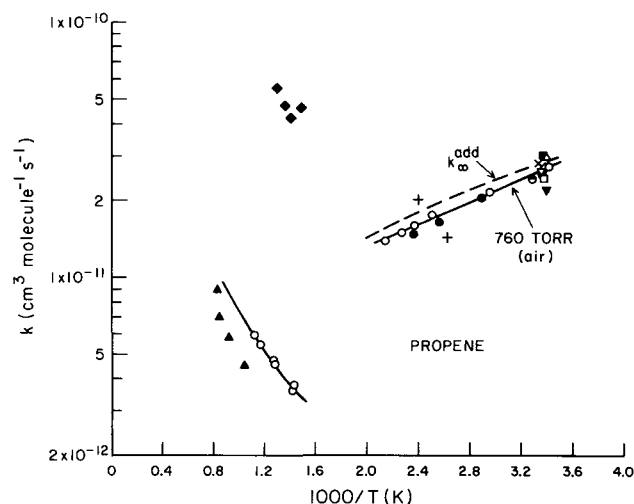


FIG. 41. Arrhenius plot of rate constants obtained at, or close to, the high-pressure limit, for the reaction of the OH radical with propene. (+) Gordon and Mulac;⁴ (●) Atkinson and Pitts;²⁶ (⊙) Winer *et al.*,^{28,29} (∇) Ravishankara *et al.*,³⁰ (□) Nip and Paraskevopoulos;³¹ (■) Zellner and Lorenz;¹¹ (◆) Baldwin *et al.*,³⁵ (Δ) Klein *et al.*,¹³ (∇) Schmidt *et al.*,¹⁴ (○) Tully and Goldsmith,³⁷ (▲) Smith *et al.*,³⁸ (x) Barnes *et al.*,³⁹ (◇) Atkinson and Aschmann;⁴¹ (— — —, —) recommendations (see text).

In the rate constant study of Atkinson and Aschmann,¹² relative rate constants for a series of alkenes (and *n*-butane and *n*-hexane) were obtained at 295 ± 1 K. Analogous to the procedure of Atkinson and Aschmann¹² and Atkinson,⁶³ a least-squares fit of these relative rate constants at 295 ± 1 K¹² to the absolute rate constants at 295 K for propene,^{26,30,31,37} 1-butene,^{26,30,31} 3-methyl-1-butene,⁴⁸ 2-methylpropene,²⁶ *cis*-2-butene,²⁶ *trans*-2-butene,²⁶ 2-methyl-2-butene,⁵⁰ propadiene⁴⁸ and 1,3-butadiene⁴⁸ (using the observed temperature dependencies or an estimated temperature dependence of $B = -500$ K to extrapolate or interpolate these observed absolute rate constants to 295 K) has been used to obtain a value of

$$k(\text{propene}) = 2.68 \\ \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 295 \text{ K,}$$

with an estimated overall uncertainty of $\sim 15\%$.

Use of this 295 K rate constant, together with the temperature dependence derived above, yields the recommended Arrhenius expression of

$$k(\text{propene}, T \leq 467 \text{ K}) = (4.85^{+0.66}_{-0.59}) \\ \times 10^{-12} \text{ e}^{(504 \pm 45)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

applicable to ~ 760 Torr total pressure of air, where the indicated error limits are two least-squares standard deviations, and

$$k(\text{propene}) = 2.63 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated uncertainty at 298 K of $\pm 15\%$. This expression is $\sim 3\%$ higher than that derived solely from the absolute rate data. In the discussions below, this recommended value of $k(\text{propene})$ at 295 K is used to derive rate constants at 295 K and atmospheric pressure for the other alkenes and dialkenes studied by Atkinson and Aschmann.¹²

As for ethene, values of k_o , k_∞ and F , and their temperature dependencies, are required to define the fall-off behavior for the OH radical reaction rate constant for propene. As discussed by Klein *et al.*,¹³ this reaction approaches the high-pressure limit at relatively low total pressures, and hence few reliable data are available concerning the low pressure rate constant k_o . The recent studies of Zellner and Lorenz¹¹ and Klein *et al.*¹³ have derived values of

$$k_o^{\text{Ar}} \sim 8.3 \times 10^{-28} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \text{ }^{11}$$

and

$$k_o^{\text{Ar}} = k_o^{\text{air}} \sim 8 \times 10^{-27} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}, \text{ }^{13}$$

both at room temperature. The discrepancy between these derived values of k_o arises, in part, because the fall-off does not become obvious until low total pressures ($\lesssim 10$ Torr), and only a small number of data points have been obtained in this low-pressure region. Indeed, at the lowest pressure studied, the rate constants measured by Zellner and Lorenz¹¹ and Klein *et al.*¹³ disagree by less than a factor of 2 (and almost agree within the combined cited error limits).

Accordingly, a geometric mean of

$$k_o^{\text{Ar}} = k_o^{\text{air}} \approx 3 \times 10^{-27} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

at 298 K is used. By analogy with OH radical addition to ethene, a T^{-3} dependency is assumed, leading to

$$k_o^{\text{Ar}} = k_o^{\text{air}} = 3 \times 10^{-27} (T/298)^{-3} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

With $F = 0.5$ at 298 K¹³ and $T^* = 430$ K, the measured rate constants at ~ 760 Torr total pressure of argon or air are $\sim 5\text{--}6\%$ and $\sim 8\text{--}9\%$ lower than the limiting high-pressure rate constants k_∞ at 298 K and 420 K, respectively. Based upon the rate constant expression given above of

$$k(\text{propene}) = 4.85 \times 10^{-12} \text{ e}^{504/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

applicable for ~ 760 Torr total pressure of air, then

$$k_\infty = 2.8 \times 10^{-11} (T/298)^{-1.3} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range $\sim 290\text{--}470$ K, and this expression is plotted in Fig. 41 as the dashed line.

At elevated temperatures, $\gtrsim 700$ K, the reaction is expected to proceed by H-atom abstraction and, possibly, initial OH radical addition followed by rapid rearrangement and decomposition of the adduct. Rate constants for the reaction of OH radicals with propene have been measured in this temperature range by Tully and Goldsmith³⁷ and Smith *et al.*³⁸ using absolute methods and by Baldwin *et al.*³⁵ from a product study. The rate constants derived from the relative rate/product study of Baldwin *et al.*³⁵ are an order of magnitude higher than those of Tully and Goldsmith³⁷ and Smith *et al.*³⁸ and also lie above the extrapolated high pressure addition rate constant k_∞ , for reasons which are not presently known. While the rate constants determined by Tully and Goldsmith³⁷ and Smith *et al.*³⁸ are in general agreement, there are discrepancies of the order of 50% between these studies (Fig. 41).

The data of Tully and Goldsmith³⁷ have been used to derive the rate constant in this temperature region. Using the expression $k = CT^2 e^{-D/T}$, a unit-weighted least-squares analysis of the data of Tully and Goldsmith³⁷ yields the recommendation of

$$k(\text{propene}; T > 700 \text{ K}) = (7.20^{+1.98}_{-1.55}) \\ \times 10^{-18} T^2 \text{ e}^{(31 \pm 189)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 701–896 K, where the indicated error limits are two least-squares standard deviations. Hence the abstraction reaction will account for $< 3\%$ of the observed overall high-pressure rate constant at 298 K. This estimate is totally consistent with the room temperature product data of Cvetanovic,⁷⁷ Hoyer-mann and Sievert⁷⁸ and Biermann *et al.*,⁴³ which showed that the abstraction reaction accounts for $\lesssim 5\%$,⁷⁷ $< 5\%$,⁷⁸ and $< 2\%$ ⁴³ of the overall reaction rate constant under the conditions employed.

Under conditions where the rate constants were close to the high pressure limit, the rate constants measured by Tully and Goldsmith³⁷ for propene- d_6 at < 470 K are essentially identical to those for the reaction of OH radicals with propene. This is totally consistent with the occurrence of an OH radical addition reaction under these conditions.

At >700 K, the rate constants measured by Tully and Goldsmith³⁷ for propene- d_6 are $\sim 35\%$ lower than those for propene. However, these rate constants for propene- d_6 at temperatures ≥ 700 K may also include other reaction processes, such as OD radical formation, in addition to D-atom abstraction, and thus these measured rate constants for propene- d_6 at >700 K may not be solely those for the D-atom abstraction pathway (as indicated by the similar temperature dependencies of the propene and propene- d_6 reactions, despite the fact that the temperature dependence of D-atom abstraction from propene- d_6 should be higher than for H-atom abstraction from propene).

(3) 1-Butene and 1-Butene- d_8

The available rate constants are listed in Table 5. The kinetics of the OH radical reactions with 1-butene and 1-butene- d_8 are analogous to those for propene, with OH radical addition dominating at temperatures $\lesssim 425$ K and OH radical addition with rapid subsequent isomerization/decomposition to products other than the initial reactants and/or H- (or D-) atom abstraction occurring at elevated temperatures ($\gtrsim 600$ K). As for propene, the limiting high-pressure second-order rate constants at around room temperature are closely approached at total pressures of helium $\gtrsim 20$ Torr.³⁰ In the lower temperature ($\lesssim 425$ K) region, the most recent kinetic data of Atkinson and Pitts,²⁶ Wu *et al.*,²⁷ Ravishankara *et al.*,³⁰ Nip and Paraskevopoulos,³¹ Barnes *et al.*,³³ Biermann *et al.*⁴³ (which is possibly still in the fall-off region between second- and third-order kinetics), Ohta⁴⁴ and Atkinson and Aschmann¹² are in good agreement. These rate constants of Atkinson and Pitts,²⁶ Wu *et al.*,²⁷ Ravishankara *et al.*,³⁰ Nip and Paraskevopoulos,³¹ Barnes *et al.*,³³ Ohta⁴⁴ and Atkinson and Aschmann¹² and the elevated temperature rate constants of Smith¹⁵ and Tully¹⁶ are plotted in Arrhenius form in Fig. 42.

At temperatures $\lesssim 425$ K, the sole reported temperature dependence is that of Atkinson and Pitts,²⁶ and hence this temperature dependence is recommended. As for ethene and propene, the rate constant derived from the best-fit analysis of the relative rate constant data of Atkinson and Aschmann¹² for a series of alkenes and dialkenes with the available absolute data (as described above) is recommended. This yields

$$k(1\text{-butene}) = 3.19$$

$$\times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 295 \text{ K.}$$

This rate constant, when combined with the temperature dependence of Atkinson and Pitts,²⁶ leads to the recommended Arrhenius expression of

$$k(1\text{-butene}; T \leq 425 \text{ K}) = 6.55$$

$$\times 10^{-12} e^{467/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 298–424 K, and

$$k(1\text{-butene}) = 3.14$$

$$\times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of $\pm 20\%$.

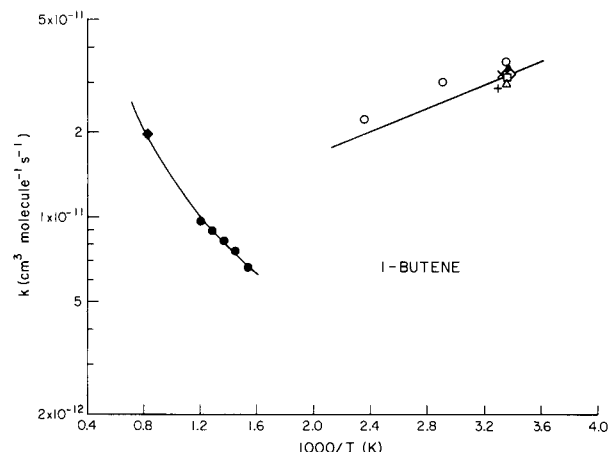


FIG. 42. Arrhenius plot of rate constants obtained at, or close to, the high-pressure limit for the reaction of the OH radical with 1-butene. (○) Atkinson and Pitts,²⁶ (+) Wu *et al.*,²⁷ (Δ) Ravishankara *et al.*,³⁰ (▲) Nip and Paraskevopoulos,³¹ (x) Barnes *et al.*,³³ (□) Ohta,⁴⁴ (◇) Atkinson and Aschmann,¹² (◆) Smith,¹⁵ (●) Tully,¹⁶ (—) recommendations, see text.

The room temperature kinetic data of Barnes *et al.*,³³ Biermann *et al.*⁴³ and Ohta,⁴⁴ which were not used in the evaluation, are in good agreement with this recommended rate constant.

At temperatures ≥ 650 K the measured rate constants^{15,16} increase with increasing temperatures (but for $T < 1225$ K are still lower than those at ~ 425 K). A unit-weighted least-squares analysis of the rate constants of Smith¹⁵ and Tully,¹⁶ using the expression $k = CT^2e^{-D/T}$, yields the recommendation of

$$k(1\text{-butene}; T > 650 \text{ K}) = (1.04^{+0.13}_{-0.11})$$

$$\times 10^{-17} T^2 e^{(273 \pm 85)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 650–1225 K, where the indicated errors are two least-squares standard deviations [use of the rate constants of Tully¹⁶ only leads to calculated rate constants which agree with those from the above recommendation to within $\pm 5\%$ over the temperature range 650–1225 K].

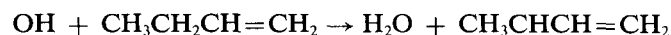
Extrapolation of these expressions to room temperature indicates that H-atom abstraction will account for $< 10\%$ of the measured overall high-pressure rate constant at 298 K. This estimated contribution of H-atom abstraction to the overall OH radical reaction rate con-

stant at 298 K is in agreement with the estimates of <10% obtained from the product studies of Hoyermann and Sievert⁷⁹ and Atkinson *et al.*,⁸⁰ but disagrees with the percentage (20 ± 6%) measured by Biermann *et al.*⁴³ Thus, at temperatures ≲425 K the reaction of the OH radical with 1-butene proceeds mainly by OH radical addition [note, however, that extrapolation of the recommended high temperature (>650 K) rate expression predicts that the "direct" reaction channel involving decomposition of the OH-1-butene adduct to products other than the reactants and/or H-atom abstraction will account for ~20% of the overall reaction rate constant at 425 K]. At ~760 Torr total pressure of helium, argon or air diluent this OH radical addition reaction is close to the high-pressure limit, since the low pressure rate constant k_0 is expected to be greater than that for propene.

As for ethene and propene, the thermal decomposition of the OH-1-butene adduct will become increasingly important above ~550–650 K, with the result that, unless this adduct radical rapidly rearranges and/or decomposes to products other than the original reactants, the addition process becomes of no importance above ~700 K. Above this temperature, H-atom abstraction, together with any "direct" reaction arising from the OH radical addition pathway (which cannot exceed the rate constant for OH addition to 1-butene to form the initially energy rich adduct), are the only reaction channels observed. That the major reaction pathway in this temperature region is H-atom abstraction is supported by the deuterium isotope effect observed by Tully¹⁶ for the OH radical reactions with 1-butene and 1-butene-*d*₈, with¹⁶

$$k(1\text{-butene})/k(1\text{-butene-}d_8) = 1.05 e^{258/T}$$

Furthermore, the magnitude of this isotope effect is consistent with the H- or D-atom abstraction occurring mainly from the allylic C–H or C–D bonds



over the temperature range 650–830 K. As the temperature increases, H- or D-atom abstraction from the terminal –CH₃ or –CD₃ group will become increasingly important.¹⁵

(4) 2-Methylpropene

The available kinetic data are given in Table 5 and are plotted in Arrhenius form in Fig. 43. At temperatures ≲425 K the sole absolute study carried out is that of Atkinson and Pitts,²⁶ which is also the only temperature dependence study. Thus, this temperature dependence,²⁶ equivalent to $B = -504$ K, is used in combination with the best-fit 295 K rate constant derived from the relative rate constant data of Atkinson and Aschmann¹² of

$$k(2\text{-methylpropene}) = 5.23$$

$$\times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 295 \text{ K,}$$

to yield the recommended Arrhenius expression of

$$k(2\text{-methylpropene}; T \leq 425 \text{ K}) = 9.47$$

$$\times 10^{-12} e^{504/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 297–424 K, and

$$k(2\text{-methylpropene}) = 5.14 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

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

The relative rate constants obtained by Wu *et al.*,²⁷ Barnes *et al.*³³ and Ohta⁴⁴ at room temperature are in good agreement with this recommendation.

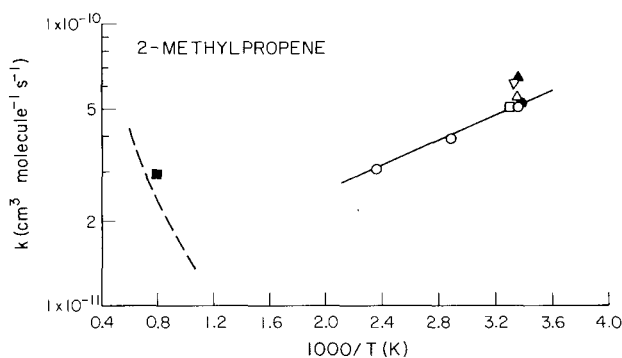


FIG. 43. Arrhenius plot of rate constants for the reaction of the OH radical with 2-methylpropene. (▲) Morris and Niki;⁴² (○) Atkinson and Pitts;²⁶ (□) Wu *et al.*;²⁷ (∇) Barnes *et al.*;³³ (Δ) Ohta;⁴⁴ (●) Atkinson and Aschmann;¹² (■) Smith;¹⁵ (—) recommendation for $T \lesssim 425$ K (see text); (---) tentatively recommended rate constant for H-atom abstraction (see text).

As for propene and 1-butene, at temperatures ≲425 K the OH radical reaction with 2-methylpropene proceeds predominantly by OH radical addition, with the rate constant being close to the high pressure limit at total pressures of ~50 Torr of helium, argon or air diluent. The OH-2-methylpropene adduct will thermally decompose at temperatures ≳550–750 K and, unless this adduct can rearrange and/or decompose more rapidly to products other than the initial reactants, at elevated temperatures only the H-atom abstraction reaction from the two –CH₃ groups will be important. The rate constant measured by Smith¹⁵ of $2.96 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 1259 K is consistent with this expectation, since this measured rate constant for 2-methylpropene¹⁵ is 2.5 k (propene).

Hence, it is tentatively recommended that the rate constant for H-atom abstraction from 2-methylpropene is given by

$$k(2\text{-methylpropene}; T \geq 700 \text{ K}) \approx 1.5$$

$$\times 10^{-17} T^2 e^{30/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

Extrapolation of this H-atom abstraction rate constant to room temperature leads to the conclusion that at 298 K the H-atom abstraction channel accounts for $\sim 3\%$ of the overall high pressure rate constant, in agreement with the product study of Hoyermann and Sievert⁷⁹ (which yielded $< 5\%$ abstraction at ~ 1 Torr total pressure).

(5) *cis*-2-Butene

The available rate constants are given in Table 5 and are plotted in Arrhenius form in Fig. 44. At room temperature the absolute rate constant determined by Atkinson and Pitts²⁶ is in good agreement with the relative rate constants derived by Lloyd *et al.*,⁵ Ohta⁴⁴ and Atkinson and Aschmann.¹² As for the alkenes discussed above, the temperature dependence determined by Atkinson and Pitts²⁶ is used, together with the best-fit rate constant at 295 K derived from the relative rate constant data of Atkinson and Aschmann¹² and the available absolute rate data for a series of alkenes and dialkenes (see above), to recommend that

$$k(\textit{cis}\text{-}2\text{-butene}) = 5.71 \\ \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 295 \text{ K,}$$

$$k(\textit{cis}\text{-}2\text{-butene}; T \lesssim 425 \text{ K}) = 1.10 \\ \times 10^{-11} e^{487/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

and

$$k(\textit{cis}\text{-}2\text{-butene}) = 5.64 \\ \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of $\pm 20\%$.

The relative rate constant of Ohta⁴⁴ is in excellent agreement with this recommendation. However, as discussed previously, the absolute rate constant determined by Ravishankara *et al.*³⁰ at 298 K appears to be $\sim 20\%$ low, possibly because of wall losses of the *cis*-2-butene reactant in the static reaction system used.

(6) *trans*-2-Butene

The available kinetic data (apart from that of Cox,⁶¹ as noted above) are given in Table 5 and those of Morris and Niki,⁴² Atkinson and Pitts,²⁶ Wu *et al.*,²⁷ Ohta,⁴⁵ Atkinson and Aschmann,¹² Edney *et al.*⁴⁶ and Smith¹⁵ are plotted in Arrhenius form in Fig. 45. The room temperature rate constants of Morris and Niki,⁴² Atkinson and Pitts,²⁶ Wu *et al.*,²⁷ Ohta,⁴⁵ Atkinson and Aschmann,¹² Edney *et al.*⁴⁶ and Rogers⁴⁷ are in reasonable agreement. Consistent with the previous criteria, the temperature dependence determined by Atkinson and Pitts²⁶ of $B = -550 \text{ K}$ is used, together with the best-fit of the relative rate constants of Atkinson and Aschmann¹² to the abso-

lute rate constant data for a series of alkenes and dialkenes (see above), to yield

$$k(\textit{trans}\text{-}2\text{-butene}) = 6.51 \\ \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 295 \text{ K,}$$

$$k(\textit{trans}\text{-}2\text{-butene}; T \lesssim 425 \text{ K}) = 1.01 \\ \times 10^{-11} e^{550/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

and

$$k(\textit{trans}\text{-}2\text{-butene}) = 6.40 \\ \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of $\pm 20\%$.

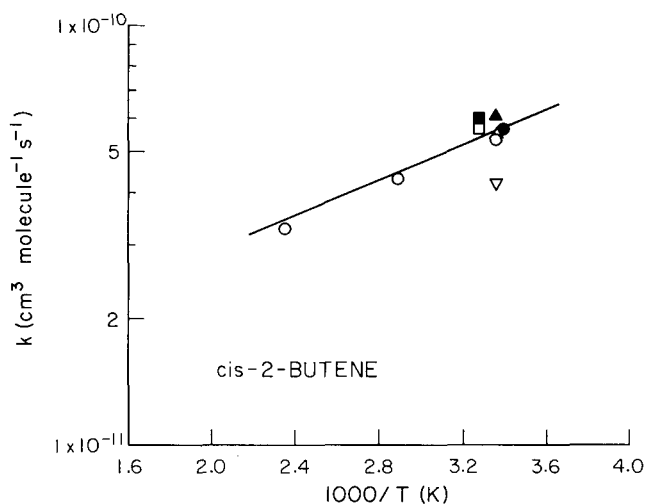


FIG. 44. Arrhenius plot of rate constants for the reaction of the OH radical with *cis*-2-butene. (\blacktriangle) Morris and Niki;⁴² (\circ) Atkinson and Pitts;²⁶ (\square) Lloyd *et al.*;⁵ (\blacksquare) Winer *et al.*;²⁸ (∇) Ravishankara *et al.*;³⁰ (Δ) Ohta;⁴⁴ (\bullet) Atkinson and Aschmann;¹² (—) recommendation (see text).

As for 2-methylpropene, 1-butene and propene, at temperatures $\lesssim 425 \text{ K}$ this OH radical reaction with *trans*-2-butene proceeds predominantly by OH radical addition, with the rate constant being close to the high pressure limit at total pressures of $\gtrsim 50$ Torr of helium, argon or air diluent. The OH-*trans*-2-butene adduct will thermally decompose at temperatures $\gtrsim 550\text{--}750 \text{ K}$, and hence at higher temperatures only the rate constant for a "direct" reaction involving OH radical addition with rapid rearrangement and decomposition to products other than the initial reactants (which must have a rate constant $\leq k_{\infty}$) and/or H-atom abstraction is measured.

The rate constant determined by Smith¹⁵ at 1275 K of $2.70 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is a factor of 2.25 higher than that calculated from the recommended expression

for propene at this temperature, consistent with the number of substituent $-\text{CH}_3$ groups. Hence, it is tentatively recommended that the rate constant for H-atom abstraction from *trans*-2-butene is given by

$$k(\textit{trans}\text{-}2\text{-butene}); T \gtrsim 700 \text{ K} \approx 1.5 \\ \times 10^{-17} T^2 e^{30/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

identical to that for 2-methylpropene (and *cis*-2-butene). Extrapolation of this expression to room temperature leads to the conclusion that at 298 K the contribution of the H-atom abstraction pathway to the overall high-pressure rate constant is $\sim 2\%$. This is consistent with the product study of Hoyermann and Sievert,⁷⁹ which showed that the abstraction channel accounts for $< 10\%$ of the overall reaction at ~ 1 Torr total pressure.

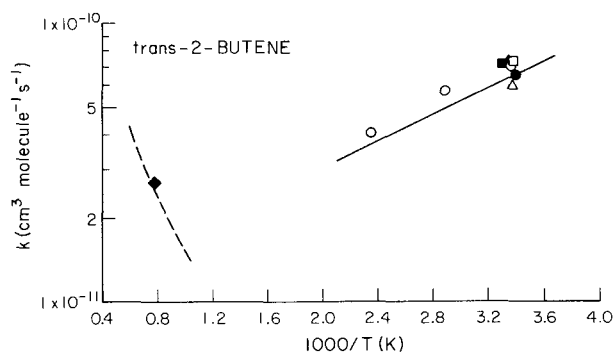


FIG. 45. Arrhenius plot of rate constants for the reaction of the OH radical with *trans*-2-butene. (\blacktriangle) Morris and Niki;⁴² (\circ) Atkinson and Pitts;²⁶ (\square) Wu *et al.*;²⁷ (\triangle) Ohta;⁴⁵ (\bullet) Atkinson and Aschmann;¹² (\square) Edney *et al.*;⁴⁶ (\blacklozenge) Smith;¹⁵ (—) recommendation for $T \lesssim 425$ K (see text); (---) tentatively recommended rate constant for H-atom abstraction (see text).

(7) 1-Pentene

The available rate constants, all obtained at room temperature, are given in Table 5. These rate constants exhibit a significant amount of scatter, with those of Morris and Niki⁴² and Nip and Paraskevopoulos³¹ being $\sim 30\%$ higher than the remaining data. As for the C_2 through C_4 alkenes (see above), the rate constant derived from the relative rate study of Atkinson and Aschmann¹² is used to recommend that

$$k(1\text{-pentene}) = 3.19 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 295 K. Combined with an estimated temperature dependence of $B = -500$ K (similar to the recommended temperature dependencies for propene, 1-butene, 2-

methylpropene and *cis*- and *trans*-2-butene for temperatures ≤ 425 K), this leads to

$$k(1\text{-pentene}) = 5.86 \times 10^{-12} e^{500/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at around 300 K (this expression is definitely not applicable above ~ 425 K), and

$$k(1\text{-pentene}) = 3.14 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty at 298 K of $\pm 20\%$.

(8) 3-Methyl-1-butene

The only rate constants available for this alkene (Table 5) are those from the absolute rate constant study of Atkinson *et al.*⁴⁸ and the relative rate constant study of Atkinson and Aschmann,¹² and these data are plotted in Arrhenius form in Fig. 46.

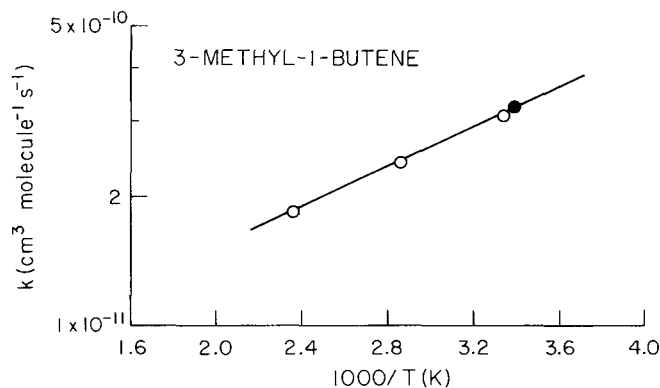


FIG. 46. Arrhenius plot of rate constants for the reaction of the OH radical with 3-methyl-1-butene. (\circ) Atkinson *et al.*;⁴⁸ (\bullet) Atkinson and Aschmann;¹² (—) recommendation (see text).

These data are in excellent agreement. The best-fit rate constant from an analysis of the relative rate data of Atkinson and Aschmann¹² and the absolute rate constants for a series of alkenes and dialkenes (see above) leads to

$$k(3\text{-methyl-1-butene}) = 3.24 \\ \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 295 K. Combined with the temperature dependence of Atkinson *et al.*,⁴⁸ this leads to the recommended Arrhenius expression of

$$k(3\text{-methyl-1-butene}) = 5.32 \\ \times 10^{-12} e^{533/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 299–423 K, and

$$k(3\text{-methyl-1-butene}) = 3.18 \times 10^{-11} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of $\pm 20\%$. This OH radical reaction proceeds mainly by OH radical addition at temperatures $\lesssim 425$ K, with the rate constants being close to the high-pressure limit above ~ 20 Torr total pressure of diluent.

(9) 2-Methyl-2-butene

The available kinetic data are given in Table 5 and are plotted in Arrhenius form in Fig. 47. It can be seen that at room temperature the more recent absolute and relative rate constants of Atkinson and Pitts,⁵⁰ Atkinson *et al.*,^{9,51} Ohta⁴⁵ and Atkinson and Aschmann¹² are in excellent agreement [the absolute rate constant study of Atkinson *et al.*⁴⁹ has been superseded by that of Atkinson and Pitts,⁵⁰ although it is in agreement with this later study⁵⁰ within the experimental error limits].

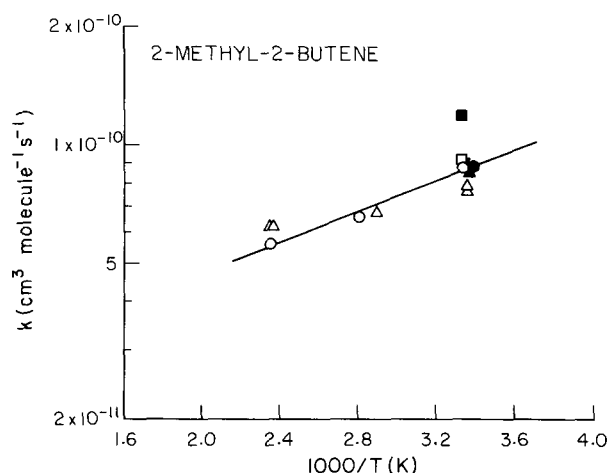


FIG. 47. Arrhenius plot of rate constants for the reaction of the OH radical with 2-methyl-2-butene. (■) Morris and Niki;⁴² (△) Atkinson *et al.*;⁴⁹ (○) Atkinson and Pitts;⁵⁰ (□) Atkinson *et al.*;⁵¹ (▼) Atkinson *et al.*;⁹ (▲) Ohta;⁴⁵ (●) Atkinson and Aschmann;¹² (—) recommendation (see text).

Again, consistent with the above recommendations for the alkenes, the temperature dependence of Atkinson and Pitts,⁵⁰ of $B = -450$ K, is used, together with the best-fit rate constant obtained from the relative rate study of Atkinson and Aschmann¹² and the absolute rate constants for a series of alkenes and dialkenes of

$$k(2\text{-methyl-2-butene}) = 8.84$$

$$\times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 295 \text{ K,}$$

to recommend the Arrhenius expression of

$$k(2\text{-methyl-2-butene}) = 1.92$$

$$\times 10^{-11} e^{450/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 299–426 K, and

$$k(2\text{-methyl-2-butene}) = 8.69$$

$$\times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty at 298 K of $\pm 20\%$. As for ethene, propene and 1-butene, at elevated temperatures ($\gtrsim 500$ K) this OH radical addition reaction will changeover to an H-atom abstraction process (from the three $-\text{CH}_3$ groups).

(10) 2,3-Dimethyl-2-butene

The available rate constants (all but one obtained at around room temperature) are given in Table 5. At room temperature the most recent rate constants of Atkinson *et al.*,^{9,53-56} Atkinson and Aschmann^{12,57} and Ohta⁴⁴ are in good agreement. Using an assumed temperature dependence of $B = -500$ K for this reaction to extrapolate the measured rate constants to 298 K, a unit-weighted average of these data^{9,12,44,53-57} yields the recommendation of

$$k(2,3\text{-dimethyl-2-butene}) = 1.10$$

$$\times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty of $\pm 20\%$.

As discussed previously,^{63,65} the room temperature rate constant obtained by Ravishankara *et al.*³⁰ is low, by a factor of ~ 2 , presumably due to wall losses of the 2,3-dimethyl-2-butene reactant in the static reaction system used.

As for the alkenes discussed above, this rate constant primarily reflects OH radical addition. At elevated temperatures in the region of ~ 550 – 750 K the OH-2,3-dimethyl-2-butene adduct will thermally decompose and, unless this adduct more rapidly rearranges and/or decomposes to products other than the reactants, at temperatures $\gtrsim 700$ K the observed reaction process will be H-atom abstraction from the four $-\text{CH}_3$ groups. Indeed, the rate constant of

$$k = 3.70 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 1237 \text{ K}$$

measured by Smith¹⁵ is consistent with an H-atom abstraction reaction, being a factor of 3.3 times that of the calculated H-atom abstraction reaction rate constant for propene at 1237 K.

Thus, it is tentatively recommended that H-atom abstraction from 2,3-dimethyl-2-butene has a rate constant of

$k(2,3\text{-dimethyl-2-butene}; T > 700 \text{ K}) = 3.0$

$$\times 10^{-17} T^2 e^{30/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

with this H-atom abstraction process being a minor contributor ($\sim 3\%$) to the overall reaction at room temperature and the high-pressure limit.

(11) Other Acyclic Monoalkenes

For the remaining acyclic monoalkenes for which data are available, only one or two studies have been carried out, and no specific recommendations are made. However, in general it is recommended that the room temperature rate constants derived from the relative rate studies of Ohta^{44,45} and Atkinson and Aschmann¹² be used.

(12) Propadiene

The available rate constants of Bradley *et al.*,²² Atkinson *et al.*,⁴⁸ Ohta,⁴⁵ Atkinson and Aschmann¹² and Liu *et al.*⁵⁹ are given in Table 6. At temperatures $\lesssim 425 \text{ K}$ the rate constants of Atkinson *et al.*,⁴⁸ Ohta,⁴⁵ Atkinson and Aschmann¹² and Liu *et al.*⁵⁹ are in good agreement and the data from these studies are plotted in Arrhenius form in Fig. 48. Atkinson *et al.*⁴⁸ showed that at room temperature the rate constant for this reaction exhibits fall-off behavior between second- and third-order kinetics below $\sim 50 \text{ Torr}$ total pressure of argon, with the bimolecular rate constant at 100 Torr total pressure being $\sim 10\%$ higher than that at 25 Torr total pressure.

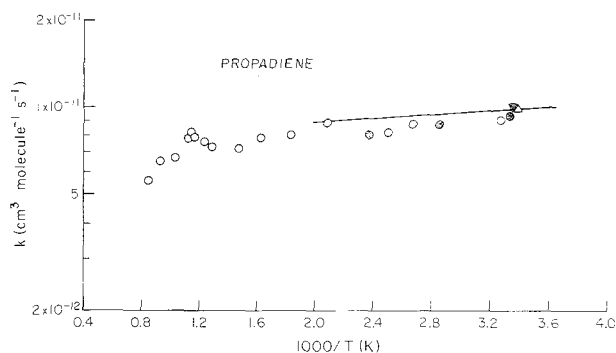


FIG. 48. Arrhenius plot of rate constants obtained at, or close to, the high-pressure limit for the reaction of the OH radical with propadiene. (●) Atkinson *et al.*;⁴⁸ (▼) Ohta;⁴⁵ (Δ) Atkinson and Aschmann;¹² (○) Liu *et al.*;⁵⁹ (—) recommendation (see text).

These observations indicate that the rate constants determined by Atkinson *et al.*⁴⁸ at 100 Torr total pressure of argon diluent were not totally at the high-pressure limit. At 298 K , a value of the low pressure third-order

rate constant of

$$k_o^{\text{Ar}} \sim 4 \times 10^{-28} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1},$$

combined with a limiting high-pressure second-order rate constant of

$$k_{\infty} = 1.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

accounts for this observed fall-off behavior (though obviously the value of k_o is only very approximate). The rate constants at 298 K and 100 Torr and 760 Torr total pressures of argon diluent are then calculated to be $\sim 10\%$ and $\sim 5\%$ below the high-pressure limit, respectively.

A unit-weighted least-squares analysis of the absolute rate constants obtained by Atkinson *et al.*⁴⁸ and Liu *et al.*⁵⁹ at temperatures $\leq 500 \text{ K}$ yields the Arrhenius expression of

$$k(\text{propadiene}; T \leq 500 \text{ K}) = (7.08^{+1.64}_{-1.33}) \times 10^{-12} e^{(74 \pm 75)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range $299\text{--}478 \text{ K}$ and at a total pressure of argon diluent of $100\text{--}760 \text{ Torr}$, where the indicated error limits are two least-squares standard deviations. From a best-fit of the relative rate constants of Atkinson and Aschmann¹² and selected literature room temperature absolute rate constants for a series of alkenes and dialkenes (see above), a rate constant of

$$k(\text{propadiene}) = 9.84$$

$$\times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 295 \text{ K}$$

is recommended, applicable to $\sim 760 \text{ Torr}$ total pressure of air. Combined with the temperature dependence derived above, this yields the recommendation of

$$k(\text{propadiene}; T < 500 \text{ K}) = (7.66^{+1.78}_{-1.44}) \times 10^{-12} e^{(74 \pm 75)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range $295\text{--}478 \text{ K}$, where the indicated errors are two least-squares standard deviations, and

$$k(\text{propadiene}) = 9.82 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K , with an estimated overall uncertainty at 298 K of $\pm 20\%$. This recommendation is applicable to one atmosphere total pressure of air, and is expected to be slightly ($\lesssim 5\%$) into the fall-off region at 298 K (and will be further into the fall-off region at higher temperatures).

The rate constant reported by Bradley *et al.*,²² obtained at a total pressure of $\sim 1 \text{ Torr}$, is almost certainly well into the fall-off region. The data of Liu *et al.*⁵⁹ show

no obvious deviation from a linear Arrhenius plot, with a slight negative temperature dependence, up to ~ 900 K. Above this temperature, a slightly enhanced decrease in the rate constants with increasing temperature is evident.⁵⁹ By analogy with the monoalkenes, this could be interpreted as the onset of thermal decomposition of the OH-propadiene adduct, although this phenomenon is observed to occur at ~ 500 – 600 K for the monoalkenes. It is also possible that this observed enhanced decrease in the rate constants with increasing temperatures above ~ 900 K is due to fall-off behavior. Clearly, further kinetic data are needed at elevated temperatures, $\gtrsim 500$ K, to better define the onset of thermal decomposition of the OH-propadiene adduct and of the H-atom abstraction process.

(13) 1,3-Butadiene

The available kinetic data of Lloyd *et al.*,⁵ Atkinson *et al.*,⁴⁸ Barnes *et al.*,³³ Ohta,⁴⁵ Atkinson and Aschmann¹² and Liu *et al.*⁵⁹ are given in Table 6 and are plotted in Arrhenius form in Fig. 49. It can be seen that the room temperature rate constants from the studies of Lloyd *et al.*,⁵ Atkinson *et al.*,⁴⁸ Barnes *et al.*,³³ Ohta,⁴⁵ Atkinson *et al.*¹² and Liu *et al.*⁵⁹ are in very good agreement. Furthermore, the temperature-dependencies obtained by Atkinson *et al.*⁴⁸ and Liu *et al.*⁵⁹ are in good agreement.

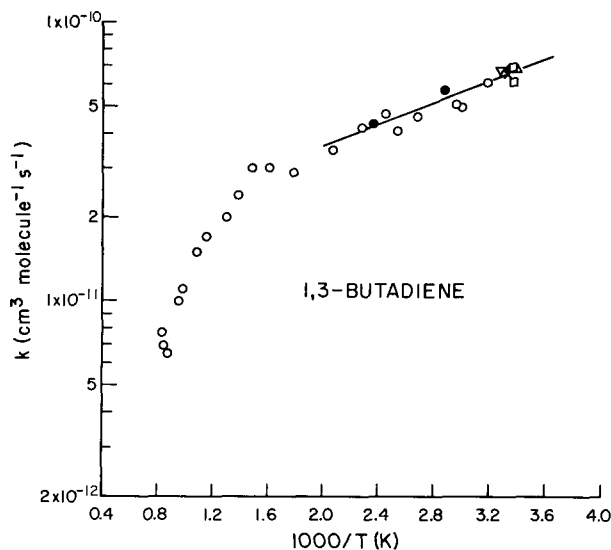


FIG. 49. Arrhenius plot of rate constants for the reaction of the OH radical with 1,3-butadiene. (∇) Lloyd *et al.*,⁵ (\bullet) Atkinson *et al.*,⁴⁸ (\times) Barnes *et al.*,³³ (\square) Ohta,⁴⁵ (Δ) Atkinson and Aschmann,¹² (\circ) Liu *et al.*,⁵⁹ (—) recommendation (see text).

A unit-weighted least-squares analysis of the data of Atkinson *et al.*⁴⁸ and Liu *et al.*⁵⁹ at temperatures < 500 K yields the Arrhenius expression of

$$k(1,3\text{-butadiene}; T < 500 \text{ K}) = (1.44^{+0.54}_{-0.40}) \times 10^{-11} e^{(448 \pm 117)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 299–483 K, where the indicated errors are two least-squares standard deviations. The relative rate study of Atkinson and Aschmann¹² for a series of alkenes and dialkenes, when combined with the literature absolute rate constants (see above), leads to the recommendation of

$$k(1,3\text{-butadiene}) = 6.78 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 295 K. Combined with the above temperature dependence, this yields the recommended Arrhenius expression of

$$k(1,3\text{-butadiene}; T < 500 \text{ K}) = (1.48^{+0.56}_{-0.42}) \times 10^{-11} e^{(448 \pm 117)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 295–483 K, where the indicated errors are two least-squares standard deviations, and

$$k(1,3\text{-butadiene}) = 6.66 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty at 298 K of $\pm 20\%$.

The relative rate constants of Lloyd *et al.*,⁵ Barnes *et al.*,³³ and Ohta⁴⁵ are in very good agreement with this recommendation.

By analogy with the alkenes such as ethene, propene and the butenes, this rate constant is that for the OH radical addition pathway and will be very close to the high-pressure limit, at least up to ~ 500 K. Indeed, the above recommendation provides a good fit to the rate constants measured by Liu *et al.*⁵⁹ in one atmosphere of argon diluent up to ~ 700 K. Above ~ 700 K, the rate constants measured by Liu *et al.*⁵⁹ decrease more rapidly with increasing temperature than calculated from extrapolation of the above recommendation, and this is expected to be due to the onset of thermal decomposition of the OH-1,3-butadiene adduct back to reactants. At higher temperatures, H-atom abstraction will be the major process observed, and some evidence of the contribution of this reaction pathway is seen from the data at 1153–1203 K,⁵⁹ which may indicate an increasing rate constant with increasing temperature.

As for propadiene, more data are needed at temperatures > 500 K (preferably as a function of pressure) to quantitatively define any fall-off behavior and the onset of thermal decomposition of the addition adduct and of the H-atom abstraction process.

(14) 2-Methyl-1,3-butadiene

The available rate constants of Cox *et al.*,³² Atkinson *et al.*,⁹ Kleindienst *et al.*,⁶⁰ Ohta,⁴⁵ Atkinson and Aschmann¹²

and Edney *et al.*⁴⁶ are given in Table 6 and are plotted in Arrhenius form in Fig. 50.

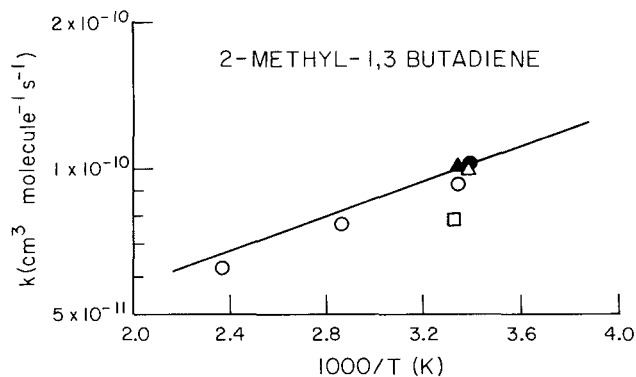


FIG. 50. Arrhenius plot of rate constants for the reaction of the OH radical with 2-methyl-1,3-butadiene (isoprene). (□) Cox *et al.*;³² (▲) Atkinson *et al.*;⁹ (○) Kleindienst *et al.*;⁶⁰ (Δ) Ohta;⁴⁵ (●) Atkinson and Aschmann,¹² Edney *et al.*;⁴⁶ (—) recommendation (see text).

The most recent room temperature data of Atkinson *et al.*,⁹ Atkinson and Aschmann,¹² Kleindienst *et al.*,⁶⁰ Ohta⁴⁵ and Edney *et al.*⁴⁶ are in good agreement. Consistent with the above recommendations for the alkenes, the temperature dependence observed by Kleindienst *et al.*⁶⁰ of $B = -410$ K is used, together with the rate constant resulting from a best fit of the relative rate constants of Atkinson and Aschmann¹² for a series of alkenes and dialkenes to the available absolute rate constant data of

$$k(2\text{-methyl-1,3-butadiene}) = 1.02 \\ \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 295 \text{ K,}$$

to recommend

$$k(2\text{-methyl-1,3-butadiene}) = 2.54 \\ \times 10^{-11} e^{410/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 295–422 K, and

$$k(2\text{-methyl-1,3-butadiene}) = 1.01 \\ \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of $\pm 25\%$.

This reaction proceeds by OH radical addition, and the above rate constant will be very close to the high-pressure limit over this temperature range. At elevated temperatures thermal decomposition of the OH-2-methyl-1,3-butadiene adduct will become important, and

the reaction pathways observed will then be OH radical addition followed by rapid rearrangement and/or decomposition of the adduct to products other than the reactants and/or H-atom abstraction from the $-\text{CH}_3$ group and vinyl C–H bonds.

(15) Remaining Acyclic Di- and Trialkenes

For the remaining acyclic di- and trialkenes, only single studies have been carried out, and no recommendations are made.

(16) Cyclohexene

The available rate constants of Wu *et al.*,²⁷ Darnall *et al.*,⁵⁸ Cox *et al.*,³² Barnes *et al.*,³³ Ohta,⁴⁵ Atkinson *et al.*⁵³ and Rogers⁴⁷ are given in Table 7. While no temperature dependent data are available, the reported room temperature rate constants of Wu *et al.*,²⁷ Darnall *et al.*,⁵⁸ Cox *et al.*,³² Barnes *et al.*,³³ Ohta⁴⁵ and Atkinson *et al.*⁵³ are in good agreement (though $\sim 20\%$ higher than that of Rogers⁴⁷). Based upon the recent study of Atkinson *et al.*,⁵³ it is recommended that

$$k(\text{cyclohexene}) = 6.77 \\ \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty of $\pm 25\%$.

(17) α -Pinene

The available kinetic data of Winer *et al.*,²⁸ Kleindienst *et al.*⁶⁰ and Atkinson *et al.*⁵⁵ are given in Table 7 and are plotted in Arrhenius form in Fig. 51. The room temperature rate constants of Winer *et al.*,²⁸ Kleindienst *et al.*⁶⁰ and Atkinson *et al.*⁵⁵ are in reasonable agreement. The temperature dependence obtained from the data of Kleindienst *et al.*⁶⁰ of $B = -444$ K is used together with the 294 K rate constant of Atkinson *et al.*⁵⁵ to recommend

$$k(\alpha\text{-pinene}) = (1.21_{-0.38}^{+0.54}) \\ \times 10^{-11} e^{(444 \pm 127)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 294–422 K, where the indicated errors are two least-squares standard deviations, and

$$k(\alpha\text{-pinene}) = 5.37 \\ \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of $\pm 25\%$.

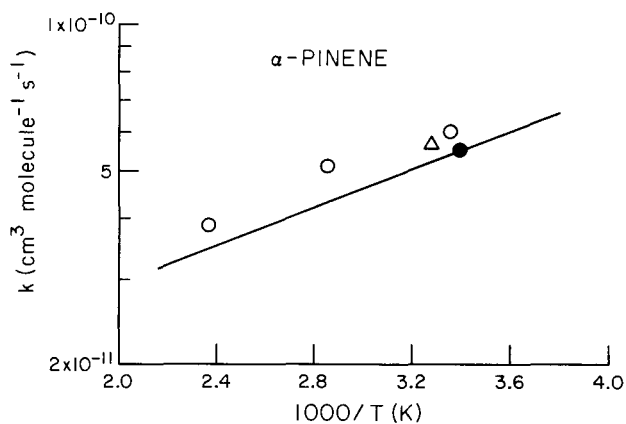


FIG. 51. Arrhenius plot of rate constants for the reaction of the OH radical with α -pinene. (Δ) Winer *et al.*,²⁸ (\circ) Kleindienst *et al.*,⁶⁰ (\bullet) Atkinson *et al.*,⁵⁵ (—) recommendation (see text).

(18) β -Pinene

The available kinetic data of Winer *et al.*,²⁸ Kleindienst *et al.*,⁶⁰ and Atkinson *et al.*,⁵⁵ are given in Table 7 and are plotted in Arrhenius form in Fig. 52. The relative rate constant of Atkinson *et al.*,⁵⁵ is in excellent agreement with the absolute room temperature rate constant of Kleindienst *et al.*,⁶⁰ and in reasonable agreement with that of Winer *et al.*,²⁸ As for α -pinene, the recommendation uses the temperature dependence determined by Kleindienst *et al.*,⁶⁰ of $B = -357$ K, in conjunction with the 294 K rate constant of Atkinson *et al.*,⁵⁵ to derive

$$k(\beta\text{-pinene}) = (2.38^{+0.91}_{-0.67}) \times 10^{-11} e^{(357 \pm 111)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 294–423 K, where the indicated errors are two least-squares standard deviations, and

$$k(\beta\text{-pinene}) = 7.89$$

$$\times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of $\pm 25\%$.

(19) Other Cycloalkenes

For the other cycloalkenes, cyclodialkenes and cyclo-trialkenes listed in Table 7, no specific recommendations are made. However, it is recommended that the room temperature rate constants derived from the relative rate constant studies of Ohta⁴⁵ and Atkinson *et al.*,⁵³⁻⁵⁵ be used (see, for example, the excellent agreement between the

room temperature rate constants of Ohta⁴⁵ and Atkinson *et al.*,⁵³ for 1,4-cyclohexadiene).

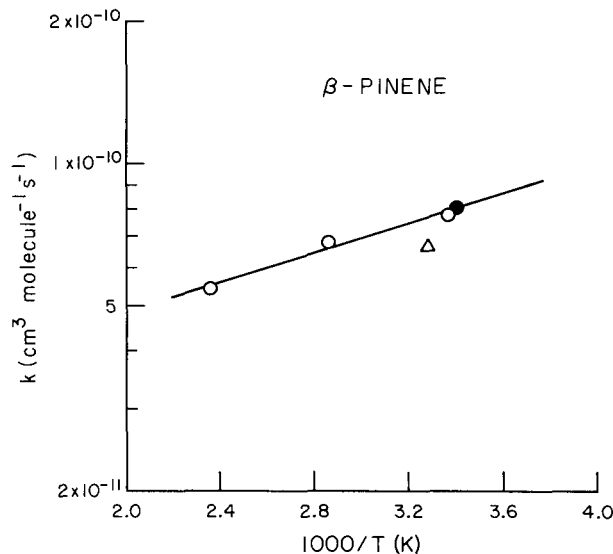


FIG. 52. Arrhenius plot of rate constants for the reaction of the OH radical with β -pinene. (Δ) Winer *et al.*,²⁸ (\circ) Kleindienst *et al.*,⁶⁰ (\bullet) Atkinson *et al.*,⁵⁵ (—) recommendation (see text).

As discussed in detail previously,^{63,81} the room temperature rate constants for the monoalkenes increase monotonically with the number of substituents around the double bond, and the rate constants for the acyclic and cyclic mono-alkenes and the non-conjugated di- and trialkenes can be estimated to a good degree of accuracy ($\pm 30\%$) from the number and position(s) of alkyl substituents around the double bond(s). Similarly, for alkenes containing conjugated double bond systems, reasonably accurate predictions of the room temperature rate constants can be made from the rate constants for $>C=C-C=C<$ systems with the varying numbers of substituents around this double bond system.^{63,81}

b. Mechanisms

The kinetic data discussed above for the reactions of the OH (or OD) radical with alkenes show that three distinct temperature regimes exist, for temperatures $\lesssim 500$ K, ~ 500 – 700 K, and $\gtrsim 700$ K, with the precise temperatures which define these regimes depending on the specific alkene, the total pressure and identity of the third body, and the experimental technique used. These temperature regimes, and the behaviors of the measured high pressure rate constants in the low and high temperature regimes (which approximate the recommendations for *trans*-2-butene) are shown in Fig. 53. To an approximation, these temperature regimes correspond to: (a)

≈ 500 K, OH radical addition to the $>C=C<$ bond(s) which may be in the fall-off regime between second- and third-order kinetics, with the rate constant at a given total pressure decreasing with increasing temperature, (b) ~ 500 – 700 K, the occurrence of thermal decomposition of the OH radical-alkene addition adduct and, for the smaller alkenes such as ethene, propene and possibly propadiene, increasing fall-off behavior with increasing temperature, and (c) ≈ 700 K, the occurrence of H-atom abstraction as the major or sole reaction pathway, with the rate constant increasing rapidly with increasing temperature. These processes are discussed briefly below.

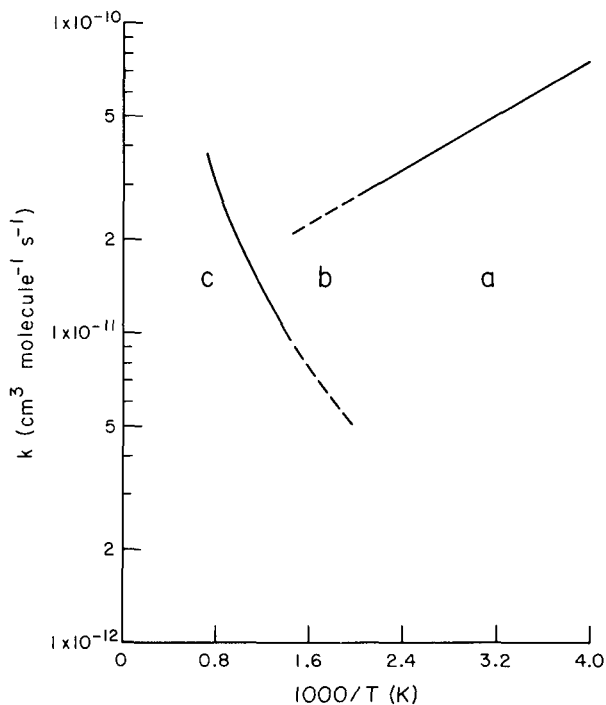
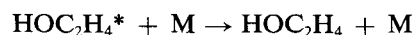
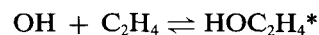


FIG. 53. Schematic Arrhenius plot (which approximates the OH radical rate constant behavior of *trans*-2-butene at the high-pressure limit) showing the three temperature regimes (a) ≈ 500 K, (b) ~ 500 – 700 K and (c) ≈ 700 K (see text).

The available kinetic and mechanistic data show that at ≈ 500 – 600 K the reaction of OH radicals to the alkenes proceeds predominantly via addition of the OH radical to the carbon-carbon double bond(s). Thus, in the discharge flow-mass spectrometric study of Morris *et al.*,²¹ mass peaks corresponding to the OH-alkene adducts were observed for ethene and propene. These adduct peaks increased in intensity as the total pressure was increased from 1 to 4 Torr,²¹ showing that OH radical addition was occurring and that these addition adducts were being collisionally stabilized.

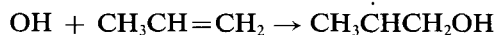
As noted above, numerous kinetic studies have shown for ethene^{7,8,10,11,13,67,72,73} and propene^{11,13,37} that the rate

constants are in the fall-off region between second-order and third-order kinetics at total pressures below approximately one atmosphere for ethene and below ~ 30 Torr for propene. These observations show that these reactions proceed via initial addition of OH radicals to the alkene to form an initially energy-rich OH-alkene adduct, which can decompose back to the reactants or be collisionally stabilized. For example, for ethene



For ethene, Howard⁶⁷ has shown from a kinetic study over the total pressure range 0.7–7 Torr of helium that the rate constant extrapolates to essentially zero at zero pressure. Thus, as expected from the high C–H bond energy in ethene, H-atom abstraction from ethene is essentially negligible at room temperature. This prediction from kinetic studies is confirmed by the recent discharge flow-mass spectrometric study of Bartels *et al.*,⁶⁸ in which the abstraction channel was shown to account for $< 2.5\%$ of the overall reaction channels at 295 K and at ~ 2 Torr total pressure. These investigations^{67,68} thus show, in contradiction to the earlier product study of Meagher and Heicklen⁸² (involving a difficult to interpret final product analysis which can be re-interpreted as indicating an $\sim 10\%$ H-atom abstraction route at the high-pressure limit),⁶⁵ that H-atom abstraction from ethene under atmospheric conditions is totally negligible.

For propene and the butenes, Hoyermann and Sievert^{78,79} have shown from discharge flow-mass spectroscopic studies that H-atom abstraction from these alkenes is also insignificant, being $< 5\%$ for propene and 2-methylpropene and $< 10\%$ for 1-butene and *cis*- and *trans*-2-butene at room temperature. That H-atom abstraction from propene is negligible is totally consistent with the product study of Cvetanovic,⁷⁷ who, from a comprehensive investigation of the products formed and their formation reactions (mainly via radical-radical processes), concluded that the OH radical addition pathway was the major, if not exclusive, reaction pathway, and that addition to the terminal carbon atom



occurs $\sim 65\%$ of the time at room temperature.⁷⁷ As shown above, extrapolation of elevated temperature (> 650 K) kinetic data to 298 K indicates that H-atom abstraction from the vinyl C–H bonds and/or C–H bonds of substituent alkyl groups for ethene, propene, the butenes and 2,3-dimethyl-2-butene contributes $< 5\%$ of the overall reaction rate at the high-pressure limit.

Hence, it appears that at ≈ 425 K H-atom abstraction from acyclic alkenes containing $\leq \text{C}_2$ side chains is of minimal importance, and that at room temperature the reactions of OH radicals with these alkenes can be considered to proceed almost totally via OH radical addition to the $>C=C<$ double bonds. Of course, for the 1-alk-

nes and other alkenes with long side chains it must be expected that H-atom abstraction from the $>CH-$, $-CH_2-$, and $-CH_3$ groups will occur, with rate constants for H-abstraction from these groups being approximately similar to those for the corresponding alkane groups.⁸¹ Moreover, Ohta⁸³ has shown that benzene is a minor, but significant, product formed during room temperature irradiations of $CH_3ONO-NO$ -cyclohexadiene-air mixtures, accounting for 8.9% and 15.3% of the overall reaction pathways for 1,3-cyclohexadiene and 1,4-cyclohexadiene, respectively. These data⁸³ show that H-atom abstraction from the allylic C-H bonds (of bond dissociation energy 73 ± 5 kcal mol⁻¹⁸⁴) in these cyclohexadienes does occur, with a rate constant per allylic C-H bond of $\sim 3.7 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ for both 1,3- and 1,4-cyclohexadiene.

The formation of the OH-ethene adduct is calculated to be ~ 32 kcal mol⁻¹ exothermic⁷⁶ (formation of the other OH-alkene adducts have similar calculated exothermicities) and formation of an H-atom together with $HOCH=CH_2$ is endothermic from the OH radical and ethene reactants by ~ 7 kcal mol⁻¹.⁷⁶ Melius *et al.*⁸⁵ and Sosa and Schlegel⁸⁶ have calculated that the thermochemically most favorable decomposition pathway for the OH-ethene adduct involves redissociation back to the reactants. At elevated temperatures decomposition of the thermalized OH-ethene adduct, and the thermalized OH-alkene adducts in general, then occurs as experimentally observed by Tully¹⁰ and Tully and Goldsmith.³⁷ For example, in the recent flash photolysis studies of Tully¹⁰ and Tully and Goldsmith³⁷ for ethene¹⁰ and propene,³⁷ non-exponential OH radical decays were observed to occur at temperatures of $\sim 500-700$ K, and the derived rate constants decreased rapidly with increasing temperature over this temperature range.

This is totally consistent with the increasing importance of thermal decomposition of the thermalized OH-alkene adducts at elevated temperature, with the adduct decomposing within the time-scale of these experimental observations^{10,37} for temperatures $\sim 500-700$ K. At still higher temperatures the addition pathway, at least for ethene, becomes unimportant due to the extremely rapid decomposition rate of the OH-alkene adduct back to reactants, and for ethene the reaction is then expected to proceed via H-atom abstraction from the vinyl C-H bonds⁸⁵ with a positive temperature dependence.

For the higher alkenes, as noted above, other decomposition pathways of the OH-alkene adducts (for example, CH_3 radical elimination and isomerization followed by decomposition reactions) may also become of importance in this temperature regime. Thus, the situation at elevated temperatures where thermal decomposition of the OH-alkene adduct becomes important may be more complex,^{37,85} involving other reaction pathways as well as direct H-atom abstraction. However, for the methyl-substituted ethenes for which high temperature (> 650 K) kinetic data are available (propene, 2-methylpropene, *trans*-2-butene and 2,3-dimethyl-2-butene), the magnitude of the rate constants depends almost linearly

on the number of substituent $-CH_3$ groups, as shown in Fig. 54. This indicates that for these alkenes the high temperature reaction pathway involves H-atom abstraction from the $-CH_3$ groups, with the rate constant per $-CH_3$ group being approximately constant at a given temperature.

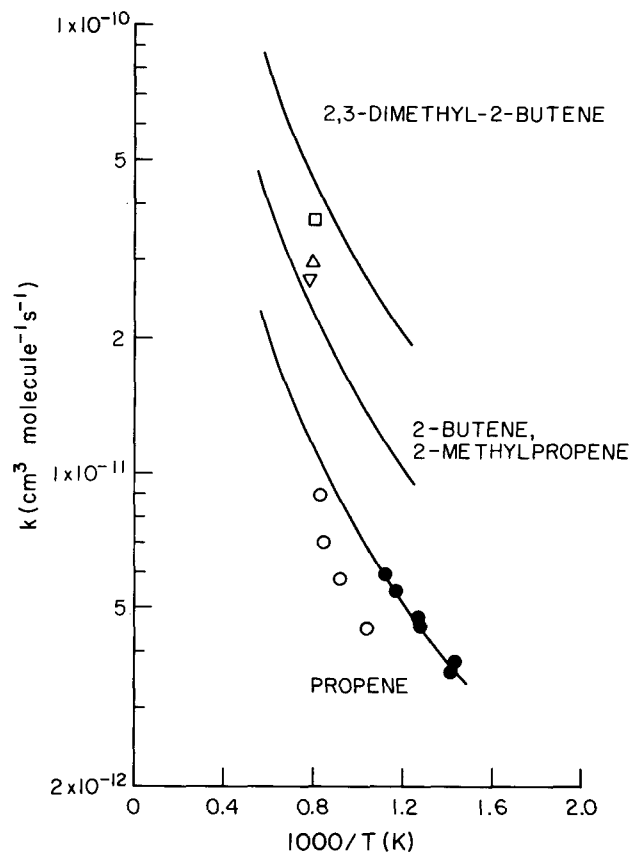
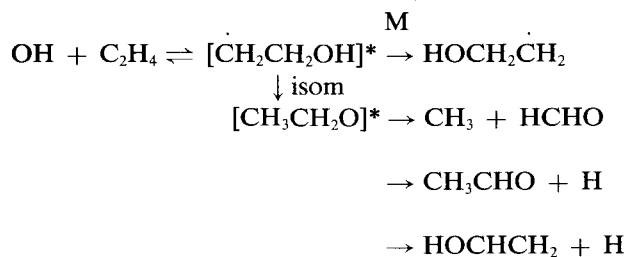


FIG. 54. Arrhenius plot of the available high-temperature (> 650 K) rate constants for the reactions of the OH radical with methyl-substituted ethenes. Propene: (○) Smith *et al.*;³⁸ (●) Tully.¹⁶ 2-Methylpropene: (Δ) Smith.¹⁵ *trans*-2-Butene: (▽) Smith.¹⁵ 2,3-Dimethyl-2-butene: (□) Smith.¹⁵ (—) Calculated based upon the recommended H-atom abstraction rate constant for propene and the number of substituent $-CH_3$ groups (see text).

At low total pressures other reactions of the chemically activated OH-alkene adducts can occur.⁸⁶ Thus, for example, Bartels *et al.*⁶⁸ have observed the formation of $HCHO + CH_3$ and $CH_3CHO + H$ as decomposition products of the OH-ethene adduct at total pressures of ~ 2 Torr. Under these low pressure conditions the reaction sequence for ethene appears to be^{68,86}



Clearly, at low total pressures and/or high temperatures, the dynamics of these OH radical reactions, even for ethene, are complex,^{85,86} and further experimental and theoretical studies are required.

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2.4. Haloalkenes

a. Kinetics

The available second-order rate constants obtained at, or close to, the high pressure limit are listed in Table 9. In addition, Howard⁵ has determined, using a discharge flow-laser magnetic resonance (DF-LMR) technique, rate constants for the reactions of OH radicals with CH₂=CHCl, CH₂=CF₂ and CF₂=CFCl at 296 K over the total pressure range of 0.7 to 7 Torr of helium. For these three haloalkenes the measured rate constants were in the fall-off region between second- and third-order kinetics,⁵ with second-order rate constants at 296 K and 7 Torr total pressure of helium diluent of 2.1×10^{-12} cm³ molecule⁻¹ s⁻¹ for CH₂=CF₂⁵ and 7×10^{-12} cm³ molecule⁻¹ s⁻¹ for CF₂=CFCl.⁵ For CHCl=CCl₂, the rate constant at 296 K is in the fall-off region below ~2 Torr total pressure of helium.⁵

Kinetic data for the individual haloalkenes for which multiple studies have been carried out are discussed below.

(1) Trichloroethene

The available rate constants of Winer *et al.*,⁴ Howard,⁵ Davis *et al.*,⁶ Chang and Kaufman,⁷ Kirchner,⁸ Klöpffer *et al.*⁹ and Edney *et al.*² are given in Table 9, and those of Howard,⁵ Davis *et al.*,⁶ Chang and Kaufman,⁷ Kirchner,⁸ and Edney *et al.*,² which are in reasonably good agreement, are plotted in Arrhenius form in Fig. 55. The relative rate constant of Winer *et al.*⁴ was at, or close to, the lower limit of values able to be derived by the experi-

mental technique used,¹³ and is hence neglected in the evaluation. The rate constants reported by Kirchner⁸ and Klöpffer *et al.*⁹ at around room temperature have not been used in the evaluation because of a lack of details available.

Thus, a unit-weighted least-squares analysis of the rate constant data of Howard,⁵ Davis *et al.*⁶ and Chang and Kaufman⁷ yields the recommended Arrhenius expression of

$$k(\text{trichloroethene}) = (5.63^{+1.54}_{-1.20}) \times 10^{-13} e^{(427 \pm 70)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 234–420 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{trichloroethene}) = 2.36 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of $\pm 30\%$. This recommendation is identical to that of Atkinson.¹³

(2) Tetrachloroethene

The kinetic data of Winer *et al.*,⁴ Howard,⁵ Davis *et al.*,⁶ Chang and Kaufman⁷ and Kirchner⁸ are given in Table 9, and those of Howard,⁵ Davis *et al.*,⁶ Chang and Kaufman⁷ and Kirchner,⁸ which are in good agreement, are plotted in Arrhenius form in Fig. 56. (Only the reported rate constants at 298 K and 305 K for the studies of Davis *et al.*⁶ and Kirchner,⁸ respectively, can be plotted, together with the reported Arrhenius expressions,^{6,8} since the individual rate constants at the temperatures studied were not given.^{6,8}) Analogous to the case for trichloroethene, the relative rate constant reported by Winer *et al.*⁴ has been neglected and the rate constant of Kirchner⁸ has not been used in the evaluation.

A unit-weighted least-squares analysis of the rate constants of Howard,⁵ Chang and Kaufman⁷ and the 298 K rate constant of Davis *et al.*⁶ leads to the recommended Arrhenius expression of

$$k(\text{tetrachloroethene}) = (9.64^{+2.92}_{-2.24}) \times 10^{-12} e^{-(1209 \pm 90)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 296–420 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{tetrachloroethene}) = 1.67 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of $\pm 30\%$. This recommendation is identical to that of Atkinson.¹³

TABLE 9. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with haloalkenes at, or close to, the high pressure limit

Haloalkene	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Tempera- ture range covered (K)	
CH ₂ =CHF			5.56 ± 0.56	299.2	FP-RF	Perry <i>et al.</i> ¹	299–426	
			4.44 ± 0.45	346.8				
	1.48	-390 ± 151	3.76 ± 0.38	426.1				
CH ₂ =CHCl			6.60 ± 0.66	299.2	FP-RF	Perry <i>et al.</i> ¹	299–423	
			5.01 ± 0.51	357.8				
	1.14	-526 ± 151	3.95 ± 0.40	422.5				
CH ₂ =CHBr			6.81 ± 0.69	298.6	FP-RF	Perry <i>et al.</i> ¹	299–424	
			6.00 ± 0.60	350.0				
	1.79	-405 ± 151	4.56 ± 0.46	423.7				
CH ₂ =CCl ₂			14.8 ± 2.1	296	RR [relative to $k(n\text{-butane}) =$ $2.51 \times 10^{-12}]^a$	Edney <i>et al.</i> ²		
			14.6	298				RR [relative to $k(n\text{-pentane}) =$ $3.94 \times 10^{-12}]^a$
			8.11 ± 0.24	298 ± 2				RR [relative to $k(\text{dimethyl ether}) =$ $2.98 \times 10^{-12}]^a$
<i>cis</i> -CHCl=CHCl			2.38 ± 0.14	298 ± 2	RR [relative to $k(\text{dimethyl ether}) =$ $2.98 \times 10^{-12}]^a$	Tuazon <i>et al.</i> ³		
<i>trans</i> - CHCl=CHCl			1.80 ± 0.03	298 ± 2	RR [relative to $k(\text{dimethyl ether}) =$ $2.98 \times 10^{-12}]^a$	Tuazon <i>et al.</i> ³		
CHCl=CCl ₂			4.3 ± 1.3	305 ± 2	RR [relative to $k(2\text{-methylpropene}) =$ $4.94 \times 10^{-11}]^a$	Winer <i>et al.</i> ⁴		
			2.0 ± 0.4	296	DF-LMR	Howard ⁵		
			2.35 ± 0.25	298	FP-RF	Davis <i>et al.</i> ⁶		
			3.12 ± 0.24	234	DF-RF	Chang and Kaufman ⁷	234–420	
			3.65 ± 0.21	237				
			3.73 ± 0.18	243				
			3.14 ± 0.16	250				
			3.06 ± 0.07	260				
			2.78 ± 0.17	268				
			2.37 ± 0.10	296				
			1.74 ± 0.04	343				
			1.86 ± 0.13	357				
			1.67 ± 0.03	420				
			1.55 ± 0.06	420				
	0.532 ± 0.071	-445 ± 41	1.68 ± 0.04	420				
		2.11	305	DF-MS	Kirchner ⁸			
		2.8	300	RR [relative to $k(\text{toluene}) =$ $5.91 \times 10^{-12}]^a$	Klöpffer <i>et al.</i> ⁹			
		2.85 ± 0.40	296	RR [relative to $k(n\text{-butane}) =$ $2.51 \times 10^{-12}]^a$	Edney <i>et al.</i> ²			

TABLE 9. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with haloalkenes at, or close to, the high pressure limit — Continued

Haloalkene	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
$\text{CCl}_2=\text{CCl}_2$			2.2 ± 0.7	305 ± 2	RR [relative to $k(2\text{-methylpropene}) =$ $4.94 \times 10^{-11}]^a$	Winer <i>et al.</i> ⁴	
			0.170 ± 0.034	296	DF-LMR	Howard ⁵	
	10.6 ± 5	1295 ± 150	0.155 ± 0.015	298	FP-RF	Davis <i>et al.</i> ⁶	250–375
			0.169 ± 0.007	297	DF-RF	Chang and Kaufman ⁷	297–420
			0.270 ± 0.009	341			
			0.276 ± 0.010	341			
			0.303 ± 0.034	350			
			0.424 ± 0.016	378			
			0.477 ± 0.014	403			
		9.44 ± 1.34	1199 ± 55	0.526 ± 0.061	420		
	5.53	1034	0.179	305	DF-MS	Kirchner ⁸	~305–430 ^b
$\text{CH}_2\text{ClCH}=\text{CH}_2$			17 ± 7	298	RR [relative to $k(n\text{-butane}) =$ $2.54 \times 10^{-12}]^a$	Edney <i>et al.</i> ¹⁰	
			19.5 ± 3.2	296	RR [relative to $k(n\text{-butane}) =$ $2.51 \times 10^{-12}]^a$	Edney <i>et al.</i> ²	
			16.9 ± 0.7	298 ± 2	RR [relative to $k(\text{propene}) =$ $2.63 \times 10^{-11}]^a$	Tuazon <i>et al.</i> ¹¹	
<i>cis</i> - $\text{CH}_2\text{ClCH}=\text{CHCl}$			7.36 ± 0.12^c	295 ± 2	RR [relative to $k(n\text{-octane}) =$ $8.57 \times 10^{-12}]^a$	Tuazon <i>et al.</i> ¹²	
			8.41 ± 0.40	298 ± 2	RR [relative to $k(n\text{-octane}) =$ $8.68 \times 10^{-12}]^a$	Tuazon <i>et al.</i> ³	
<i>trans</i> - $\text{CH}_2\text{ClCH}=\text{CHCl}$			12.4 ± 0.4^c	295 ± 2	RR [relative to $k(n\text{-octane}) =$ $8.57 \times 10^{-12}]^a$	Tuazon <i>et al.</i> ¹²	
			14.3 ± 0.8	298 ± 2	RR [relative to $k(n\text{-octane}) =$ $8.68 \times 10^{-12}]^a$	Tuazon <i>et al.</i> ³	
$(\text{CH}_2\text{Cl})_2\text{C}=\text{CH}_2$			40.2 ± 5.4	295 ± 2	RR [relative to $k(2\text{-methyl-1,3-butadiene}) =$ $1.02 \times 10^{-10}]^a$	Tuazon <i>et al.</i> ¹²	
			33.5 ± 3.0	298 ± 2	RR [relative to $k(2\text{-methyl-1,3-butadiene}) =$ $1.01 \times 10^{-10}]^a$	Tuazon <i>et al.</i> ³	

^aFrom the present recommendations (see text).^bTemperature range covered estimated from the graphical presentation given.^cNo effort made to minimize possible effects of Cl atom reactions,³ and these rate constants are superseded by those determined by Tuazon *et al.*³

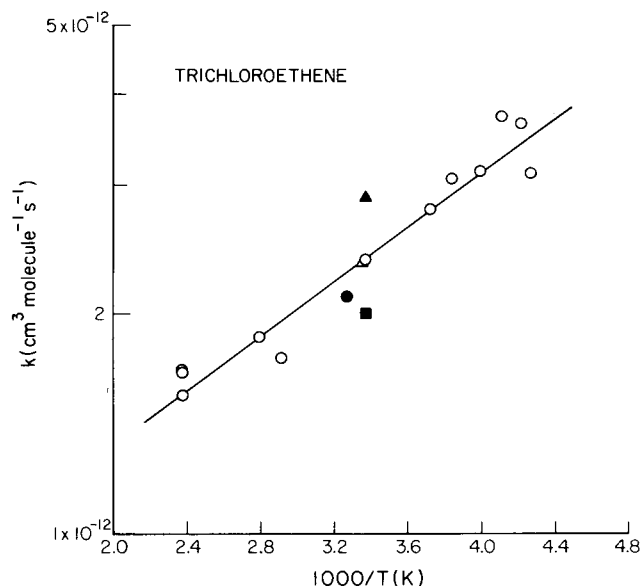


FIG. 55. Arrhenius plot of rate constants for the reaction of the OH radical with trichloroethene. (■) Howard;⁵ (Δ) Davis *et al.*;⁶ (○) Chang and Kaufman;⁷ (●) Kirchner;⁸ (▲) Edney *et al.*;² (—) recommendation (see text).

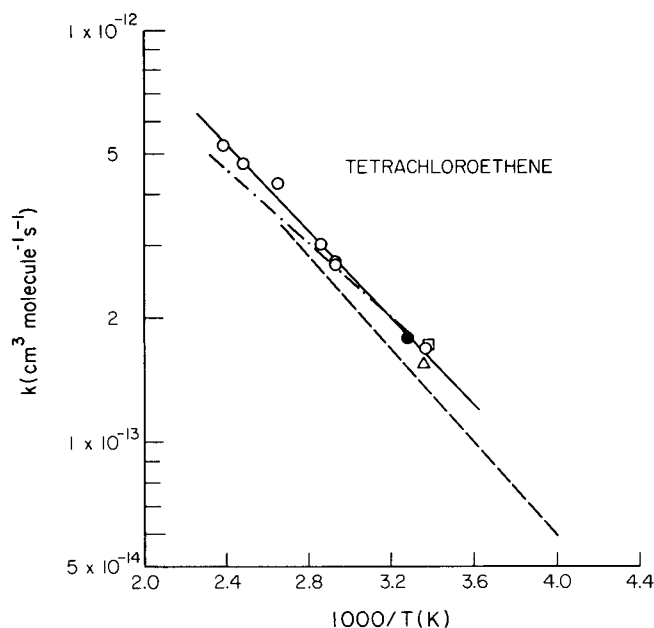


FIG. 56. Arrhenius plot of rate constants for the reaction of the OH radical with tetrachloroethene. (□) Howard;⁵ (Δ, — —) Davis *et al.*;⁶ (○) Chang and Kaufman;⁷ (●, - - -) Kirchner;⁸ (—) recommendation (see text).

(3) 3-Chloropropene (allyl chloride)

Rate constants have been obtained at room temperature by Edney *et al.*^{2,10} and Tuazon *et al.*¹¹ Relative rate techniques were used in all three of these studies,^{2,10,11} and the involvement of Cl atom reactions (with the Cl

atoms being generated from the overall OH radical reaction with 3-chloropropene) was observed by Edney *et al.*,^{2,10} but not by Tuazon *et al.*¹¹ The rate constants^{2,10,11} given in Table 9 were obtained under experimental conditions designed to minimize the effects of any Cl atom reactions with the 3-chloropropene and the reference organic, and the rate constants obtained^{2,10,11} are in agreement within the experimental error limits.

Based mainly upon the study of Tuazon *et al.*¹¹ in which any Cl atom reactions were suppressed by the addition of ethane to the reactant mixtures, a rate constant of

$$k(3\text{-chloropropene}) = 1.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

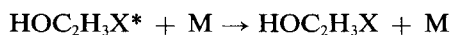
at 298 K is recommended, with an estimated overall uncertainty of $\pm 30\%$. This rate constant is expected to exhibit a small negative temperature dependence at around room temperature.

(4) Other Haloalkenes

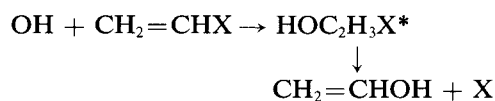
For the remaining haloalkenes for which kinetic data are available at, or close to, the high pressure second-order limit, there are either significant discrepancies between the reported data (1,1-dichloroethene), or data have only been obtained by one research group. Accordingly, until further studies are carried out these data must be used with correspondingly large uncertainty limits. In particular, relative rate studies of the reaction of the OH radical with chloroalkenes can be complicated by the production of Cl atoms from reaction steps subsequent to the initial OH radical addition step, followed by reactions of these Cl atoms with the haloalkene and the reference organic(s). The most recent relative rate studies of Edney *et al.*^{2,10} and Tuazon *et al.*^{3,11} have attempted to avoid or take into account these complicating Cl atom reactions (although for 1,1-dichloroethene discrepancies of a factor of ~ 2 still remain between the room temperature rate constants obtained by these two groups^{2,3}).

b. Mechanism

For the haloalkenes studied, the available kinetic data show that the reactions proceed via OH radical addition to the carbon-carbon double bond,¹³ with H-atom abstraction from the vinyl C-H bonds or the alkyl-substituent C-H bonds being of essentially negligible significance. This situation is analogous to the OH radical reactions with the alkenes at temperatures $\lesssim 425$ K, and is consistent with the observed fall-off dependence of several of these rate constants over the range 0.7–7 Torr total pressure of helium diluent.⁵ Hence, taking the vinyl halides as an example, these reactions proceed via addition of the OH radical to the haloalkenes to form an initially energy-rich OH-haloalkene adduct. This adduct can decompose back to the reactants or be collisionally stabilized, as shown, for example, for the vinyl halides (X = F, Cl, or Br).



For $\text{CH}_2=\text{CHF}$, $\text{CH}_2=\text{CHCl}$ and $\text{CH}_2=\text{CHBr}$, the limiting high-pressure second-order kinetic regime is approached at total pressures of argon diluent of ~ 50 Torr at 298 K,¹ with the high pressure limit for $\text{CHCl}=\text{CCl}_2$ being approached at a total pressure of ~ 2 Torr of helium⁵ at 296 K. The reaction to form the OH-haloalkene adduct is ~ 35 kcal mol⁻¹ exothermic for all three halogen substituents¹⁴ (similar to the situation for the alkenes). Elimination of an F-atom from the initially-formed OH-vinyl fluoride adduct is endothermic, with the overall reaction process



being ~ 19 kcal mol⁻¹ endothermic for $\text{X} = \text{F}$. Hence, for the reactions of the OH radical with vinyl fluoride, and with other haloalkenes containing no Cl or Br atoms attached to the double bond, the rate constants at temperatures $\lesssim 500$ –600 K will exhibit similar behavior to that for ethene, showing fall-off behavior from second- to third-order kinetics as the total pressure decreases.

For the reaction of OH radicals with vinyl chloride and vinyl bromide (and by analogy, probably also for other haloalkenes with Cl or Br atoms attached to the $>\text{C}=\text{C}<$ double bond), the elimination of Cl or Br atoms from the OH-haloalkene adducts is thermochemically favorable,⁵ with the overall reactions being exothermic by ~ 11 kcal mol⁻¹ and ~ 24 kcal mol⁻¹ for $\text{X} = \text{Cl}$ and Br , respectively.¹ In order for these Cl or Br atom eliminations to occur, the OH radical must add at the carbon atom to which the halogen substituent is located (the α -carbon atom) or, after OH radical addition to the β -carbon atom, a rapid 1,2-migration of OH must occur. If these elimination reactions occur, then the observed rate constants will exhibit second-order kinetics even at low total pressures where collisional stabilization of the OH-haloalkene adducts is not effective. At higher total pressures collisional stabilization of the adducts will become competitive with Cl or Br atom elimination, although the observed rate constant will remain pressure-independent and still be that for the initial reaction to form the adduct.

However, Howard⁵ has shown that for the reaction of OH radicals with vinyl chloride at 296 K, the rate constant approaches a limiting low pressure value of $\lesssim 1 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹, a factor of $\gtrsim 7$ lower than the limiting high pressure rate constant.¹ Thus, the elimination of a Cl atom is, at most, a relatively minor reaction pathway. This then implies that for the reaction of OH radicals with vinyl chloride (and presumably for other haloalkenes with Cl or Br atoms attached to the double bond) the two extreme reaction pathways involve either (a) OH radical addition only to the β -carbon atom and

that a 1,2-migration of OH has an activation energy of $\gtrsim 35$ kcal mole⁻¹, so that this 1,2-migration becomes rate determining, or (b) OH radical addition occurs at both the α - and β -positions, but mainly at the β position, the 1,2-migration of OH is negligible slow, and hence the elimination reaction occurs only after OH radical addition at the α position. While this latter situation is the most likely,¹ further work concerning both the pressure dependencies of the overall rate constants and the amount of reaction proceeding via halogen atom elimination is required for this class of organic compounds.

At elevated temperatures of $\gtrsim 600$ K, H-atom abstraction from the vinyl C–H bonds or alkyl-substituent C–H bonds is expected to become significant. Furthermore, at temperatures $\gtrsim 500$ –700 K the thermal back decomposition of the thermalized OH-haloalkene adducts to reactants will become sufficiently rapid that, unless these adducts rearrange and/or decompose more rapidly by other channels, the OH radical addition pathway (with a rate constant which cannot exceed that for the addition of the OH radical to yield the energy-rich adduct) will become of no consequence. While this is expected to be the case for $\text{CH}_2=\text{CHF}$ and other fluoroalkenes, the rearrangement and/or decomposition pathways for other OH-haloalkene adducts are not experimentally known, and hence it cannot be predicted whether or not the observed rate constants will exhibit a discontinuity from the “high” ($\gtrsim 600$ K) to the “low” ($\lesssim 450$ K) temperature regimes (as for the alkenes; see Fig. 54) or exhibit a smooth, curved, Arrhenius plot with a minimum in the ~ 500 –700 K temperature region. Clearly, further kinetic and mechanistic data are required for this class of organic compounds at temperatures > 450 K.

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2.5. Alkynes

a. Kinetics and Mechanisms

The available kinetic data reported to be at, or close to, the high-pressure limit, or obtained at one atmosphere total pressure of argon diluent,¹⁶ are given in Table 10. In addition to these cited kinetic data, a number of rate constant studies have been carried out for acetylene which are now recognized to have been in the fall-off region between second- and third-order kinetics.²²⁻²⁶ The data for the individual reactions are discussed below.

(1) Acetylene

Despite earlier evidence that at around room temperature the rate constant for the reaction of OH radicals

with acetylene did not exhibit a pressure dependence,^{4,23-25} the more recent flash or laser photolysis studies of Perry *et al.*,⁵ Michael *et al.*,⁷ Perry and Williamson,⁸ Schmidt *et al.*¹¹ and Wahner and Zetzsch¹² show conclusively that at ~ 298 K the rate constant for this reaction exhibits fall-off behavior below ~ 1000 Torr total pressure of argon or nitrogen diluent.

Analogous to the situation for the reaction of OH radicals with ethene, these kinetic data^{5,7,8,11,12} show that at temperatures $\lesssim 450$ K the reaction of the OH radical with acetylene proceeds by initial addition, with the rate constant being in the fall-off region at total pressures of less than one atmosphere. At temperatures $\gtrsim 500$ – 800 K the OH radical addition pathway becomes increasingly less important due to the increasingly important effects of fall-off with increasing temperature, and to the expectation that the thermal decomposition of the thermalized C_2H_2OH adduct will begin to become important at temperatures $\gtrsim 650$ K.¹³ Thus, at elevated temperatures representative of combustion conditions the observed reaction pathway involves H-atom abstraction¹³



TABLE 10. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with alkynes at, or close to, the high pressure limit

Alkyne	$10^{12} \times A$ (cm^3 mole- cule $^{-1}$ s $^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 molecule $^{-1}$ s $^{-1}$)	at T (K)	Technique	Reference	Tempera- ture range covered (K)
Acetylene			3.3	1700–2000	Flame-equilibrium calculations	Fenimore and Jones ¹	1700–2000
			2.0	1600	Flame-RA	Porter <i>et al.</i> ²	
	10 ($C_2H + H_2O$) ^a	3520		1000–1600	Flame-RA; product analysis	Browne <i>et al.</i> ³	1000–1600
			0.165 ± 0.015	300	FP-RF	Davis <i>et al.</i> ⁴	
			0.679 ± 0.070	298.1	FP-RF	Perry <i>et al.</i> ⁵	298–422
			0.763 ± 0.100	350.2			
	1.91	312 ± 201	0.926 ± 0.120	422.4			
	0.53 ($H + CH_2CO$) ^b	101		570–850	Flame-MS	Vandooren and Van Tiggelen ⁶	570–850
	91 ($CH_3 + CO$) ^b	6895		650–1100	Flame-MS	Vandooren and Van Tiggelen ⁶	650–1100
			0.384 ± 0.025	228	FP-RF	Michael <i>et al.</i> ⁷	228–413
			0.597 ± 0.050	257			
			0.776 ± 0.073	298			
	6.83 ± 1.19	646 ± 47	1.056 ± 0.156	362			
		1.499 ± 0.163	413				
		0.675 ± 0.070	297	FP-RF	Perry and Williamson ⁸	297–429	
		0.798 ± 0.100	429				

TABLE 10. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with alkynes at, or close to, the high pressure limit — Continued

Alkyne	$10^{12} \times A$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{molecule}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
			2.2 ± 0.5 (H + CH ₂ CO) ^b	1700–1900	Flame-MS	Bittner and Howard ⁹	1700–1900
			0.88 ± 0.11	298 ± 2	RR [relative to $k(\text{cyclohexane}) =$ $7.49 \times 10^{-12}]^c$	Atkinson and Aschmann ¹⁰	
			0.83 ± 0.08	295	LP-LIF	Schmidt <i>et al.</i> ¹¹	
			0.9^d	298 ± 3	LP-RA	Wahner and Zetzsch ¹²	
			0.09 ± 0.06^e	880 ± 60	LH-LIF	Smith <i>et al.</i> ¹³	880–1330
			0.27 ± 0.06	1140 ± 90			
			0.58 ± 0.08	1330 ± 60			
			0.81	300	RR [relative to $k(\text{propane}) =$ $1.17 \times 10^{-12}]^c$	Klöpffer <i>et al.</i> ¹⁴	
			0.87 ± 0.19	297 ± 2	RR [relative to $k(\text{cyclohexane}) =$ $7.47 \times 10^{-12}]^c$	Hatakeyama <i>et al.</i> ¹⁵	
			1.05	333	PR-RA	Liu <i>et al.</i> ¹⁶	333–1273
			1.23	353			
			1.26	363			
			1.35	373			
			1.46	393			
			1.42	423			
			1.37	478			
			1.34	518			
			1.41	573			
			1.08	673			
			0.918	723			
			0.595	773			
			0.525	873			
			0.548	973			
			0.640	1073			
			0.583	1123			
			0.687	1173			
			0.869	1223			
			1.17	1273			
Acetylene- d_2			1.26	358	PR-RA	Liu <i>et al.</i> ¹⁶	358–1173
			1.32	383			
			1.93	443			
			1.84	448			
			2.18	478			
			1.97	573			
			1.75	673			
			1.73	773			
			1.05	878			
			0.480	1073			
			0.530	1173			
Propyne			0.95 ± 0.17	300	DF-EPR	Bradley <i>et al.</i> ¹⁷	
			6.15 ± 0.30	298 ± 2	RR [relative to $k(\text{cyclohexane}) =$ $7.49 \times 10^{-12}]^c$	Atkinson and Aschmann ¹⁰	

TABLE 10. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with alkynes at, or close to, the high pressure limit

Alkyne	$10^{12} \times A$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{molecule}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference	Tempera- ture range covered (K)
			5.63 ± 0.15	297 ± 2	RR [relative to $k(\text{cyclohexane}) =$ $7.47 \times 10^{-12}]^c$	Hatakeyama <i>et al.</i> ¹⁵	
			3.73 ± 0.28	253	DF-RF	Boodaghians <i>et al.</i> ¹⁸	253–343
			3.05 ± 0.14	298			
			2.39 ± 0.12	343			
1-Butyne			8.16 ± 0.23	298 ± 2	RR [relative to $k(\text{cyclohexane}) =$ $7.49 \times 10^{-12}]^c$	Atkinson and Aschmann ¹⁰	
			6.58 ± 1.24	253	DF-RF	Boodaghians <i>et al.</i> ¹⁸	253–343
			4.95 ± 0.91	273			
			10.42 ± 1.38	300			
			8.81 ± 0.88	323			
			6.32 ± 0.93	343			
2-Butyne			29.7 ± 2.7	297 ± 2	RR [relative to $k(\text{cyclohexane}) =$ $7.47 \times 10^{-12}]^c$	Hatakeyama <i>et al.</i> ¹⁵	
			25.5 ± 1.8	253	DF-RF	Boodaghians <i>et al.</i> ¹⁸	253–343
			24.6 ± 1.9	298			
			18.9 ± 1.5	343			
1-Pentyne			9.63 ± 0.81	253	DF-RF	Boodaghians <i>et al.</i> ¹⁸	253–343
			11.17 ± 0.80	298			
			11.51 ± 0.61	343			
1-Hexyne			13.5 ± 1.1	253	DF-RF	Boodaghians <i>et al.</i> ¹⁸	253–343
			12.6 ± 0.4	298			
			12.6 ± 0.7	343			
Butadiyne (Diacetylene)			83 ± 33	1700–1900	Flame*MS	Bittner and Howard ⁹	1700–1900
			50	f	DF-RF	Homann <i>et al.</i> ¹⁹	
			16.0 ± 0.6	297 ± 2	RR [relative to $k(\text{cyclohexane}) =$ $7.47 \times 10^{-12}]^c$	Atkinson and Aschmann ²⁰	
			15.6 ± 0.2	297 ± 2	RR [relative to $k(n\text{-octane}) =$ $8.65 \times 10^{-12}]^c$	Atkinson and Aschmann ²⁰	
			22.0 ± 1.1	296	FP-RF	Perry ²¹	296–688
			19.5 ± 1.4	365			
			18.2 ± 2.0	475			
	11.1	-206 ± 151	14.5 ± 0.9	688			

^aAssumed products.^bProducts assumed; rate constants determined are dependent on the product species assumed.^cFrom the present recommendations (see text).^dRate constants of $(8.3 \pm 0.6) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $(8.1 \pm 0.7) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ were determined at total pressures of N_2 diluent of 749 Torr and 771 Torr, respectively.¹²^eRate constant extrapolated to zero pressure; rate constant of $(3.5 \pm 1.0) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ determined at 100 Torr effective pressure of N_2 .¹³^fRoom temperature, not reported.

The rate constants obtained at temperatures $\gtrsim 500$ K and those obtained at $\lesssim 500$ K which were either reported to be at, or close to, the high-pressure limit or obtained at ~ 760 Torr total pressure of argon or air are given in Table 10. In the studies of Vandooren and Van Tiggelen⁶ and Bittner and Howard,⁹ rate constants were obtained by assuming specific reaction products, involving initial OH radical addition, to be formed. The study of Bittner and Howard⁹ was carried out at sufficiently high temperatures (1700–1900 K) that the OH radical addition pathway would be of negligible importance, and hence the rate constant obtained⁹ was not utilized in this evaluation. The study of Vandooren and Van Tiggelen⁶ was carried out at a low total pressure (40 Torr) and at temperatures such that the addition channel would again be expected to be well into the fall-off region. Because of the uncertainties of the reaction pathways and the difficulties of extracting rate data from complex reaction systems, the data obtained by Vandooren and Van Tiggelen⁶ were also not used in this evaluation.

The high-pressure rate constants of Perry *et al.*,⁵ Michael *et al.*,⁷ Perry and Williamson,⁸ Atkinson and Aschmann,¹⁰ Schmidt *et al.*,¹¹ Wahner and Zetzsch,¹² Hatakeyama *et al.*,¹⁵ and Liu *et al.*¹⁶ and the elevated temperature data of Fenimore and Jones,¹ Porter *et al.*,² Browne *et al.*,³ and Smith *et al.*¹³ (including the rate constants determined at 880 K at 100 Torr total pressure and extrapolated to zero pressure)¹³ are plotted in Arrhenius form in Fig. 57.

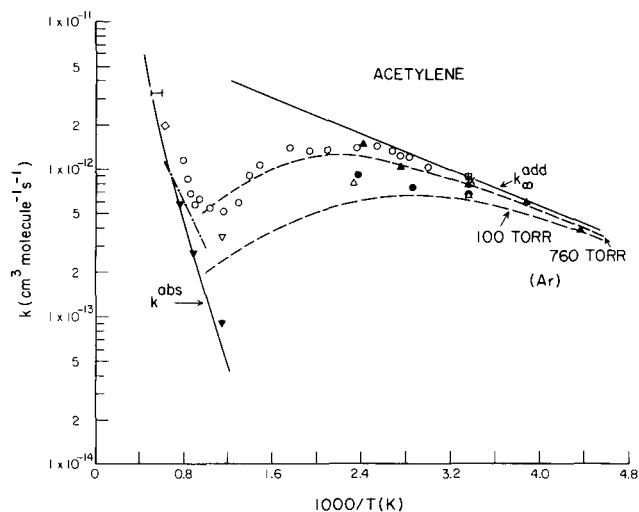


FIG. 57. Arrhenius plot of rate constants, reportedly at, or close to, the high pressure limit for argon or air diluent, for the reaction of the OH radical with acetylene. (—) Fenimore and Jones;¹ (◇) Porter *et al.*;² (---) Browne *et al.*;³ (●) Perry *et al.*;⁵ (▲) Michael *et al.*;⁷ (Δ) Perry and Williamson;⁸ (+) Atkinson and Aschmann,¹⁰ Hatakeyama *et al.*;¹⁵ (x) Schmidt *et al.*;¹¹ (□) Wahner and Zetzsch;¹² (▼) Smith *et al.*,¹³ pressure-independent (1140 K and 1330 K) or extrapolated to zero pressure (880 K); (▽) Smith *et al.*,¹³ at 100 Torr effective pressure of N₂ diluent; (○) Liu *et al.*;¹⁶ (—, — —) recommendations (see text).

The laser heating-laser induced fluorescence study of Smith *et al.*¹³ provided important information concerning the kinetics and reaction processes occurring. At 1140 and 1330 K, the rate constants obtained were observed to be independent of the total pressure,¹³ while at 880 K the rate constant increased with the diluent pressure. The observation that the rate constants at 1140 and 1330 K and the extrapolated zero pressure rate constant at 880 K increase markedly with increasing temperature (Fig. 57), in conjunction with the lower temperature data showing the rate constant to be highly pressure dependent (at least up to several hundred Torr of argon diluent) at 295–429 K^{5,7,8,11,12} and to decrease with increasing temperature over the temperature range ~ 500 –900 K at a given pressure,¹⁶ shows that the rate constants of Smith *et al.*¹³ given in Table 10 and plotted as the filled inverted triangles in Fig. 57 are those for the H-atom abstraction process. Furthermore, only at temperatures $\lesssim 1000$ K is the OH radical addition process of importance.¹³

The recent studies of Schmidt *et al.*¹¹ and Wahner and Zetzsch¹² show that the rate constants reported by Perry *et al.*⁵ and Perry and Williamson⁸ were still in the fall-off regime. The kinetic data of Schmidt *et al.*¹¹ and Wahner and Zetzsch,¹² obtained over wide pressure ranges utilizing argon and nitrogen as the diluent gases, allow the limiting low-pressure third-order rate constant k_0 and high-pressure second-order rate constant k_∞ to be derived. Based upon the study of Wahner and Zetzsch¹² with the more efficient N₂ as the diluent gas, it is recommended that

$$k_\infty(\text{acetylene}) = 9.0$$

$$\times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

From the data of Schmidt *et al.*¹¹ and Wahner and Zetzsch,¹² values of

$$k_0^{\text{Ar}}(\text{acetylene}) = 2.5 \times 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

and

$$k_0^{\text{N}_2}(\text{acetylene}) = 5.0 \times 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1},$$

both at 298 K, are recommended. These rate constants k_∞ and k_0^{Ar} , together with $F = 0.6^{11-13}$ and the Troe fall-off expression,

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

allow the experimental room temperature rate constants measured by Perry *et al.*,⁵ Michael *et al.*⁷ and Perry and Williamson⁸ to be fit reasonably well.

The temperature dependence of $k_\infty(\text{acetylene})$ can be derived from the high pressure rate constants determined by Michael *et al.*⁸ and the rate constants of Liu *et al.*¹⁶ at 760 Torr total pressure of argon. With the

above value of k_{∞} at 298 K, this leads to the recommendation of

$$k_{\infty}(\text{acetylene}) = 9.4 \times 10^{-12} e^{-700/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range ~ 230 – 500 K, and this expression is plotted in Fig. 57. While no definitive experimental data exist for the limiting low pressure rate constant k_0 at other than room temperature, a $T^{-1.5}$ dependence of k_0 allows the ~ 350 – 360 K and ~ 410 – 430 K rate constant data of Perry *et al.*,⁵ Michael *et al.*⁷ and Perry and Williamson⁸ to be duplicated well, and this temperature dependence of k_0 is very similar to that derived by Smith *et al.*¹³ from transition state calculations.

Accordingly, rate constants k_0 of

$$k_0^{Ar}(\text{acetylene}) = 2.5$$

$$\times 10^{-30} (T/298)^{-1.5} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

and

$$k_0^{N_2}(\text{acetylene}) = 5.0$$

$$\times 10^{-30} (T/298)^{-1.5} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

are recommended. With $F = 0.6$ at 298 K and $F = e^{-T/T^*} + e^{-4T^*/T}$, a value of $T^* = 580$ K is obtained.

The rate constants obtained by Schmidt *et al.*¹¹ and Wahner and Zetzsch¹² and, to a much lesser extent, by Perry *et al.*⁵ and Perry and Williamson⁸ show that any limiting low pressure bimolecular reaction is negligible at room temperature (with a rate constant of $< 8 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). This is in contrast to the data of Michael *et al.*⁷ which suggested a limiting low pressure bimolecular reaction with a rate constant of $\sim 4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 228–413 K. The reasons for this observation⁷ are not known, but the more recent data show that at temperatures $\lesssim 450$ K the OH radical reaction with acetylene proceeds entirely by OH radical addition and that the rate constant exhibits the expected fall-off behavior with no observable limiting low-pressure bimolecular component. Also plotted in Fig. 57 as the dashed lines are the addition rate constants calculated from the above values of k_{∞} , k_0^{Ar} and F for total pressures of argon diluent of 100 and 760 Torr.

For the H-atom abstraction reaction pathway, the pressure-independent rate constants measured by Smith *et al.*¹³ at 1140 and 1330 K are employed, using the expression $k = CT^2 e^{-D/T}$ with $C \sim 5 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (similar to the values of C for methane and ethene), to yield the recommendation of

$$k^{abs}(\text{acetylene}) = 4.9$$

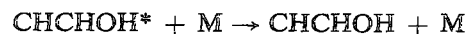
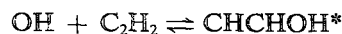
$$\times 10^{-18} T^2 e^{-3600/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range ~ 1100 – 1350 K. This expres-

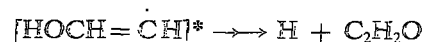
sion is also plotted in Fig. 57. It can be seen from Fig. 57 that these expressions k_{∞}^{add} , k_{Ar}^{add} (760 Torr total pressure) and k^{abs} provide a reasonably good representation of the experimental kinetic data for acetylene plotted in Fig. 57. In particular, the calculated values of k_{Ar}^{add} at 760 Torr total pressure agree reasonably well with the data obtained by Michael *et al.*⁷ (at total pressures of argon diluent varying from 10–100 Torr at 228 K to 450–1100 Torr at 413 K) and with the rate constants of Liu *et al.*¹⁶ determined at 760 Torr of argon diluent. Furthermore, the rate constant calculated for one atmosphere total pressure of air (making the reasonable assumption that O_2 and N_2 are equally efficient third-bodies) of $k = 8.15 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K agrees well with the relative rate data of Atkinson and Aschmann,¹⁰ Klöpffer *et al.*¹⁴ and Hatakeyama *et al.*¹⁵ Also relevant is the good agreement between the pressure-dependent portion of the 880 K rate constant determined by Smith *et al.*¹³ at an effective pressure of 100 Torr of N_2 of $(2.6 \pm 0.4) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and the calculated value of

$$k_{N_2}^{add}(100 \text{ Torr}) = 3.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

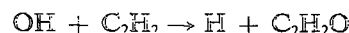
Thus, at temperatures < 650 K the OH radical reaction with acetylene is characterized by initial OH radical addition to form the initially energy-rich C_2H_2OH adduct, which can decompose back to reactants or be stabilized



A further possible decomposition pathway for the adduct is via the elimination of an H atom⁵

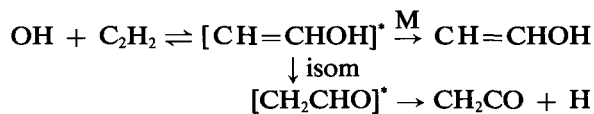


The overall reaction



is exothermic by ~ 26 kcal mole⁻¹ if the C_2H_2O product is ketene, but if the initial product formed after H-atom elimination is $HOC\equiv CH$, then the elimination reaction will be much less exothermic.⁵

The formation of C_2H_2O and C_2DHO from the reaction of OH radicals with C_2H_2 and C_2D_2 , respectively, has been observed by Gutman and co-workers²⁷ using crossed molecular beams with photoionization mass spectrometric detection. These observations indicate that this elimination reaction does occur, with the H (or D) atom eliminated originating from the acetylene.²⁷ More recently, the C_2H_2O product has been identified as ketene by Hack *et al.*²⁶ from a discharge flow-mass spectrometry study of this reaction at a total pressure of ~ 2 Torr. Under these low pressure conditions, the initially formed, energy-rich, $OH-C_2H_2$ adduct can thus either be stabilized or isomerize (presumably to the vinyloxy radical) with subsequent decomposition.²⁶



This reaction sequence explains the observed formation of CHDCO from the reactions of OH radicals with C_2D_2 ²⁷ and of OD radicals with C_2H_2 .²⁶ Recent room temperature product data at higher pressure indicates that the thermalized OH— C_2H_2 adduct can also isomerize to the vinyloxy radical.¹¹

As the temperature increases above ~ 650 K the thermal decomposition of the $\text{C}_2\text{H}_2\text{OH}$ adduct is expected to become increasingly important and, unless this adduct can rapidly react with other species (such as O_2) or undergo isomerization and decomposition to products other than the reactants, the addition pathway will become of no significance. At these elevated temperatures, the H-atom abstraction pathway will then take over, with a rate constant which increases rapidly with increasing temperature.

These expectations are borne out by the experimental data and the recommended expressions shown in Fig. 57. In particular, the study of Liu *et al.*¹⁶ may not have clearly differentiated the abstraction/addition regimes, with the OH radical addition channel contributing to the measure overall rate constants at temperatures up to ≈ 1000 K. The abstraction rate constant expression is consistent with a C—H bond strength in acetylene of $133 \text{ kcal mol}^{-1}$,²⁸ although the parameters in the recommended expression for k^{abs} are not well determined. The same is true for the temperature dependencies of the rate constants k_∞ and k_o . However, for example, values of

$$k_\infty^{\text{add}} = 9.0 \times 10^{-13} (T/298)^{1.5} \text{ or } 7.0$$

$$\times 10^{-12} e^{-610/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

do not change the calculated addition rate constants for 100 and 760 Torr total pressure of argon diluent shown in Fig. 57 to any significant extent.

(2) Acetylene- d_2

Rate constants for the reaction of the OH radical with acetylene- d_2 are available only from the pulsed radiolysis study of Liu *et al.*¹⁶ carried out at 760 Torr total pressure of argon diluent. The reaction mechanism is expected to be totally analogous to that for the reaction of OH radicals with C_2H_2 . No OD production from this reaction was observed,¹⁶ showing that scrambling in the initially formed CDCDOH radical does not occur. These data of Liu *et al.*¹⁶ are plotted in Arrhenius form in Fig. 58, together with the limiting high-pressure addition rate constant k_∞^{add} assuming (by analogy with the OH radical reactions with ethene and ethene- d_4) that

$$k_\infty^{\text{add}}(\text{acetylene-}d_2) = k_\infty^{\text{add}}(\text{acetylene}) = 9.4$$

$$\times 10^{-12} e^{-700/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

While no experimental data are available concerning the value of the low pressure third-order rate constant k_o , this rate constant for C_2D_2 is expected to be higher than that for C_2H_2 on account of the higher density of states in $\text{C}_2\text{D}_2\text{OH}$ than in $\text{C}_2\text{H}_2\text{OH}$.^{29,30} For the reactions of the OH radical with ethene and ethene- d_4 , $k_o(\text{ethene-}d_4) \approx 3 k_o(\text{ethene})$. Since there are less C—D bonds in C_2D_2 than in C_2D_4 , a ratio of $k_o(\text{acetylene-}d_2)/k_o(\text{acetylene}) \approx 2$, leading to

$$k_o^{\text{Ar}}(\text{acetylene-}d_2) = 5.0$$

$$\times 10^{-30} (T/298)^{-1.5} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1},$$

has been used to calculate the addition rate constant at 760 Torr total pressure of argon diluent, and these calculated rate constants are also plotted in Fig. 58 [use of

$$k_o^{\text{Ar}}(\text{acetylene-}d_2) = 7.5$$

$$\times 10^{-30} (T/298)^{-1.5} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

increases the addition rate constant at 760 Torr of argon by $< 10\%$ at 500 K].

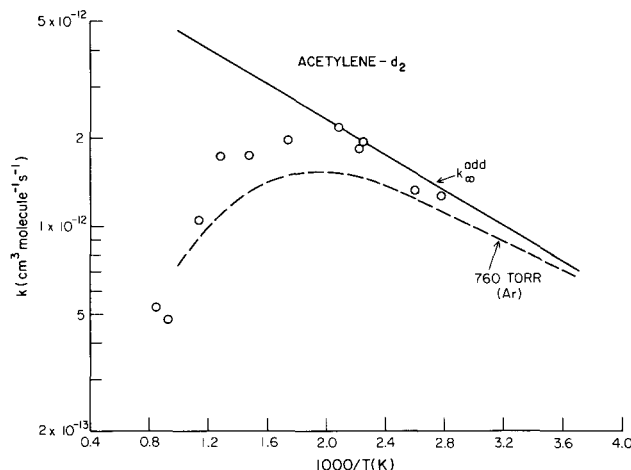
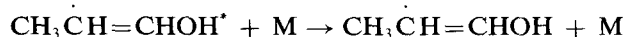


FIG. 58. Arrhenius plot of rate constants obtained at one atmosphere total pressure of argon diluent for the reaction of the OH radical with acetylene- d_2 . (O) Liu *et al.*;¹⁶ (—, — — —) recommendations (see text).

The agreement between the calculated and experimental data¹⁶ is reasonable (Fig. 58), and it is clear that further rate data need to be obtained as a function of both pressure and temperature. The H-atom abstraction rate constant will be significantly lower than that for acetylene.

(3) Propyne

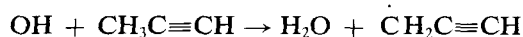
The rate constants obtained by Bradley *et al.*,¹⁷ Atkinson and Aschmann,¹⁰ Hatakeyama *et al.*¹⁵ and Boodaghians *et al.*¹⁸ are given in Table 10. These measured rate constants vary by a factor of ~ 6 at room temperature, with those studies conducted at lower total pressures yielding the lower rate constants. It is thus likely that this reaction, which is expected to proceed by OH radical addition,



is in the fall-off region at the total pressures characteristic of discharge flow system studies, although Boodaghians *et al.*¹⁸ did not observe any effect of pressure on the room temperature rate constant over the total pressure range 1.7–6.4 Torr of helium diluent. That the data of Boodaghians *et al.*¹⁸ for propyne are in the fall-off regime is supported by the good agreement of their data for 1- and 2-butyne, the more complex alkynes, with the relative rate data of Atkinson and Aschmann¹⁰ and Hatakeyama *et al.*¹⁵ obtained at ~ 750 Torr total pressure of air. Accordingly, a unit-weighted average of the atmospheric pressure rate constants of Atkinson and Aschmann¹⁰ and Hatakeyama *et al.*¹⁵ leads to the recommendation of

$$k(\text{propyne}) = 5.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty of $\pm 40\%$. As for acetylene and acetylene- d_2 , at elevated temperatures (≥ 800 – 1000 K) this reaction of the OH radical with propyne is expected to change over from OH radical addition to H-atom abstraction, mainly from the $-\text{CH}_3$ group:



(4) 1-Butyne

The rate constants obtained by Atkinson and Aschmann¹⁰ and Boodaghians *et al.*¹⁸ are given in Table 10 and are plotted in Arrhenius form in Fig. 59. While the data of Boodaghians *et al.*¹⁸ as a function of temperature exhibit a significant degree of scatter, they are consistent with the room temperature rate constant of Atkinson and Aschmann.¹⁰ This presumably indicates that for 1-butyne the OH radical addition reaction is at, or close to, the high pressure limit at total pressures of a few Torr at around room temperature. Based upon these rate constants of Atkinson and Aschmann¹⁰ and Boodaghians *et al.*,¹⁸ it is recommended that

$$k(1\text{-butyne}) = 8.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

independent of temperature over the range 253–343 K, with an estimated overall uncertainty of $\pm 30\%$ at 298 K.

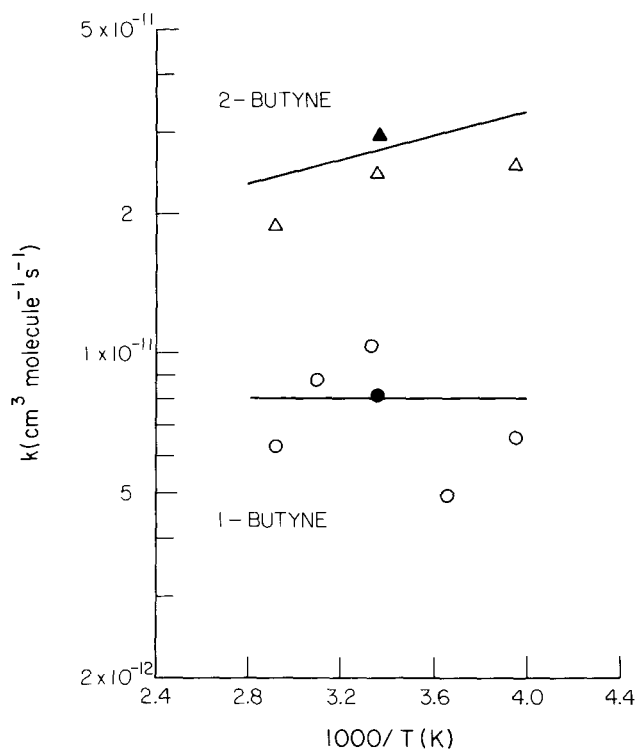


FIG. 59. Arrhenius plots of rate constants for the reactions of the OH radical with 1-butyne and 2-butyne. (●) Atkinson and Aschmann¹⁰ (1-butyne); (▲) Hatakeyama *et al.*¹⁵ (2-butyne); (○, Δ) Boodaghians *et al.*,¹⁸ (—) recommendations (see text).

(5) 2-Butyne

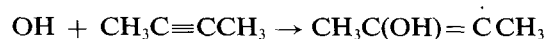
The rate constants obtained by Hatakeyama *et al.*¹⁵ and Boodaghians *et al.*¹⁸ are given in Table 10 and are plotted in Arrhenius form in Fig. 59. The agreement at room temperature is reasonable, and a unit-weighted average of the room temperature rate constants of Hatakeyama *et al.*¹⁵ and Boodaghians *et al.*,¹⁸ combined with the temperature dependence of Boodaghians *et al.*,¹⁸ leads to the tentative recommendation of

$$k(2\text{-butyne}) = 1.0 \times 10^{-11} e^{(300 \pm 300)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 253–343 K, and

$$k(2\text{-butyne}) = 2.74 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty at 298 K of $\pm 35\%$. As for 1-propyne and 1-butyne, at around room temperature this OH radical reaction with 2-butyne is expected to proceed by OH radical addition,



with the reaction being at, or close to, the high pressure limit at total pressures of a few Torr.

(6) Butadiyne

The rate constants of Bittner and Howard,⁹ Homann *et al.*,¹⁹ Atkinson and Aschmann²⁰ and Perry²¹ are given in Table 10 and are plotted in Arrhenius form in Fig. 60.

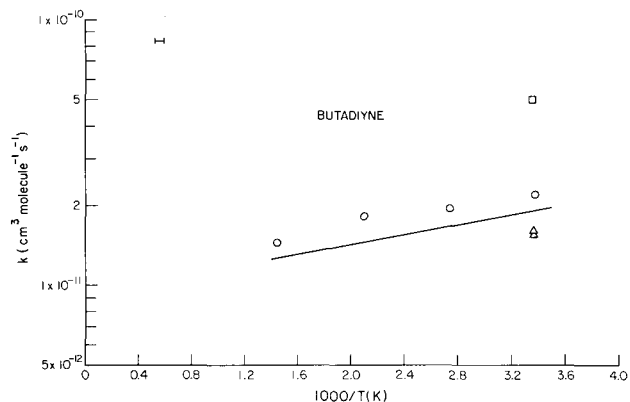


FIG. 60. Arrhenius plot of rate constants for the reaction of the OH radical with butadiyne. (—) Bittner and Howard,⁹ (□) Homann *et al.*,¹⁹ assuming a temperature of 298 K; (Δ) Atkinson and Aschmann;²⁰ (○) Perry;²¹ (—) recommendation (see text).

At room temperature the reported rate constants of Homann *et al.*,¹⁹ Atkinson and Aschmann²⁰ and Perry²¹ disagree by a factor of ~3. This reaction will proceed by OH radical addition at temperatures $\lesssim 700$ K, and the temperature dependence measured by Perry²¹ is consistent with such an OH radical addition process, which is expected to be at the high pressure limit at total pressures of a few Torr. The data obtained by Perry²¹ and Atkinson and Aschmann²⁰ at room temperature disagree by ~35%, for reasons which are not presently understood, although the rate constants obtained by Atkinson and Aschmann²⁰ using two different reference organics are in excellent agreement. The recommended room temperature rate constant of

$$k(\text{butadiyne}) = 1.89 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty of $\pm 40\%$, is a unit-weighted average of the room temperature rate constants from these studies,^{20,21} using an average rate constant of $1.58 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the Atkinson and Aschmann²⁰ study. The temperature dependence obtained by Perry²¹ has been combined with

this 298 K value to yield the recommendation of

$$k(\text{butadiyne}) = 9.45 \times 10^{-12} e^{206/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 296–688 K.

No recommendation is made for temperatures > 700 K.

(7) Other Alkynes

Boodaghians *et al.*¹⁸ have obtained rate constant data for 1-pentyne and 1-hexyne. Since these are the only available data, no recommendations are made.

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2.6. Oxygen-Containing Organics

a. Kinetics and Mechanisms

The available kinetic data are given in Tables 11 (OH radical reactions) and 12 (OD radical reactions), and are discussed below by class of oxygenate. The experimental data concerning the mechanisms of these reactions are discussed for the individual oxygenates.

(1) Aldehydes

(a) Formaldehyde, Formaldehyde-¹³C and Formaldehyde-d₁

The available kinetic data are given in Table 11. The rate constants obtained by Hoare,^{1,5} Baldwin and Cowe,² Blundell *et al.*,³ Westenberg and Fristrom,⁴ Hoare and Peacock,⁶ Morris and Niki,^{8,9} Peeters and Mahnen,¹⁰

Vandooren and Van Tiggelen,¹¹ Niki *et al.*,¹² Atkinson and Pitts,¹³ Stief *et al.*,¹⁵ Temps and Wagner¹⁶ and Zabarnick *et al.*¹⁷ for ¹²CH₂O and of Niki *et al.*¹⁸ for ¹³CH₂O are plotted in Arrhenius form in Fig. 61. A significant amount of scatter in these data is evident. Since the rate constant for the self reaction of OH radicals is subject to significant uncertainties,¹⁰⁵ the rate constants derived from the study of Smith¹⁴ are not plotted in Fig. 61 and are not used in the evaluation of the rate constant for this reaction.

It can be seen from Fig. 61 that the rate constant for this reaction appears to be approximately independent of temperature over the range ~230–500 K, but that at temperatures >500 K the rate constant increases with increasing temperature. At around room temperature, absolute rate constants have been determined by Morris and Niki,⁸ Atkinson and Pitts,¹³ Stief *et al.*,¹⁵ Temps and Wagner¹⁶ and Zabarnick *et al.*¹⁷ Again, a significant amount of scatter is observed, with Morris and Niki⁸ and Zabarnick *et al.*¹⁷ obtaining rate constants of $(1.2\text{--}1.4) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, Atkinson and Pitts¹³ and Stief *et al.*¹⁵ rate constants of $(9.4\text{--}9.9) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and Temps and Wagner¹⁶ a rate constant of $8.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. At elevated temperatures, there are again significant discrepancies, especially between the various studies of Hoare and co-workers^{1,3,5,6} and that of Baldwin and Cowe,² and between those of Zabarnick *et al.*¹⁷ and Vandooren and Van Tiggelen¹¹ (the rate constants from this study¹¹ being dependent upon those for the self reaction of OH radicals and the reaction of OH radicals with H₂, and cannot be reevaluated). Interestingly, the rate constants obtained from the flame studies of Westenberg and Fristrom⁴ and Peeters and Mahnen¹⁰ are in good agreement as to the magnitude of the rate constant at ~1400 K.

TABLE 11. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with oxygen-containing organics

Oxygenate	$10^{12} \times A$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	n	B (K)	$10^{12} \times k$ (cm^3 $\text{molecule}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
<i>Aldehydes</i>								
Formaldehyde				28 ± 8	773	RR [relative to $k(\text{CH}_4) = 6.95 \times 10^{-18}$ $T^3 e^{-1282/T}$] ^a	Hoare ¹	773–923
				29	798			
				33	873			
				33	923			
				47	813	RR [relative to $k(\text{H}_2)$ $= 1.12 \times 10^{-12}$] ^b	Baldwin and Cowe ²	
				26 ± 3	773	RR [relative to $k(\text{CH}_4)$ $= 7.91 \times 10^{-13}$] ^a	Blundell <i>et al.</i> ³	
	~880		~4265		1250–1400	RR [relative to $k(\text{CO})$ $= 1.12 \times$ $10^{-13} e^{0.000907T}$] ^b	Westenberg and Fristrom ⁴	1250–1400

TABLE 11. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with oxygen-containing organics — Continued

Oxygenate	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	n	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
				25	723	RR [relative to $k(\text{CH}_4)$ $= 6.95 \times 10^{-18}$ $T^2 e^{-1282/T}]^a$	Hoare ⁵	723–923
				29	798			
				33	923			
				25	798	RR [relative to $k(\text{CH}_4)$ $= 8.88 \times 10^{-13}]^a$	Hoare and Peacock ⁶	
				14	798	RR [relative to $k(\text{C}_2\text{H}_6)$ $= 5.07 \times 10^{-12}]^a$	Hoare and Peacock ⁶	
				≥ 6.6	300	DF-MS	Herron and Penzhorn ⁷	
				14 ± 3.5	298	DF-MS	Morris and Niki ⁸	
				15.3	298	DF-MS	Morris and Niki ⁹	
			~ 500	42	1600	Flame-MS	Peeters and Mahnen ¹⁰	1400–1800
				17	485	Flame-MS	Vandooren and Van Tiggelen ¹¹	485–570
				22	570			
				15.8 ± 0.9	298 ± 2	RR [relative to $k(\text{ethene-}d_4) =$ $8.78 \times 10^{-12}]^c$	Niki <i>et al.</i> ¹²	
				9.4 ± 1.0	299.3	FP-RF	Atkinson and Pitts ¹³	299–426
				9.4 ± 1.0	356.5			
	12.5		88 ± 151	10.3 ± 1.1	426.4			
				5.5 ± 0.7	268	DF-MS [relative to $k(\text{OH} + \text{OH}) =$ $4.2 \times 10^{-12} e^{-240/T}]^d$	Smith ¹⁴	268–334
				5.5 ± 0.7	298			
				7.4 ± 1.0	334			
				11.22 ± 0.98	228	FP-RF	Stief <i>et al.</i> ¹⁵	228–362
				10.28 ± 0.90	257			
				9.86 ± 1.13	298			
	10.5 ± 1.1		0	10.46 ± 1.50	362			
				8.1 ± 1.7	296	DF-LMR	Temps and Wagner ¹⁶	
				10.7 ± 1.3	296	LP-LIF	Zabarnick <i>et al.</i> ¹⁷	296–576
				12.5 ± 0.5	297			
				11.4 ± 0.6	297			
				13.6 ± 1.0	297			
				13.2 ± 0.4	298			
				13.1 ± 0.4	298			
				13.7 ± 0.5	299			
				12.0 ± 0.3	301			
				13.9 ± 0.4	378			
				13.3 ± 0.3	473			
				11.4 ± 0.5	567			
				15.8 ± 1.2	572			
				14.1 ± 0.5	574			
	16.6 ± 2.0		86 ± 40	16.7 ± 0.8	576			
Formaldehyde- ¹³ C				8.40 ± 0.51	299 ± 2	RR [relative to $k(\text{ethene}) =$ $8.48 \times 10^{-12}]^a$	Niki <i>et al.</i> ¹⁸	
Formaldehyde- d_1				~ 14	298	DF-MS	Morris and Niki ⁸	
Acetaldehyde				15 ± 3.8	300	DF-MS	Morris <i>et al.</i> ¹⁹	

TABLE 11. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with oxygen-containing organics — Continued

Oxygenate	$10^{12} \times A$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	n	B (K)	$10^{12} \times k$ (cm^3 $\text{molecule}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
				15.3	298	DF-MS	Morris and Niki ⁹	
				≤ 14	295 ± 2	RR [relative to $k(\text{HONO})$ $= 4.80 \times 10^{-12}]^b$	Cox <i>et al.</i> ²⁰	
				≥ 3.0	1100	RR [relative to $k(\text{CO})$ $= 3.04 \times 10^{-13}]^b$	Colket <i>et al.</i> ²¹	
				16.2 ± 1.8	298 ± 2	RR [relative to $k(\text{ethene}) =$ $8.52 \times 10^{-12}]^a$	Niki <i>et al.</i> ¹²	
				16.0 ± 1.6	299.4	FP-RF	Atkinson and Pitts ¹³	299–426
				14.4 ± 1.5	355.0			
6.87			-257 ± 151	12.4 ± 1.3	426.1			
				12.8 ± 4.3	298 ± 4	RR [relative to $k(\text{ethene}) =$ $8.52 \times 10^{-12}]^a$	Kerr and Sheppard ²²	
				14.0 ± 3.1	253	FP-RF	Semmes <i>et al.</i> ²³	253–424
				12.2 ± 2.7	298			
				10.7 ± 2.3	356			
7.1 ± 0.2			-165 ± 91	11.0 ± 2.3	424			
				21.0 ± 1.4	244	DF-RF	Michael <i>et al.</i> ²⁴	244–528
				19.2 ± 0.6	244			
				18.9 ± 1.4	259			
				17.9 ± 1.2	259			
				15.6 ± 0.8	273			
				16.3 ± 1.2	273			
				17.8 ± 0.6	273			
				19.6 ± 1.2	273			
				14.2 ± 1.0	298			
				14.7 ± 2.8	298			
				13.0 ± 1.2	333			
				14.0 ± 0.8	355			
				14.0 ± 0.4	367			
				14.3 ± 1.0	367			
				15.0 ± 1.0	373			
				11.6 ± 0.6	393			
				11.7 ± 0.8	420			
				10.6 ± 0.6	424			
				11.0 ± 0.6	433			
				11.5 ± 0.8	466			
				10.4 ± 0.4	468			
				10.4 ± 0.4	492			
				9.2 ± 1.4	499			
5.52 ± 0.80			-307 ± 52	9.9 ± 0.4	528			
Glycolaldehyde [HOCH ₂ CHO]				9.9 ± 1.0	298 ± 2	RR [relative to $k(\text{acetaldehyde}) =$ $1.58 \times 10^{-11}]^a$	Niki <i>et al.</i> ²⁵	
1-Propanal				5.2	713	RR [relative to $k(\text{CO}) = 2.14 \times 10^{-13}]^b$	Baldwin <i>et al.</i> ²⁶	
				30.6	298	DF-MS	Morris and Niki ⁹	
				22.2 ± 0.9	298 ± 2	RR [relative to $k(\text{ethene}) =$ $8.52 \times 10^{-12}]^a$	Niki <i>et al.</i> ¹²	

TABLE 11. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with oxygen-containing organics — Continued

Oxygenate	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	n	B (K)	$10^{12} \times k$ (cm^3 $\text{molecule}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
				19.4 ± 1.5	298 ± 4	RR [relative to $k(\text{ethene}) =$ $8.52 \times 10^{-12}]^a$	Kerr and Sheppard ²²	
				18.0 ± 2.1	298	RR [relative to $k(\text{acetaldehyde}) =$ $1.58 \times 10^{-11}]^a$	Audley <i>et al.</i> ²⁷	
				≤ 30	553	RR [relative to $k(\text{trans-2-butene}) =$ $2.73 \times 10^{-11}]^a$	Kaiser ²⁸	
				17.1 ± 2.4	298	FP-RF	Semmes <i>et al.</i> ²³	
				≤ 28	296	RR [relative to $k(\text{HONO}) =$ $4.82 \times 10^{-12}]^b$	Kerr and Stocker ²⁹	
1-Butanal [$\text{CH}_3(\text{CH}_2)_2\text{CHO}$]				25.2 ± 0.6	298 ± 4	RR [relative to $k(\text{ethene}) =$ $8.52 \times 10^{-12}]^a$	Kerr and Sheppard ²²	
				25.6 ± 3.2	298	RR [relative to $k(\text{acetaldehyde}) =$ $1.58 \times 10^{-11}]^a$	Audley <i>et al.</i> ²⁷	
				30.8 ± 4.2	258	FP-RF	Semmes <i>et al.</i> ²³	258–422
				20.6 ± 3.0	298			
				18.2 ± 2.6	361			
	5.7 ± 0.3		-411 ± 164	15.4 ± 2.3	422			
2-Methyl- 1-propanal [$(\text{CH}_3)_2\text{CHCHO}$]				29.0 ± 5.7	298 ± 4	RR [relative to $k(\text{ethene}) =$ $8.52 \times 10^{-12}]^a$	Kerr and Sheppard ²²	
				17.7 ± 2.1	298	RR [relative to $k(\text{acetaldehyde}) =$ $1.58 \times 10^{-11}]^a$	Audley <i>et al.</i> ²⁷	
				33.4 ± 4.5	255	FP-RF	Semmes <i>et al.</i> ²³	255–423
				24.2 ± 3.3	298			
				19.7 ± 2.7	354			
	6.8 ± 0.3		-393 ± 125	18.2 ± 2.7	423			
1-Pentanal [$\text{CH}_3(\text{CH}_2)_3\text{CHO}$]				27.6 ± 4.2	298 ± 4	RR [relative to $k(\text{ethene}) =$ $8.52 \times 10^{-12}]^a$	Kerr and Sheppard ²²	
				13.9 ± 1.8	298	RR [relative to $k(\text{acetaldehyde}) =$ $1.58 \times 10^{-11}]^a$	Audley <i>et al.</i> ²⁷	
				38.9 ± 5.7	253	FP-RF	Semmes <i>et al.</i> ²³	253–410
				26.9 ± 3.9	298			
				23.3 ± 3.4	355			
	6.3 ± 0.2		-451 ± 108	19.0 ± 2.8	410			
3-Methyl- 1-butanol [$(\text{CH}_3)_2\text{CHCH}_2\text{CHO}$]				28.9 ± 0.9	298 ± 4	RR [relative to $k(\text{ethene}) =$ $8.52 \times 10^{-12}]^a$	Kerr and Sheppard ²²	
				18.6 ± 2.1	298	RR [relative to $k(\text{acetaldehyde}) =$ $1.58 \times 10^{-11}]^a$	Audley <i>et al.</i> ²⁷	

TABLE 11. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with oxygen-containing organics — Continued

Oxygenate	$10^{12} \times A$ ($\text{cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$)	n	B (K)	$10^{12} \times k$ (cm^3 $\text{molecule}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
				25.8 ± 4.0	298	FP-RF	Semmes <i>et al.</i> ²³	
2,2-Dimethyl- 1-propanal [(CH_3) ₂ CCHO]				22.4 ± 6.3	298 ± 4	RR [relative to $k(\text{ethene}) =$ 8.52×10^{-12}] ^a	Kerr and Sheppard ²²	
				8.53 ± 0.95	298	RR [relative to $k(\text{acetaldehyde}) =$ 1.58×10^{-11}] ^a	Audley <i>et al.</i> ²⁷	
				33.9 ± 6.4	254	FP-RF	Semmes <i>et al.</i> ²³	254–425
				30.6 ± 4.4	298			
				21.8 ± 3.1	354			
	6.7 ± 0.3		-423 ± 154	17.6 ± 2.9	425			
Benzaldehyde [$\text{C}_6\text{H}_5\text{CHO}$]				14.0 ± 0.9	298 ± 2	RR [relative to $k(\text{ethene-}d_4) =$ 8.78×10^{-12}] ^c	Niki <i>et al.</i> ¹²	
				11.8 ± 2.3	298 ± 4	RR [relative to $k(\text{ethene}) =$ 8.52×10^{-12}] ^a	Kerr and Sheppard ²²	
CCl_3CHO				1.73	298 ± 3	RR [relative to $k(\text{ethyl acetate}) =$ 1.6×10^{-12}] ^a	Nelson <i>et al.</i> ³⁰	
CH_3CClO				0.068	298 ± 3	RR [relative to $k(\text{trichloromethane}) =$ 1.03×10^{-13}] ^a	Nelson <i>et al.</i> ³⁰	
<i>Ketones</i>								
Acetone				≤ 0.53	300	RR [relative to $k(\text{ethene}) =$ 8.44×10^{-12}] ^a	Cox <i>et al.</i> ³¹	
				0.23 ± 0.03	300	FP-RF	Zetzsch ³²	
				0.63 ± 0.09	298	RR [relative to $k(n\text{-hexane}) =$ 5.61×10^{-12}] ^a	Chiorboli <i>et al.</i> ³³	
				0.27 ± 0.01	303 ± 2	RR [relative to $k(\text{ethene}) =$ 8.32×10^{-12}] ^a	Kerr and Stocker ³⁴	
				0.145 ± 0.015	240	FP-RF	Wallington and Kurylo ³⁵	240–440
				0.216 ± 0.016	296			
				0.292 ± 0.023	350			
				0.407 ± 0.030	400			
	1.7 ± 0.4		600 ± 75	0.436 ± 0.050	440			
2-Butanone				3.5 ± 1.0	305 ± 2	RR [relative to $k(2\text{-methylpropene}) =$ 4.94×10^{-11}] ^a	Winer <i>et al.</i> ³⁶	
				2.74	300	RR [relative to $k(\text{ethene}) =$ 8.44×10^{-12}] ^a	Cox <i>et al.</i> ³¹	
				0.95 ± 0.09	295 ± 2	RR [relative to $k(\text{ethene}) =$ 8.65×10^{-12}] ^a	Cox <i>et al.</i> ³⁷	

TABLE 11. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with oxygen-containing organics — Continued

Oxygenate	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	n	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
				1.2 ± 0.2	300	FP-RF	Zetzsch ³²	
				0.97 ± 0.17	297	RR [relative to $k(\text{propane}) =$ $1.14 \times 10^{-12}]^a$	Edney <i>et al.</i> ³⁸	
				1.23 ± 0.10	240	FP-RF	Wallington and Kurylo ³⁵	240–440
				1.15 ± 0.10	296			
				1.41 ± 0.09	350			
				1.55 ± 0.07	400			
	2.3 ± 1.1		170 ± 120	1.65 ± 0.09	440			
2-Pentanone				4.70 ± 0.14	299 ± 2	RR [relative to $k(\text{cyclohexane}) =$ $7.51 \times 10^{-12}]^a$	Atkinson <i>et al.</i> ³⁹	
				4.00 ± 0.29	296	FP-RF	Wallington and Kurylo ³⁵	
				5.07 ± 0.26	296 ± 2	RR [relative to $k(\text{cyclohexane}) =$ $7.45 \times 10^{-12}]^a$	Atkinson and Aschmann ⁴⁰	
3-Pentanone				1.84 ± 0.34	299 ± 2	RR [relative to $k(\text{cyclohexane}) =$ $7.51 \times 10^{-12}]^a$	Atkinson <i>et al.</i> ³⁹	
				2.85 ± 0.17	240	FP-RF	Wallington and Kurylo ³⁵	240–440
				2.74 ± 0.13	296			
				2.91 ± 0.17	350			
				2.79 ± 0.32	400			
	2.8 ± 0.3		-10 ± 35	2.78 ± 0.40	440			
				2.09 ± 0.15	296 ± 2	RR [relative to $k(\text{cyclohexane}) =$ $7.45 \times 10^{-12}]^a$	Atkinson and Aschmann ⁴⁰	
2-Hexanone				9.09 ± 0.61	299 ± 2	RR [relative to $k(\text{cyclohexane}) =$ $7.51 \times 10^{-12}]^a$	Atkinson <i>et al.</i> ³⁹	
				6.64 ± 0.56	296	FP-RF	Wallington and Kurylo ³⁵	
				9.09 ± 0.45	296 ± 2	RR [relative to $k(\text{cyclohexane}) =$ $7.45 \times 10^{-12}]^a$	Atkinson and Aschmann ⁴⁰	
3-Hexanone				6.90 ± 0.29	299 ± 2	RR [relative to $k(\text{cyclohexane}) =$ $7.51 \times 10^{-12}]^a$	Atkinson <i>et al.</i> ³⁹	
4-Methyl- 2-pentanone				15 ± 5	305 ± 2	RR [relative to $k(2\text{-methylpropene}) =$ $4.94 \times 10^{-11}]^a$	Winer <i>et al.</i> ³⁶	
				13.1	300	RR [relative to $k(\text{ethene}) =$ $8.44 \times 10^{-12}]^a$	Cox <i>et al.</i> ³¹	
				13.9 ± 0.4	295 ± 2	RR [relative to $k(\text{ethene}) =$ $8.65 \times 10^{-12}]^a$	Cox <i>et al.</i> ³⁷	

TABLE 11. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with oxygen-containing organics — Continued

Oxygenate	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	n	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
				14.3 ± 0.7	299 ± 2	RR [relative to $k(\text{cyclohexane})$ $= 7.51 \times 10^{-12}]^a$	Atkinson <i>et al.</i> ³⁹	
3,3-Dimethyl- 2-butanone				1.21 ± 0.05	296	FP-RF	Wallington and Kurylo ³⁵	
2-Heptanone				8.67 ± 0.84	296	FP-RF	Wallington and Kurylo ³⁵	
2,4-Dimethyl- 3-pentanone				5.38 ± 0.41	299 ± 2	RR [relative to $k(\text{cyclohexane})$ $= 7.51 \times 10^{-12}]^a$	Atkinson <i>et al.</i> ³⁹	
2-Octanone				11.0 ± 0.9	296	FP-RF	Wallington and Kurylo ³⁵	
2-Nonanone				12.2 ± 1.3	296	FP-RF	Wallington and Kurylo ³⁵	
2,6-Dimethyl- 4-heptanone				25 ± 8	305 ± 2	RR [relative to $k(2\text{-methylpropene})$ $= 4.94 \times 10^{-11}]^a$	Winer <i>et al.</i> ³⁶	
				27.5 ± 1.5	299 ± 2	RR [relative to $k(\text{cyclohexane})$ $= 7.51 \times 10^{-12}]^a$	Atkinson <i>et al.</i> ³⁹	
2-Decanone				13.2 ± 1.2	296	FP-RF	Wallington and Kurylo ³⁵	
Cyclobutanone				0.87 ± 0.06	298	FP-RF	Dagaut <i>et al.</i> ⁴¹	
Cyclopentanone				2.94 ± 0.18	298	FP-RF	Dagaut <i>et al.</i> ⁴¹	
Cyclohexanone				6.39 ± 0.51	298	FP-RF	Dagaut <i>et al.</i> ⁴¹	
<i>α, β-Unsaturated Carbonyls</i>								
Acrolein [$\text{CH}_2=\text{CHCHO}$]				25.4 ± 3.2	298 ± 2	RR [relative to $k(n\text{-butane}) =$ $2.54 \times 10^{-12}]^a$	Maldotti <i>et al.</i> ⁴²	
				20.3 ± 2.4	298 ± 4	RR [relative to $k(\text{ethene}) =$ $8.52 \times 10^{-12}]^a$	Kerr and Sheppard ²²	
				19.0 ± 1.4	299 ± 2	RR [relative to $k(\text{propene}) =$ $2.62 \times 10^{-11}]^a$	Atkinson <i>et al.</i> ⁴³	
				20.4 ± 0.1	297	RR [relative to $k(\text{propene}) =$ $2.65 \times 10^{-11}]^a$	Edney <i>et al.</i> ³⁸	
Crotonaldehyde [<i>trans</i> - $\text{CH}_3\text{CH}=\text{CHCHO}$]				35.1 ± 6.9	298 ± 4	RR [relative to $k(\text{ethene}) =$ $8.52 \times 10^{-12}]^a$	Kerr and Sheppard ²²	
				36.4 ± 4.2	299 ± 2	RR [relative to $k(\text{propene}) =$ $2.62 \times 10^{-11}]^a$	Atkinson <i>et al.</i> ⁴³	
Methacrolein [$\text{CH}_2=\text{C}(\text{CH}_3)\text{CHO}$]				31.4 ± 4.9	300	FP-RF	Kleindienst <i>et al.</i> ⁴⁴	300-423
				29.9 ± 4.8	350			
	17.7		-175 ± 52	26.5 ± 3.9	423			

TABLE 11. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with oxygen-containing organics — Continued

Oxygenate	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	n	B (K)	$10^{12} \times k$ (cm^3 $\text{molecule}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
				29.6 ± 2.4	299 ± 2	RR [relative to $k(\text{propene}) =$ $2.62 \times 10^{-11}]^a$	Atkinson <i>et al.</i> ⁴³	
				39.2 ± 3.1	298	RR [relative to $k(\text{propene}) =$ $2.63 \times 10^{-11}]^a$	Edney <i>et al.</i> ³⁸	
Methyl vinyl ketone [$\text{CH}_2=\text{CHCOCH}_3$]				14.8	300	RR [relative to $k(\text{ethene}) =$ $8.44 \times 10^{-12}]^a$	Cox <i>et al.</i> ³¹	
				17.9 ± 2.8	298	FP-RF	Kleindienst <i>et al.</i> ⁴⁴	298–424
				13.5 ± 2.4	350			
	3.85		-456 ± 73	11.4 ± 2.1	424			
				19.6 ± 1.5	299 ± 2	RR [relative to $k(\text{propene}) =$ $2.62 \times 10^{-11}]^a$	Atkinson <i>et al.</i> ⁴³	
<i>Ketenes</i>								
Ketene [$\text{CH}_2=\text{CO}$]			0	46.5	480–1000	Flame-MS	Vandooren and Van Tiggelen ¹¹	480–1000
				> 1.7	295	RR [relative to $k(\text{C}_3\text{O}_2) = 1.4 \times 10^{-12}]^e$	Faubel <i>et al.</i> ⁴⁵	
				17.3 ± 2.3	299 ± 2	RR [relative to $k(\text{cyclohexane}) =$ $7.51 \times 10^{-12}]^a$	Hatakeyama <i>et al.</i> ⁴⁶	
Methylketene [$\text{CH}_3\text{CH}=\text{CO}$]				60 ± 13	299 ± 2	RR [relative to $k(\text{cyclohexane}) =$ $7.51 \times 10^{-12}]^a$	Hatakeyama <i>et al.</i> ⁴⁶	
				79 ± 14	299 ± 2	RR [relative to $k(\text{propene}) =$ $2.62 \times 10^{-11}]^a$	Hatakeyama <i>et al.</i> ⁴⁶	
Ethylketene [$\text{C}_2\text{H}_5\text{CH}=\text{CO}$]				118 ± 29	299 ± 2	RR [relative to $k(\text{propene}) =$ $2.62 \times 10^{-11}]^a$	Hatakeyama <i>et al.</i> ⁴⁶	
Dimethylketene [$(\text{CH}_3)_2\text{C}=\text{CO}$]				107 ± 29	299 ± 2	RR [relative to $k(\text{propene}) =$ $2.62 \times 10^{-11}]^a$	Hatakeyama <i>et al.</i> ⁴⁶	
<i>Dicarbonyls</i>								
Glyoxal [$(\text{CHO})_2$]				11.4 ± 0.4	298 ± 2	RR [relative to $k(\text{cyclohexane}) =$ $7.49 \times 10^{-12}]^a$	Plum <i>et al.</i> ⁴⁷	
				14.2 ± 2.1	298 ± 2	RR [relative to $k(\text{cyclohexane}) =$ $7.49 \times 10^{-12}]^a$	Becker and Klein ⁴⁸	
Methylglyoxal [CH_3COCHO]				7.1 ± 1.6	297	FP-RF	Kleindienst <i>et al.</i> ⁴⁴	
				17.2 ± 1.2	298 ± 2	RR [relative to $k(\text{cyclohexane}) =$ $7.49 \times 10^{-12}]^a$	Plum <i>et al.</i> ⁴⁷	

TABLE 11. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with oxygen-containing organics — Continued

Oxygenate	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	n	B (K)	$10^{12} \times k$ (cm^3 $\text{molecule}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)				
2,3-Butanedione	1.12 ± 0.65		450 ± 90	$0.24^{+0.08}_{-0.06}$	298	FP-RF	Darnall <i>et al.</i> ⁴⁹					
				0.19 ± 0.02	240	FP-RF	Dagaut <i>et al.</i> ⁴¹	240-440				
				0.23 ± 0.02	298							
				0.26 ± 0.02	350							
				0.39 ± 0.02	400							
Pentane-1,5-dial [CHO(CH ₂) ₃ CHO]				25.2 ± 1.1	298 ± 3	RR [relative to $k(\text{propene}) =$ $2.63 \times 10^{-11}]^a$	Rogers ⁵⁰					
				22.4 ± 1.1	298 ± 3	RR [relative to $k(\text{trans-2-butene}) =$ $6.40 \times 10^{-11}]^a$	Rogers ⁵⁰					
2,4-Pentanedione				1.15 ± 0.15	298	FP-RF	Dagaut <i>et al.</i> ⁴¹					
2,5-Hexanedione	1.49 ± 0.43		-450 ± 90	9.4 ± 1.2	240	FP-RF	Dagaut <i>et al.</i> ⁴¹	240-440				
				7.13 ± 0.34	298							
				5.07 ± 0.47	350							
				4.29 ± 0.38	400							
				4.35 ± 0.53	440							
<i>Unsaturated 1,4-Dicarbonyls</i>												
<i>cis</i> -3-Hexene- 2,5-dione				63.1 ± 6.1	298 ± 2	RR [relative to $k(\text{propene}) =$ $2.63 \times 10^{-11}]^a$	Tuazon <i>et al.</i> ⁵¹					
<i>trans</i> -3-Hexene- 2,5-dione				53.1 ± 2.4	298 ± 2	RR [relative to $k(\text{propene}) =$ $2.63 \times 10^{-11}]^a$	Tuazon <i>et al.</i> ⁵¹					
<i>Alcohols</i>												
Methanol				1.01 ± 0.11	292	RR [relative to $k(n\text{-butane}) =$ $2.47 \times 10^{-12}]^a$	Campbell <i>et al.</i> ⁵²					
				1.06 ± 0.10	296 ± 2	FP-RA	Overend and Paraskevopoulos ⁵³					
				1.00 ± 0.10	298	FP-RF	Ravishankara and Davis ⁵⁴					
				80	2265	1000-2000	Flame-MS	Vandooren and Van Tiggelen ⁵⁵	1000-2000			
								1.10	300	RR [relative to $k(\text{ethene}) =$ $8.44 \times 10^{-12}]^a$	Barnes <i>et al.</i> ⁵⁶	
								0.75 ± 0.15	293	LP-RF	Hägele <i>et al.</i> ⁵⁷	293-420
								0.94 ± 0.19	294			
								0.71 ± 0.15	295			
								0.97 ± 0.20	324			
								1.33 ± 0.27	372			
12 ± 3	810 ± 50			1.74 ± 0.35	420							
				0.945 ± 0.073	300 ± 3	RR [relative to $k(\text{dimethyl ether}) =$ $3.01 \times 10^{-12}]^a$	Tuazon <i>et al.</i> ⁵⁸					

TABLE 11. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with oxygen-containing organics — Continued

Oxygenate	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	n	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
	11 ± 3		798 ± 45	0.77	300	DF-LIF	Meier <i>et al.</i> ^{59,60}	300–1010
				0.71 ± 0.08	296	FP-RF	Zetzsch ⁶¹	
				0.54 ± 0.04	260	FP-RA	Greenhill and O'Grady ⁶²	260–803
				0.76 ± 0.04	292			
				0.75 ± 0.08	300			
				1.13 ± 0.05	331			
				1.44 ± 0.06	362			
				1.44 ± 0.09	453			
				1.35 ± 0.08	465			
				2.06 ± 0.17	570			
				2.67 ± 0.24	597.5			
				2.79 ± 0.25	669			
	8.0 ± 1.9		664 ± 88	5.76 ± 0.59	803			
				0.657 ± 0.046	240	FP-RF	Wallington and Kurylo ⁶³	240–440
				0.861 ± 0.047	296			
				1.25 ± 0.080	350			
				1.41 ± 0.12	400			
	4.8 ± 1.2		480 ± 70	1.62 ± 0.14	440			
				0.934 ± 0.041	294	LP-LIF	Hess and Tully ⁶⁴	294–866
				1.09 ± 0.05	332			
				1.33 ± 0.06	380			
				1.69 ± 0.07	441			
				2.10 ± 0.09	505			
				2.31 ± 0.10	527.5			
				3.01 ± 0.13	626			
				3.96 ± 0.20	709			
				5.05 ± 0.24	786.5			
	5.89×10^{-8}		$2.65 - 444$	6.18 ± 0.32	865.5			
				1.01 ± 0.10	298 ± 2	DF-LIF	McCaulley <i>et al.</i> ⁶⁵	
Methanol- d_3 [CD ₃ OH]				0.50 ± 0.02	293	FP-RA	Greenhill and O'Grady ⁶²	
				0.435 ± 0.019	293	LP-LIF	Hess and Tully ⁶⁴	293–862
				0.529 ± 0.022	331			
				0.682 ± 0.030	384			
				0.920 ± 0.041	438.5			
				1.27 ± 0.06	530			
				1.88 ± 0.09	634			
				2.81 ± 0.12	730			
	1.28×10^{-10}		$3.48 - 642$	4.85 ± 0.25	861.5			
				0.335 ± 0.072	298 ± 2	DF-LIF	McCaulley <i>et al.</i> ⁶⁵	
Methanol- d_4 [CD ₃ OD]				0.193 ± 0.045	298 ± 2	DF-LIF	McCaulley <i>et al.</i> ⁶⁵	
Ethanol				3.2 ± 0.4	292	RR [relative to $k(n\text{-butane}) =$ $2.47 \times 10^{-12}]^a$	Campbell <i>et al.</i> ⁵²	
				3.74 ± 0.37	296 ± 2	FP-RA	Overend and Paraskevopoulos ⁵³	
				2.62 ± 0.36	298	FP-RF	Ravishankara and Davis ⁵⁴	
				3.5 ± 0.6	295 ± 2	RR [relative to $k(\text{propene}) =$ $2.68 \times 10^{-11}]^a$	Cox and Goldstone ⁶⁶	

TABLE 11. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with oxygen-containing organics — Continued

Oxygenate	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	n	B (K)	$10^{12} \times k$ (cm^3 $\text{molecule}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
	5.16 ± 1		274 ± 90	2.07	300	DF-LIF	Meier <i>et al.</i> ^{60,67,68}	300–1000
				3.0 ± 0.6	296	LP-RF	Lorenz <i>et al.</i> ⁶⁹	296–609
				2.9 ± 0.6	296			
				3.0 ± 0.6	298			
				2.5 ± 0.5	339			
				3.3 ± 0.6	386			
				3.1 ± 0.6	386			
				3.6 ± 0.7	452			
				4.3 ± 0.8	524			
				4.0 ± 0.8	525			
	5.6 ± 0.6		200 ± 50	3.7 ± 0.8	609			
				3.66 ± 0.42	303 ± 2	RR [relative to $k(\text{ethene}) =$ $8.32 \times 10^{-12}]^a$	Kerr and Stocker ³⁴	
				2.84 ± 0.15	255	FP-RA	Greenhill and O'Grady ⁶²	255–459
				3.40 ± 0.14	273			
				3.80 ± 0.24	289			
				3.40 ± 0.17	293			
				4.26 ± 0.19	331			
				4.26 ± 0.18	360			
				5.21 ± 0.36	369			
	12.5 ± 2.4		360 ± 52	5.63 ± 0.48	459			
				2.75 ± 0.14	240	FP-RF	Wallington and Kurylo ⁶³	240–440
				3.33 ± 0.23	296			
				3.25 ± 0.39	350			
				4.07 ± 0.40	400			
	7.4 ± 3.2		240 ± 110	4.58 ± 0.29	440			
				3.26 ± 0.14	293	LP-LIF	Hess and Tully ⁷⁰	293–750
				3.32 ± 0.16^f	295			
				3.33 ± 0.14	326.5			
				3.63 ± 0.15	380			
				3.94 ± 0.16	441			
				4.65 ± 0.19	520.5			
				4.78 ± 0.23	544			
				4.74 ± 0.22	561			
				4.74 ± 0.22	582			
				4.65 ± 0.21	598			
				5.47 ± 0.34^f	599			
				4.79 ± 0.22	620.5			
				5.06 ± 0.23	645			
				5.66 ± 0.30	677			
				6.12 ± 0.35	706			
				6.62 ± 0.37	749.5			
1-Propanol				4.1 ± 0.4	292	RR [relative to $k(n\text{-butane}) =$ $2.47 \times 10^{-12}]^a$	Campbell <i>et al.</i> ⁵²	
				5.33 ± 0.54	296 ± 2	FP-RA	Overend and Paraskevopoulos ⁵³	
				5.34 ± 0.29	296	FP-RF	Wallington and Kurylo ⁶³	
2-Propanol				6.9 ± 2.1	305 ± 2	RR [relative to $k(2\text{-methylpropene}) =$ $4.94 \times 10^{-11}]^a$	Lloyd <i>et al.</i> ⁷¹	
				5.48 ± 0.55	296 ± 2	FP-RA	Overend and Paraskevopoulos ⁵³	

TABLE 11. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with oxygen-containing organics — Continued

Oxygenate	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	n	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
				4.8	300	RR [relative to $k(\text{propane}) =$ $1.17 \times 10^{-12}]^a$	Klöpffer <i>et al.</i> ⁷²	
				5.12 ± 0.31	240	FP-RF	Wallington and Kurylo ⁶³	240-440
				5.81 ± 0.34	296			
				5.27 ± 0.38	350			
				5.16 ± 0.44	400			
	5.8 ± 1.9		30 ± 90	5.75 ± 0.55	440			
1-Butanol				7.2 ± 1.1	292	RR [relative to $k(n\text{-butane}) =$ $2.47 \times 10^{-12}]^a$	Campbell <i>et al.</i> ⁵²	
				8.31 ± 0.63	296	FP-RF	Wallington and Kurylo ⁶³	
2-Methyl- 2-propanol [(CH_3) ₂ COH]				1.08 ± 0.13	295 ± 2	RR [relative to $k(\text{ethene}) =$ $8.65 \times 10^{-12}]^a$	Cox and Goldstone ⁶⁶	
				1.00 ± 0.06	240	FP-RF	Wallington <i>et al.</i> ⁷³	240-440
				1.07 ± 0.08	298			
				1.23 ± 0.08	350			
				1.63 ± 0.07	400			
	3.3 ± 1.6		310 ± 150	1.77 ± 0.17	440			
1-Pentanol				10.8 ± 1.1	296	FP-RF	Wallington and Kurylo ⁶³	
2-Pentanol				11.8 ± 0.8	298	FP-RF	Wallington <i>et al.</i> ⁷⁴	
3-Pentanol				12.2 ± 0.7	298	FP-RF	Wallington <i>et al.</i> ⁷⁴	
Cyclopentanol				10.7 ± 0.7	298	FP-RF	Wallington <i>et al.</i> ⁷⁴	
3-Methyl- 2-butanol				12.4 ± 0.7	298	FP-RF	Wallington <i>et al.</i> ⁷⁴	
1-Hexanol				12.4 ± 0.7	298	FP-RF	Wallington <i>et al.</i> ⁷⁴	
2-Hexanol				12.1 ± 0.7	298	FP-RF	Wallington <i>et al.</i> ⁷⁴	
1-Heptanol				13.6 ± 1.3	298	FP-RF	Wallington <i>et al.</i> ⁷⁴	
Allyl alcohol [$\text{CH}_2=\text{CHCH}_2\text{OH}$]				25.9 ± 3.4	440	PR-RA	Gordon and Mulac ⁷⁵	
2-Chloroethanol				1.4 ± 0.1	295	FP-RF	Wiedelmann and Zetzsch ⁷⁶	
<i>Glycols, Hydroxyethers and Ketoethers</i>								
1,2-Ethandiol [$\text{HOCH}_2\text{CH}_2\text{OH}$]				7.7 ± 1.1	295	FP-RF	Wiedelmann and Zetzsch ⁷⁶	
Hydroxyacetone [$\text{CH}_3\text{COCH}_2\text{OH}$]				3.02 ± 0.30	298	FP-RF	Dagaut <i>et al.</i> ⁷⁷	
1,2-Propanediol [$\text{HOCH}_2\text{CHOHCH}_3$]				12 ± 1	295	FP-RF	Wiedelmann and Zetzsch ⁷⁶	
2-Methoxyethanol [$\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$]				18.8 ± 1.3	240	FP-RF	Dagaut <i>et al.</i> ⁷⁷	240-440
				12.5 ± 0.7	298			
				11.0 ± 0.6	350			

TABLE 11. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with oxygen-containing organics — Continued

Oxygenate	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	n	B (K)	$10^{12} \times k$ (cm^3 $\text{molecule}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
	4.5 ± 1.4		-325 ± 100	10.4 ± 0.8 10.1 ± 0.6	400 440			
Methoxyacetone [$\text{CH}_3\text{OCH}_2\text{COCH}_3$]				6.77 ± 0.61	298	FP-RF	Dagaut <i>et al.</i> ⁷⁷	
2-Hydroxyethyl ether [$\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$]				30 ± 2	295	FP-RF	Wiedelmann and Zetzsch ⁷⁶	
2-Ethoxyethanol [$\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$]	18 ± 4		120 ± 30	12 ± 3 14 ± 3	298 485	LP-RF	Hartmann <i>et al.</i> ⁷⁸	298–485
				18.7 ± 2.0	298	FP-RF	Dagaut <i>et al.</i> ⁷⁷	
3-Ethoxy-1-propanol [$\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{OH}$]				22.0 ± 1.3	298	FP-RF	Dagaut <i>et al.</i> ⁷⁷	
3-Methoxy-1-butanol [$\text{CH}_3\text{OCH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{OH}$]				23.6 ± 1.6	298	FP-RF	Dagaut <i>et al.</i> ⁷⁷	
2-Butoxyethanol [$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$]	14 ± 3		0	14 ± 3 14 ± 3	298 505	LP-RF	Hartmann <i>et al.</i> ⁷⁸	298–505
				23.1 ± 0.9	298	FP-RF	Dagaut <i>et al.</i> ⁷⁷	
<i>Ethers and Cycloethers</i>								
Dimethyl ether				3.50 ± 0.35 4.31 ± 0.43 5.13 ± 0.51	298.9 350.5 423.9	FP-RF	Perry <i>et al.</i> ⁷⁹	299–424
	12.9		388 ± 151	2.95 ± 0.12 3.40 ± 0.14 3.81 ± 0.16 4.52 ± 0.19	295 332 377.5 442	LP-LIF	Tully and Droege ⁸⁰	295–442
	10.4 ± 1.0		372 ± 34	1.92 ± 0.22 2.49 ± 0.22 2.87 ± 0.40 3.02 ± 0.22 3.69 ± 0.35	240 296 350 400 440	FP-RF	Wallington <i>et al.</i> ⁸¹	240–440
Diethyl ether				9.1 ± 1.8	305 ± 2	RR [relative to $k(2\text{-methylpropene})$ $= 4.94 \times 10^{-11}]^a$	Lloyd <i>et al.</i> ⁷¹	
				13.4 ± 0.6 12.9 ± 0.5 12.4 ± 0.5 11.8 ± 0.5	295 332 377.5 442	LP-LIF	Tully and Droege ⁸⁰	295–442
	9.13 ± 0.35		-115 ± 14	17.7 ± 1.5 13.6 ± 0.9 11.4 ± 1.2 11.5 ± 1.2 11.4 ± 1.7	240 296 350 400 440	FP-RF	Wallington <i>et al.</i> ⁸¹	240–440
	5.6 ± 1.7		-270 ± 100	12.0 ± 1.0	294 ± 2	RR [relative to $k(2\text{-methylpropene})$ $= 5.26 \times 10^{-11}]^a$	Bennett and Kerr ⁸²	

TABLE 11. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with oxygen-containing organics — Continued

Oxygenate	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	n	B (K)	$10^{12} \times k$ (cm^3 $\text{molecule}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
Diethyl ether- d_{10} [$\text{C}_2\text{D}_5\text{OC}_2\text{D}_5$]				6.70 ± 0.40	296	LP-LIF	Tully ⁸³	296-441
				6.54 ± 0.39	333			
				6.61 ± 0.40	375			
				6.84 ± 0.41	441			
Di- n -propyl ether				16.8 ± 3.4	305 ± 2	RR [relative to $k(2\text{-methylpropene})$ $= 4.94 \times 10^{-11}]^a$	Lloyd <i>et al.</i> ⁷¹	
				21.8 ± 2.4	240	FP-RF	Wallington <i>et al.</i> ⁸¹	240-440
				18.0 ± 2.2	296			
				16.3 ± 1.8	350			
				15.9 ± 1.0	400			
		11 ± 3		-150 ± 80	16.4 ± 2.0	440		
				15.3 ± 1.7	294 ± 2	RR [relative to $k(2\text{-methylpropene})$ $= 5.26 \times 10^{-11}]^a$	Bennett and Kerr ⁸²	
Methyl n -butyl ether				16.4 ± 0.6	298	FP-RF	Wallington <i>et al.</i> ⁷⁴	
Methyl t -butyl ether [$\text{CH}_3\text{OC}(\text{CH}_3)_3$]				2.85 ± 0.52	295 ± 2	RR [relative to $k(\text{ethene}) =$ $8.65 \times 10^{-12}]^a$	Cox and Goldstone ⁶⁶	
				2.44 ± 0.39	295 ± 2	RR [relative to $k(n\text{-hexane}) =$ $5.55 \times 10^{-12}]^a$	Cox and Goldstone ⁶⁶	
				2.74 ± 0.19	240	FP-RF	Wallington <i>et al.</i> ⁷³	240-440
				3.09 ± 0.15	298			
				3.20 ± 0.26	350			
		5.1 ± 1.6		155 ± 100	3.21 ± 0.25	400		
				3.97 ± 0.36	440			
Ethyl n -butyl ether [$\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$]				22.8 ± 0.9	298	FP-RF	Wallington <i>et al.</i> ⁷⁴	
				13.4 ± 0.6	294 ± 2	RR [relative to $k(2\text{-methylpropene})$ $= 5.26 \times 10^{-11}]^a$	Bennett and Kerr ⁸²	
Ethyl $tert$ -butyl ether [$\text{C}_2\text{H}_5\text{OC}(\text{CH}_3)_3$]				8.12 ± 0.32	298	FP-RF	Wallington <i>et al.</i> ⁷⁴	
				5.63 ± 0.58	294 ± 2	RR [relative to $k(2\text{-methylpropene})$ $= 5.26 \times 10^{-11}]^a$	Bennett and Kerr ⁸²	
Methyl $tert$ - amyl ether [$\text{CH}_3\text{OC}(\text{CH}_3)_2\text{CH}_2\text{CH}_3$]				7.91 ± 0.42	298	FP-RF	Wallington <i>et al.</i> ⁷⁴	
Di- n -butyl ether				27.8 ± 3.6	296	FP-RF	Wallington <i>et al.</i> ⁸¹	
				17.0 ± 0.9	294 ± 2	RR [relative to $k(2\text{-methylpropene})$ $= 5.26 \times 10^{-11}]^a$	Bennett and Kerr ⁸²	
Di-isobutyl ether				26.0 ± 1.6	294 ± 2	RR [relative to $k(2\text{-methylpropene})$ $= 5.26 \times 10^{-11}]^a$	Bennett and Kerr ⁸²	

TABLE 11. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with oxygen-containing organics — Continued

Oxygenate	$10^{12} \times A$ ($\text{cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$)	n	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
Di- <i>n</i> -pentyl ether				34.7 ± 2.0	296	FP-RF	Wallington <i>et al.</i> ⁸¹	
Trimethylene oxide ⁸				10.3 ± 0.6	298	FP-RF	Dagaut <i>et al.</i> ⁷⁷	
Tetrahydrofuran ⁸				14.3 ± 2.9	305 ± 2	RR [relative to $k(2\text{-methylpropene})$ $= 4.94 \times 10^{-11}$] ^a	Winer <i>et al.</i> ⁸⁴	
				16.2 ± 2.3	298	FP-RF	Ravishankara and Davis ⁵⁴	
				17.8 ± 1.6	296	FP-RF	Wallington <i>et al.</i> ⁸¹	
Tetrahydropyran ⁸				13.8 ± 0.7	298	FP-RF	Dagaut <i>et al.</i> ⁷⁷	
Oxepane ⁸				15.4 ± 1.3	298	FP-RF	Dagaut <i>et al.</i> ⁷⁷	
1,1-Dimethoxyethane [(CH ₃ O) ₂ CHCH ₃]				8.89 ± 0.95	298	FP-RF	Dagaut <i>et al.</i> ⁷⁷	
Diethoxymethane [CH ₃ CH ₂ OCH ₂ OCH ₂ CH ₃]				16.8 ± 1.6	298	FP-RF	Dagaut <i>et al.</i> ⁷⁷	
2,2-Dimethoxypropane [CH ₃ OC(CH ₃) ₂ OCH ₃]				4.09 ± 0.89	240	FP-RF	Dagaut <i>et al.</i> ⁷⁷	240–440
				3.92 ± 0.22	298			
				3.75 ± 0.18	350			
				3.80 ± 0.51	400			
3.55 ± 0.39		-30 ± 35		3.93 ± 0.35	440			
1,2-Dimethoxypropane [CH ₃ OCH ₂ CH(CH ₃)OCH ₃]				14.3 ± 1.5	298	FP-RF	Dagaut <i>et al.</i> ⁷⁷	
2,2-Diethoxypropane [CH ₃ CH ₂ OC(CH ₃) ₂ OCH ₂ CH ₃]				11.1 ± 1.7	240	FP-RF	Dagaut <i>et al.</i> ⁷⁷	240–440
				11.7 ± 1.3	298			
				10.5 ± 1.0	350			
				11.7 ± 1.0	400			
1.06 ± 0.25		-15 ± 15		10.6 ± 0.7	440			
2-Methoxyethyl ether [CH ₃ OCH ₂ CH ₂ OCH ₂ CH ₂ OCH ₃]				17.5 ± 1.1	298	FP-RF	Dagaut <i>et al.</i> ⁷⁷	
1,1,3-Trimethoxypropane [(CH ₃ O) ₂ CHCH ₂ CH ₂ OCH ₃]				19.2 ± 1.0	298	FP-RF	Dagaut <i>et al.</i> ⁷⁷	
2-Ethoxyethyl ether [CH ₃ CH ₂ OCH ₂ CH ₂ OCH ₂ CH ₂ OCH ₂ CH ₃]				26.8 ± 2.4	298	FP-RF	Dagaut <i>et al.</i> ⁷⁷	
1,3-Dioxane ⁸				10.0 ± 0.5	240	FP-RF	Dagaut <i>et al.</i> ⁷⁷	240–440
				9.15 ± 0.43	298			
				10.6 ± 0.2	350			
				9.65 ± 0.31	400			
9.4 ± 0.2		-10 ± 60		9.72 ± 1.18	440			
1,4-Dioxane ⁸				11.8 ± 0.8	240	FP-RF	Dagaut <i>et al.</i> ⁷⁷	240–440
				10.9 ± 0.5	298			
				9.55 ± 0.58	350			
				9.68 ± 0.83	400			
8.3 ± 2.2		-80 ± 90		10.4 ± 0.9	440			
4-Methyl-1,3-dioxane ⁸				11.3 ± 0.6	298	FP-RF	Dagaut <i>et al.</i> ⁷⁷	

TABLE 11. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with oxygen-containing organics — Continued

Oxygenate	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	n	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
1,3,5-Trioxane ⁶	13.6 ± 2.0		232 ± 50	6.71 ± 0.21	292	LP-LIF	Zabarnick <i>et al.</i> ¹⁷	292–597
				6.85 ± 0.18	293			
				5.85 ± 0.15	294			
				6.35 ± 0.17	373			
				7.64 ± 0.17	434			
				7.94 ± 0.37	487			
				9.82 ± 0.14	542			
				9.86 ± 0.15	597			
Vinyl methyl ether [CH ₂ =CHOCH ₃]	6.10		–511 ± 151	33.5 ± 3.4	299.1	FP-RF	Perry <i>et al.</i> ⁷⁹	299–427
				26.0 ± 2.6	352.4			
				20.1 ± 2.0	427.0			
Furan ⁸	13.2 ± 2.9		–333 ± 67	105 ± 8	295 ± 1	DF-RF	Lee and Tang ⁸⁵	254–424
				39.5 ± 2.9	298 ± 2	RR [relative to $k(n\text{-hexane}) =$ 5.61×10^{-12}] ^a	Atkinson <i>et al.</i> ⁸⁶	
				49.6 ± 3.3	254	FP-RF	Wine and Thompson ⁸⁷	
				40.8 ± 1.8	297			
				43.1 ± 1.2	297			
				38.7 ± 2.2	299			
				41.6 ± 3.5	299			
				38.3 ± 4.5	300			
				31.9 ± 1.6	365			
				29.9 ± 2.0	424			
				42.3 ± 3.2	295 ± 2	RR [relative to $k(2\text{-methyl-1,3-butadiene}) =$ 1.02×10^{-10}] ^a	Tuazon <i>et al.</i> ⁸⁸	
				46.6 ± 3.9	298	FP-RF	Witte and Zetzsch ⁸⁹	
				46.6 ± 9.0	299			
				49.1 ± 2.7	299			
				43.6 ± 2.3	323			
				46.4 ± 2.9	349			
				38.9 ± 2.8	350			
				34.4 ± 5.4	372			
				38.5 ± 2.5	373			
35.3 ± 1.9	399							
34.0 ± 2.2	422							
35.1 ± 2.2	422							
32.4 ± 1.4	424							
35.7 ± 3.1	424							
29.4 ± 1.7	440							
3-Methylfuran ⁸				93.5 ± 2.4	296 ± 2	RR [relative to $k(2,3\text{-dimethyl-2-butene}) =$ 1.11×10^{-10}] ^a	Atkinson <i>et al.</i> ⁹⁰	
Oxazole ⁸				10.11 ± 0.24	299	FP-RF	Witte and Zetzsch ⁸⁹	299–468
				9.83 ± 0.26	299			
				8.96 ± 0.38	299			
				9.17 ± 0.55	299			
				8.29 ± 0.19	324			
				7.68 ± 0.38	348			
				7.68 ± 0.24	349			
				7.25 ± 0.23	373			
				6.84 ± 0.10	398			
				6.67 ± 0.18	398			
				6.44 ± 0.18	423			

TABLE 11. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with oxygen-containing organics — Continued

Oxygenate	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	n	B (K)	$10^{12} \times k$ (cm^3 $\text{molecule}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
				6.04 ± 0.17	448			
				6.18 ± 0.19	449			
	2.8 ± 0.1		-350 ± 30	5.99 ± 0.22	468			
<i>Esters</i>								
Methyl formate [HC(O)OCH ₃]				0.227 ± 0.034	296	FP-RF	Wallington <i>et al.</i> ⁹¹	
Ethyl formate [HC(O)OCH ₂ CH ₃]				1.02 ± 0.14	296	FP-RF	Wallington <i>et al.</i> ⁹¹	
<i>n</i> -Propyl formate [HC(O)OCH ₂ CH ₂ CH ₃]				2.38 ± 0.27	296	FP-RF	Wallington <i>et al.</i> ⁹¹	
<i>n</i> -Butyl formate [HC(O)OCH ₂ CH ₂ CH ₂ CH ₃]				3.12 ± 0.33	296	FP-RF	Wallington <i>et al.</i> ⁹¹	
Methyl acetate [CH ₃ C(O)OCH ₃]				0.17 ± 0.06	292	RR [relative to $k(n\text{-butane}) =$ $2.47 \times 10^{-12}]^a$	Campbell and Parkinson ⁹²	
				0.486 ± 0.037	240	FP-RF	Wallington <i>et al.</i> ⁹¹	240-440
				0.419 ± 0.032	263			
				0.341 ± 0.029	296			
				0.414 ± 0.030	350			
				0.395 ± 0.038	400			
	0.83 ± 0.35		260 ± 150 (296-440 K)	0.474 ± 0.066	440			
Methyl trifluoroacetate [CF ₃ C(O)OCH ₃]				0.037 ± 0.003	240	FP-RF	Wallington <i>et al.</i> ⁹¹	240-440
				0.052 ± 0.008	296			
				0.064 ± 0.005	350			
				0.083 ± 0.011	400			
	0.30 ± 0.07		512 ± 78	0.099 ± 0.008	440			
Ethyl acetate [CH ₃ C(O)OCH ₂ CH ₃]				1.84 ± 0.37	292	RR [relative to $k(n\text{-butane}) =$ $2.47 \times 10^{-12}]^a$	Campbell and Parkinson ⁹²	
				1.7 ± 0.2	296	FP-RF	Zetzsch ⁶¹	
				3.26 ± 0.21	240	FP-RF	Wallington <i>et al.</i> ⁹¹	240-440
				2.40 ± 0.15	263			
				1.51 ± 0.14	296			
				1.57 ± 0.10	350			
				1.72 ± 0.13	400			
	2.3 ± 0.2		131 ± 28 (296-440 K)	1.73 ± 0.13	440			
<i>n</i> -Propyl acetate [CH ₃ C(O)OCH ₂ CH ₂ CH ₃]				4.2 ± 0.9	305 ± 2	RR [relative to $k(2\text{-methylpropene}) =$ $4.94 \times 10^{-11}]^a$	Winer <i>et al.</i> ⁸⁴	
				2.50 ± 0.25	303 ± 2	RR [relative to $k(\text{ethene}) =$ $8.32 \times 10^{-12}]^a$	Kerr and Stocker ³⁴	
				3.45 ± 0.34	296	FP-RF	Wallington <i>et al.</i> ⁹¹	
Isopropyl acetate [CH ₃ C(O)OCH(CH ₃) ₂]				3.08 ± 0.84	303 ± 2	RR [relative to $k(\text{ethene}) =$ $8.32 \times 10^{-12}]^a$	Kerr and Stocker ³⁴	

TABLE 11. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with oxygen-containing organics — Continued

Oxygenate	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	n	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
				3.72 ± 0.29	296	FP-RF	Wallington <i>et al.</i> ⁹¹	
<i>n</i> -Butyl acetate [$\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{-}$ $\text{CH}_2\text{CH}_2\text{CH}_3$]	31 ± 7		594 ± 126	4.3 ± 0.8 6.8 ± 1.3 10 ± 2	298 400 516	LP-RF	Hartmann <i>et al.</i> ⁷⁸	298–516
				4.15 ± 0.30	296	FP-RF	Wallington <i>et al.</i> ⁹¹	
<i>sec</i> -Butyl acetate [$\text{CH}_3\text{C}(\text{O})\text{OCH}(\text{CH}_3)\text{-}$ CH_2CH_3]				5.4 ± 1.1	305 ± 2	RR [relative to $k(2\text{-methylpropene})$ $= 4.94 \times 10^{-11}$] ^a	Winer <i>et al.</i> ⁸⁴	
				5.65 ± 0.59	296	FP-RF	Wallington <i>et al.</i> ⁹¹	
Methyl propionate [$\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{OCH}_3$]				0.27 ± 0.11	292	RR [relative to $k(n\text{-butane}) =$ 2.47×10^{-12}] ^a	Campbell and Parkinson ⁹²	
				1.03 ± 0.04	296	FP-RF	Wallington <i>et al.</i> ⁹¹	
Ethyl propionate [$\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{OCH}_2\text{CH}_3$]				1.68 ± 0.36	292	RR [relative to $k(n\text{-butane}) =$ 2.47×10^{-12}] ^a	Campbell and Parkinson ⁹²	
				2.14 ± 0.30	296	FP-RF	Wallington <i>et al.</i> ⁹¹	
<i>n</i> -Propyl propionate [$\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{OCH}_2\text{-}$ CH_2CH_3]				4.02 ± 0.32	296	FP-RF	Wallington <i>et al.</i> ⁹¹	
				3.04 ± 0.33	296	FP-RF	Wallington <i>et al.</i> ⁹¹	
Methyl butyrate [$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{-}$ OCH_3]				4.94 ± 0.38	296	FP-RF	Wallington <i>et al.</i> ⁹¹	
Ethyl butyrate [$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{-}$ OCH_2CH_3]				7.41 ± 0.32	296	FP-RF	Wallington <i>et al.</i> ⁹¹	
<i>n</i> -Propyl butyrate [$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{-}$ $\text{OCH}_2\text{CH}_2\text{CH}_3$]				10.6 ± 1.3	296	FP-RF	Wallington <i>et al.</i> ⁹¹	
<i>n</i> -Butyl butyrate [$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{-}$ $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$]				13 ± 2 9 ± 2 8 ± 2	298 401 506	LP-RF	Hartmann <i>et al.</i> ⁷⁸	298–506
1-Acetoxy-2-ethoxyethane [$\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_3$]	3.6 ± 0.8		-383 ± 80					
<i>Carboxylic Acids</i>								
Formic acid				0.32 ± 0.10	298	FP-RF	Zetzsch and Stuhl ⁹³	
				0.461 ± 0.051	298	FP-RF	Wine <i>et al.</i> ⁹⁴	298–430
				0.405 ± 0.047	298			
				0.545 ± 0.012	298			
				0.448 ± 0.032	298			
				0.432 ± 0.065	298			
				0.446 ± 0.011	298			
				0.449 ± 0.026	298			
				0.428 ± 0.049	298			

TABLE 11. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with oxygen-containing organics — Continued

Oxygenate	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	n	B (K)	$10^{12} \times k$ (cm^3 $\text{molecule}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
				0.481 ± 0.059	298			
				0.482 ± 0.042	298			
				0.523 ± 0.030	299			
				0.466 ± 0.007	299			
				0.480 ± 0.075	299			
				0.464 ± 0.037	299			
				0.495 ± 0.081	299			
				0.490 ± 0.094	300			
				0.539 ± 0.076	300			
				0.446 ± 0.033	300			
				0.443 ± 0.053	300			
				0.495 ± 0.050	320			
				0.406 ± 0.024	337			
				0.433 ± 0.037	374			
				0.505 ± 0.002	378			
				0.479 ± 0.068	402			
				0.407 ± 0.034	428			
				0.409 ± 0.051	428			
				0.439 ± 0.072	430			
	0.363 ± 0.089 [0.462 ± 0.078]		-77 ± 75 0]	0.434 ± 0.053	430			
				0.490 ± 0.012	296	FP-RA	Jolly <i>et al.</i> ⁹⁵	
				0.37 ± 0.04	298	FP-RF	Dagaut <i>et al.</i> ⁹⁶	
				0.447 ± 0.028	296.9	LP-RA	Singleton <i>et al.</i> ⁹⁷	297-445
				0.365 ± 0.030	326.3			
				0.369 ± 0.032	356.2			
				0.367 ± 0.012	396.2			
	0.291 ± 0.159 [0.365 ± 0.033]		-102 ± 194 0]	0.390 ± 0.028	445.2			
Formic acid dimer				≤ 0.025	296	FP-RA	Jolly <i>et al.</i> ^{95,98}	
				0.0802 ± 0.0206	296.9	LP-RA	Singleton <i>et al.</i> ⁹⁷	297-326
				0.223 ± 0.103	326.3			
Formic acid- d_1 [DCOOH]				0.435 ± 0.038	298	FP-RF	Wine <i>et al.</i> ⁹⁴	
				0.498 ± 0.099	298			
				0.456 ± 0.028	298			
				0.400 ± 0.033	296.0	LP-RA	Singleton <i>et al.</i> ⁹⁷	
Formic acid dimer- d_2 [(DCOOH) $_2$]				-0.0203 ± 0.0113	296.0	LP-RA	Singleton <i>et al.</i> ⁹⁷	
Acetic acid				0.6 ± 0.2	298	FP-RF	Zetzsch and Stuhl ⁹³	
				0.74 ± 0.06	298	FP-RF	Dagaut <i>et al.</i> ⁹⁶	298-440
				0.81 ± 0.09	350			
				0.87 ± 0.14	400			
	1.3 ± 0.1		170 ± 20	0.88 ± 0.08	440			
Propionic acid				1.6 ± 0.5	298	FP-RF	Zetzsch and Stuhl ⁹³	
				1.22 ± 0.12	298	FP-RF	Dagaut <i>et al.</i> ⁹⁶	298-440
				1.28 ± 0.13	350			
				1.36 ± 0.13	400			
	1.8 ± 0.2		120 ± 30	1.37 ± 0.10	440			

TABLE 11. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with oxygen-containing organics — Continued

Oxygenate	$10^{12} \times A$ ($\text{cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$)	n	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
Butyric acid				2.4 ± 0.7	298	FP-RF	Zetzsch and Stuhl ⁹³	
Isobutyric acid [(CH_3) ₂ CHCOOH]				2.00 ± 0.20 2.09 ± 0.18 2.12 ± 0.13 2.17 ± 0.17	298 350 400 440	FP-RF	Dagaut <i>et al.</i> ⁹⁶	298–440
	2.6 ± 0.2		70 ± 25					
<i>Oxides</i>								
Epoxyethane				0.080 ± 0.016 0.18 ± 0.04 0.40 ± 0.08 1.6 ± 0.1 2.7 ± 0.5	297 377 435 501 515	LP-RF	Lorenz and Zellner ⁹⁹	297–515
	11 ± 4		1460 ± 150 (297–435 K)					
				0.053 ± 0.01	295	FP-RF	Zetzsch ¹⁰⁰	
				<0.10	300	RR [relative to $k(\text{propane}) =$ $1.17 \times 10^{-12}]^a$	Klöpffer <i>et al.</i> ⁷²	
				0.095 ± 0.005	296	FP-RF	Wallington <i>et al.</i> ⁸¹	
1,2-Epoxypropane				1.2 ± 0.7	300 ± 1	RR [relative to $k(n\text{-butane})-k(\text{neopentane})$ $= 1.70 \times 10^{-12}]^a$	Winer <i>et al.</i> ¹⁰¹	
				0.52 ± 0.1	295	FP-RF	Zetzsch ¹⁰⁰	
				1.11 ± 0.75	296	RR [relative to $k(n\text{-butane}) =$ $2.51 \times 10^{-12}]^a$	Edney <i>et al.</i> ³⁸	
				0.495 ± 0.052	296	FP-RF	Wallington <i>et al.</i> ⁸¹	
1,2-Epoxybutane				2.1 ± 0.7	300 ± 1	RR [relative to $k(n\text{-butane})-k(\text{neopentane})$ $= 1.70 \times 10^{-12}]^a$	Winer <i>et al.</i> ¹⁰¹	
1-Chloro-2,3- epoxypropane				0.44 ± 0.05	295	FP-RF	Zetzsch ¹⁰⁰	
				≥ 0.55	297	RR [relative to $k(n\text{-butane}) =$ $2.53 \times 10^{-12}]^a$	Edney <i>et al.</i> ³⁸	
<i>Hydroperoxides</i>								
Methyl hydroperoxide				10.2 ± 0.8	h	RR [relative to $k(\text{ethene}) =$ $8.52 \times 10^{-12}]^a$	Niki <i>et al.</i> ¹⁰²	
				10.7 ± 1.2	h	RR [relative to $k(\text{acetaldehyde}) =$ $1.58 \times 10^{-11}]^a$	Niki <i>et al.</i> ¹⁰²	
				5.13 ± 0.19 5.00 ± 0.29 4.33 ± 0.54 3.85 ± 0.23 3.29 ± 0.32	203 223 244 298 348	FP/LP-LIF	Vaghjiani and Ravishankara ¹⁰³	203–348
	1.78 ± 0.25		-220 ± 21					
				6.93 ± 0.26^f 6.45 ± 0.20^f	223 244	FP/LP-LIF	Vaghjiani and Ravishankara ¹⁰³	223–373

TABLE 11. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with oxygen-containing organics — Continued

Oxygenate	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	n	B (K)	$10^{12} \times k$ (cm^3 $\text{molecule}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
	3.08 ± 0.36		-179 ± 18	5.48 ± 0.20^f	298			
				5.06 ± 0.14^f	373			
<i>t</i> -Butyl hydroperoxide [(CH_3) ₃ COOH]				3.0 ± 0.8	298	FP-RA	Anastasi <i>et al.</i> ¹⁰⁴	

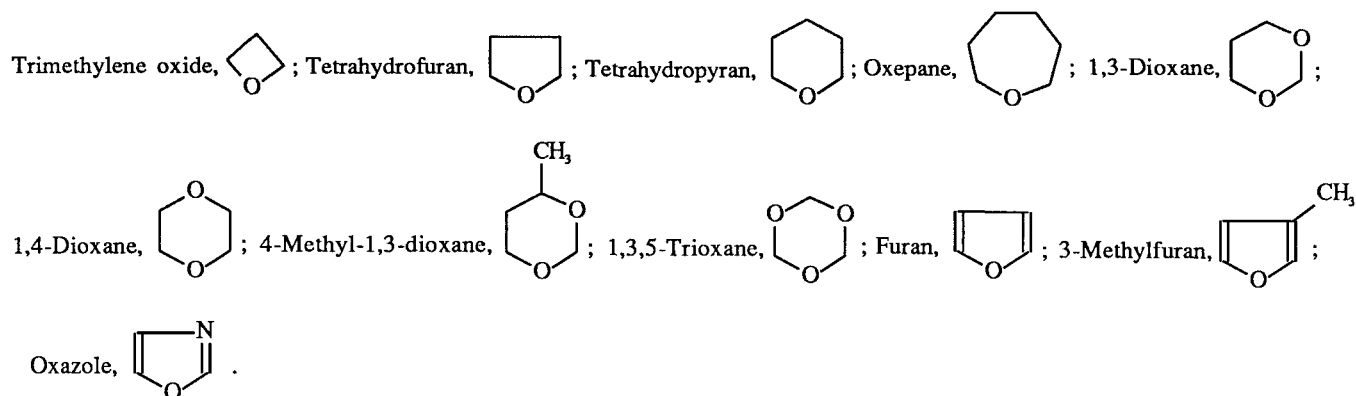
^aFrom the present recommendations (see text).^bSee Introduction.^cFrom the rate constant ratio $k(\text{OH} + \text{ethene-}d_4)/k(\text{OH} + \text{ethene})^{12}$ and the present recommendation for ethene (see text).^dFrom DeMore *et al.*¹⁰⁵^eFrom Faubel *et al.*⁴⁵^fRate constants for reactions of the ¹⁸OH radical.^gStructures:^hRoom temperature not reported. 298 K has been assumed, based on previous studies carried out by Niki and co-workers.^{12,25}

TABLE 12. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OD radical with oxygen-containing organics

Oxygenate	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Tempera- ture range covered (K)
Methanol			0.95 ± 0.12	298 ± 2	DF-LIF	McCaulley <i>et al.</i> ⁶⁵	
Methanol- d_1 (CH_3OD)			0.93 ± 0.11	298 ± 2	DF-LIF	McCaulley <i>et al.</i> ⁶⁵	
Methanol- d_3 (CD_3OH)			0.286 ± 0.037	298 ± 2	DF-LIF	McCaulley <i>et al.</i> ⁶⁵	
Methanol- d_4 (CD_3OD)			0.167 ± 0.016	298 ± 2	DF-LIF	McCaulley <i>et al.</i> ⁶⁵	
Formic acid- d_1 (HCOOD)			$\lesssim 0.15$	a	LP-RA	Singleton <i>et al.</i> ⁹⁷	
Formic acid- d_2 (DCOOD)			0.0636 ± 0.0130 0.0674 ± 0.0052 0.0864 ± 0.0039 0.0943 ± 0.0045	298.0 324.0 355.9 396.1	LP-RA	Singleton <i>et al.</i> ⁹⁷	298–445
	0.447 ± 0.169	594 ± 134	0.123 ± 0.0055	445.3			
Formic acid dimer- d_4 [(DCOOD) ₂]			0.0137 ± 0.0135 0.0181 ± 0.0135	298.0 324.0	LP-RA	Singleton <i>et al.</i> ⁹⁷	298–324
Methyl hydroperoxide			6.29 ± 0.23 5.27 ± 0.13 4.97 ± 0.48 4.61 ± 0.41	249 298 348 423	LP-LIF	Vaghjiani and Ravishankara ¹⁰³	249–423
	2.94 ± 0.38	-185 ± 24					
Methyl hydroper- oxide- d_1 (CH_3OOD)			1.94 ± 0.09	298	LP-LIF	Vaghjiani and Ravishankara ¹⁰³	

^aRoom temperature, not reported.

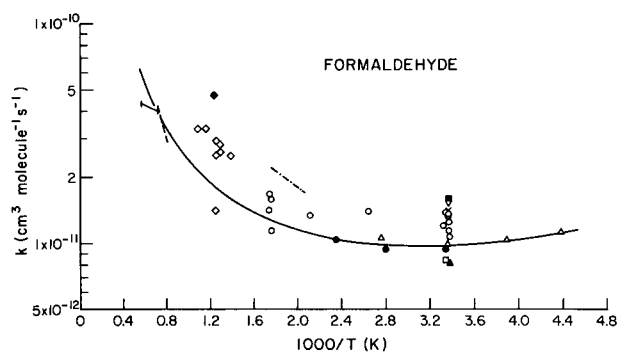


FIG. 61. Arrhenius plot of rate constants for the reaction of the OH radical with formaldehyde. (\diamond) Hoare,^{1,5} Blundell *et al.*,³ Hoare and Peacock,⁶ (\blacklozenge) Baldwin and Cowe,² (— — —) Westenberg and Fristrom,⁴ (x) Morris and Niki,⁸ (∇) Morris and Niki,⁹ (—) Peeters and Mahnen,¹⁰ (— · — ·) Vandooren and Van Tiggelen,¹¹ (\blacksquare) Niki *et al.*,¹² (\bullet) Atkinson and Pitts,¹³ (Δ) Stief *et al.*,¹⁵ (\blacktriangle) Temps and Wagner,¹⁶ (\circ) Zabarnick *et al.*,¹⁷ (\square) Niki *et al.*¹⁸ (for reaction with formaldehyde-¹³C); (—) recommendation (see text).

Based upon the data shown in Fig. 61, the Arrhenius plot exhibits significant curvature. A unit-weighted least-squares analysis of the absolute rate constants determined by Atkinson and Pitts¹³ and Stief *et al.*¹⁵ (which are in excellent agreement), using the expression $k = CT^2 e^{-D/T}$, yields the recommendation of

$$k(\text{formaldehyde}) = (1.25^{+0.20}_{-0.18}) \times 10^{-17} T^2 e^{(648 \pm 45)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 228–426 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{formaldehyde}) = 9.77 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty at 298 K of $\pm 30\%$. This recommendation is $\sim 10\%$ higher than that recommended by Atkinson¹⁰⁶ of

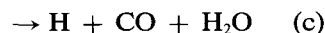
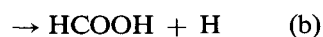
$$k(\text{formaldehyde}) = 9.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

independent of temperature over the same range of 228–426 K. At elevated temperatures, the recommended ex-

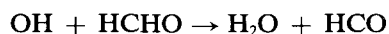
pression yields calculated rate constants in good agreement with those obtained from the flame studies of Westenberg and Fristrom⁴ and Peeters and Mahnen¹⁰ (Fig. 61).

As expected, the rate constant for the reaction of OH radicals with formaldehyde-¹³C is, within the likely experimental errors, essentially identical to that for formaldehyde-¹²C.¹⁸ Similarly, Morris and Niki⁸ determined that the room temperature rate constant for the reaction of formaldehyde-*d*₁ with the OH radical is essentially identical with that for the reaction of the OH radical with formaldehyde, showing that any deuterium isotope effect is small. This is consistent with the essential lack of a temperature dependence for the reaction of OH radicals with formaldehyde at around room temperature and indicates that this reaction of the OH radical with formaldehyde proceeds by an initial addition pathway (although the overall reaction involves H-atom abstraction) [compare with the kinetics of the reactions of the OH radical with diethyl ether and diethyl ether-*d*₁₀, see below].

This OH radical reaction with formaldehyde can proceed by the pathways



Morrison and Heicklen,¹⁰⁷ Temps and Wagner¹⁶ and Niki *et al.*¹⁸ have shown from product studies that reaction pathway (b) is negligible, accounting for $\approx 2\%$ of the overall reaction.¹⁸ Morrison and Heicklen¹⁰⁷ did not observe any formation ($<10\%$) of HCOOH, and concluded that reaction pathways (a) and (c) occur with approximately equal probability. More recently, Temps and Wagner,¹⁶ using a discharge flow technique with LMR detection to monitor both OH and HCO radicals, have shown that reaction pathway (a) accounts for $100 \pm 5\%$ of the overall reaction. Thus, at room temperature the OH radical reaction with formaldehyde proceeds essentially entirely by the H-atom abstraction process.



(b) Acetaldehyde

The available kinetic data are given in Table 11, and those of Morris *et al.*,¹⁹ Morris and Niki,⁹ Niki *et al.*,¹² Atkinson and Pitts,¹³ Kerr and Sheppard,²² Semmes *et al.*²³ and Michael *et al.*²⁴ are plotted in Arrhenius form in Fig. 62. Within the cited experimental errors, the room temperature rate constants of Morris *et al.*,¹⁹ Morris and Niki,⁹ Niki *et al.*,¹² Atkinson and Pitts,¹³ Kerr and Sheppard,²² Semmes *et al.*²³ and Michael *et al.*²⁴ are in reason-

ably good agreement, although those of Kerr and Sheppard²² and Semmes *et al.*²³ are somewhat lower than the remaining data. The Arrhenius plot (Fig. 62) does not show any definitive evidence of curvature, and hence the experimental data have been fitted to the Arrhenius expression $k = Ae^{-B/T}$.

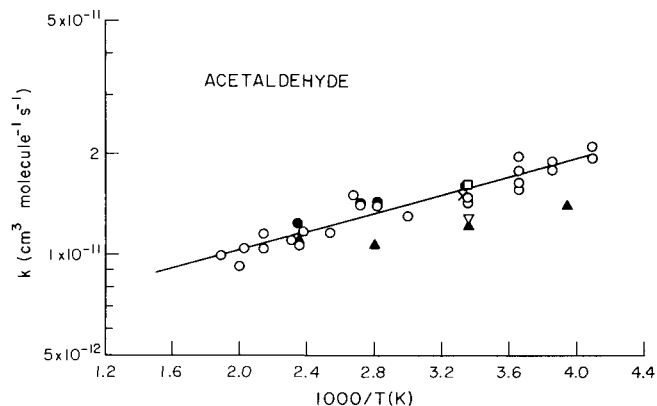


FIG. 62. Arrhenius plot of rate constants for the reaction of the OH radical with acetaldehyde. (x) Morris *et al.*,¹⁹ Morris and Niki;⁹ (□) Niki *et al.*,¹² (●) Atkinson and Pitts,¹³ (∇) Kerr and Sheppard,²² (▲) Semmes *et al.*,²³ (○) Michael *et al.*,²⁴ (—) recommendation (see text).

A unit-weighted least-squares analysis of the rate constants of Niki *et al.*,¹² Atkinson and Pitts¹³ and Michael *et al.*²⁴ leads to the recommendation of

$$k(\text{acetaldehyde}) = (5.55^{+0.76}_{-0.66}) \times 10^{-12} e^{(311 \pm 42)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 244–528 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{acetaldehyde}) = 1.58 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty at 298 K of $\pm 20\%$.

Using the three-parameter expression $k = CT^2e^{-D/T}$, a unit-weighted least-squares analysis of these same kinetic data^{12,13,24} yields

$$k(\text{acetaldehyde}) = (6.03^{+1.07}_{-0.92}) \times 10^{-18} T^2 e^{(999 \pm 54)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

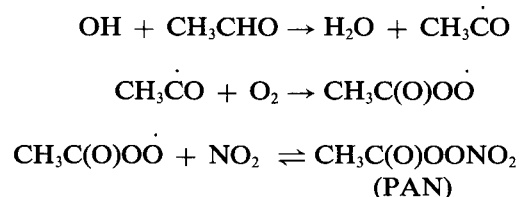
over the temperature range 244–528 K, where the indicated errors are again the two least-squares standard deviations, and

$$k(\text{acetaldehyde}) = 1.53 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K. Over a wider temperature range extending to temperatures $\gtrsim 600$ K, curvature in the Arrhenius plot is expected, and the above three-parameter expression should probably then be used. Clearly, rate constants are needed for this reaction at temperatures $\gtrsim 600$ K.

The recent rate constants of Semmes *et al.*²³ were not included in the evaluation of this rate constant since they reported difficulties in adequately determining the acetaldehyde concentrations in their reactant mixtures.

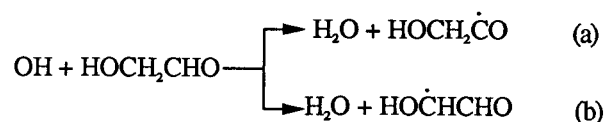
While definite product and mechanistic data are not available for the OH radical reaction with acetaldehyde, the observation of peroxyacetyl nitrate (PAN) from the reaction of the OH radical with CH_3CHO in air in the presence of NO_x ¹⁰⁸ shows that at room temperature this reaction must also proceed via overall H-atom abstraction from the $-\text{CHO}$ group.



This is consistent with the observation that the room temperature rate constants for the $\geq \text{C}_2$ aldehydes are reasonably similar, increasing only slightly with the length of the alkyl side chain (Table 11) and showing that the alkyl substituent group has only a minimal effect on the OH radical rate constant. As for formaldehyde, the observed negative temperature dependence suggests that, although the reaction proceeds by overall H-atom abstraction, the reaction involves initial OH radical addition followed by rapid decomposition of the adduct to the observed products. While H-atom abstraction from the $-\text{CH}_3$ group is expected to be of minimal importance at room temperature,¹⁰⁹ this process will become of more significance at higher temperatures.¹⁰⁹

(c) Glycolaldehyde

The sole kinetic study conducted to date is that of Niki *et al.*²⁵ (Table 11). From the associated product study, Niki *et al.*²⁵ determined the branching ratio for the two reaction pathways,



and rate constant ratios of $k_a/(k_a + k_b) = 0.80$ and $k_b/(k_a + k_b) = 0.20$ were obtained from the $(\text{CHO})_2$, HCHO and CO_2 products observed in the presence of NO and air at atmospheric pressure.

(d) 1-Propanal

The available rate constants, or upper limits to the rate constants, for 1-propanal are given in Table 11. The room temperature rate constants of Morris and Niki,⁹ Niki *et al.*,¹² Kerr and Sheppard,²² Audley *et al.*²⁷ and Semmes *et al.*²³ and the upper limit to the rate constant of Kerr and Stocker²⁹ are in reasonable agreement. While the rate constant of Audley *et al.*²⁷ for 1-propanal agrees well with those of Kerr and Sheppard²² and Semmes *et al.*²³ (and with the rate constant of Niki *et al.*¹²), significant discrepancies exist between the data of Audley *et al.*²⁷ and those of Kerr and Sheppard²² and Semmes *et al.*²³ for the other aldehydes studied.^{23,106} Accordingly, the rate constants of Audley *et al.*²⁷ were not used in the rate constant evaluations for any of the aldehydes. Hence, a unit-weighted average of the room temperature rate constants of Niki *et al.*,¹² Kerr and Sheppard²² and Semmes *et al.*²³ yields the recommendation of

$$k(1\text{-propanal}) = 1.96 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

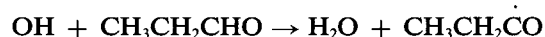
at 298 K, with an estimated overall uncertainty of $\pm 25\%$.

Rate constants have been derived from relative rate studies carried out at elevated temperatures by Baldwin *et al.*²⁶ and Kaiser.²⁸ The rate constant cited in Table 11 from the study of Kaiser²⁸ is an upper limit, since under the conditions employed (~ 50 Torr total pressure, mainly of O_2) the rate constant for the reaction of the OH radical with *trans*-2-butene may have been somewhat into the fall-off regime, and a fraction (measured to be $\sim 0.17 \pm 0.10$) of the 1-propanal decay rate was possibly due to loss processes other than reaction with the OH radical.²⁸ Based upon the discussion in Sec. 2.3 for ethene and propene, the rate constant for the reaction of the OH radical with *trans*-2-butene at 553 K and 50 Torr total pressure of O_2 is estimated to be $\sim 2.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ($\sim 20\%$ below the high-pressure limit), and this yields a value of

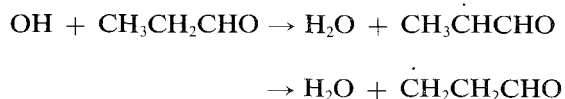
$$k(1\text{-propanal}) \sim 1.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 553 K. The observation that the relative decay rates of propene and *trans*-2-butene were 0.45:1²⁸ (close to the calculated relative high-pressure limit values) further indicates that these OH radical reactions with the alkenes were not far into the fall-off region.

These data²⁸ suggest that the rate constant for the overall OH radical reaction with 1-propanal at ~ 550 K is similar to that at 298 K, and that the rate constant derived from the experimental study of Baldwin *et al.*²⁶ at 713 K is erroneously low. At room temperature, the major reaction pathway is by H-atom abstraction from the $-\text{CHO}$ group^{23,29,106,109}



At elevated temperatures, H-atom abstraction from the $-\text{CH}_2-$ and, at still higher temperatures, the $-\text{CH}_3$ groups will become significant.¹⁰⁹



(e) 1-Butanal, 2-Methyl-1-propanal, 1-Pentanal and 2,2-Dimethyl-1-propanal

The available rate constants of Kerr and Sheppard,²² Audley *et al.*²⁷ and Semmes *et al.*²³ are given in Table 11, and those of Kerr and Sheppard²² and Semmes *et al.*²³ are plotted in Arrhenius form in Figs. 63 to 66. At 298 K the rate constants obtained by Kerr and Sheppard²² and Semmes *et al.*²³ are in reasonable agreement, especially when the rate constants of Semmes *et al.*²³ as calculated from their Arrhenius expressions are used.

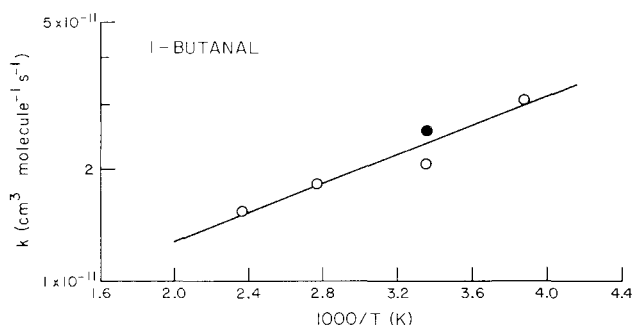


FIG. 63. Arrhenius plot of rate constants for the reaction of the OH radical with 1-butanal. (●) Kerr and Sheppard;²² (○) Semmes *et al.*;²³ (—) recommendation (see text).

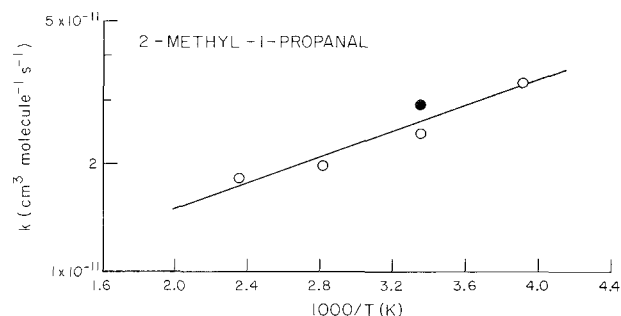


FIG. 64. Arrhenius plot of rate constants for the reaction of the OH radical with 2-methyl-1-propanal. (●) Kerr and Sheppard;²² (○) Semmes *et al.*;²³ (—) recommendation (see text).

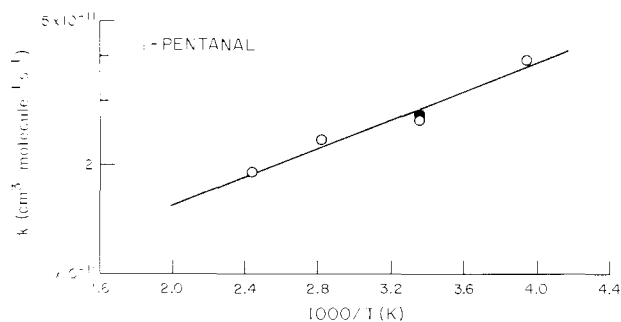


FIG. 65. Arrhenius plot of rate constants for the reaction of the OH radical with 1-pentanal. (●) Kerr and Sheppard;²² (○) Semmes *et al.*;²³ (—) recommendation (see text).

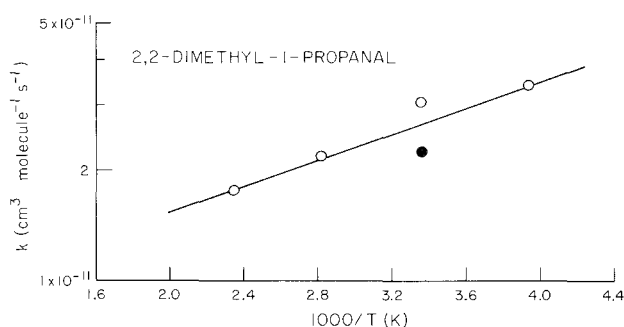


FIG. 66. Arrhenius plot of rate constants for the reaction of the OH radical with 2,2-dimethyl-1-propanal. (●) Kerr and Sheppard;²² (○) Semmes *et al.*;²³ (—) recommendation (see text).

However, for 2-methyl-1-propanal, 1-pentanal and, especially, 2,2-dimethyl-1-propanal, the data of Audley *et al.*²⁷ are significantly lower, and are hence not used in the rate constant evaluations.

Unit-weighted least-squares analyses of the rate constant data of Kerr and Sheppard²² and Semmes *et al.*,²³ using the Arrhenius expression (since no clear evidence of curvature in the Arrhenius plots is evident), leads to the recommendations of:

$$k(1\text{-butanal}) = (5.26^{+3.33}_{-2.04}) \times 10^{-12} e^{(446 \pm 154)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 258–422 K,

$$k(2\text{-methyl-1-propanal}) = (6.61^{+4.02}_{-2.51}) \times 10^{-12} e^{(411 \pm 149)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 255–423 K,

$$k(1\text{-pentanal}) = (6.34^{+2.12}_{-1.59}) \times 10^{-12} e^{(448 \pm 90)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 253–410 K, and

$$k(2,2\text{-dimethyl-1-propanal}) = (6.82_{-3.39}^{+6.72}) \\ \times 10^{-12} e^{(405 \pm 214)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 254–425 K; where in all cases the indicated error limits are two least-squares standard deviations, and

$$k(1\text{-butanal}) = 2.35 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

$$k(2\text{-methyl-1-propanal}) = 2.63$$

$$\times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

$$k(1\text{-pentanal}) = 2.85 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \text{ and}$$

$$k(2,2\text{-dimethyl-1-propanal}) = 2.65$$

$$\times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with estimated overall uncertainties at 298 K of $\pm 30\%$ for all four of these reactions.

At room temperature and below, these reactions are expected to proceed almost entirely by H-atom abstraction from the —CHO group,^{106,109} consistent with the independence of the rate constants at 298 K on the substituent alkyl group.²³ At elevated temperatures, however, H-atom abstraction from the alkyl substituent groups will become increasingly important, and hence the above recommended Arrhenius expressions should not be used outside of the temperature ranges from which they were derived.

(f) 3-Methyl-1-butanal

Rate constants have been determined at 298 K by Kerr and Sheppard,²² Audley *et al.*²⁷ and Semmes *et al.*²³ (Table 11) and, consistent with the above recommendations for the aldehydes, a unit-weighted average of the rate constants of Kerr and Sheppard²² and Semmes *et al.*²³ leads to the recommendation of

$$k(3\text{-methyl-1-butanal}) = 2.74$$

$$\times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty of $\pm 30\%$.

This OH radical reaction at room temperature and below is again expected to proceed mainly by H-atom abstraction from the —CHO group.

(g) Benzaldehyde

Room temperature rate constants have been determined by Niki *et al.*¹² and Kerr and Sheppard²² (Table

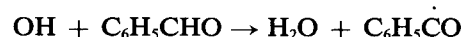
11). These rate constants are in good agreement, and it is recommended from a unit-weighted average of these data^{12,22} that

$$k(\text{benzaldehyde}) = 1.29$$

$$\times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty of $\pm 25\%$.

Benzaldehyde is included in the aldehydes rather than with the aromatic compounds since it is apparent^{12,106,109} that at room temperature the reaction proceeds essentially totally ($\approx 90\%$) by overall H-atom abstraction from the —CHO group,



and not by OH radical addition to the aromatic ring. This H-atom abstraction process is expected to be by far the dominant reaction pathway up to at least 1000 K.

(2) Ketones

The available kinetic data are given in Table 11. Only for acetone, 2-butanone, 2- and 3-pentanone, 2-hexanone, 4-methyl-2-pentanone and 2,6-dimethyl-4-heptanone have more than one study been carried out.

(a) Acetone

The available rate constant data of Cox *et al.*,³¹ Zetzsch,³² Chiorboli *et al.*,³³ Kerr and Stocker³⁴ and Wallington and Kurylo³⁵ are given in Table 11, and those of Zetzsch,³² Kerr and Stocker³⁴ and Wallington and Kurylo³⁵ are plotted in Arrhenius form in Fig. 67. The rate constant reported by Chiorboli *et al.*³³ was obtained from irradiations of NO_x-organic-air mixtures, and it is possible that photolysis of acetone contributed to its removal. The upper limit to the rate constant of Cox *et al.*³¹ is consistent with the remaining data,^{32,34,35} which are in good agreement. The only temperature-dependent study is that of Wallington and Kurylo.³⁵

A unit-weighted least-squares analysis of the rate constant data of Zetzsch,³² Kerr and Stocker³⁴ and Wallington and Kurylo,³⁵ using the expression $k = CT^2 e^{-D/T}$, leads to the recommendation of

$$k(\text{acetone}) = (2.13_{-0.61}^{+0.85})$$

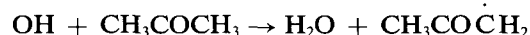
$$\times 10^{-18} T^2 e^{(53 \pm 106)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 240–440 K, where the indicated error limits are two least-squares standard deviations, and

$$k(\text{acetone}) = 2.26 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty at 298 K of $\pm 35\%$.

This reaction proceeds by H-atom abstraction from the $-\text{CH}_3$ groups.



The magnitude of the temperature dependence is somewhat less than may be expected by analogy with the alkanes¹⁰⁹ (for example, ethane, which has a similar room temperature rate constant).

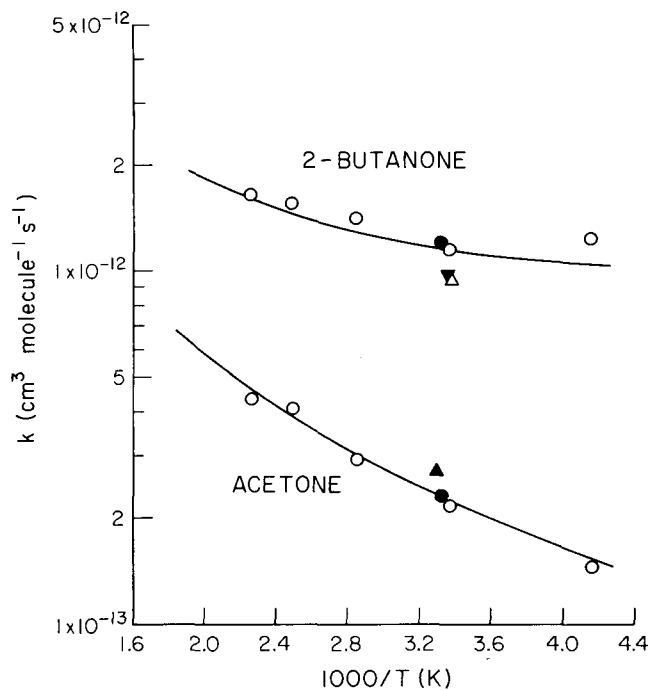


FIG. 67. Arrhenius plot of rate constants for the reactions of the OH radical with acetone and 2-butanone. (Δ) Cox *et al.*,³⁷ (\bullet) Zetzsch,³² (\blacktriangle) Kerr and Stocker,³⁴ (\blacktriangledown) Edney *et al.*,³⁸ (\circ) Wallington and Kurylo,³⁵ (—) recommendations (see text).

(b) 2-Butanone

The available rate constants of Winer *et al.*,³⁶ Cox *et al.*,^{31,37} Zetzsch,³² Edney *et al.*,³⁸ and Wallington and Kurylo³⁵ are given in Table 11, and those of Cox *et al.*,³⁷ Zetzsch,³² Edney *et al.*,³⁸ and Wallington and Kurylo³⁵ are plotted in Arrhenius form in Fig. 67. The rate constants obtained from the relative rate studies of Winer *et al.*³⁶ and Cox *et al.*³¹ are a factor of ~ 2 – 3 higher than the more recent absolute^{32,35} and relative^{37,38} rate data, and are not consistent with the kinetic data of Atkinson *et al.*³⁹ for the higher ketones.

Accordingly, a unit-weighted least-squares analysis of the rate constants of Cox *et al.*,³⁷ Zetzsch,³² Edney *et al.*,³⁸ and Wallington and Kurylo³⁵ (the only temperature-dependent study), using the expression $k = CT^2e^{-D/T}$, leads to the recommendation of

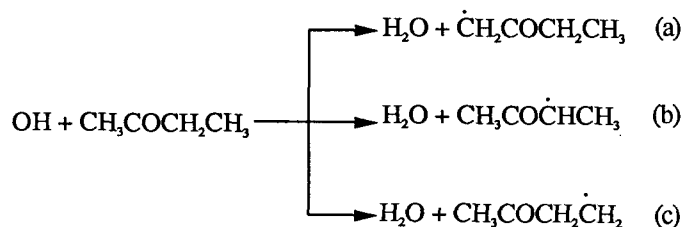
$$k(2\text{-butanone}) = (3.24_{-1.34}^{+2.29}) \times 10^{-18} T^2 e^{(414 \pm 167)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 240–440 K, where the indicated errors are two least-squares standard deviations, and

$$k(2\text{-butanone}) = 1.15 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty at 298 K of $\pm 25\%$. As for acetone, the magnitude of the temperature dependence is less than expected by analogy with the reactions of the OH radical with alkanes¹⁰⁹ (for example, propane, which has a similar room temperature rate constant).

The OH radical reaction with 2-butanone, as for the other ketones, occurs by H-atom abstraction from the C—H bonds:



From a product study, Cox *et al.*³⁷ determined that at 295 ± 2 K the rate constant ratio $k_b/(k_a + k_b + k_c) = 0.62 \pm 0.02$, and approximate values of the fractions of the overall reaction proceeding by the three pathways (a), (b) and (c) are available from estimation methods.¹⁰⁹

(c) 2-Pentanone, 3-Pentanone and 2-Hexanone

For these three ketones, rate constants have been determined by Atkinson *et al.*,³⁹ Wallington and Kurylo³⁵ and Atkinson and Aschmann⁴⁰ (Table 11). As discussed by Atkinson and Aschmann,⁴⁰ the rate constants obtained from the relative rate studies^{39,40} (which are in good agreement) exhibit significant discrepancies with the room temperature absolute rate constants of Wallington and Kurylo³⁵ which are independent of the uncertainties associated with the rate constant for the reference organic (cyclohexane) used in the relative rate studies. Furthermore, these discrepancies are of a random nature, ranging from -25% for 2-pentanone to $+25$ – 35% for 3-pentanone and 2-hexanone. These data suggest that the absolute rate constants obtained by Wallington and Kurylo³⁵ for these, and possibly the higher, ketones were subject to significant systematic uncertainties which are not reflected in the cited error limits. From the relative rate studies of Atkinson *et al.*³⁹ and Atkinson and Aschmann,⁴⁰ the following 298 K rate constants are recommended,

$$k(2\text{-pentanone}) = 4.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

$k(3\text{-pentanone}) = 2.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$,
and

$k(2\text{-hexanone}) = 9.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$,

all with estimated overall uncertainties of $\pm 30\%$.

(d) *4-Methyl-2-pentanone*

The four reported room temperature rate constants of Winer *et al.*,³⁶ Cox *et al.*^{31,37} and Atkinson *et al.*³⁹ are in good agreement (Table 11), and a unit-weighted average of the two most recent (and supposedly accurate) determinations of Cox *et al.*³⁷ and Atkinson *et al.*³⁹ yields the recommendation of

$k(4\text{-methyl-2-pentanone}) = 1.41$
 $\times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

at 298 K, with an estimated overall uncertainty of $\pm 30\%$.

(e) *2,6-Dimethyl-4-heptanone*

The two reported room temperature rate constants of Winer *et al.*³⁶ and Atkinson *et al.*³⁹ are in good agreement (Table 11), and the most recent and precise rate constant of Atkinson *et al.*³⁹ of

$k(2,6\text{-dimethyl-4-heptanone}) = 2.75$
 $\times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

is recommended at 298 K, with an estimated overall uncertainty of $\pm 30\%$.

(f) *Other Ketones*

For the remaining ketones, only single studies have been carried out to date and no recommendations are made. All of these OH radical reactions with the ketones proceed by H-atom abstraction from the C—H bonds.^{31,37,106} The kinetic study of Atkinson *et al.*³⁹ shows that at room temperature the carbonyl $>C=O$ group decreases the reactivity of the C—H bonds on the α -carbon atom towards attack by the OH radical, relative to the C—H bonds in the analogous alkane, but increases the reactivity of the C—H bonds on the β -carbon atom. Those effects have been incorporated into an estimation method¹⁰⁹ for the calculation of the overall OH radical reaction rate constants and the contributions of the differing C—H bond abstraction pathways to the overall reaction rate constant over the temperature range $\sim 250\text{--}1000$ K.

(3) α,β -Unsaturated Carbonyls

The available rate constant data are given in Table 11. For all four of the α,β -unsaturated carbonyls investigated, two or more studies have been carried out.

(a) *Acrolein*

The four room temperature rate constants obtained by Maldotti *et al.*,⁴² Kerr and Sheppard,²² Atkinson *et al.*⁴³ and Edney *et al.*³⁸ are in reasonable agreement. A unit-weighted average of the rate constants from the three most recent studies of Kerr and Sheppard,²² Atkinson *et al.*⁴³ and Edney *et al.*³⁸ leads to the recommendation of

$k(\text{acrolein}) = 1.99 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

at 298 K, with an estimated overall uncertainty of $\pm 30\%$.

This recommended room temperature rate constant is of a similar magnitude to those for the saturated aldehydes. By analogy, it is expected that the OH radical reaction with acrolein proceeds mainly by H-atom abstraction from the —CHO group, with the OH radical addition pathway being of minor importance at 298 K.^{106,109,110} Thus, it is expected that this reaction will have a negative temperature dependence of $B \sim -250$ K at around room temperature.

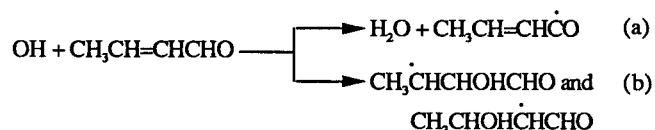
(b) *Crotonaldehyde*

The room temperature rate constants of Kerr and Sheppard²² and Atkinson *et al.*⁴³ (Table 11) are in excellent agreement, and a unit-weighted average of these rate constants yields the recommendation of

$k(\text{crotonaldehyde}) = 3.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

at 298 K, with an estimated overall uncertainty of $\pm 30\%$.

At around room temperature this reaction proceeds by H-atom abstraction from the —CHO group and OH radical addition to the $>C=C<$ bond,



with $k_a/(k_a + k_i)$ being estimated to be ~ 0.5 at 298 K.¹⁰⁹ By analogy with methacrolein (see below), a negative temperature dependence equivalent to $B \sim -150$ K is expected at around room temperature. At elevated temperatures $\gtrsim 500\text{--}600$ K, only the H-atom abstraction route is expected to be of importance due to thermal decomposition of the addition radicals formed in reaction pathway (b).

(c) *Methacrolein*

The available rate constants of Kleindienst *et al.*,⁴⁴ Atkinson *et al.*⁴³ and Edney *et al.*³⁸ are given in Table 11 and are plotted in Arrhenius form in Fig. 68.

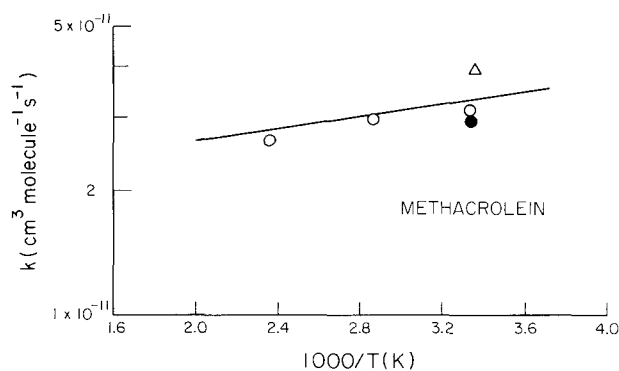


FIG. 68. Arrhenius plot of rate constants for the reaction of the OH radical with methacrolein. (○) Kleindienst *et al.*;⁴⁴ (●) Atkinson *et al.*;⁴³ (Δ) Edney *et al.*;³⁸ (—) recommendation (see text).

At room temperature the rate constants of Kleindienst *et al.*⁴⁴ and Atkinson *et al.*⁴³ are in excellent agreement, with that of Edney *et al.*³⁸ being ~30% higher. Since the sole temperature-dependent study is that of Kleindienst *et al.*,⁴⁴ a unit-weighted average of the three room temperature rate constants^{38,43,44} is used in conjunction with the temperature dependence obtained from the study of Kleindienst *et al.*⁴⁴ to recommend that

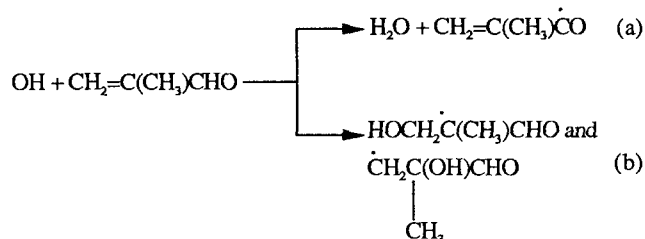
$$k(\text{methacrolein}) = (1.86_{-0.41}^{+0.51}) \times 10^{-11} e^{(175 \pm 83)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 298–423 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{methacrolein}) = 3.35 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty at 298 K of $\pm 30\%$.

As for crotonaldehyde, at room temperature this OH radical reaction proceeds by H-atom abstraction from the —CHO group and OH radical addition to the $>C=C<$ bond,



with $k_a/(k_a + k_b)$ being estimated to be ~ 0.5 at 298 K.^{106,109}

(d) Methyl vinyl ketone

The available rate constants of Cox *et al.*,³¹ Kleindienst *et al.*⁴⁴ and Atkinson *et al.*⁴³ are given in Table 11 and are plotted in Arrhenius form in Fig. 69.

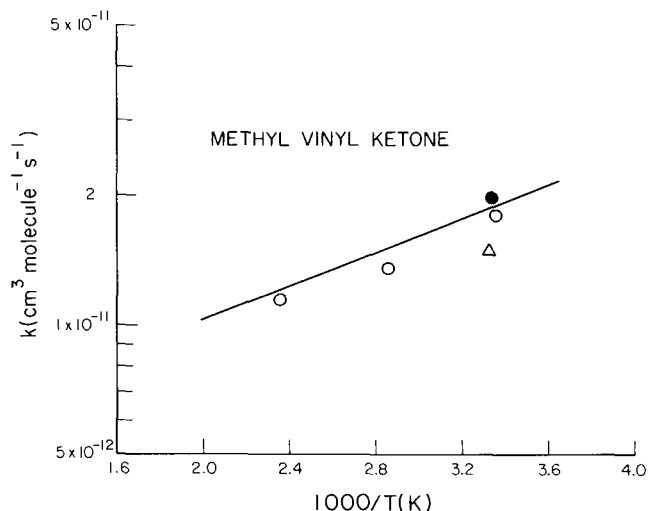


FIG. 69. Arrhenius plot of rate constants for the reaction of the OH radical with methyl vinyl ketone. (Δ) Cox *et al.*;³¹ (○) Kleindienst *et al.*;⁴⁴ (●) Atkinson *et al.*;⁴³ (—) recommendation (see text).

Again, the room temperature rate constants of Kleindienst *et al.*⁴⁴ and Atkinson *et al.*⁴³ are in good agreement, with that of Cox *et al.*³¹ being ~20% lower. From a unit-weighted average of the room temperature rate constants of Kleindienst *et al.*⁴⁴ and Atkinson *et al.*⁴³ and the temperature dependence of Kleindienst *et al.*,⁴⁴ it is recommended that

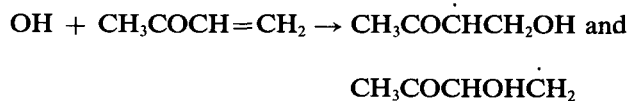
$$k(\text{methyl vinyl ketone}) = (4.13_{-1.30}^{+1.88}) \times 10^{-12} e^{(452 \pm 130)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 298–424 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{methyl vinyl ketone}) = 1.88 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

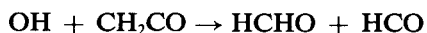
at 298 K, with an estimated overall uncertainty at 298 K of $\pm 30\%$.

This OH radical reaction will proceed essentially totally by OH radical addition to the $>C=C<$ bond at temperatures $\lesssim 500$ K, with the rate constant for this reaction being at, or close to, the high-pressure limit at total pressures $\gtrsim 50$ Torr. At 298 ± 2 K, the $\text{CH}_3\text{COCHCH}_2\text{OH}$ and $\text{CH}_3\text{COCHOHCH}_2$ radicals are formed in an $\sim 70\%:30\%$ distribution.¹¹¹

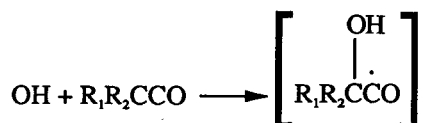


(4) Ketenes

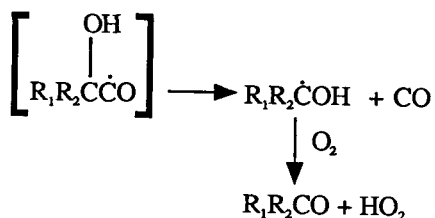
The available kinetic data for the reactions of the OH radical with ketene, methylketene, ethylketene and dimethylketene are given in Table 11. No recommendations are made. The rate constant for ketene derived by Vandoooren and Van Tiggelen¹¹ from flame measurements was based upon the measured formation of HCHO. It was assumed that the reaction occurred by



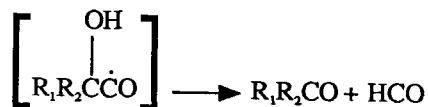
and was hence not a direct rate study. The room temperature kinetic and product data of Hatakeyama *et al.*⁴⁶ show that these reactions of the OH radical with the ketenes proceed by initial OH radical addition, with the ultimate formation (under the experimental conditions employed) of carbonyl compounds.⁴⁶



followed by either



or



in a direct reaction. In the presence of O₂ these reactions yield identical products, since HCO reacts rapidly with O₂ to form HO₂ and CO.¹⁰⁵

(5) Dicarboxyls

Rate constants have been measured for the α-dicarboxyls glyoxal,^{47,48} methylglyoxal,^{44,47} and 2,3-butanedione (biacetyl)^{41,49} and for pentane-1,5-dial,⁵⁰ 2,4-pentanedione⁴¹ and 2,5-hexanedione.⁴¹

(a) Glyoxal

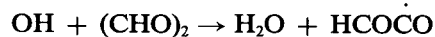
The available rate constant data of Plum *et al.*⁴⁷ and Becker and Klein⁴⁸ are given in Table 11. Both of these

studies were relative rate measurements carried out at room temperature. The agreement is good, and the rate constant of Plum *et al.*⁴⁷ of

$$k(\text{glyoxal}) = 1.14 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K is recommended, with an estimated overall uncertainty of ±40%.

As for the aliphatic aldehydes such as HCHO and CH₃CHO, the OH radical reaction proceeds by H-atom abstraction,



and the subsequent reactions of the HCOCO radical (involving decomposition and reaction with O₂) have been investigated at room temperature by Niki *et al.*¹¹² in the presence of 700 Torr of O₂ + N₂ diluent.

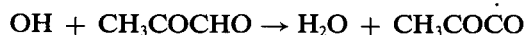
(b) Methylglyoxal

The available rate constants of Kleindienst *et al.*⁴⁴ and Plum *et al.*⁴⁷ are given in Table 11. The rate constant derived from the relative rate study of Plum *et al.*⁴⁷ is a factor of 2.4 higher than the absolute value of Kleindienst *et al.*⁴⁴ It is possible that the methylglyoxal sample prepared and used by Kleindienst *et al.*⁴⁴ contained a significant amount of non-reactive impurities (such as CO and CO₂), and the rate constant of Plum *et al.*⁴⁷ of

$$k(\text{methylglyoxal}) = 1.72 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K is recommended, with an estimated overall uncertainty of ±40%.

At around room temperature this reaction will proceed by H-atom abstraction from the —CHO group



By analogy with the HCOCO radical formed from glyoxal, the resulting CH₃COCO radical is expected to decompose or react with O₂, with decomposition (to CH₃CO and CO) being expected to dominate at ~298 K and atmospheric pressure of air. At elevated temperatures H-atom abstraction from the —CH₃ group will become significant.¹⁰⁹

(c) 2,3-Butanedione

The rate constants of Darnall *et al.*⁴⁹ and Dagaut *et al.*⁴¹ are given in Table 11 and are plotted in Arrhenius form in Fig. 70. At room temperature the measured rate constants are in excellent agreement. A unit-weighted least-squares analysis of the kinetic data of Darnall *et al.*⁴⁹ and Dagaut *et al.*⁴¹ using the expression $k = CT^2e^{-D/T}$, leads to the recommendation of

$$k(2,3\text{-butanedione}) = (1.40^{+0.59}_{-0.42})$$

$$\times 10^{-18} T^2 e^{(194 \pm 112)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 240–440 K, where the indicated errors are two least-squares standard deviations, and

$$k(2,3\text{-butanedione}) = 2.38 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty at 298 K of $\pm 35\%$.

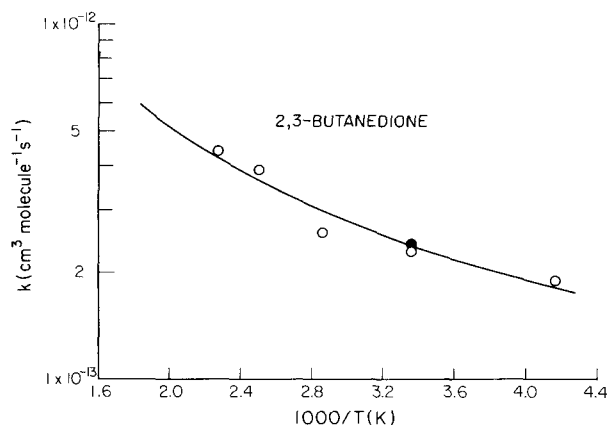
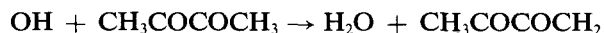


FIG. 70. Arrhenius plot of rate constants for the reaction of the OH radical with 2,3-butanedione (biacetyl). (●) Darnall *et al.*;⁴⁹ (○) Dagaut *et al.*;⁴¹ (—) recommendation (see text).

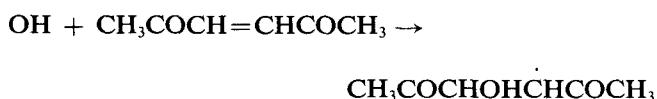
This OH radical reaction proceeds by H-atom abstraction from the $-\text{CH}_3$ groups



At room temperature this rate constant is similar to those for the reactions of the OH radical with ethane and acetone and, as for acetone, the magnitude of the temperature dependence appears somewhat low when compared to the alkanes (for example, ethane for which $C = 1.42 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $D = 462 \text{ K}$). Accordingly, until further temperature-dependent studies are carried out, the above recommended expression should be used with caution outside of the temperature range $\sim 240\text{--}440 \text{ K}$.

(6) Unsaturated 1,4-Dicarbonyls

The sole kinetic data for this class of organic compounds arise from the room temperature relative rate study of Tuazon *et al.*⁵¹ for *cis*- and *trans*-3-hexene-2,5-dione. At around room temperature these reactions are expected to proceed essentially entirely by OH radical addition to the $>\text{C}=\text{C}<$ bond,



with the rate constant being at, or very close to, the high-pressure limit under atmospheric conditions.

(7) Alcohols and Glycols

(a) Methanol and Methanol- d_3 (CD_3OH)

The available rate constants of Campbell *et al.*,⁵² Overend and Paraskevopoulos,⁵³ Ravishankara and Davis,⁵⁴ Vandooren and Van Tiggelen,⁵⁵ Barnes *et al.*,⁵⁶ Hägele *et al.*,⁵⁷ Tuazon *et al.*,⁵⁸ Meier *et al.*,^{59,60} Zetzsch,⁶¹ Greenhill and O'Grady,⁶² Wallington and Kurylo,⁶³ Hess and Tully⁶⁴ and McCaulley *et al.*⁶⁵ are given in Table 11 and those of Campbell *et al.*,⁵² Overend and Paraskevopoulos,⁵³ Ravishankara and Davis,⁵⁴ Vandooren and Van Tiggelen,⁵⁵ Barnes *et al.*,⁵⁶ Hägele *et al.*,⁵⁷ Tuazon *et al.*,⁵⁸ Meier *et al.*,^{59,60} Greenhill and O'Grady,⁶² Wallington and Kurylo⁶³ and Hess and Tully⁶⁴ for methanol are plotted in Arrhenius form in Fig. 71.

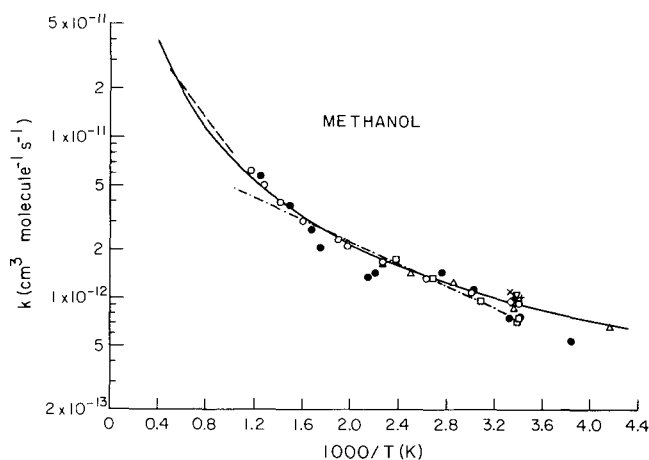


FIG. 71. Arrhenius plot of rate constants for the reaction of the OH radical with methanol. (+) Campbell *et al.*;⁵² (∇) Overend and Paraskevopoulos;⁵³ (▲) Ravishankara and Davis;⁵⁴ (— —) Vandooren and Van Tiggelen;⁵⁵ (x) Barnes *et al.*;⁵⁶ (□) Hägele *et al.*;⁵⁷ (◇) Tuazon *et al.*;⁵⁸ (- - -) Meier *et al.*;^{59,60} (●) Greenhill and O'Grady;⁶² (Δ) Wallington and Kurylo;⁶³ (○) Hess and Tully;⁶⁴ (—) recommendation (see text).

In addition to the rate constants given in Table 11, Osif *et al.*¹¹³ also determined rate constants for methanol at 298 and 345 K, relative to those for the reaction of OH radicals with CO, at total pressures of 28–203 Torr of $\text{CH}_3\text{OH} + \text{N}_2\text{O} + \text{CO}$. While no quantitative estimate of this reference reaction rate constant can be made, a lower limit of $1.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K is applicable, and the data of Osif *et al.*¹¹³ yield a rate constant of $\geq (9.5 \pm 1.5) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K, with a likely upper limit at this temperature of

$\approx 2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Since this rate constant is lower by a factor of ~ 4 – 10 than the room temperature rate constants listed in Table 11, the data of Osif *et al.*¹¹³ are neglected in the evaluation of the rate constant.

In general, the agreement between these studies is reasonably good, although the rate constants determined by Greenhill and O'Grady⁶² exhibit a significant degree of scatter and, together with the rate data of Hägele *et al.*⁵⁷ and Zetzsch,⁶¹ are substantially lower at ~ 290 – 300 K than the rate constants from the remaining studies. Of particular concern for atmospheric purposes is the disagreement at temperatures < 290 K between the measurement of Greenhill and O'Grady⁶² and that of Wallington and Kurylo.⁶³

The data from the studies of Vandooren and Van Tiggelen⁵⁵ and Meier *et al.*^{59,60} cannot be used in the evaluation because the rate constants at the specific temperatures studied were not tabulated. The absolute rate constants of Overend and Paraskevopoulos,⁵³ Ravishankara and Davis,⁵⁴ Wallington and Kurylo⁶³ and Hess and Tully⁶⁴ and the rate constant from the relative rate study of Tuazon *et al.*⁵⁸ have been used to evaluate the rate constant for the methanol reaction. A unit-weighted least-squares analysis of these data,^{53,54,58,63,64} using the expression $k = CT^2 e^{-D/T}$, yields the recommendation of

$$k(\text{methanol}) = (6.39^{+0.60}_{-0.54}) \times 10^{-18} T^2 e^{(148 \pm 33)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

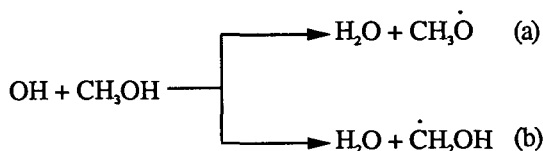
over the temperature range 240–866 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{methanol}) = 9.32 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty at 298 K of $\pm 25\%$.

The data of Vandooren and Van Tiggelen⁵⁵ at 1000–2000 K are in excellent agreement with this recommendation (Fig. 71), suggesting that the recommended expression can be used with some confidence up to ~ 2000 K. However, it is clear that further rate constant data are needed at temperatures $\lesssim 290$ K.

The reaction of the OH radical with methanol proceeds by H-atom abstraction, from either the $-\text{CH}_3$ group or the $-\text{OH}$ group.



Based upon the C–H and O–H bond dissociation energies of 94.1 kcal mol⁻¹ and 104.5 kcal mol⁻¹, respectively,¹¹⁴ reaction pathway (b) would be expected to

totally dominate at room temperature and below. The room temperature rate constants of Greenhill and O'Grady,⁶² Hess and Tully⁶⁴ and McCaulley *et al.*⁶⁵ for CD₃OH are in reasonable agreement, and the deuterium isotope effect observed by Hess and Tully⁶⁴ of

$$k(\text{CH}_3\text{OH})/k(\text{CD}_3\text{OH}) = k^{\text{H}}/k^{\text{D}} = 460 T^{-0.83} e^{-198/T}$$

(equivalent to $k^{\text{H}}/k^{\text{D}} = 1.15 e^{217/T}$ centered at 500 K) is consistent (Section 2.1) with H- (or D-) atom abstraction from the $-\text{CH}_3$ (or $-\text{CD}_3$) group dominating over the temperature range studied.

However, Hägele *et al.*⁵⁷ and Meier *et al.*^{59,60} have experimentally investigated the relative importance of pathways (a) and (b), and derived, from LIF measurements of the CH₃O radical, ratios of $k_a/(k_a + k_b)$ at ~ 298 K of 0.11 ± 0.03 ⁵⁷ (increasing to 0.22 ± 0.07 at 393 K⁵⁷) and 0.25 ± 0.08 .^{59,60} Meier *et al.*⁵⁹ also determined a ratio of $k_b/(k_a + k_b)$ of 0.83 ± 0.13 at room temperature using mass spectrometry. From their kinetic measurements on the various methanol isotopes, McCaulley *et al.*⁶⁵ derived a ratio of

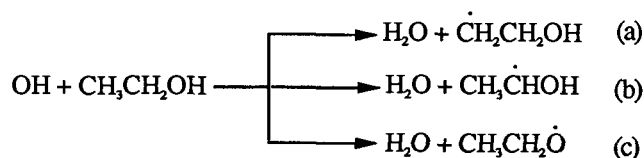
$$k_a/(k_a + k_b) = 0.15 \pm 0.08 \text{ at } 298 \pm 2 \text{ K.}$$

Thus, for CH₃OH H-atom abstraction occurs to a significant extent from both the C–H and O–H bonds, with abstraction from the stronger O–H bonds increasing in importance with increasing temperature.

(b) Ethanol

The rate constant data of Campbell *et al.*,⁵² Overend and Paraskevopoulos,⁵³ Ravishankara and Davis,⁵⁴ Cox and Goldstone,⁶⁶ Meier *et al.*,⁶⁸ Lorenz *et al.*,⁶⁹ Kerr and Stocker,³⁴ Greenhill and O'Grady,⁶² Wallington and Kurylo⁶³ and Hess and Tully⁷⁰ are given in Table 11 and are plotted in Arrhenius form in Fig. 72. Clearly, there is a large amount of scatter between the various studies, with the rate constants of Ravishankara and Davis⁵⁴ and Meier *et al.*⁶⁸ being lower than the data from the remaining studies.

As recognized and experimentally demonstrated by Hess and Tully,⁷⁰ kinetic studies which involve monitoring the decay rates of the OH radical in the presence of C₂H₅OH are subject to regeneration of the OH radical at elevated temperatures from the reaction pathway involving H-atom abstraction from the $-\text{CH}_3$ group, leading to erroneously low measured rate constants. The three possible reaction pathways are,



and the $\text{CH}_2\text{CH}_2\text{OH}$ radical formed in pathway (a) is identical to that formed from the addition reaction of the OH radical to ethene. As discussed in Section 2.3 above, the thermalized $\text{CH}_2\text{CH}_2\text{OH}$ radical thermally decomposes to the OH radical and ethene at a significant rate at temperatures above $\sim 450\text{--}500\text{ K}$. Thus, in absolute studies employing ^{16}OH and ^{16}O -ethanol, at temperatures $\lesssim 450\text{--}500\text{ K}$ all three channels are observed and the measured rate constant is $k_{\text{obs}} = k_a + k_b + k_c$. At temperatures $\gtrsim 500\text{ K}$ where thermal decomposition of the $\text{CH}_2\text{CH}_2\text{OH}$ radical is sufficiently rapid, only channels (b) and (c) are observed, with $k_{\text{obs}} = k_b + k_c$. At intermediate temperatures ($\sim 450\text{--}700\text{ K}$, depending on the experimental conditions employed), bi-exponential OH radical decays should be observed.

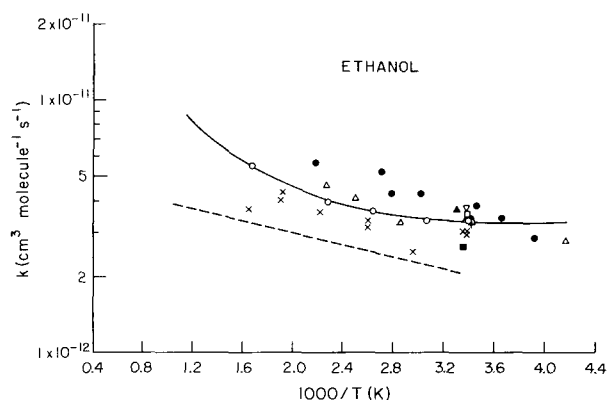


FIG. 72. Arrhenius plot of rate constants for the reaction of the OH radical with ethanol. (+) Campbell *et al.*;⁵² (∇) Overend and Paraskevopoulos;⁵³ (■) Ravishankara and Davis;⁵⁴ (□) Cox and Goldstone;⁵⁶ (— — —) Meier *et al.*;⁶⁸ (x) Lorenz *et al.*;⁶⁹ (▲) Kerr and Stocker;³⁴ (●) Greenhill and O'Grady;⁶² (Δ) Wallington and Kurylo;⁶³ (○) Hess and Tully,⁷⁰ rate constant for ^{18}OH reaction only plotted for temperatures $>441\text{ K}$; (—) recommendation for overall reaction rate constant (see text).

The recent absolute study of Hess and Tully⁷⁰ confirms these expectations.⁷⁰ As shown by the Arrhenius plot in Fig. 73, the measured rate constants for the reaction of the ^{16}OH radical with ethanol exhibit a plateau region at $\sim 520\text{--}600\text{ K}$. Moreover, the measured rate constant for the reaction of the ^{18}OH radical with ethanol [which is not subject to regeneration of the ^{18}OH radical from the thermal decomposition of the $\text{CH}_2\text{CH}_2^{16}\text{OH}$ radical formed in pathway (a)] at 599 K is $\sim 15\%$ higher than that measured for the ^{16}OH reaction. These data indicate that pathway (a) accounts for $\sim 15\%$ of the overall reaction at $\sim 600\text{ K}$ (which agrees well with the calculated value of 20% from the estimation procedure of Atkinson¹⁰⁹), and show that the measured rate constants for the reaction of the ^{16}OH radical with ^{16}O -ethanol at temperatures $\gtrsim 500\text{ K}$ cannot be used to derive the overall rate constant for this reaction.

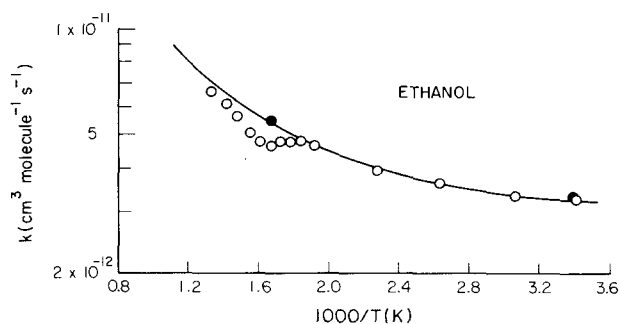


FIG. 73. Arrhenius plot of rate constants obtained by Hess and Tully⁷⁰ for the reactions of ^{16}OH and ^{18}OH radicals with ethanol. (○) ^{16}OH radical reaction; (●) ^{18}OH radical reaction; (—) recommendation for the overall reaction rate constant, $k = k_a + k_b + k_c$ (see text).

Accordingly, the rate constant data of Hess and Tully⁷⁰ have been used in the recommendation of the rate constant for this reaction, using only the ^{18}OH radical rate constant data above 500 K . A unit-weighted least-squares analysis of these data,⁷⁰ using the expression $k = CT^2e^{-D/T}$, yields the recommendation of

$$k(\text{ethanol}) = (6.18^{+0.36}_{-0.34}) \times 10^{-18} T^2 e^{(532 \pm 21)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range $293\text{--}599\text{ K}$, where the indicated errors are two least-squares standard deviations, and

$$k(\text{ethanol}) = 3.27 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K , with an estimated overall uncertainty at 298 K of $\pm 20\%$.

The rate constants of Greenhill and O'Grady⁶² are somewhat higher than the recommendation, while those of Lorenz *et al.*⁶⁹ (obtained at $\leq 500\text{ K}$) and Wallington and Kurylo⁶³ are in reasonable agreement. It is possible that the decrease in the measured rate constants of Lorenz *et al.*⁶⁹ as the temperature was raised above 525 K was due to the changeover from observing all of the reaction channels to observing only channels (b) and (c).

The sole direct product study carried out to date is that of Meier *et al.*,^{60,67} in which mass spectrometry was used to show that reaction channel (b) accounted for $75 \pm 15\%$ of the overall reaction at 300 K . As noted above, the kinetic data of Hess and Tully⁷⁰ indicate that channel (a) accounts for $\sim 15\%$ of the overall reaction at 600 K . At combustion temperatures (indeed, above $\sim 500\text{ K}$), channel (a) in effect proceeds by



(c) 1-Propanol

Rate constants have been determined at room temperature by Campbell *et al.*,⁵² Overend and Paraskevopoulos

los⁵³ and Wallington and Kurylo⁶³ (Table 11). The absolute rate constants of Overend and Paraskevopoulos⁵³ and Wallington and Kurylo⁶³ are in excellent agreement, and it is recommended from a unit-weighted average of these data^{53,63} that

$$k(1\text{-propanol}) = 5.34 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty of $\pm 40\%$. (The rate constant of Campbell *et al.*⁵² was not used in the evaluation because of questions concerning the validity of the experimental technique used¹⁰⁶). Consistent with the discussion above for ethanol, H-atom abstraction from the β $-\text{CH}_2-$ group will lead to the formation of the radical $\text{CH}_3\dot{\text{C}}\text{HCH}_2\text{OH}$, identical to that formed by terminal OH radical addition to propene. This radical will thermally decompose to regenerate the OH radical above ~ 500 K and hence this reaction channel will not be observed at temperatures $\gtrsim 500$ K in absolute techniques monitoring the decay rates of the ¹⁶OH radical.

(d) 2-Propanol

The available rate constant data of Lloyd *et al.*,⁷¹ Overend and Paraskevopoulos,⁵³ Klöpffer *et al.*⁷² and Wallington and Kurylo⁶³ are given in Table 11 and are plotted in Arrhenius form in Fig. 74.

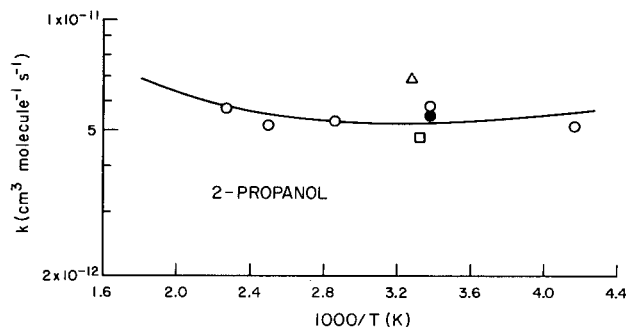


FIG. 74. Arrhenius plot of rate constants for the reaction of the OH radical with 2-propanol. (Δ) Lloyd *et al.*,⁷¹ (\bullet) Overend and Paraskevopoulos,⁵³ (\square) Klöpffer *et al.*,⁷² (\circ) Wallington and Kurylo,⁶³ (—) recommendation (see text).

At 296 K, the absolute rate constants of Overend and Paraskevopoulos⁵³ and Wallington and Kurylo⁶³ are in good agreement. A unit-weighted least-squares analysis of the data of Overend and Paraskevopoulos⁵³ and Wallington and Kurylo,⁶³ using the expression $k = CT^2e^{-D/T}$, yields the recommendation of

$$k(2\text{-propanol}) = (7.32^{+2.89}_{-2.07})$$

$$\times 10^{-18} T^2 e^{(620 \pm 106)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

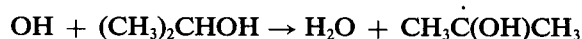
over the temperature range 240–440 K, where the indi-

cated errors are two least-squares standard deviations, and

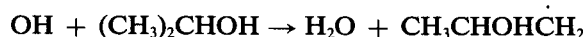
$$k(2\text{-propanol}) = 5.21 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty at 298 K of $\pm 40\%$.

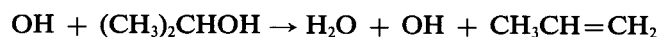
At around room temperature and below, the dominant reaction pathway will be H-atom abstraction from the tertiary C—H bond:



At elevated temperatures H-atom abstraction from the $-\text{CH}_3$ groups will become significant,



leading to the radical also formed by OH radical addition to propene. At temperatures $\gtrsim 500$ K this radical will thermally decompose to regenerate the OH radical together with propene,⁷⁰ and hence under these conditions this reaction channel becomes an OH radical catalyzed conversion of the alcohol to the alkene.⁷⁰



Hess and Tully⁷⁰ have confirmed the occurrence of this reaction process from kinetic studies of the reactions of ¹⁶OH and ¹⁸OH radicals with $(\text{CH}_3)_2\text{CH}^{16}\text{OH}$.

(e) 2-Methyl-2-propanol (tert-butyl alcohol)

The rate constants of Cox and Goldstone⁶⁶ and Wallington *et al.*⁷³ are given in Table 11 and are plotted in Arrhenius form in Fig. 75.

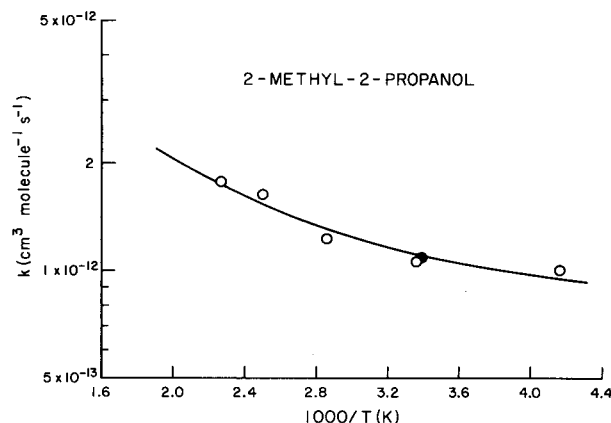


FIG. 75. Arrhenius plot of rate constants for the reaction of the OH radical with 2-methyl-2-propanol. (\bullet) Cox and Goldstone,⁶⁶ (\circ) Wallington *et al.*,⁷³ (—) recommendation (see text).

The room temperature rate constants from these studies are in excellent agreement, and a unit-weighted least-

squares analysis of these data,^{66,73} using the expression $k = CT^2e^{-D/T}$, leads to the recommendation of

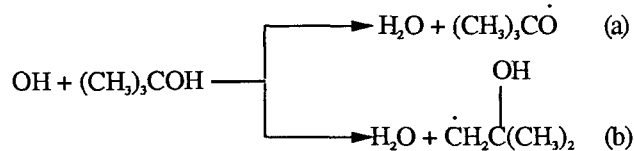
$$k(\text{2-methyl-2-propanol}) = (4.29^{+1.24}_{-0.97}) \times 10^{-18} T^2 e^{(322 \pm 81)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 240–440 K, where the indicated errors are two least-squares standard deviations, and

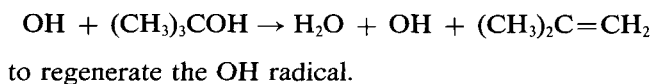
$$k(\text{2-methyl-2-propanol}) = 1.12 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty at 298 K of $\pm 40\%$.

The two reaction channels involve H-atom abstraction



It is expected that the major reaction pathway will be (b).¹⁰⁹ The radical formed from this reaction channel is that also formed from the addition reaction of the OH radical with 2-methylpropene and, as discussed above, this radical will thermally decompose to the OH radical and 2-methylpropene at temperatures $\gtrsim 500$ K. Hence, at these temperatures, reaction channel (b) will proceed by the overall reaction



(f) Other Alcohols and Glycols, Hydroxyethers and Ketoethers

The available kinetic data for a number of alcohols and glycols not dealt with above are given in Table 11. Apart from 1-butanol, 2-ethoxyethanol and 2-butoxyethanol these data were obtained from single studies (for 1-butanol one of the two studies was that of Campbell *et al.*,⁵² which is not used in the evaluations). No recommendations are made for these alcohols and glycols.

(8) Ethers and Cycloethers

The available kinetic data are given in Table 11, and it can be seen that studies have been carried out by more than one research group for dimethyl ether, diethyl ether, di-*n*-propyl ether, methyl *t*-butyl ether, ethyl *n*-butyl ether, ethyl *t*-butyl ether, di-*n*-butyl ether, tetrahydrofuran and furan. The data for these compounds are discussed as follows.

(a) Dimethyl ether

The available rate constant data of Perry *et al.*,⁷⁹ Tully and Droege⁸⁰ and Wallington *et al.*,⁸¹ all obtained using

flash or laser photolysis techniques, are given in Table 11 and are plotted in Arrhenius form in Fig. 76.

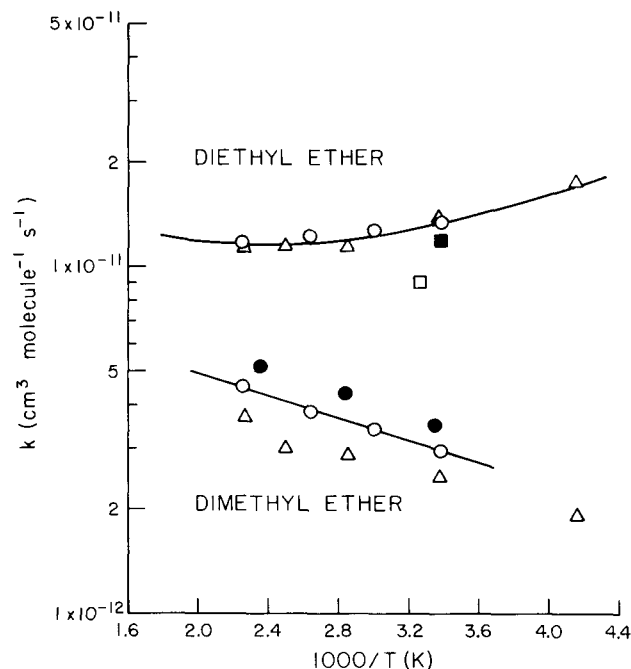


FIG. 76. Arrhenius plots of rate constants for the reactions of the OH radical with dimethyl ether and diethyl ether. (□) Lloyd *et al.*,⁷¹ (●) Perry *et al.*,⁷⁹ (○) Tully and Droege,⁸⁰ (Δ) Wallington *et al.*,⁸¹ (■) Bennett and Kerr,⁸² (—) recommendations (see text).

The rate constants determined by Perry *et al.*⁷⁹ are uniformly $\sim 15\%$ higher than those of Tully and Droege⁸⁰ over the entire temperature range studied, while those of Wallington *et al.*⁸¹ are $\sim 20\%$ lower over the temperature range common to both studies. This implies the existence of systematic errors in at least two of these studies. The rate constants of Tully and Droege,⁸⁰ which lie in between those of the other studies,^{79,81} are used to recommend, from a unit-weighted least-squares analysis, that

$$k(\text{dimethyl ether}) = (1.04^{+0.13}_{-0.11}) \times 10^{-11} e^{-(372 \pm 39)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 295–442 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{dimethyl ether}) = 2.98 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty at 298 K of $\pm 25\%$. This recommended Arrhenius expression is applicable only over the temperature range cited, since it is expected that non-Arrhenius behavior will be observed over a wider temperature range.¹⁰⁹ This reaction proceeds by H-atom abstraction from the $-\text{CH}_3$ groups.



(b) Diethyl ether and Diethyl ether- d_{10}

The rate constants for diethyl ether obtained by Lloyd *et al.*,⁷¹ Tully and Droege,⁸⁰ Wallington *et al.*⁸¹ and Bennett and Kerr⁸² are given in Table 11 and are plotted in Arrhenius form in Fig. 76. In this case, the absolute rate constants of Tully and Droege⁸⁰ and Wallington *et al.*⁸¹ are in good agreement and agree reasonably well with the room temperature rate constant of Bennett and Kerr.⁸² However, at room temperature the rate constants from these studies⁸⁰⁻⁸² are ~30–50% higher than the rate constant derived from the relative rate study of Lloyd *et al.*⁷¹ While the data of Tully and Droege,⁸⁰ obtained over the temperature range 295–442 K, show no evidence of non-Arrhenius behavior, the combined data set of Tully and Droege⁸⁰ and Wallington *et al.*⁸¹ do suggest that the Arrhenius plot exhibits curvature. A unit-weighted least-squares analysis of the rate constants of Tully and Droege,⁸⁰ Wallington *et al.*⁸¹ and Bennett and Kerr,⁸² using the expression $k = CT^2e^{-D/T}$, yields the recommendation of

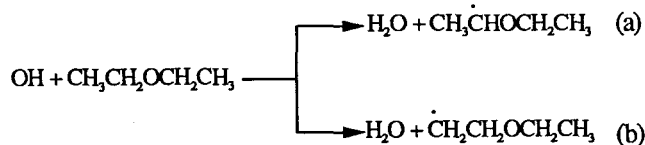
$$k(\text{diethyl ether}) = (8.80^{+1.73}_{-1.46}) \times 10^{-18} T^2 e^{(844 \pm 60)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 240–442 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{diethyl ether}) = 1.33 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty at 298 K of $\pm 25\%$.

The kinetic data of Tully⁸³ for diethyl ether- d_{10} (Table 11) show a significant deuterium isotope effect of $k(\text{diethyl ether})/k(\text{diethyl ether-}d_{10}) = 1.7\text{--}2.0$ over the temperature range 295–440 K, showing that these OH radical reactions with diethyl ether and diethyl ether- d_{10} proceed by H (or D) atom abstraction from the C—H (or C—D) bonds.



Pathway (a) is expected to dominate at essentially all temperatures.¹⁰⁹

(c) Di-*n*-propyl ether

The available rate constants of Lloyd *et al.*,⁷¹ Wallington *et al.*⁸¹ and Bennett and Kerr⁸² are given in Table 11 and are plotted in Arrhenius form in Fig. 77. The room temperature rate constants from these studies^{71,81,82} are in good agreement, and a unit-weighted least-squares anal-

ysis of the data of Wallington *et al.*⁸¹ and Bennett and Kerr,⁸² using the expression $k = CT^2e^{-D/T}$, yields the recommendation of

$$k(\text{di-}n\text{-propyl ether}) = (1.42^{+0.47}_{-0.36}) \times 10^{-17} T^2 e^{(778 \pm 90)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 240–440 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{di-}n\text{-propyl ether}) = 1.72 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty at 298 K of $\pm 35\%$. As for dimethyl ether and diethyl ether, this OH radical reaction will proceed by H-atom abstraction from the various C—H bonds.

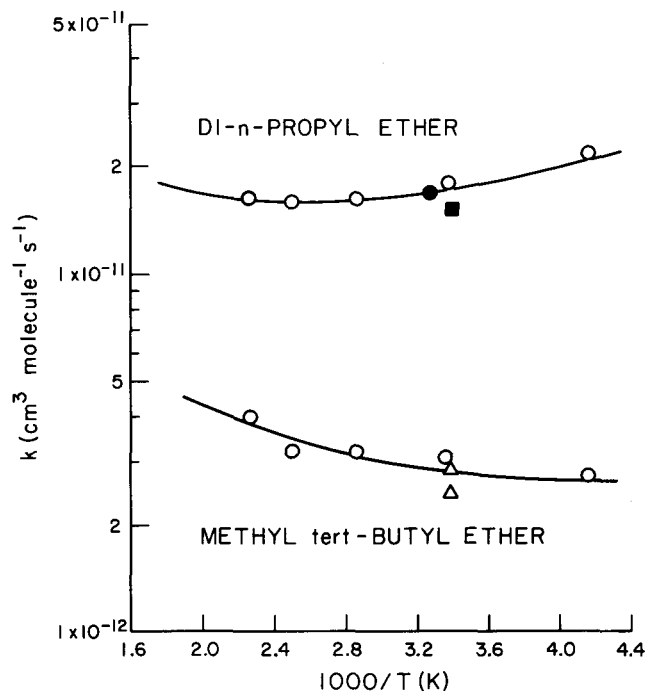


FIG. 77. Arrhenius plots of rate constants for the reactions of the OH radical with di-*n*-propyl ether and methyl *t*-butyl ether. (●) Lloyd *et al.*,⁷¹ (Δ) Cox and Goldstone,⁶⁶ (○) Wallington *et al.*⁸¹ (di-*n*-propyl ether) and Wallington *et al.*⁷³ (methyl *t*-butyl ether); (■) Bennett and Kerr,⁸² (—) recommendations (see text).

(d) Methyl *tert*-butyl ether

The rate constants of Cox and Goldstone⁶⁶ and Wallington *et al.*⁷³ are given in Table 11 and are plotted in Arrhenius form in Fig. 77. Within the combined overall experimental error limits, the room temperature rate constants from these studies^{66,73} are in agreement. The

rate constants obtained by Cox and Goldstone⁶⁶ at 295 ± 2 K using both *n*-hexane and ethene as the reference organics are in good agreement, showing a self-consistency of the data and suggesting the absence of significant systematic errors.

Although the Arrhenius plot (Fig. 77) does not show clear evidence for curvature, a unit-weighted least-squares analysis of the rate constant data of Cox and Goldstone⁶⁶ and Wallington *et al.*,⁷³ using the equation $k = CT^2e^{-D/T}$, has been carried out to yield the recommendation of

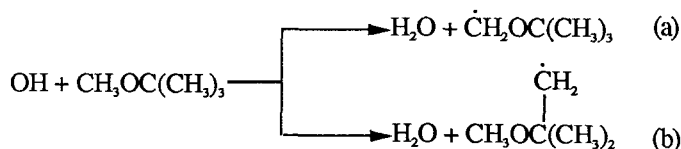
$$k(\text{methyl } t\text{-butyl ether}) = (6.81^{+2.91}_{-2.04}) \times 10^{-18} T^2 e^{(460 \pm 112)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 240–440 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{methyl } t\text{-butyl ether}) = 2.83 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty at 298 K of $\pm 35\%$.

This OH radical reaction will proceed by H-atom abstraction from all of the C—H bonds¹⁰⁹



with pathways (a) and (b) being calculated¹⁰⁹ to be of approximately comparable importance at around room temperature, with channel (b) becoming increasingly important with increasing temperature.

(e) Tetrahydrofuran

The available rate constants of Winer *et al.*,⁸⁴ Ravishankara and Davis⁵⁴ and Wallington *et al.*,⁸¹ all obtained at room temperature, are given in Table 11. These room temperature rate constants^{54,81,84} are in reasonably good agreement. A unit-weighted average of these rate constants^{54,81,84} leads to the recommendation of

$$k(\text{tetrahydrofuran}) = 1.61 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at ~ 298 K, with an estimated uncertainty of $\pm 30\%$. The temperature dependence of the rate constant for this reaction is expected to be essentially zero at around room temperature.

(f) Furan

The available rate constants of Lee and Tang,⁸⁵ Atkinson *et al.*,⁸⁶ Wine and Thompson,⁸⁷ Tuazon *et al.*,⁸⁸ and Witte and Zetzsch⁸⁹ are given in Table 11 and are plotted in Arrhenius form in Fig. 78.

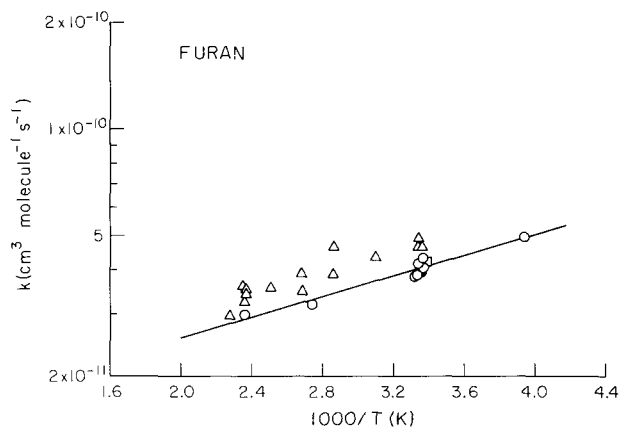


FIG. 78. Arrhenius plot of rate constants for the reaction of the OH radical with furan. (▲) Lee and Tang,⁸⁵ (●) Atkinson *et al.*,⁸⁶ (○) Wine and Thompson,⁸⁷ (□) Tuazon *et al.*,⁸⁸ (△) Witte and Zetzsch,⁸⁹ (—) recommendation (see text).

The room temperature rate constants from the studies of Atkinson *et al.*,⁸⁶ Wine and Thompson,⁸⁷ Tuazon *et al.*,⁸⁸ and Witte and Zetzsch⁸⁹ are a factor of ~ 2.0 – 2.5 lower than that of Lee and Tang.⁸⁵ It should be noted that a similar discrepancy occurs for the analogous reaction of OH radicals with thiophene (see Sec. 2.7 below), suggesting the occurrence of a systematic error in the discharge flow study of Lee and Tang,⁸⁵ at least for these two heterocycles [their room temperature rate constant for ethane⁸⁵ is consistent with other literature data (Sec. 2.1)].

The rate constants of Witte and Zetzsch⁸⁹ are uniformly $\sim 20\%$ higher than those of Atkinson *et al.*,⁸⁶ Wine and Thompson⁸⁷ and Tuazon *et al.*,⁸⁸ which are in excellent agreement at room temperature. A unit-weighted least-squares analysis of the data of Atkinson *et al.*,⁸⁶ Wine and Thompson⁸⁷ and Tuazon *et al.*,⁸⁸ yields the recommended Arrhenius expression of

$$k(\text{furan}) = (1.32^{+0.30}_{-0.24}) \times 10^{-11} e^{(334 \pm 61)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 254–424 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{furan}) = 4.05 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated uncertainty at 298 K of $\pm 25\%$ (which encompasses the rate constants of Witte and Zetzsch⁸⁹).

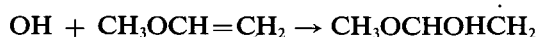
Consistent with the magnitude of the room temperature rate constant and the negative temperature dependency, the OH radical reaction with furan (and 3-methylfuran) almost certainly proceeds via initial OH radical addition to the $>\text{C}=\text{C}<$ double bond, with the measured rate constants^{86–89} being at, or close to, the

high-pressure limit. At elevated temperatures the resulting OH radical addition adduct is expected to undergo thermal decomposition, and hence kinetic studies are required to determine the rate constant at temperatures $\gtrsim 500$ K.

(g) *Other Ethers*

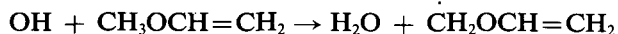
For the remaining ethers, no recommendations are made, although it should be noted that significant discrepancies exist between the room temperature rate constants of Wallington *et al.*⁷⁴ and Bennett and Kerr⁸² for ethyl *n*-butyl ether, ethyl *t*-butyl ether and di-*n*-butyl ether. These discrepancies, of up to a factor of 1.7, indicate the presence of systematic errors in at least one of these two studies.^{74,82} The OH radical reactions with the saturated ethers will proceed by H-atom abstraction from the C—H bonds, as discussed above for dimethyl, diethyl, di-*n*-propyl and methyl *t*-butyl ether.

For methyl vinyl ether, at temperatures $\lesssim 400$ –500 K the OH radical reaction will proceed mainly by OH radical addition to the $>C=C<$ bond.



and (mainly) $\text{CH}_3\text{OCHCH}_2\text{OH}$

Analogous to the reactions of the OH radical with the alkenes, at elevated temperatures ($\gtrsim 500$ –700 K) this OH radical adduct will undergo rapid thermal decomposition and the major reaction pathway then observed will be H-atom abstraction from the —CH₃ group:



(9) *Esters*

The available rate constant data are given in Table 11. For methyl acetate, ethyl acetate, *n*-propyl acetate, isopropyl acetate, *n*-butyl acetate, sec-butyl acetate, methyl propionate and ethyl propionate, studies have been carried out by two or three groups. However, as discussed previously¹⁰⁶ (and above), the rate constants obtained by Campbell and Parkinson⁹² are suspect due to questions concerning the validity of the experimental technique used (and discrepancies between the data of Campbell and Parkinson⁹² and Wallington *et al.*⁹¹ are evident for methyl acetate and methyl propionate, but not for ethyl acetate or ethyl propionate). For ethyl acetate, *n*-propyl acetate, isopropyl acetate, *n*-butyl acetate and sec-butyl acetate, the room temperature rate constants measured by various combinations of the studies of Winer *et al.*,⁸⁴ Zetzsch,⁶¹ Kerr and Stocker,³⁴ Hartmann *et al.*⁷⁸ and Wallington *et al.*⁹¹ are in reasonable agreement.

However, the temperature dependences (for $T \geq 296$ K) obtained by Wallington *et al.*⁹¹ for methyl acetate and ethyl acetate (and methyl trifluoroacetate) are surprisingly low considering the low magnitude of the room temperature rate constants for these acetates ($\lesssim 1.5 \times$

10^{-12} cm³ molecule⁻¹ s⁻¹), especially when compared with the significant temperature dependence observed by Hartmann *et al.*⁷⁸ for *n*-butyl acetate ($B = 594 \pm 126$ K for *n*-butyl acetate,⁷⁸ $B = 131 \pm 28$ K for ethyl acetate⁹¹). It would be expected that the absolute magnitude of the temperature dependences would decrease with the increasing room temperature rate constants associated with the increasing —OR chain lengths.

Accordingly, no recommendations are made concerning the temperature dependencies of the OH radical reactions with the esters. However, based upon the reasonable agreement of the studies of Winer *et al.*,⁸⁴ Zetzsch,⁶¹ Kerr and Stocker,³⁴ Hartmann *et al.*⁷⁸ and Wallington *et al.*⁹¹ for the room temperature rate constants for the esters studied by two or more of these groups, the following recommendations are made at 298 K

$$k(\text{ethyl acetate}) = 1.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

based upon the data of Zetzsch⁶¹ and Wallington *et al.*;⁹¹

$$k(\textit{n}\text{-propyl acetate}) = 3.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

based upon the data of Winer *et al.*,⁸⁴ Kerr and Stocker³⁴ and Wallington *et al.*⁹¹ (though significant discrepancies exist between the relative rate constants obtained by Winer *et al.*⁸⁴ and Kerr and Stocker³⁴);

$$k(\text{isopropyl acetate}) = 3.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

based upon the data of Kerr and Stocker³⁴ and Wallington *et al.*,⁹¹

$$k(\textit{n}\text{-butyl acetate}) = 4.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

based upon the data of Hartmann *et al.*⁷⁸ and Wallington *et al.*,⁹¹ and

$$k(\text{sec-butyl acetate}) = 5.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

based upon the data of Winer *et al.*⁸⁴ and Wallington *et al.*⁹¹

For these and the other esters for which no recommendations are made (including $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_3$), the rate constant data given in Table 11 indicate that the OH radical reaction with $\text{R}_1\text{C}(\text{O})\text{OR}_2$ occurs mainly at the —OR₂ entity rather than at the R₁CO-entity (thus the room temperature rate constants for ethyl formate, ethyl acetate and ethyl propionate increase only slowly with increasing length of the R₁C(O)O- chain, while there is a marked increase in the room temperature rate constant for the formates, acetates, propionates and butyrates as the —OR₂ chain length increases⁹¹). The magnitude of the rate constants for the acetate series further shows that they increase with the number of secondary and tertiary C—H bonds, as expected for H-atom abstraction reactions.^{106,109} Furthermore, analogous to the ethers, the rate

constants per C—H bond for the —OR₂ entities are higher than those for the corresponding alkanes.^{106,109}

(10) Carboxylic Acids

The available kinetic data for the carboxylic acids are given in Table 11.

(a) Formic Acid, Formic Acid-d₁ (DCOOH and HCOOD) and Formic Acid-d₂ (DCOOD)

The available rate constant data of Zetzsch and Stuhl,⁹³ Wine *et al.*,⁹⁴ Jolly *et al.*,⁹⁵ Dagaut *et al.*,⁹⁶ and Singleton *et al.*⁹⁷ for the reactions of the OH radical with HCOOH and DCOOH are given in Table 11, and rate data for the reactions of the OD radical with HCOOD⁹⁷ and DCOOD⁹⁷ are given in Table 12. The data for HCOOH^{93–97} are plotted in Arrhenius form in Fig. 79.

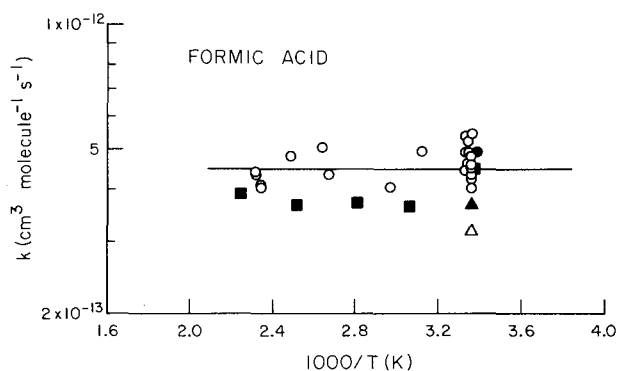


FIG. 79. Arrhenius plot of rate constants for the reaction of the OH radical with formic acid. (Δ) Zetzsch and Stuhl,⁹³ (○) Wine *et al.*,⁹⁴ (●) Jolly *et al.*,⁹⁵ (▲) Dagaut *et al.*,⁹⁶ (■) Singleton *et al.*,⁹⁷ (—) recommendation (see text).

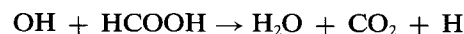
At room temperature the rate constants determined by Wine *et al.*,⁹⁴ Jolly *et al.*,⁹⁵ and Singleton *et al.*⁹⁷ are in good agreement, with those of Zetzsch and Stuhl⁹³ and Dagaut *et al.*⁹⁶ being somewhat lower (but in agreement within the combined overall error limits). The rate constants obtained by Wine *et al.*⁹⁴ and Singleton *et al.*⁹⁷ over the temperature range 297–445 K show no temperature dependence within the experimental uncertainties.

Problems associated with dimerization of HCOOH occur during the measurement of the rate constant for the reaction of the OH radical with the formic acid monomer. In the studies of Wine *et al.*,⁹⁴ Jolly *et al.*⁹⁵ and Singleton *et al.*,⁹⁷ the HCOOH concentrations were monitored by ultraviolet absorption, and hence the data determined from these studies^{94,95,97} are used in the evaluation of the rate constant for this reaction. From a unit-weighted average of the rate constants reported by Wine *et al.*,⁹⁴ Jolly *et al.*⁹⁵ and Singleton *et al.*,⁹⁷ a rate constant of

$$k(\text{formic acid}) = 4.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

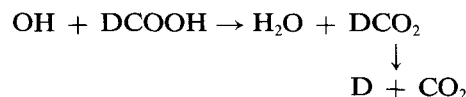
is recommended, independent of temperature over the range 296–445 K, with an estimated overall uncertainty of $\pm 35\%$ over this temperature range.

The data of Wine *et al.*⁹⁴ and Singleton *et al.*⁹⁷ show that the rate constant for the reaction of the OH radical with DCOOH is identical to that for HCOOH at 298 K, within the experimental uncertainties. Using resonance fluorescence detection of H-atoms, Wine *et al.*⁹⁴ estimated that the H-atom production yield from the OH radical reaction with HCOOH was 0.75 ± 0.25 , indicating that the major reaction pathway proceeds via,



and this is consistent with the observations of Jolly *et al.*⁹⁵

Singleton *et al.*⁹⁷ have determined that the room temperature rate constants for the reactions of the OD radical with HCOOD and DCOOD (Table 12) are significantly lower than those for the reactions of the OH radical with HCOOH and DCOOH (Table 12). These observations, together with the similarity of the room temperature rate constants for the reactions of the OH radical with HCOOH and DCOOH,^{94,97} indicate that abstraction of the H (or D) atom from the —OH (or —OD) group is the major reaction pathway at around room temperature



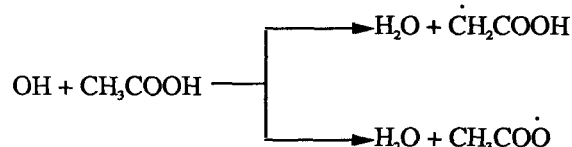
This conclusion⁹⁷ is consistent with the low reactivity of the various formic acid dimers studied.^{95,97,98} The detailed reaction dynamics are not known, i.e., initial formation of a HO—HCOOH adduct followed by decomposition to H₂O + (mainly) HCOO, or direct H-atom abstraction to yield H₂O and (mainly) HCOO. The observation of an essentially zero temperature dependence of the rate constant for HCOOH suggests the initial formation of an HO—HCOOH adduct.^{94,95,97,98}

(b) Other Carboxylic Acids

Rate constants have been measured for acetic, propionic and butyric acids at room temperature by Zetzsch and Stuhl,⁹³ and for acetic, propionic and isobutyric acids over the temperature range 298–440 K by Dagaut *et al.*⁹⁶ For acetic and propionic acid, the agreements between the room temperature rate constants determined from these studies are within the combined experimental error limits. The rate constants obtained by Zetzsch and Stuhl⁹³ required a knowledge of the vapor pressures of the carboxylic acids studied at 298 K, and are hence subject to significant uncertainties.⁹³ Consequently, no firm recommendations are made for the reactions of the OH radical with these carboxylic acids. However, until further experimental data become available, the rate constants of Dagaut *et al.*⁹⁶ should be used

over the temperature range of 298–440 K studied, with accordingly large overall uncertainties.

These reactions are expected to proceed by an overall H-atom abstraction process; for example,



although the observed near-zero temperature dependences measured by Dagaut *et al.*⁹⁶ would indicate that these reactions proceed by initial OH radical addition to form a complex which then, presumably, rapidly decomposes to products.

(11) Epoxides

(a) Kinetics

The available kinetic data are given in Table 11. Only for epoxyethane, 1,2-epoxypropane and 1-chloro-2,3-epoxypropane have multiple studies been carried out, and for 1-chloro-2,3-epoxypropane the relative rate study of Edney *et al.*³⁸ leads only to a lower limit to the rate constant.

(i) Epoxyethane

At room temperature, the absolute rate constants determined by Lorenz and Zellner,⁹⁹ Zetzsch¹⁰⁰ and Wallington *et al.*⁸¹ exhibit a spread of a factor of 1.8, but are consistent with the upper limit to the rate constant derived by Klöpffer *et al.*⁷² The only temperature-dependent study is that of Lorenz and Zellner,⁹⁹ who observed a rapid increase in the rate constant above 435 K, leading to marked non-Arrhenius behavior. A unit-weighted average of the room temperature rate constants of Lorenz and Zellner,⁹⁹ Zetzsch¹⁰⁰ and Wallington *et al.*⁸¹ yields the recommendation of

$$k(\text{epoxyethane}) = 7.6 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty of $\pm 50\%$.

Because of the high magnitude of the temperature dependence measured by Lorenz and Zellner,⁹⁹ leading to an Arrhenius pre-exponential factor of $1.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for rate data obtained over the range 297–435 K and a markedly higher value for data obtained over the temperature range 435–515 K, no temperature dependence is recommended.

(ii) 1,2-Epoxypropane

The two absolute measurements of the room temperature rate constant by Zetzsch¹⁰⁰ and Wallington *et al.*⁸¹ are in good agreement, but are a factor of ~ 2 lower than the relative rate data of Winer *et al.*¹⁰¹ and Edney *et al.*³⁸ The absolute flash photolysis-resonance fluorescence

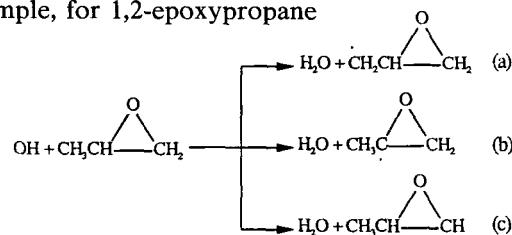
data are preferred, and a unit-weighted average of the room temperature rate constants of Zetzsch¹⁰⁰ and Wallington *et al.*⁸¹ yields the recommendation of

$$k(1,2\text{-epoxypropane}) = 5.2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

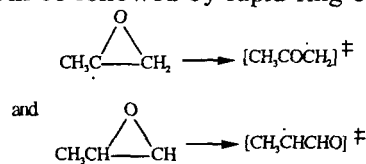
at 298 K (assuming a temperature dependence of $B \sim 1000 \text{ K}$ to extrapolate the measured data from 295–296 K to 298 K), with an estimated overall uncertainty of $\pm 40\%$.

(b) Mechanism

The OH radical reactions with the epoxides proceed by initial H-atom abstraction from the C—H bonds, for example, for 1,2-epoxypropane

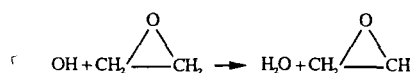


At around room temperature, reaction pathway (a) is estimated to dominate,^{106,109} since the three-membered ring structure decreases the reactivity of the C—H bonds on the carbon atoms in the ring^{106,109} (of course, for epoxyethane a reaction pathway analogous to (a) cannot occur). It is also expected that reaction pathways (b) and (c) will be followed by rapid ring cleavage:

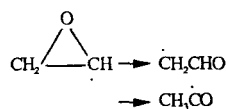


with the resulting species being initially energy-rich.

For epoxyethane, the initially formed OH radical is



and it is expected that this radical will rapidly undergo ring cleavage.



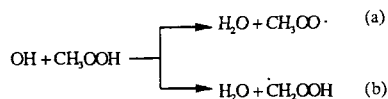
Using LIF detection to monitor the vinoxy (CH_2CHO) radical, Lorenz and Zellner⁹⁹ have measured CH_2CHO yields at 298 K of 0.08 ± 0.03 and 0.23 ± 0.08 at 10 and 60 Torr total pressure of helium, respectively.

(12) Hydroperoxides

(a) Methylhydroperoxide and Methylhydroperoxide-*d*₁ (CH_3OOD)

The available rate constant data are given in Tables 11 (¹⁶OH and ¹⁸OH radical reactions with CH_3OOH) and 12 (¹⁶OD radical reactions with CH_3OOH and CH_3OOD).

The most comprehensive of the two studies^{102,103} is that of Vaghjiani and Ravishankara,¹⁰³ who studied the kinetics and mechanisms of the reactions of ¹⁶OH, ¹⁸OH and ¹⁶OD radicals with CH₃OOH and of ¹⁶OD radicals with CH₃OOD. The reaction of the OH radical with CH₃OOH proceeds by the two pathways



with the $\dot{\text{C}}\text{H}_2\text{OOH}$ radical rapidly decomposing to yield an OH radical and HCHO.¹⁰³ Thus, relative rate studies yield the overall rate constant $k = k_a + k_b$, while flash or laser photolysis studies monitoring the disappearance of the OH radical measure only the rate constant k_a if the OH radical regenerated contains the same oxygen isotope as the reactant OH radical.

Thus, reaction of the ¹⁶OH radical with CH₃O¹⁶OH (or of the ¹⁶OD radical with CH₃O¹⁶OD) yields the rate constant k_a , while reaction of the ¹⁸OH radical with CH₃O¹⁶OH yields $k = (k_a + k_b)$. Similarly, reaction of the OD radical with CH₃OOH yields the overall reaction rate constant $(k_a + k_b)$ for the OD radical reaction.

The overall room temperature rate constant $k = (k_a + k_b)$ derived from the data of Niki *et al.*¹⁰² is a factor of ~ 2 higher than those obtained by Vaghjiani and Ravishankara¹⁰³ from the reactions of ¹⁸OH and OD radicals with CH₃OOH, for unknown reasons. The rate constants for the reaction of the OD radical with CH₃OOH (Table 12) are essentially identical to those for the reaction of the ¹⁸OH radical with CH₃OOH (Table 11), as expected, while a significant isotope effect on reaction channel (a) is shown by the lower room temperature rate constant for the OD radical reaction with CH₃OOD compared to the ¹⁶OH radical reaction with CH₃OOH. These observations confirm the occurrence of the two H-atom abstraction channels (a) and (b).

Unit-weighted least-squares analyses of the data of Vaghjiani and Ravishankara¹⁰³ lead to:

from the data for the ¹⁶OH radical reaction with CH₃OOH;

$$k_a = (1.79_{-0.30}^{+0.36}) \times 10^{-12} e^{(219 \pm 46)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 203–348 K, where the indicated errors are two least-squares standard deviations, and

$$k_a = 3.73 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

and from the data for the ¹⁸OH and OD radical reactions with CH₃OOH;

$$(k_a + k_b) = (2.93_{-0.28}^{+0.30}) \times 10^{-12} e^{(190 \pm 28)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

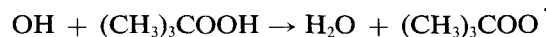
over the temperature range 223–423 K, where the indicated errors are two least-squares standard deviations, and

$$(k_a + k_b) = 5.54 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

These rate constant expressions yield the rate constant ratio $k_a/(k_a + k_b) = 0.611 e^{29/T} = 0.67$ at 298 K. Despite the disagreement concerning the overall rate constant, this rate constant ratio derived from the data of Vaghjiani and Ravishankara¹⁰³ is in agreement with that of $k_a/(k_a + k_b) = 0.58 \pm 0.09$ obtained from the product study of Niki *et al.*¹⁰²

(b) *t*-Butylhydroperoxide

For (CH₃)₃COOH, because of the stronger C—H bonds than the O—H bond, the reaction is expected to proceed mainly via H-atom abstraction from the weak O—H bond,



and this is consistent with the magnitude of the rate constant measured by Anastasi *et al.*¹⁰⁴

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2.7. Sulfur-Containing Organics

The available kinetic data are given in Tables 13 and 14. Table 13 gives the rate constants obtained in the absence of O₂ and from relative rate studies carried out in the presence of one atmosphere total pressure of air, while Table 14 gives the available kinetic data obtained from studies designed to investigate the effect of the O₂ concentration on the measured rate constants. The rate constants and mechanisms of the reactions of the OH radical with the inorganic reduced sulfur compounds H₂S, COS and CS₂ are not included in this article; these reactions are dealt with in the NASA²⁸ and IUPAC²⁹ evaluations.

a. Thiols

(1) Kinetics

(a) Methanethiol, Methanethiol-d₁ (CH₃SD) and Methanethiol-d₃ (CD₃SH)

The available rate constants obtained by Atkinson *et al.*,¹ Cox and Sheppard,² Wine *et al.*,^{3,7} Mac Leod *et al.*,^{4,5} Lee and Tang,⁶ Barnes *et al.*⁸ and Hynes and Wine⁹ are given in Tables 13 and 14. While the rate constant obtained by Cox and Sheppard² from a relative rate study involving the photolysis of HONO-NO-ethene-methanethiol-air mixtures is a factor of ~3 higher than the flash photolysis data,^{1,3,7,9} the more recent data of Barnes *et al.*^{8,21,26} show that secondary reactions, possibly involving CH₃SO,¹⁸ occur in reaction systems which include NO. The relative rate study of Barnes *et al.*⁸ utilized the photolysis of H₂O₂ to generate OH radicals in the absence of oxides of nitrogen, and the rate constants obtained for CH₃SH⁸ are in reasonably good agreement with the absolute rate data of Atkinson *et al.*,¹ Wine *et al.*,^{3,7} and Hynes and Wine.⁹

For both CH₃SH and CD₃SH, Hynes and Wine⁹ have shown that the rate constant is independent of the O₂ concentration (Table 14). Furthermore, the rate constants for CH₃SH^{1,3,7,9} and CD₃SH⁹ are independent of the total pressure of the diluent gas.

The rate constants for the reaction of the OH radical with CH₃SH obtained by Atkinson *et al.*,¹ Wine *et al.*,^{3,7} Mac Leod *et al.*,^{4,5} Lee and Tang⁶ and Barnes *et al.*⁸ and the unit-weighted averages of the rate constants determined by Hynes and Wine⁹ in the presence and absence of O₂ at 270 and 300 K are plotted in Arrhenius form in Fig. 80.

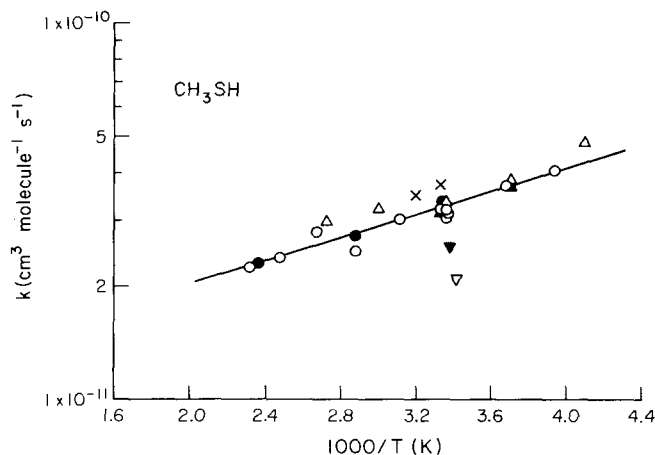


FIG. 80. Arrhenius plot of rate constants for the reaction of the OH radical with methanethiol. (●) Atkinson *et al.*,¹ (Δ) Wine *et al.*,³ (∇) Mac Leod *et al.*,^{4,5} (▼) Lee and Tang,⁶ (○) Wine *et al.*,⁷ (x) Barnes *et al.*,⁸ (▲) Hynes and Wine,⁹ (—) recommendation (see text).

The flash and laser photolysis studies of Atkinson *et al.*,¹ Wine *et al.*,^{3,7} and Hynes and Wine⁹ are in excellent agreement and agree within the experimental error limits with the rate constants obtained from the relative rate study of Barnes *et al.*⁸ However, the room temperature rate constants of Atkinson *et al.*,¹ Wine *et al.*,^{3,7} and Hynes and Wine⁹ are somewhat higher, by up to 50%, than the room temperature values of Mac Leod *et al.*^{4,5} and Lee and Tang.⁶ Since similar discrepancies occur for ethanethiol, the data of Mac Leod *et al.*^{4,5} and Lee and Tang⁶ are not used in the evaluation of the rate constant for CH₃SH.

A unit-weighted least-squares analysis of the rate constant data of Atkinson *et al.*,¹ Wine *et al.*,^{3,7} Barnes *et al.*⁸ and Hynes and Wine⁹ leads to the recommended Arrhenius expression of

$$k(\text{methanethiol}) = (9.97^{+2.15}_{-1.77}) \times 10^{-12} e^{(356 \pm 60)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 244–430 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{methanethiol}) = 3.29 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty at 298 K of $\pm 25\%$. This recommendation is essentially identical to that of

$$k(\text{methanethiol}) = 9.70$$

$$\times 10^{-12} e^{366/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

recommended by Atkinson.³⁰

The rate constants determined by Wine *et al.*⁷ for CH₃SD are essentially identical to those for CH₃SH, while the rate constants for CD₃SH⁹ are $\sim 15\%$ lower than those for CH₃SH (Tables 13 and 14).

TABLE 13. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with sulfur-containing organics in the absence of O₂ (unless indicated)

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)	
<i>Thiols</i>								
Methanethiol [CH ₃ SH]			33.9 \pm 3.4	299.8	FP-RF	Atkinson <i>et al.</i> ¹	300–423	
	8.89	–398 \pm 151	27.3 \pm 2.8	347.2				
			23.0 \pm 2.3	423.1				
			96.8 \pm 9.5 ^a	297 \pm 2	RR [relative to $k(\text{ethene}) =$ 8.57×10^{-12}] ^b	Cox and Sheppard ²		
			48.3 \pm 9.8	244	FP-RF	Wine <i>et al.</i> ³	244–366	
			38.4 \pm 5.8	270				
			33.7 \pm 4.1	298				
			32.2 \pm 6.2	333				
11.5 \pm 3.9	–338 \pm 100		29.7 \pm 4.7	366				
			21 \pm 2	293	DF-EPR			Mac Leod <i>et al.</i> ^{4,5}
			25.6 \pm 4.4	296	DF-RF			Lee and Tang ⁶
			40.8 \pm 4.2	254	FP-RF	Wine <i>et al.</i> ⁷	254–430	
			37.3 \pm 4.3	272				
			32.2 \pm 3.2	298				
			31.6 \pm 4.3	298				
			30.4 \pm 1.9	298				
			32.5 \pm 0.9	298				
			30.9 \pm 1.0	298				
			32.5 \pm 2.8	299				
			32.3 \pm 3.7	300				
			30.3 \pm 2.6	322				
			24.9 \pm 3.1	347				
			28.0 \pm 2.8	375				
			23.9 \pm 1.3	403				
10.1 \pm 1.9	–347 \pm 59		22.5 \pm 1.4	430				
			37.2 \pm 3.7	300	RR [relative to $k(\text{propene}) =$ $4.85 \times 10^{-12} e^{504/7}$] ^b	Barnes <i>et al.</i> ⁸	300–313	
			35.0 \pm 4.9	313				

TABLE 13. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with sulfur-containing organics in the absence of O₂ (unless indicated) — 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)
			36.6 ± 2.1	270	LP-LIF	Hynes and Wine ⁹	270–300
			36.9 ^c	270			
			33.0	300			
			31.7 ^c	300			
Methanethiol- <i>d</i> ₁ [CH ₃ SD]			40.4 ± 2.2	253	FP-RF	Wine <i>et al.</i> ⁷	253–429
			34.3 ± 3.9	268			
			34.1 ± 4.1	276			
			31.9 ± 2.8	295			
			30.8 ± 2.1	297			
			28.7 ± 1.8	346			
			24.3 ± 1.0	384			
			24.0 ± 1.8	412			
	11.2 ± 1.5	−310 ± 43	23.4 ± 0.7	429			
Methanethiol- <i>d</i> ₃ [CD ₃ SH]			27.4	273	LP-LIF	Hynes and Wine ⁹	273–300
			27.9	300			
			27.6 ^c	300			
Ethanethiol [CH ₃ CH ₂ SH]			27 ± 2	293	DF-EPR	MacLeod <i>et al.</i> ^{4,5}	
			36.7 ± 1.8	296	DF-RF	Lee and Tang ⁶	
			65.5 ± 5.1	252	FP-RF	Wine <i>et al.</i> ⁷	252–425
			51.5 ± 3.5	278			
			45.2 ± 6.2	298			
			43.1 ± 6.1	298			
			42.1 ± 3.2	298			
			46.5 ± 2.9	300			
			40.2 ± 1.4	343			
			33.2 ± 3.6	381			
			34.1 ± 3.1	397			
	12.3 ± 3.3	−396 ± 84	33.2 ± 2.7	425			
			46.5 ± 6.0	300	RR [relative to	Barnes <i>et al.</i> ⁸	300–313
			46.9 ± 4.7	313	$k(\text{propene}) =$ $4.85 \times 10^{-12} e^{504/T}]^b$		
1-Propanethiol [CH ₃ CH ₂ CH ₂ SH]			63.1 ± 2.0	257	FP-RF	Wine <i>et al.</i> ⁷	257–419
			45.6 ± 1.8	298			
			41.8 ± 5.7	298			
			45.5 ± 2.5	298			
			36.3 ± 1.6	353			
	8.89 ± 2.80	−489 ± 98	29.1 ± 0.9	419			
			55.4 ± 6.5	300	RR [relative to	Barnes <i>et al.</i> ⁸	300–313
			52.7 ± 7.3	313	$k(\text{propene}) =$ $4.85 \times 10^{-12} e^{504/T}]^b$		
2-Propanethiol [(CH ₃) ₂ CHSH]			56.9 ± 9.0	256	FP-RF	Wine <i>et al.</i> ⁷	256–429
			40.7 ± 3.7	297			
			42.2 ± 7.1	299			
			39.5 ± 4.4	300			
			31.2 ± 0.9	358			
			33.0 ± 3.4	380			
			35.5 ± 2.6	423			
	11.6 ± 5.5	−386 ± 155	25.1 ± 2.3	429			
			40.8 ± 3.9	300	RR [relative to	Barnes <i>et al.</i> ⁸	300–313
			38.6 ± 2.7	313	$k(\text{propene}) =$ $4.85 \times 10^{-12} e^{504/T}]^b$		

TABLE 13. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with sulfur-containing organics in the absence of O₂ (unless indicated) — Continued

Organic	$10^{12} \times A$ (cm ³ mole- ⁻¹ s ⁻¹)	B (K)	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at T (K)	Technique	Reference	Tempera- ture range covered (K)		
1-Butanethiol [CH ₃ CH ₂ CH ₂ CH ₂ SH]			43.8 ± 6.6	298	FP-RF	Wine <i>et al.</i> ⁷			
			58.2 ± 4.5	300	RR [relative to $k(\text{propene}) =$ $4.85 \times 10^{-12} e^{504/T}]^b$	Barnes <i>et al.</i> ⁸	300-313		
			57.3 ± 5.4	313					
2-Methyl-1- propanethiol [(CH ₃) ₂ CHCH ₂ SH]			41.8 ± 6.3	298	FP-RF	Wine <i>et al.</i> ⁷			
			47.8 ± 5.5	300	RR [relative to $k(\text{propene}) =$ $4.85 \times 10^{-12} e^{504/T}]^b$	Barnes <i>et al.</i> ⁸	300-313		
			39.1 ± 5.9	313					
2-Butanethiol [CH ₃ CH ₂ CH(CH ₃)SH]			39.8 ± 5.9	298	FP-RF	Wine <i>et al.</i> ⁷			
			39.5 ± 7.1	300	RR [relative to $k(\text{propene}) =$ $4.85 \times 10^{-12} e^{504/T}]^b$	Barnes <i>et al.</i> ⁸	300-313		
			32.8 ± 2.7	313					
2-Methyl-2- propanethiol [(CH ₃) ₂ CSH]			47.2 ± 2.3	257	FP-RF	Wine <i>et al.</i> ⁷	257-409		
			34.2 ± 1.3	298					
			35.7 ± 0.8	298					
			26.3 ± 4.2	348					
	6.22 ± 1.35	-516 ± 67	22.7 ± 0.5	409					
			30.7 ± 3.9	300				RR [relative to $k(\text{propene}) =$ $4.85 \times 10^{-12} e^{504/T}]^b$	Barnes <i>et al.</i> ⁸
		24.1 ± 3.7	313						
2-Methyl- 1-butanethiol [CH ₃ CH ₂ CH(CH ₃)CH ₂ SH]			54.3 ± 2.9	300	RR [relative to $k(\text{propene}) =$ $4.85 \times 10^{-12} e^{504/T}]^b$	Barnes <i>et al.</i> ⁸	300-313		
			44.0 ± 5.9	313					
<i>Sulfides</i>									
Dimethyl sulfide [CH ₃ SCH ₃]	5.47	-179 ± 151	9.8 ± 1.2	299.9	FP-RF	Atkinson <i>et al.</i> ¹⁰	300-427		
			9.3 ± 1.2	355.3					
			8.2 ± 1.2	426.5	FP-RF	Kurylo ¹¹	273-400		
			10.98 ± 3.37	273					
			8.28 ± 0.87	296					
			10.75 ± 2.85	323					
			7.99 ± 1.37	362					
			9.28 ± 2.01	400					
			6.25 ± 4.19	-131 ± 215	9.77 ± 1.55 ^a	297 ± 2	RR [relative to $k(\text{ethene}) =$ $8.57 \times 10^{-12}]^b$	Cox and Sheppard ²	
					3.89 ± 0.38	248	FP-RF	Wine <i>et al.</i> ³	248-363
					4.15 ± 0.55	271			
					4.26 ± 0.56	298			
4.50 ± 0.68	334								
4.67 ± 0.51	363								
6.8 ± 1.1	138 ± 46	9.2 ± 0.6	373	DF-EPR	MacLeod <i>et al.</i> ^{4,5}	373-573			
		7.8 ± 1	573						
		10.0 ± 0.5 ^a	296 ± 2	RR [relative to $k(n\text{-hexane}) =$ $5.57 \times 10^{-12}]^b$	Atkinson <i>et al.</i> ¹²				

TABLE 13. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with sulfur-containing organics in the absence of O₂ (unless indicated) — Continued

Organic	$10^{12} \times A$ (cm ³ mole- cule ⁻¹ s ⁻¹)	B (K)	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at T (K)	Technique	Reference	Tempera- ture range covered (K)
			3.80 ± 0.30	273	DF-EPR	Martin <i>et al.</i> ¹³	273–318
			3.22 ± 0.16	293			
			3.66 ± 0.19	318			
			3.6 ± 0.2	297	FP-RF	Wallington <i>et al.</i> ¹⁴	297–400
			3.8 ± 0.7	320			
			3.7 ± 0.9	332			
			3.7 ± 0.4	359			
			3.4 ± 0.4	369			
			3.4 ± 0.4	377			
	2.5 ^{+0.9} -0.6	-130 ± 102	3.3 ± 0.3	400			
			5.36 ± 0.44	296 ± 2	RR [relative to $k(\text{cyclohexane}) =$ 7.45×10^{-12}] ^b	Wallington <i>et al.</i> ¹⁴	
			9.36 ± 0.67 ^a	296 ± 2	RR [relative to $k(n\text{-hexane}) =$ 5.57×10^{-12}] ^b	Wallington <i>et al.</i> ¹⁴	
			4.17 ± 0.87	276	FP-RF	Hynes <i>et al.</i> ¹⁵	276–397
			4.09 ± 1.16	298			
			4.44 ± 0.23	298			
			4.75 ± 0.71	300			
			5.45 ± 0.89	359			
			5.97 ± 0.07	374			
			5.46 ± 0.52	374			
	13.6 ± 4.0	332 ± 96	5.69 ± 0.46	397			
			4.29 ± 0.48	261	LP-LIF	Hynes <i>et al.</i> ¹⁵	261–321
			4.80 ± 0.11	298			
			4.75 ± 0.15	298			
			3.5 ± 0.4	d	PR-RA	Nielsen <i>et al.</i> ¹⁶	
			4.94 ± 0.15	260	DF-RF	Hsu <i>et al.</i> ¹⁷	260–393
			4.51 ± 0.15	265			
			5.09 ± 0.11	278			
			5.54 ± 0.15	298			
			5.92 ± 0.27	333			
			6.00 ± 0.13	363			
	11.8 ± 2.2	236 ± 150	6.44 ± 0.26	393			
			4.69 ± 0.43	298 ± 3	RR [relative to $k(\text{ethene}) =$ 8.52×10^{-12}]	Barnes <i>et al.</i> ¹⁸	
			4.85 ± 0.14	299	FP-RF	Witte and Zetzsch ¹⁹	299–469
			4.76 ± 0.32	299			
			5.20 ± 0.16	323			
			5.43 ± 0.27	348			
			5.36 ± 0.30	348			
			5.79 ± 0.19	373			
			6.09 ± 0.20	398			
			6.13 ± 0.28	398			
			6.22 ± 0.38	423			
			6.63 ± 0.36	442			
			6.13 ± 0.28	447			
			6.29 ± 0.26	448			
			6.57 ± 0.38	453			
			6.28 ± 0.31	459			
			6.67 ± 0.24	463			

TABLE 13. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with sulfur-containing organics in the absence of O_2 (unless indicated) — Continued

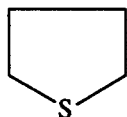
Organic	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{molecule}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
	11 ± 1	250 ± 30	6.59 ± 0.47 6.43 ± 0.58	468 469			
Dimethyl sulfide- d_6 [CD_3SCD_3]			1.46 ± 0.14 1.95 ± 0.13 1.87 ± 0.16 1.98 ± 0.18 2.53 ± 0.19 2.72 ± 0.21 3.11 ± 0.18	253 299 299 299 360 360 418	FP-RF	Hynes <i>et al.</i> ¹⁵	253–418
	10.3 ± 1.7	498 ± 51	1.82 ± 0.11	298	LP-LIF	Hynes <i>et al.</i> ¹⁵	261–361
Methyl ethyl sulfide			8.50	299	FP-RF	Hynes <i>et al.</i> ¹⁵	
Diethyl sulfide			12 ± 1.4 11.6 ± 2.2	293 300	DF-EPR RR [relative to $k(\text{ethene}) = 8.44 \times 10^{-12}]^b$	Martin <i>et al.</i> ¹³ Barnes <i>et al.</i> ²⁰	
	13.9 ± 6.3 [15.5 ± 2.2]	-31 ± 132 0]	14.2 ± 1.8 17.6 ± 2.5 15.4 ± 1.6 14.5 ± 1.2 16.1 ± 2.1 15.4 ± 2.3 15.1 ± 2.2	255 255 269 299 299 338 370	FP-RF	Hynes <i>et al.</i> ¹⁵	255–370
			4.5 ± 0.5	d	PR-RA	Nielsen <i>et al.</i> ¹⁶	
Ethyl propyl sulfide			4.9 ± 0.5	d	PR-RA	Nielsen <i>et al.</i> ¹⁶	
Di- <i>n</i> -propyl sulfide			20.0 ± 2.2	300	RR [relative to $k(\text{ethene}) = 8.44 \times 10^{-12}]^b$	Barnes <i>et al.</i> ²⁰	
			5.2 ± 0.5	d	PR-RA	Nielsen <i>et al.</i> ¹⁶	
Dimethyl disulfide [CH_3SSCH_3]			240 ± 86^a	297 ± 2	RR [relative to $k(\text{ethene}) = 8.57 \times 10^{-12}]^b$	Cox and Sheppard ²	
	59 ± 33	-380 ± 160	280 ± 18 198 ± 18 171 ± 25	249 298 367	FP-RF	Wine <i>et al.</i> ³	249–367
			192 ± 24	300	RR [relative to $k(\text{trans-2-butene}) = 6.32 \times 10^{-11}]^b$	Barnes <i>et al.</i> ^{20,21}	
			300 ± 30	d	PR-RA	Nielsen <i>et al.</i> ¹⁶	
Di- <i>tert</i> -butyl disulfide [$(\text{CH}_3)_3\text{CSSC}(\text{CH}_3)_3$]			41 ± 4	d	PR-RA	Nielsen <i>et al.</i> ¹⁶	

TABLE 13. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with sulfur-containing organics in the absence of O_2 (unless indicated) — Continued

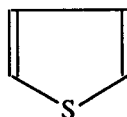
Organic	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)		
<i>Thioethers</i>									
Tetrahydrothiophene ^c			23.2 ± 1.3	255	FP-RF	Wine and Thompson ²²	255–377		
			20.9 ± 1.9	255					
			19.8 ± 3.4	298					
			18.4 ± 1.0	298					
			18.8 ± 1.8	338					
			19.5 ± 0.6	377					
			16.2 ± 1.4	377					
	11.3 ± 3.5	–166 ± 97	17.4 ± 1.3	377					
			21.2 ± 1.6	293				DF-EPR	Martin <i>et al.</i> ¹³
	9.7 ± 0.9	–240 ± 40	21.8 ^f	297				FP-RF	Witte and Zetzsch ¹⁹
Thiophene ^c			47.7 ± 6.3	295 ± 1	DF-RF	Lee and Tang ²³			
			9.42 ± 0.34 ^a	298 ± 2	RR [relative to $k(n\text{-hexane}) =$ 5.61×10^{-12}] ^b	Atkinson <i>et al.</i> ²⁴			
			50 ± 4	293	DF-EPR	MacLeod <i>et al.</i> ^{5,25}	293–473		
			22 ± 2	333					
			12 ± 2	373					
	0.13 ± 0.08	–1750 ± 200	5.2 ± 0.5	473					
			11.4 ± 0.6	255	FP-RF	Wine and Thompson ²²	255–425		
			11.5 ± 0.9	255					
			9.57 ± 1.15	298					
			9.37 ± 0.66	298					
			8.20 ± 0.68	353					
			7.28 ± 0.41	419					
			6.06 ± 0.37	425					
	3.20 ± 0.70	–325 ± 71	7.37 ± 0.41	425					
			9.6 ± 1.5 ^g	300	RR [relative to $k(\text{propene}) =$ 2.60×10^{-11}] ^b	Barnes <i>et al.</i> ²⁶			
		12 ± 1	293	DF-EPR	Martin <i>et al.</i> ¹³				
		10.1 ± 0.5	274 ± 2	FP-RF	Wallington ²⁷	274–382			
		8.9 ± 0.7	298 ± 2						
		6.1 ± 1.2	325						
		5.5 ± 0.3	349						
		6.3 ± 0.6	365						
		5.3 ± 0.5	379						
1.2 ^{+1.0} _{–0.6}	–584 ± 217	5.8 ± 0.5	382						
		10.6 ± 0.5	298				FP-RF	Witte and Zetzsch ¹⁹	298–471
		10.9 ± 0.7	298						
		13.1 ± 2.3	299						
		10.9 ± 0.5	300						
		11.7 ± 0.9	300						
		10.4 ± 0.5	312						
		10.5 ± 0.7	322						
		10.1 ± 0.5	335						
		9.4 ± 0.3	349						
		9.1 ± 0.5	360						
		8.7 ± 0.5	373						
		7.8 ± 0.3	380						
		8.3 ± 0.4	380						

TABLE 13. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with sulfur-containing organics in the absence of O_2 (unless indicated) — Continued

Organic	$10^{12} \times A$ ($\text{cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference	Tempera- ture range covered (K)
			7.7 ± 0.4	400			
			6.6 ± 0.3	414			
			7.5 ± 0.3	422			
			7.4 ± 0.2	434			
			7.5 ± 0.2	434			
			6.3 ± 0.2	438			
			7.5 ± 0.3	441			
			6.3 ± 0.3	442			
			7.2 ± 0.2	442			
			7.0 ± 0.2	442			
			6.0 ± 0.2	448			
			6.1 ± 0.2	452			
			5.6 ± 0.2	457			
			5.9 ± 0.4	463			
			5.4 ± 0.1	465			
			5.6 ± 0.3	468			
	1.9 ± 0.5	-540 ± 110	5.3 ± 0.5	471			
Thiazole ^e	0.94 ± 0.07	-120 ± 30	1.41^f	297	FP-RF	Witte and Zetzsch ¹⁹	297–423
<i>Miscellaneous</i>							
Dimethyl sulfoxide [(CH_3) ₂ SO]			62 ± 25^a	300	RR [relative to $k(\text{cis-2-butene}) =$ $5.58 \times 10^{-11}]^b$	Barnes <i>et al.</i> ²¹	

^aAt atmospheric pressure of air.^bFrom the present recommendations (see text).^cIn the presence and absence of O_2 .^dRoom temperature, not specified.^eStructures: tetrahydrothiophene,

; thiophene,



; thiazole, .

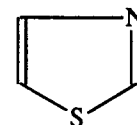
^fCalculated from cited Arrhenius expression.^gIndependent of O_2 pressure over the range 10–300 Torr.

TABLE 14. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with sulfur-containing organics as a function of the O_2 concentration

Organic	O_2 Pressure (Torr)	$10^{12} \times k$ (cm^3 molecule $^{-1}$ s $^{-1}$)	at T (K)	Technique	Reference	Tempera- ture range covered (K)
<i>Thiols</i>						
Methanethiol (CH ₃ SH)	0	36.6 ± 2.1	270	LP-LIF	Hynes and Wine ⁹	270–300
	69.3	35.9 ± 3.6	270			
	147	38.2 ± 3.6	270			
	0	32.8 ± 4.0	300			
	0	32.8 ± 1.8	300			
	0	33.8 ± 1.5	300			
	0	32.7 ± 3.6	300			
	31.5	29.3 ± 1.8	300			
	84.0	28.7 ± 1.4	300			
	94.5	33.0 ± 3.3	300			
	147	29.3 ± 1.6	300			
	147	31.5 ± 4.8	300			
	200	28.0 ± 8.0	300			
	520	35.0 ± 5.0	300			
700	33.1 ± 2.2	300				
Methanethiol- <i>d</i> ₃ (CD ₃ SH)	0, 230	27.4 ± 1.3	273	LP-LIF	Hynes and Wine ⁹	273–300
	0	27.6 ± 6.0	300			
	0	28.2 ± 3.1	300			
	21.0	26.4 ± 1.0	300			
	94.5	28.1 ± 3.3	300			
<i>Sulfides</i>						
Dimethyl sulfide (CH ₃ SCH ₃)	51	9.25 ± 1.06	296 ± 2	RR [relative to $k(n\text{-hexane})$ $= 5.57 \times 10^{-12}]^{a,b}$	Wallington <i>et al.</i> ¹⁴	261–321
	110	9.13	296 ± 2			
	154	9.36 ± 0.67	296 ± 2			
	368	10.4 ± 0.8	296 ± 2			
	740	14.0 ± 0.7	296 ± 2			
	0	5.36 ± 0.44	296 ± 2	RR [relative to $k(\text{cyclohexane})$ $= 7.45 \times 10^{-12}]^{a,c}$	Wallington <i>et al.</i> ¹⁴	
	50	7.08 ± 0.10	296 ± 2			
	160	8.64 ± 0.15	296 ± 2			
	740	10.7 ± 0.3	296 ± 2			
	0	4.29 ± 0.48	261			
	147	12.5 ± 1.7	262			
	147	9.53 ± 0.28	279			
	0	4.80 ± 0.11	298			
	0	4.75 ± 0.15	298			
	10.5	4.68 ± 0.08	298			
	27.3	5.04 ± 0.14	298			
	71.4	5.18 ± 0.34	298			
	124	5.80 ± 0.16	298			
	158	6.28 ± 0.10	298			
147	5.43 ± 0.30	321				
0	4.69 ± 0.43	298 ± 3	RR [relative to $k(\text{ethene})$ $= 8.52 \times 10^{-12}]^{a,d}$	Barnes <i>et al.</i> ¹⁸		
50	5.62 ± 0.77	298 ± 3				
100	7.16 ± 0.94	298 ± 3				
155	8.52 ± 0.52	298 ± 3				
760	12.4 ± 1.3	298 ± 3				
Dimethyl sulfide- <i>d</i> ₆ (CD ₃ SCD ₃)	147	11.6 ± 1.1	261	LP-LIF	Hynes <i>et al.</i> ¹⁵	261–361
	700	13.5 ± 1.2	266			
	700	11.9 ± 2.0	275			
	147	9.63 ± 0.63	276			
	147	5.29 ± 0.44	287			
	700	6.99 ± 0.53	287			
	0	1.82 ± 0.11	298			

TABLE 14. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with sulfur-containing organics as a function of the O_2 concentration — Continued

Organic	O_2 Pressure (Torr)	$10^{12} \times k$ (cm^3 molecule $^{-1}$ s $^{-1}$)	at T (K)	Technique	Reference	Tempera- ture range covered (K)
	21.0	2.10 ± 0.15	298			
	63.0	2.68 ± 0.09	298			
	105	2.97 ± 0.13	298			
	147	3.40 ± 0.13	298			
	700	6.50 ± 0.72	298			
	147	3.02 ± 0.18	317			
	700	3.72 ± 0.27	321			
	147	2.32 ± 0.11	340			
	700	2.30 ± 0.28	340			
	147	2.66 ± 0.11	361			

^aFrom present recommendations (see text).

^bOH radicals generated from photolysis of $CH_3ONO-NO-O_2-N_2$ mixtures.

^cOH radicals generated from the dark $N_2H_4 + O_3$ reaction.

^dOH radicals generated from photolysis of H_2O_2 in N_2-O_2 mixtures.

(b) Ethanethiol

The available rate constants of Mac Leod *et al.*,^{4,5} Lee and Tang,⁶ Wine *et al.*,⁷ and Barnes *et al.*⁸ are given in Table 13 and are plotted in Arrhenius form in Fig. 81.

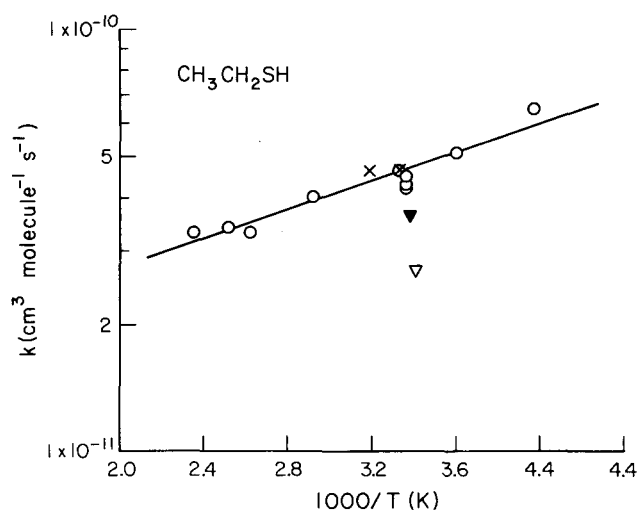


FIG. 81. Arrhenius plot of rate constants for the reaction of the OH radical with ethanethiol. (∇) Mac Leod *et al.*,^{4,5} (\blacktriangledown) Lee and Tang,⁶ (\circ) Wine *et al.*,⁷ (\times) Barnes *et al.*,⁸ (—) recommendation (see text).

As for methanethiol, the two discharge flow studies of Mac Leod *et al.*^{4,5} and Lee and Tang⁶ yield somewhat lower room temperature rate constants than do the flash photolysis study of Wine *et al.*⁷ and the relative rate study of Barnes *et al.*,⁸ which are in excellent agreement. A unit-weighted least-squares analysis of the rate constant data of Wine *et al.*⁷ and Barnes *et al.*⁸ leads to the recommended Arrhenius expression of

$$k(\text{ethanethiol}) = (1.23^{+0.36}_{-0.28}) \times 10^{-11} e^{(398 \pm 80)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 252–425 K, where the indicated error limits are two least-squares standard deviations, and

$$k(\text{ethanethiol}) = 4.68 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty at 298 K of $\pm 25\%$. This recommendation is essentially identical to that of

$$k(\text{ethanethiol}) = 1.23 \times 10^{-11} e^{396/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

recommended by Atkinson.³⁰

(c) 1-Propanethiol, 2-Propanethiol, 1-Butanethiol, 2-Methyl-1-propanethiol, 2-Butanethiol and 2-Methyl-2-propanethiol

The available rate constants determined by Wine *et al.*⁷ and Barnes *et al.*⁸ are given in Table 13, and the data for 1-propanethiol, 2-propanethiol and 2-methyl-2-propanethiol are plotted in Arrhenius form in Figs. 82 through 84, respectively. (For 1-butanethiol, 2-methyl-1-propanethiol and 2-butanethiol rate constants are available only at 298, 300 and 313 K). The room temperature rate constants from these studies of Wine *et al.*⁷ and Barnes *et al.*⁸ are in agreement within $\approx 30\%$ for these thiols.

Unit-weighted least-squares analyses of these rate constants of Wine *et al.*⁷ and Barnes *et al.*⁸ lead to the recommended Arrhenius expressions of

$$k(1\text{-propanethiol}) = (8.93^{+7.95}_{-4.21})$$

$$\times 10^{-12} e^{(503 \pm 197)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 257–419 K,

$$k(2\text{-propanethiol}) = (1.17^{+0.60}_{-0.40})$$

$$\times 10^{-11} e^{(381 \pm 133)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 256–429 K, and

$$k(2\text{-methyl-2-propanethiol}) = (6.05^{+6.69}_{-3.18})$$

$$\times 10^{-12} e^{(506 \pm 231)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 257–409 K, where the indicated errors are two least-squares standard deviations.

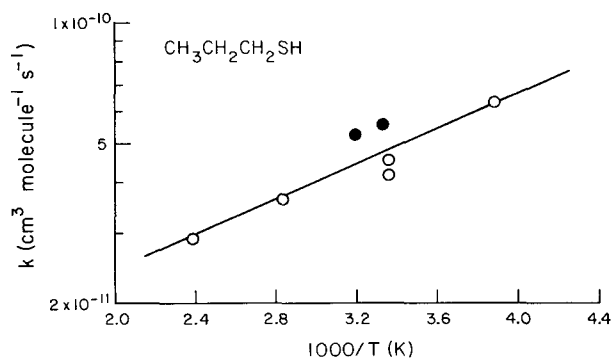


FIG. 82. Arrhenius plot of rate constants for the reaction of the OH radical with 1-propanethiol. (○) Wine *et al.*;⁷ (●) Barnes *et al.*;⁸ (—) recommendation (see text).

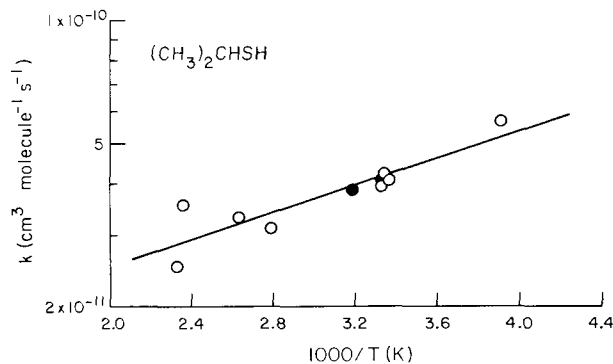


FIG. 83. Arrhenius plot of rate constants for the reaction of the OH radical with 2-propanethiol. (○) Wine *et al.*;⁷ (●) Barnes *et al.*;⁸ (—) recommendation (see text).

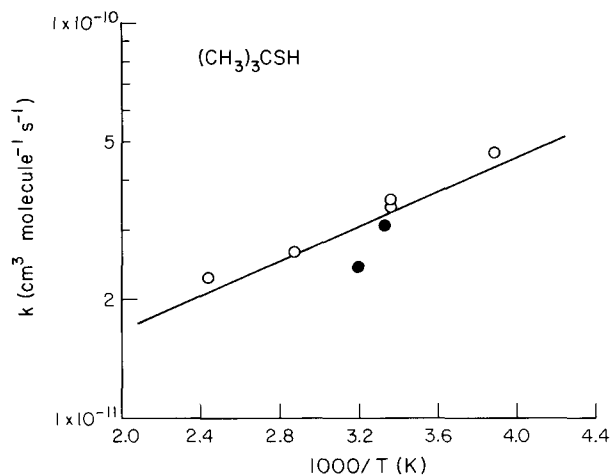


FIG. 84. Arrhenius plot of rate constants for the reaction of the OH radical with 2-methyl-2-propanethiol. (○) Wine *et al.*;⁷ (●) Barnes *et al.*;⁸ (—) recommendation (see text).

At 298 K,

$$k(1\text{-propanethiol}) = 4.83 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

$$k(2\text{-propanethiol}) = 4.20 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

and

$$k(2\text{-methyl-2-propanethiol}) = 3.31$$

$$\times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

all with estimated overall uncertainties of $\pm 30\%$ at 298 K. Unit-weighted averages of the 298–300 K rate constants of Wine *et al.*⁷ and Barnes *et al.*⁸ for 1- and 2-butanethiol and 2-methyl-1-propanethiol lead to the recommended rate constants at 298 K of

$$k(1\text{-butanethiol}) = 5.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

$$k(2\text{-methyl-1-propanethiol}) = 4.5$$

$$\times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

and

$$k(2\text{-butanethiol}) = 4.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

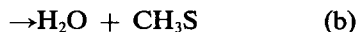
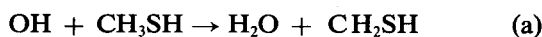
with estimated overall uncertainties of $\pm 35\%$ at 298 K.

No recommendation is made for 2-methyl-1-butanethiol, since only a single kinetic study has been carried out.

(2) Mechanism

There are three possible pathways for the reaction of OH radicals with the thiols, taking methanethiol as an

example:



The non-deuterated thiols for which kinetic data are available (Tables 13 and 14) all have reasonably similar room temperature rate constants, ranging from $3.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ to $\sim 5.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and negative temperature dependencies of $B \approx -400 \text{ K}$. These observations indicate no significant effect of the alkyl side chain on the kinetics of these reactions. This is further confirmed by the small isotope effect observed for CD_3SH compared to CH_3SH ,⁹ which suggests that H-atom abstraction from the $-\text{CH}_3$ group is a minor, but not totally negligible, reaction process for the OH radical reaction with CH_3SH . Furthermore, the rate constants for CH_3SD are virtually identical to those for CH_3SH ,⁷ indicating no deuterium isotope effect within the experimental error limits.

These kinetic observations show that over the temperature range $\sim 250\text{--}400 \text{ K}$ the H-atom abstraction channels (a) and (b) are of minor importance, and that the major reaction pathway involves OH radical addition to the S atom [reaction pathway (c)]. While this is in agreement with the conclusions of Hatakeyama and Akimoto³¹ obtained from a product study carried out in air at atmospheric pressure in the presence of NO, the now recognized occurrence of secondary reactions removing CH_3SH in these chemical systems^{26,30} may lead to added complexities in the analysis of the experimental data of Hatakeyama and Akimoto.³¹ The fate of the RS(OH)H adduct requires further study.

b. Sulfides

The available kinetic data are given in Tables 13 and 14. The majority of these data deal with the reaction of the OH radical with dimethyl sulfide and, since these kinetic studies provide the most definitive data concerning the reaction mechanisms, the kinetics and mechanisms of these OH radical reactions are discussed together in the remainder of this section.

(1) Dimethyl Sulfide and Dimethyl Sulfide- d_6 (CD_3SCD_3)

The available kinetic data of Atkinson *et al.*,^{10,12} Kurylo,¹¹ Cox and Sheppard,² Wine *et al.*,³ MacLeod *et al.*,^{4,5} Martin *et al.*,¹³ Wallington *et al.*,¹⁴ Hynes *et al.*,¹⁵ Nielsen *et al.*,¹⁶ Hsu *et al.*,¹⁷ Barnes *et al.*,¹⁸ and Witte and Zetzsch¹⁹ are given in Tables 13 and 14. In addition, preliminary data were reported for the reaction of CH_3SCH_3 at room temperature from the relative rate studies of Barnes *et al.*²⁶ and Nielsen *et al.*¹⁶

The relative rate studies of Barnes *et al.*,²⁶ Wallington *et al.*¹⁴ and Nielsen *et al.*¹⁶ show that erroneously high

rate constants are obtained for the reaction of the OH radical with dimethyl sulfide (and for CH_3SH ²⁶ and diethyl sulfide¹⁶) when these studies are conducted in the presence of oxides of nitrogen, due to secondary reactions removing CH_3SCH_3 (possibly involving the CH_3SO radical). Thus, the data obtained from the relative rate studies of Cox and Sheppard,² Atkinson *et al.*,¹² Barnes *et al.*²⁶ (not cited in Table 13 or Table 14) and Wallington *et al.*¹⁴ using irradiated HONO-NO-air^2 and $\text{CH}_3\text{ONO-NO-air}^{12,14,26}$ mixtures to generate the OH radical are in error and are not discussed further here. It is also possible that the relative rate data obtained by Wallington *et al.*,¹⁴ using the dark $\text{N}_2\text{H}_4\text{-O}_3$ reaction to generate OH radicals, were also subject to the occurrence of secondary reactions removing dimethyl sulfide, and these data must be judged to be of a qualitative nature only.¹⁴

Furthermore, the absolute rate constant data of MacLeod *et al.*^{4,5} have been shown by a subsequent study of Martin *et al.*¹³ to be in error due to the occurrence of heterogeneous reactions on the flow tube walls. The absolute rate data of Atkinson *et al.*,¹⁰ Kurylo,¹¹ Wine *et al.*,³ Martin *et al.*,¹³ Wallington *et al.*,¹⁴ Hynes *et al.*,¹⁵ Nielsen *et al.*,¹⁶ Hsu *et al.*¹⁷ and Witte and Zetzsch¹⁹ and the relative rate constant of Barnes *et al.*¹⁸ then remain to be considered. The laser photolysis-laser induced fluorescence study of Hynes *et al.*¹⁵ showed that the measured rate constants are dependent on the O_2 concentration for both CH_3SCH_3 and CD_3SCD_3 , increasing with increasing O_2 concentration, and this observation has been confirmed by the relative rate study of Barnes *et al.*,¹⁸ using the photolysis of H_2O_2 as an OH radical source. Thus, the evaluation of the rate constants for these reactions can be best carried out by first considering the data obtained in the absence of O_2 , and then dealing with the O_2 dependence of the rate constant.

The rate constants obtained in the absence of O_2 by Atkinson *et al.*,¹⁰ Kurylo,¹¹ Wine *et al.*,³ Martin *et al.*,¹³ Wallington *et al.*,¹⁴ Hynes *et al.*,¹⁵ Hsu *et al.*,¹⁷ Barnes *et al.*¹⁸ and Witte and Zetzsch¹⁹ are plotted in Arrhenius form in Fig. 85 (the absolute room temperature rate constant of Nielsen *et al.*¹⁶ is not plotted since the temperature was not specified).

Clearly, there is a significant degree of scatter in the rate constants determined from the various studies, with the reported room temperature rate constants varying by a factor of ~ 5 . The rate constants obtained by Atkinson *et al.*¹⁰ and Kurylo¹¹ are significantly higher than those from the other studies plotted,^{3,13-15,17-19} presumably due to the presence of reactive impurities in the CH_3SCH_3 reactant.^{3,14} In addition, the rate data of Martin *et al.*¹³ and Wallington *et al.*¹⁴ are lower than the rate constants of Wine *et al.*,³ Hynes *et al.*,¹⁵ Hsu *et al.*,¹⁷ Barnes *et al.*¹⁸ and Witte and Zetzsch,¹⁹ and exhibit essentially zero or slightly negative temperature dependencies, in contrast to the positive temperature dependencies observed by the absolute studies of Wine *et al.*,³ Hynes *et al.*,¹⁵ Hsu *et al.*¹⁷ and Witte and Zetzsch.¹⁹

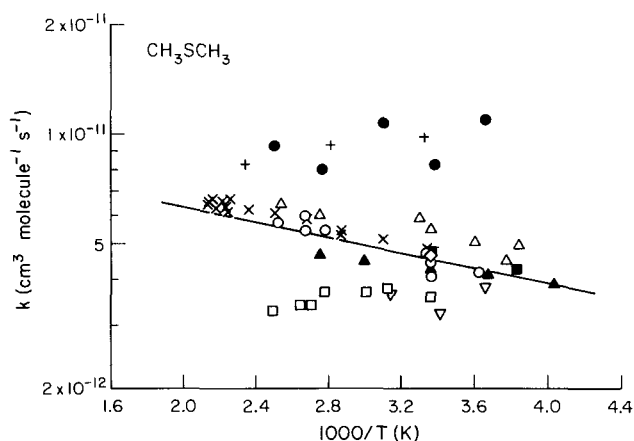


FIG. 85. Arrhenius plot of rate constants, obtained in the absence of O_2 , for the reaction of the OH radical with dimethyl sulfide. (+) Atkinson *et al.*,¹⁰ (●) Kurylo,¹¹ (▲) Wine *et al.*,³ (▽) Martin *et al.*,¹³ (□) Wallington *et al.*,¹⁴ absolute rate data; (○) Hynes *et al.*,¹⁵ FP-RF data; (■) Hynes *et al.*,¹⁵ LP-LIF data; (Δ) Hsu *et al.*,¹⁷ (◇) Barnes *et al.*,¹⁸ (x) Witte and Zetzsch;¹⁹ (—) recommendation (see text).

Since the rate constants determined from the discharge flow study of Hsu *et al.*¹⁷ are ~20% higher than the data of Wine *et al.*,³ Hynes *et al.*,¹⁵ Barnes *et al.*¹⁸ and Witte and Zetzsch,¹⁹ and few details are available concerning the study of Witte and Zetzsch,¹⁹ a unit-weighted least-squares analysis of the rate constant data of Wine *et al.*,³ Hynes *et al.*¹⁵ and Barnes *et al.*,¹⁸ using the Arrhenius expression $k = Ae^{-B/T}$, yields the recommendation of

$$k(\text{dimethyl sulfide}) = (1.03^{+0.28}_{-0.23}) \times 10^{-11} e^{-(243 \pm 76)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

in the absence of O_2 over the temperature range 248–397 K, where the indicated error limits are two least-squares standard deviations, and

$$k(\text{dimethyl sulfide}) = 4.56 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

in the absence of O_2 at 298 K, with an estimated overall uncertainty at 298 K of $\pm 30\%$. The data of Witte and Zetzsch¹⁹ are in excellent agreement (within ~10%) with this recommendation.

For the reaction of the OH radical with CD_3SCD_3 in the absence of O_2 , the flash and laser photolysis data of Hynes *et al.*¹⁵ lead to

$$k(\text{dimethyl sulfide-}d_6) = (1.05^{+0.22}_{-0.19}) \times 10^{-11} e^{-(505 \pm 60)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

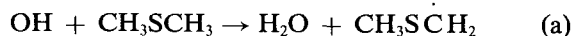
over the temperature range 253–418 K, where the indicated error limits are two least-squares standard deviations, and

$$k(\text{dimethyl sulfide-}d_6) = 1.93 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, in the absence of O_2 . These rate constant expressions for CH_3SCH_3 and CD_3SCD_3 , in the absence of O_2 , yield a deuterium isotope effect of

$$\frac{k(CH_3SCH_3)}{k(CD_3SCD_3)} = \frac{k^H}{k^D} = 0.98 e^{262/T}$$

This deuterium isotope effect is similar in magnitude to that observed for H-atom abstraction from secondary C—H bonds in the alkanes (Sec. 2.1). Since the C—H bonds in CH_3SCH_3 have a similar bond dissociation energy (96.6 kcal mol⁻¹²⁹) to the alkane secondary C—H bonds (96.1 kcal mol⁻¹ for propane²⁹), this deuterium isotope effect indicates that in the absence of O_2 the OH radical reaction proceeds by H (or D) atom abstraction from the —CH₃ (or —CD₃) groups.



Thus, the recommended rate expression given above for CH_3SCH_3 (and the analogous rate expression obtained from the data of Hynes *et al.*¹⁵ for CD_3SCD_3) is for this reaction channel (a):

$$k_a(CH_3SCH_3) = (1.03^{+0.28}_{-0.23}) \times 10^{-11} e^{-(243 \pm 76)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 248–397 K, and

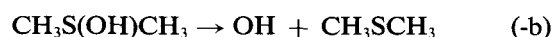
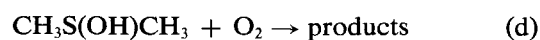
$$k_a(CH_3SCH_3) = 4.56 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K.

The observations of Hynes *et al.*¹⁵ and Barnes *et al.*¹⁸ that at around room temperature and below the measured rate constant k_{obs} increases with increasing O_2 concentration are interpreted as showing that reaction of the OH-dimethyl sulfide addition adduct with O_2 occurs in competition with rapid back-decomposition to reactants. Thus, the product of the OH radical addition channel (b),



must react with O_2 , in competition with dissociation back to the reactants:



Hence the measured rate constant k_{obs} is given by¹⁵

$$k_{\text{obs}} = k_a + \frac{k_b k_d [O_2]}{k_{-b} + k_d [O_2]} = k_{\text{abstr}} + k_{\text{add}}$$

The data of Hynes *et al.*¹⁵ for CH₃SCH₃ and CD₃CD₃ and of Barnes *et al.*¹⁸ for CH₃SCH₃ at 298 K exhibit this behavior, as shown by the plot of $k_{\text{add}} = (k_{\text{obs}} - k_a)$ in Fig. 86.

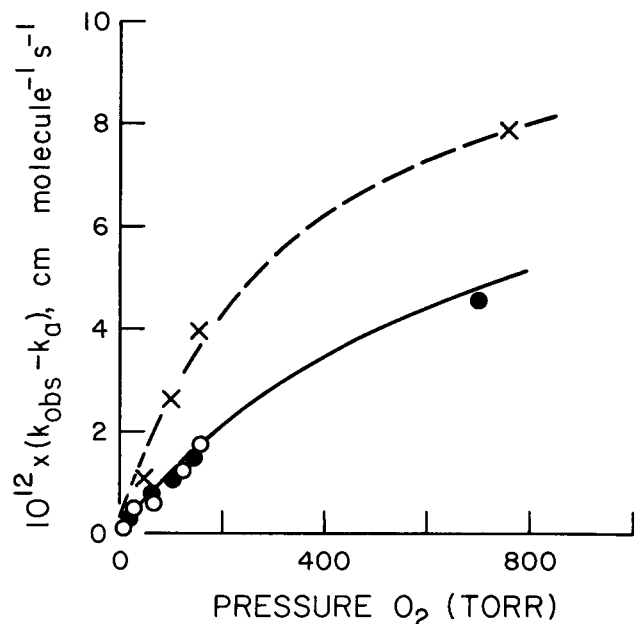


FIG. 86. Plot of the measured 298 K rate constants for OH radical addition to dimethyl sulfide and dimethyl sulfide-*d*₆ ($k_{\text{obs}} - k_a$, see text) as a function of the O₂ pressure. CH₃SCH₃: (○) Hynes *et al.*,¹⁵ (x, — —) Barnes *et al.*,¹⁸ CD₃SCD₃: (●) Hynes *et al.*,¹⁵ (—) recommendation (see text).

The effect of O₂ on the rate constant k_{add} is much more pronounced in the data obtained by Barnes *et al.*¹⁸ from a relative rate study. While the reasons for this discrepancy are not clear, the absolute rate data of Hynes *et al.*¹⁵ in the presence of O₂ (which are also available over the temperature ranges 262–321 K for CH₃SCH₃ and 261–361 K for CD₃SCD₃) are preferred. Hynes *et al.*¹⁵ derived the expression

$$k_{\text{add}} = \frac{1.68 \times 10^{-42} [\text{O}_2] e^{7812/T}}{(1 + 5.53 \times 10^{-31} [\text{O}_2] e^{7460/T})} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

from a best fit to their data for CD₃SCD₃ in the presence of 700 Torr total pressure of air or O₂ (assuming that the temperature dependence for channel (b) was $B = -350$ K, consistent with the temperature dependencies for OH radical addition to the thiols). This expression also fits the data of Hynes *et al.*¹⁵ for CH₃SCH₃ and CD₃SCD₃ as a function of the O₂ concentration at 298 K (Fig. 86), as well as the rate constants for CH₃SCH₃ at 700 Torr total pressure of air at 262, 279 and 321 K, indicating no deuterium isotope effect on k_{add} .

Accordingly, the expression

$$k_{\text{add}}(\text{CH}_3\text{SCH}_3 \text{ and } \text{CD}_3\text{SCD}_3) =$$

$$\frac{1.68 \times 10^{-42} [\text{O}_2] e^{7812/T}}{(1 + 5.53 \times 10^{-31} [\text{O}_2] e^{7460/T})} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

is recommended for pressures of O₂ ≤ 700 Torr over the temperature range 261–361 K, with an estimated overall uncertainty of ± a factor of 2 at all pressures and temperatures within the temperature and pressure limits of this recommendation. This OH radical addition channel becomes of negligible importance at temperatures ≳ 350 K.

Thus,

$$k(\text{CH}_3\text{SCH}_3) = 1.03 \times 10^{-11} e^{-243/T} +$$

$$\frac{1.68 \times 10^{-42} [\text{O}_2] e^{7812/T}}{(1 + 5.53 \times 10^{-31} [\text{O}_2] e^{7460/T})} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range ~260–400 K for O₂ pressures ≤ 700 Torr. At 760 Torr total pressure of air and 298 K the overall rate constant for CH₃SCH₃ calculated from the recommendation is

$$k(\text{CH}_3\text{SCH}_3) = 6.30 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

and ~70% of the OH radical reaction proceeds by H-atom abstraction under these conditions.

(2) Diethyl Sulfide

The available rate constant data of Martin *et al.*,¹³ Barnes *et al.*,²⁰ Hynes *et al.*¹⁵ and Nielsen *et al.*,¹⁶ all obtained in the absence of O₂, are given in Table 13, and those of Martin *et al.*,¹³ Barnes *et al.*²⁰ and Hynes *et al.*¹⁵ are plotted in Arrhenius form in Fig. 87 (the temperature of the room temperature study of Nielsen *et al.*¹⁶ was not specified).

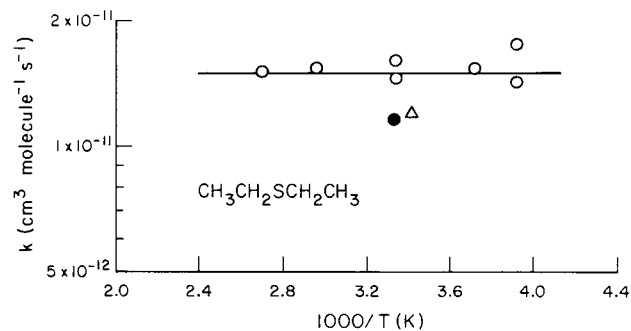
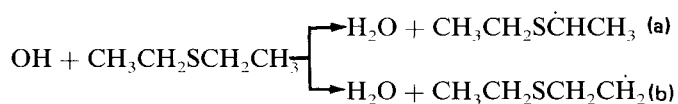


FIG. 87. Arrhenius plot of rate constants for the reaction of the OH radical with diethyl sulfide. (Δ) Martin *et al.*,¹³ (●) Barnes *et al.*,²⁰ (○) Hynes *et al.*,¹⁵ (—) recommendation (see text).

At room temperature, the rate constants of Martin *et al.*,¹³ Barnes *et al.*²⁰ and Hynes *et al.*¹⁵ are in reasonable agreement, but (Table 13) are a factor of ~ 3 higher than the pulsed radiolysis value of Nielsen *et al.*¹⁶ Due to a lack of details concerning the relative rate study of Barnes *et al.*²⁰ and the significantly low rate constants obtained by Martin *et al.*¹³ for dimethyl sulfide, these two studies are given a lower weight in the evaluation of the rate constant for this reaction. A rate constant of

$$k(\text{diethyl sulfide}) = 1.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

independent of temperature over the range 255–370 K, is recommended, with an estimated overall uncertainty of $\pm 35\%$ over this temperature range. By analogy with dimethyl sulfide, this recommended rate constant refers to the H-atom abstraction reactions,



with reaction channel (a) being estimated to dominate.³² The addition pathway is expected to be operative in the presence of O_2 , although on a relative basis its magnitude may be small compared to the H-atom abstraction process.³²

(3) Other Sulfides

The only rate constants available for other sulfides are those determined by Nielsen *et al.*¹⁶ for ethyl propyl sulfide and by Nielsen *et al.*¹⁶ and Barnes *et al.*²⁰ for di-*n*-propyl sulfide, all being obtained at room temperature. The data of Nielsen *et al.*¹⁶ and Barnes *et al.*²⁰ for di-*n*-propyl sulfide disagree by a factor of 4, and it appears that the rate constants measured by Nielsen *et al.*¹⁶ for a series of sulfides are systematically low, exhibiting essentially no variation with the increasing complexity of the sulfide, contrary to other data.^{15,18,20}

c. Disulfides

(1) Dimethyl Disulfide

The available kinetic data of Cox and Sheppard,² Wine *et al.*,³ Barnes *et al.*^{20,21} and Nielsen *et al.*¹⁶ are given in Table 13 and (apart from the rate constant of Nielsen *et al.*¹⁶ for which the temperature was not specified) are plotted in Arrhenius form in Fig. 88. The room temperature rate constants of Cox and Sheppard,² Wine *et al.*³ and Barnes *et al.*^{20,21} are in good agreement, but are $\sim 50\%$ lower than the room temperature rate constant determined by Nielsen *et al.*¹⁶ Because of the lack of details concerning the Barnes *et al.*^{20,21} study and the fact that the relative rate study of Cox and Sheppard² was carried out in the presence of oxides of nitrogen (al-

though there is no evidence that secondary consumption of CH_3SSCH_3 was occurring), the recommended Arrhenius expression is derived from a unit-weighted least-squares analysis of the absolute rate data of Wine *et al.*,³ with

$$k(\text{dimethyl disulfide}) = (5.83^{+4.53}_{-2.55}) \times 10^{-11} e^{(383 \pm 169)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 249–367 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{dimethyl disulfide}) = 2.11 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty at 298 K of $\pm 35\%$. Note that due to a calculational error³⁰ this recommendation is somewhat different to that of Atkinson³⁰ based upon the same data set. Over the temperature range studied, this reaction appears to proceed by initial OH radical addition^{3,31}

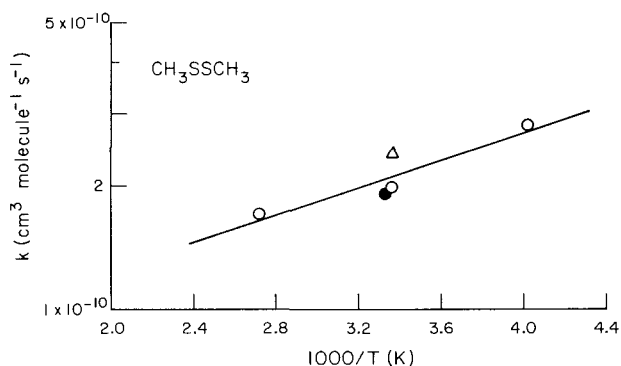
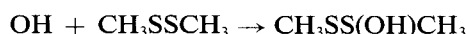


FIG. 88. Arrhenius plot of rate constants for the reaction of the OH radical with dimethyl disulfide. (Δ) Cox and Sheppard;² (○) Wine *et al.*,³ (●) Barnes *et al.*,^{20,21} (—) recommendation (see text).

d. Thioethers

(1) Tetrahydrothiophene

The rate constant data of Wine and Thompson,²² Martin *et al.*¹³ and Witte and Zetzsch¹⁹ (for which only the Arrhenius expression was available) are given in Table 13 and are plotted in Arrhenius form in Fig. 89. The rate constants obtained from these three studies^{13,19,22} are in excellent agreement.

The recommended Arrhenius expression is based upon a unit-weighted least-squares analysis of the absolute rate constants of Wine and Thompson,²² with

$$k(\text{tetrahydrothiophene}) = (1.13^{+0.42}_{-0.31}) \times 10^{-11} e^{(166 \pm 97)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 255–377 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{tetrahydrothiophene}) = 1.97 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty of $\pm 30\%$ at 298 K.

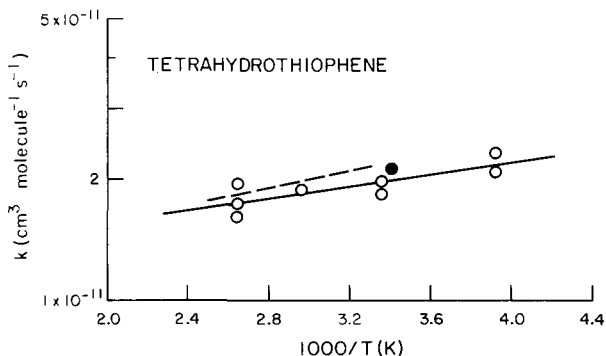
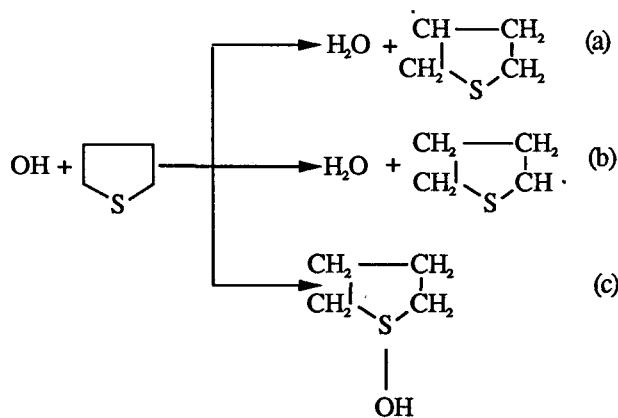


FIG. 89. Arrhenius plot of rate constants for the reaction of the OH radical with tetrahydrothiophene. (○) Wine and Thompson;²² (●) Martin *et al.*;¹³ (---) Witte and Zetzsch;¹⁹ (—) recommendation (see text).

This OH radical reaction can proceed by the reaction pathways



and it is expected that all three reaction channels will occur at around room temperature.²² Based on estimation methods,³² reaction pathway (b) is expected to dominate over pathway (a). Witte and Zetzsch¹⁹ observed bi-exponential OH radical decays at temperatures ≥ 418 K, showing the occurrence of the OH radical addition pathway (c), and obtained a rate constant of $k_{-c} = 3 \times 10^7 e^{-(6400 \pm 1000)/T} \text{ s}^{-1}$ for the thermal decomposition of the OH-tetrahydrothiophene adduct formed in reaction

channel (c) back to reactants. However, the relative importance of pathways (b) and (c) are not known, although it is likely that the H-atom abstraction channel dominates.^{19,32}

(2) Thiophene

The available rate constant data of Lee and Tang,²³ Atkinson *et al.*,²⁴ Mac Leod *et al.*,^{5,25} Wine and Thompson,²² Barnes *et al.*,²⁶ Martin *et al.*,¹³ Wallington²⁷ and Witte and Zetzsch¹⁹ are given in Table 13. The discharge flow measurements of Lee and Tang²³ and Mac Leod *et al.*^{5,25} yield room temperature rate constants which are higher by a factor of ~ 5 than those determined from the flash photolysis,^{19,22,27} the most recent discharge flow,¹³ and the relative rate^{24,26} studies, with the high rate constants obtained by Mac Leod *et al.*^{5,25} being attributed to the occurrence of heterogeneous reactions on the flow tube walls.¹³ The rate constants of Lee and Tang²³ and Mac Leod *et al.*^{5,25} were thus not used in the rate constant evaluation.

At room temperature the rate constants obtained by Witte and Zetzsch¹⁹ and Martin *et al.*¹³ are $\sim 20\%$ higher than the data of Atkinson *et al.*,²⁴ Wine and Thompson,²² Barnes *et al.*,²⁶ and Wallington²⁷ (all of which are plotted in Arrhenius form in Fig. 90), although at ≥ 380 K the data of Witte and Zetzsch¹⁹ agree well with those of Wine and Thompson.²²

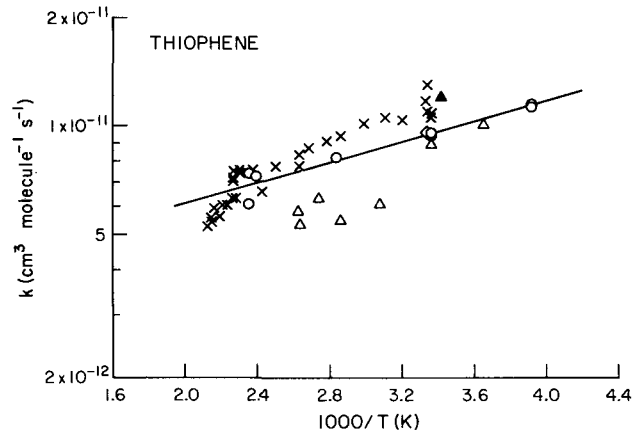


FIG. 90. Arrhenius plot of rate constants for the reaction of the OH radical with thiophene. (●) Atkinson *et al.*;²⁴ (○) Wine and Thompson;²² (◇) Barnes *et al.*;²⁶ (▲) Martin *et al.*;¹³ (Δ) Wallington;²⁷ (x) Witte and Zetzsch;¹⁹ (—) recommendation (see text).

Furthermore, while the rate constants of Atkinson *et al.*,²⁴ Wine and Thompson,²² Barnes *et al.*²⁶ and Wallington²⁷ are in excellent agreement at room temperature, significant discrepancies arise between the data of Wine and Thompson²² and Wallington²⁷ at elevated temperatures.

A unit-weighted least-squares analysis of the rate constant data of Atkinson *et al.*,²⁴ Wine and Thompson²² and Barnes *et al.*²⁶ leads to the recommendation of

$$k(\text{thiophene}) = (3.19^{+0.68}_{-0.56}) \times 10^{-12} e^{(326 \pm 61)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 255–425 K, where the indicated errors are two least-squares standard deviations, and

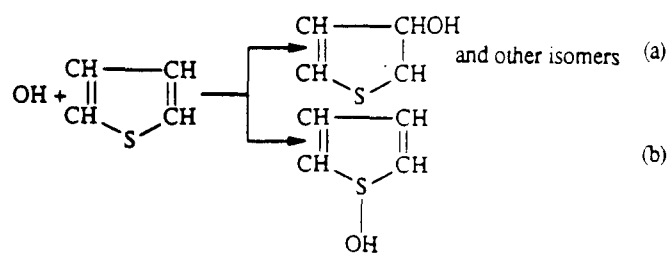
$$k(\text{thiophene}) = 9.53 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty at 298 K of $\pm 30\%$. The rate constant is independent of the total pressure or of the presence of O_2 at room temperature. This recommendation is essentially identical to that of

$$k(\text{thiophene}) = 3.20 \times 10^{-12} e^{324/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

of Atkinson.³⁰

At around room temperature the OH radical reaction with thiophene is expected to proceed by OH radical addition to the $>\text{C}=\text{C}<$ bonds and to the S atom:



At the present time the relative contributions of these two reaction pathways (a) and (b) are not known. At elevated temperatures, these OH radical adducts are expected to undergo thermal decomposition back to the reactants (at least in part), and Witte and Zetzsch¹⁹ have observed non-exponential OH radical decays at temperatures ≥ 434 K, with a rate constant for the thermal decomposition of the OH-thiophene adduct [presumably that formed in reaction channel (b)] of $k = 3 \times 10^{10} e^{-(10100 \pm 1400)/T} \text{ s}^{-1}$ over the temperature range 434–471 K. (The OH-thiophene adduct formed in reaction channel (a) is expected to have a higher barrier to thermal decomposition.) Consequently, as for all OH radical addition reactions, the recommended rate expression given above cannot be used for temperatures outside of the range of the recommendation.

e. Other Organosulfur Compounds

Rate data are available for thiazole and dimethyl sulfoxide (Table 13), but since single studies have been carried out for each of these organosulfur compounds no recommendations are made.

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2.8. Nitrogen-Containing Organics

The available rate constant data obtained at, or close to, the high pressure second-order limit are given in Tables 15 (OH radical reactions) and 16 (OD radical reactions). To date, for those OH radical reactions which proceed by OH radical addition, rate constant data in the fall-off region between second- and third-order kinetics

have been obtained only for HCN,^{22,23,44,45} C₂N₂²⁵ and CH₂=CHCN.²⁶ As seen from Table 15, for most of these nitrogen-containing organic compounds kinetic studies have been carried out by only one research group. The kinetics and mechanisms of these OH (and OD) radical reactions are discussed by the various classes of the nitrogen-containing organics.

TABLE 15. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with nitrogen-containing organics at, or close to, the high pressure limits

Organic	$10^{12} \times A$ (cm ³ mole- cule ⁻¹ s ⁻¹)	B (K)	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹) at T (K)	Technique	Reference	Tempera- ture range covered (K)
<i>Aliphatic Amines</i>						
Methyl amine			22.0 ± 2.2	FP-RF	Atkinson <i>et al.</i> ¹	299–426
			19.4 ± 2.0			
	10.2	-229 ± 151	17.5 ± 1.8			
Ethyl amine			27.7 ± 2.8	FP-RF	Atkinson <i>et al.</i> ²	300–426
			24.9 ± 2.5			
	14.7	-189 ± 151	23.0 ± 2.3			
Dimethyl amine			65.4 ± 6.6	FP-RF	Atkinson <i>et al.</i> ²	298–425
			58.3 ± 5.9			
	28.9	-247 ± 151	51.1 ± 5.2			
Trimethyl amine			60.9 ± 6.1	FP-RF	Atkinson <i>et al.</i> ²	299–425
			53.7 ± 5.4			
	26.2	-252 ± 151	47.4 ± 4.8			
Diethyl hydroxylamine			101	PR-RA	Gorse <i>et al.</i> ³	
2-(Dimethyl-amino)-ethanol			47 ± 12	FP-RF	Harris and Pitts ⁴	
			63 ± 29	FP-RF	Anderson and Stephens ⁵	234–364
			86 ± 29			
			103 ± 20			
			87 ± 15			
			93 ± 30			
90 ± 20	0					
2-Amino-2-methyl-1-propanol			28 ± 5	FP-RF	Harris and Pitts ⁴	
N-Nitroso-dimethylamine			2.53 ± 0.21	RR [relative to k (dimethyl ether) = 2.98 × 10 ⁻¹²]a	Tuazon <i>et al.</i> ⁶	
			3.6 ± 0.1	LP-LIF	Zabarnick <i>et al.</i> ⁷	
Dimethyl-nitramine			3.84 ± 0.15	RR [relative to k (dimethyl ether) = 2.98 × 10 ⁻¹²]a	Tuazon <i>et al.</i> ⁶	
<i>Hydrazines</i>						
Hydrazine			22 ± 5	DF-EPR	Hack <i>et al.</i> ⁸	
			65 ± 10	FP-RF	Harris <i>et al.</i> ⁹	298–424
			59 ± 9			
			58 ± 9			
44	-116 ± 176					
[61 ± 10	0]					

TABLE 15. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with nitrogen-containing organics at, or close to, the high pressure limits — Continued

Organic	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{molecule}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
Methylhydrazine	65 ± 13	0	65 ± 13	298–424	FP-RF	Harris <i>et al.</i> ⁹	298–424
<i>Nitrites</i>							
Methylnitrite			1.41 ± 0.19	292 ± 2	RR [relative to $k(\text{CO}) = 1.58 \times 10^{-13}$] ^b	Campbell and Goodman ¹⁰	
			1.09 ± 0.17	295 ± 3	RR [relative to $k(n\text{-butane}) = 2.50 \times 10^{-12}$] ^a	Audley <i>et al.</i> ¹¹	
			0.21 ± 0.04	300 ± 3	RR [relative to $k(n\text{-hexane}) = 5.64 \times 10^{-12}$] ^a	Tuazon <i>et al.</i> ¹²	
			0.12 ± 0.03	300 ± 3	RR [relative to $k(\text{dimethyl ether}) = 3.01 \times 10^{-12}$] ^a	Tuazon <i>et al.</i> ¹²	
			1.00 ± 0.15	295 ± 2	DF-RF	Baulch <i>et al.</i> ¹³	
Ethyl nitrite			1.77 ± 0.28	295 ± 3	RR [relative to $k(n\text{-butane}) = 2.50 \times 10^{-12}$] ^a	Audley <i>et al.</i> ¹¹	
1-Propyl nitrite [$\text{CH}_3(\text{CH}_2)_2\text{ONO}$]			2.40 ± 0.45	295 ± 3	RR [relative to $k(n\text{-butane}) = 2.50 \times 10^{-12}$] ^a	Audley <i>et al.</i> ¹¹	
			2.31 ± 0.34	295 ± 2	DF-RF	Baulch <i>et al.</i> ¹³	
1-Butyl nitrite [$\text{CH}_3(\text{CH}_2)_3\text{ONO}$]			5.23 ± 1.76	295 ± 3	RR [relative to $k(n\text{-butane}) = 2.50 \times 10^{-12}$] ^a	Audley <i>et al.</i> ¹¹	
			4.80 ± 0.72	295 ± 2	DF-RF	Baulch <i>et al.</i> ¹³	
2-Butyl nitrite [$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{ONO}$]			5.97 ± 0.71	295 ± 3	RR [relative to $k(n\text{-butane}) = 2.50 \times 10^{-12}$] ^a	Audley <i>et al.</i> ¹¹	
2-Methyl-1-propyl nitrite [$(\text{CH}_3)_2\text{CHCH}_2\text{ONO}$]			5.35 ± 0.65	295 ± 3	RR [relative to $k(n\text{-butane}) = 2.50 \times 10^{-12}$] ^a	Audley <i>et al.</i> ¹¹	
2-Methyl-2-propyl nitrite [$(\text{CH}_3)_3\text{CONO}$]			1.41 ± 0.20	295 ± 3	RR [relative to $k(n\text{-butane}) = 2.50 \times 10^{-12}$] ^a	Audley <i>et al.</i> ¹¹	
<i>Nitrates</i>							
Methylnitrate [CH_3ONO_2]			0.034 ± 0.004	298	DF-RF	Gaffney <i>et al.</i> ¹⁴	
			0.38 ± 0.10	303 ± 2	RR [relative to $k(\text{ethene}) = 8.32 \times 10^{-12}$] ^a	Kerr and Stocker ¹⁵	
Ethyl nitrate [$\text{CH}_3\text{CH}_2\text{ONO}_2$]			0.49 ± 0.21	303 ± 2	RR [relative to $k(\text{ethene}) = 8.32 \times 10^{-12}$] ^a	Kerr and Stocker ¹⁵	

TABLE 15. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with nitrogen-containing organics at, or close to, the high pressure limits — Continued

Organic	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
1-Propyl nitrate [CH ₃ CH ₂ CH ₂ ONO ₂]			0.72 ± 0.23	303 ± 2	RR [relative to $k(\text{ethene}) = 8.32 \times 10^{-12}]^a$	Kerr and Stocker ¹⁵	
			0.62 ± 0.10	298 ± 2	RR [relative to $k(\text{cyclohexane}) = 7.49 \times 10^{-12}]^a$	Atkinson and Aschmann ¹⁶	
2-Propyl nitrate [(CH ₃) ₂ CHONO ₂]			0.18 ± 0.05	299 ± 2	RR [relative to $k(\text{cyclohexane}) = 7.51 \times 10^{-12}]^a$	Atkinson <i>et al.</i> ¹⁷	
			0.41 ± 0.06	298 ± 2	RR [relative to $k(\text{cyclohexane}) = 7.49 \times 10^{-12}]^a$	Atkinson and Aschmann ¹⁶	
1-Butyl nitrate [CH ₃ (CH ₂) ₃ ONO ₂]			1.40 ± 0.11	299 ± 2	RR [relative to $k(\text{cyclohexane}) = 7.51 \times 10^{-12}]^a$	Atkinson <i>et al.</i> ¹⁷	
			1.78 ± 0.19	298 ± 2	RR [relative to $k(\text{cyclohexane}) = 7.49 \times 10^{-12}]^a$	Atkinson and Aschmann ¹⁶	
2-Butyl nitrate [CH ₃ CH ₂ CH(CH ₃)ONO ₂]			0.68 ± 0.10	299 ± 2	RR [relative to $k(\text{cyclohexane}) = 7.51 \times 10^{-12}]^a$	Atkinson <i>et al.</i> ¹⁷	
			0.92 ± 0.16	298 ± 2	RR [relative to $k(\text{cyclohexane}) = 7.49 \times 10^{-12}]^a$	Atkinson and Aschmann ¹⁶	
2-Pentyl nitrate [CH ₃ (CH ₂) ₂ CH(CH ₃)ONO ₂]			1.85 ± 0.13	299 ± 2	RR [relative to $k(\text{cyclohexane}) = 7.51 \times 10^{-12}]^a$	Atkinson <i>et al.</i> ¹⁷	
3-Pentyl nitrate [(C ₂ H ₅) ₂ CHONO ₂]			1.12 ± 0.20	299 ± 2	RR [relative to $k(\text{cyclohexane}) = 7.51 \times 10^{-12}]^a$	Atkinson <i>et al.</i> ¹⁷	
2-Methyl-3-butyl nitrate [(CH ₃) ₂ CHCH(CH ₃)ONO ₂]			1.72 ± 0.06	298 ± 2	RR [relative to $k(n\text{-butane}) = 2.54 \times 10^{-12}]^a$	Atkinson <i>et al.</i> ¹⁸	
2,2-Dimethyl-1-propyl nitrate [(CH ₃) ₃ CCH ₂ ONO ₂]			0.85 ± 0.21	298 ± 2	RR [relative to $k(n\text{-butane}) = 2.54 \times 10^{-12}]^a$	Atkinson <i>et al.</i> ¹⁸	
2-Hexyl nitrate [CH ₃ (CH ₂) ₃ CH(CH ₃)ONO ₂]			3.17 ± 0.16	299 ± 2	RR [relative to $k(\text{cyclohexane}) = 7.51 \times 10^{-12}]^a$	Atkinson <i>et al.</i> ¹⁷	
3-Hexyl nitrate [CH ₃ (CH ₂) ₂ CH(ONO ₂)CH ₂ CH ₃]			2.70 ± 0.22	299 ± 2	RR [relative to $k(\text{cyclohexane}) = 7.51 \times 10^{-12}]^a$	Atkinson <i>et al.</i> ¹⁷	
Cyclohexyl nitrate			3.30 ± 0.36	298 ± 2	RR [relative to $k(n\text{-butane}) = 2.54 \times 10^{-12}]^a$	Atkinson <i>et al.</i> ¹⁸	
2-Methyl-2-pentyl nitrate [(CH ₃) ₂ C(ONO ₂)CH ₂ CH ₂ CH ₃]			1.72 ± 0.22	298 ± 2	RR [relative to $k(n\text{-butane}) = 2.54 \times 10^{-12}]^a$	Atkinson <i>et al.</i> ¹⁸	

TABLE 15. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with nitrogen-containing organics at, or close to, the high pressure limits — Continued

Organic	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{molecule}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
3-Methyl-2-pentyl nitrate [CH ₃ CH(ONO ₂)CH(CH ₃)CH ₂ CH ₃]			3.02 ± 0.08	298 ± 2	RR [relative to $k(n\text{-butane}) = 2.54 \times 10^{-12}$] ^a	Atkinson <i>et al.</i> ¹⁸	
3-Heptyl nitrite [CH ₃ (CH ₂) ₃ CH(ONO ₂)CH ₂ CH ₃]			3.69 ± 0.43	299 ± 2	RR [relative to $k(\text{cyclohexane}) = 7.51 \times 10^{-12}$] ^a	Atkinson <i>et al.</i> ¹⁷	
3-Octyl nitrate [CH ₃ (CH ₂) ₄ CH(ONO ₂)CH ₂ CH ₃]			3.88 ± 0.79	299 ± 2	RR [relative to $k(\text{cyclohexane}) = 7.51 \times 10^{-12}$] ^a	Atkinson <i>et al.</i> ¹⁷	
<i>Nitriles</i>							
Hydrogen cyanide			0.33 ± 0.04	1950–2380	Flame	Haynes ¹⁹	1950–2380
	42	5030		1318–2400	Flame	Fenimore ²⁰	1318–2400
			0.35	1790	Flame; OH, CN by LIF	Morley ²¹	1790–2200
			0.33	1790			
			0.76	1790			
			0.67	2000			
			0.97	2130			
			1.25	2200			
	0.12 ± 0.05	400	0.03 ± 0.01	298	FP-RA	Fritz <i>et al.</i> ^{22,23}	296–433
Cyanogen [C ₂ N ₂]			≤0.03	298	FP-RF	Atkinson <i>et al.</i> ²⁴	298–424
			≤0.05	424			
	0.311	1448	0.0025 ^c	300	DF-RF	Phillips ²⁵	300–555
Acetonitrile [CH ₃ CN]			0.0494 ± 0.006	297.2	FP-RF	Harris <i>et al.</i> ²⁶	297–424
			0.0620 ± 0.007	348.0			
	0.586	755 ± 126	0.105 ± 0.015	423.8			
			0.024 ± 0.003	295	FP-RF	Fritz <i>et al.</i> ²²	
			0.019 ± 0.002	296	FP-RF	Zetzsch ^{27,28}	
			0.0102 ± 0.0022	250	FP-RF	Kurylo and Knable ²⁹	250–363
			0.0146 ± 0.0015	273			
			0.0194 ± 0.0037	298			
	0.628	1030	0.0370 ± 0.0033	363			
			0.021 ± 0.003	295	DF-EPR	Poulet <i>et al.</i> ³⁰	295–393
			0.086 ± 0.01	393			
Propionitrile [C ₂ H ₃ CN]			0.194 ± 0.020	298.2	FP-RF	Harris <i>et al.</i> ²⁶	298–423
			0.233 ± 0.025	350.8			
			0.362 ± 0.036	384.0			
	2.69	800 ± 176	0.414 ± 0.040	423.0			
Acrylonitrile [CH ₂ =CHCN]			4.80 ± 0.50	298.7	FP-RF	Harris <i>et al.</i> ²⁶	299–423
			3.4 ± 0.5	296	FP-RF	Zetzsch ²⁷	
<i>Nitrogen-Containing Heterocycles</i>							
Aziridine ^d			6.1 ± 0.5	295	FP-RF	Zetzsch ³¹	

TABLE 15. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with nitrogen-containing organics at, or close to, the high pressure limits — Continued

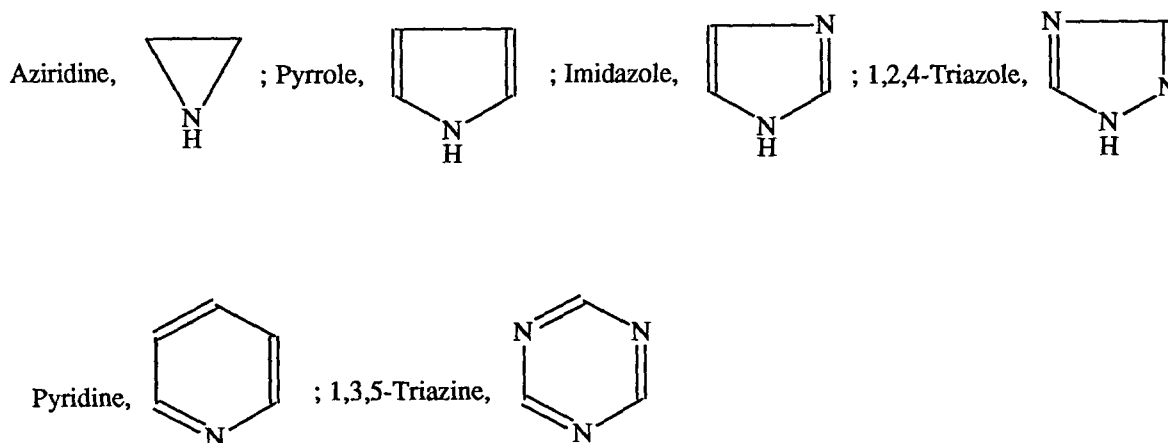
Organic	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)	
Pyrrole ^d			122 ± 4	295 ± 1	RR [relative to $k(\text{propene}) =$ $2.68 \times 10^{-11}]^a$	Atkinson <i>et al.</i> ³²		
			103 ± 6	298 ± 2	FP-RF	Wallington ³³	298–440	
			98 ± 20	325				
			83 ± 13	355				
	27_{-6}^{+8}	−403 ± 93	68 ± 10	440				
			99.1 ± 2.0	298	FP-RF	Witte and Zetzsch ³⁴	298–442	
			93.1 ± 7.3	298				
			93.1 ± 11.0	298				
			101.0 ± 21.8	298				
			83.9 ± 2.0	327				
			71.3 ± 2.0	347				
			68.7 ± 4.6	348				
	9.3 ± 3.8	−690 ± 120 (298–372 K)	59.4 ± 3.3	372				
			51.5 ± 2.0	392				
		48.5 ± 1.7	395					
		37.6 ± 2.0	422					
		24.4 ± 2.0	442					
Imidazole ^d			35.9 ± 3.3	297	FP-RF	Witte and Zetzsch ³⁴	297–440	
			31.3 ± 0.1	316				
			27.3 ± 2.5	331				
	2.2 ± 0.2	−840 ± 30 (297–344 K)	25.2 ± 0.3	344				
			22.5 ± 1.0	353				
			19.8 ± 1.0	362				
			21.2 ± 1.6	363				
			16.3 ± 0.3	386				
			13.9 ± 0.5	402				
			8.6 ± 1.2	425				
			10.4 ± 0.7	425				
			9.1 ± 1.1	440				
1,2,4-Triazole ^d			<0.2	~298	FP-RF	Witte and Zetzsch ³⁴		
Pyridine ^d			0.494 ± 0.039	296 ± 2	RR [relative to $k(\text{dimethyl ether}) =$ $2.96 \times 10^{-12}]^a$	Atkinson <i>et al.</i> ³⁵		
			0.159 ± 0.025	246	FP-RF	Witte and Zetzsch ³⁴	246–468	
			0.190 ± 0.018	258				
			0.207 ± 0.021	268				
			0.221 ± 0.021	272				
	3.5 ± 1.4	760 ± 100 (246–286 K)	0.250 ± 0.020	286				
			0.256 ± 0.014	297				
			0.254 ± 0.014	308				
			0.245 ± 0.023	323				
			0.199 ± 0.014	348				
			0.119 ± 0.016	373				
			0.175 ± 0.012	398				
			0.191 ± 0.015	423				
			0.209 ± 0.015	448				
	12 ± 7	1800 ± 240 (423–468 K)	0.252 ± 0.012	468				
	1,3,5-Triazine ^d			0.145 ± 0.027	296 ± 2	RR [relative to $k(\text{dimethyl ether}) =$ $2.96 \times 10^{-12}]^a$	Atkinson <i>et al.</i> ³⁵	

TABLE 15. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with nitrogen-containing organics at, or close to, the high pressure limits — Continued

Organic	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{molecule}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
<i>Miscellaneous</i>							
Peroxyacetyl nitrate [$\text{CH}_3\text{C}(\text{O})\text{OONO}_2$]			≤ 0.17	299 ± 1	FP-RF	Winer <i>et al.</i> ³⁶	
	1.23	651 ± 229	0.113 ± 0.006 0.137 ± 0.005	273 ± 2 297 ± 2	FP-RF	Wallington <i>et al.</i> ³⁷	273–297
			0.075 ± 0.014	298	DF-EPR	Tsalkani <i>et al.</i> ³⁸	
Nitromethane [CH_3NO_2]			1.00 ± 0.10	292 ± 2	RR [relative to $k(\text{CO}) = 1.58 \times 10^{-13}$] ^b	Campbell and Goodman ¹⁰	
			0.0174 ± 0.0038 0.0141 ± 0.0030 0.0273 ± 0.0085 0.0580 ± 0.0140 0.0735 ± 0.0071	299 300 372 473 572	LP-LIF	Zabarnick <i>et al.</i> ³⁹	299–671
	0.81 ± 0.32	1208 ± 151	0.193 ± 0.030	671			
			0.156 ± 0.012	295 ± 2	PR-RA	Nielsen <i>et al.</i> ⁴⁰	
			0.272 ± 0.084	295 ± 2	RR [relative to $k(\text{ethane}) = 2.58 \times 10^{-13}$] ^a	Nielsen <i>et al.</i> ⁴⁰	
Nitromethane- d_3 [CD_3NO_2]			0.096 ± 0.011	295 ± 2	PR-RA	Nielsen <i>et al.</i> ⁴⁰	
			0.260 ± 0.046	295 ± 2	RR [relative to $k(\text{ethane}) = 2.58 \times 10^{-13}$] ^a	Nielsen <i>et al.</i> ⁴⁰	
Nitroethane [$\text{CH}_3\text{CH}_2\text{NO}_2$]			0.15 ± 0.05	295 ± 3	PR-RA	Nielsen <i>et al.</i> ⁴¹	
1-Nitropropane [$\text{CH}_3\text{CH}_2\text{CH}_2\text{NO}_2$]			0.34 ± 0.08	295 ± 3	PR-RA	Nielsen <i>et al.</i> ⁴¹	
1-Nitrobutane [$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NO}_2$]			1.35 ± 0.18	298 ± 2	RR [relative to $k(\text{propane}) = 1.15 \times 10^{-12}$] ^a	Atkinson and Aschmann ¹⁶	
			1.55 ± 0.09	295 ± 3	PR-RA	Nielsen <i>et al.</i> ⁴¹	
1-Nitropentane [$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NO}_2$]			3.30 ± 0.05	295 ± 3	PR-RA	Nielsen <i>et al.</i> ⁴¹	
Isocyanic acid [HNCO]			0.0502 ± 0.0033 0.0723 ± 0.0048 0.100 ± 0.007 0.0942 ± 0.0075 0.133 ± 0.010	624 676 730 731 796	LP-LIF	Tully <i>et al.</i> ⁴²	624–875
	4.4 ± 0.9	2788 ± 141	0.182 ± 0.015	875			
$\text{CH}_2=\text{NOH}$			0.63 ± 0.31	300 ± 2	FP-KS	Horne and Norrish ⁴³	

TABLE 15. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with nitrogen-containing organics at, or close to, the high pressure limits — Continued

Organic	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{molecule}^{-1} \text{s}^{-1}$) at T (K)	Technique	Reference	Temperature range covered (K)
$\text{CH}_3\text{CH}=\text{NOH}$			2.2 ± 1.1	300 ± 2	FP-KS	Horne and Norrish ⁴³

^aFrom the present recommendations (see text).^bSee Introduction.^cCalculated from cited Arrhenius expression.^dStructures:TABLE 16. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OD radical with nitrogen-containing organic compounds

Organic	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{molecule}^{-1} \text{s}^{-1}$) at T (K)	Technique	Reference	Temperature range covered (K)	
Nitromethane (CH_3NO_2)	1.8 ± 1.0	1661 ± 201	0.0082 ± 0.0044	296	LP-LIF	Zabarnick <i>et al.</i> ³⁹	296-671
			0.0186 ± 0.0082	378			
			0.0443 ± 0.0004	474			
			0.0848 ± 0.0122	572			
			0.218 ± 0.010	671			
Nitromethane- d_3 (CD_3NO_2)	0.53 ± 0.24	1439 ± 171	0.0050 ± 0.0002	296	LP-LIF	Zabarnick <i>et al.</i> ³⁹	296-670
			0.0049 ± 0.0006	299			
			0.0074 ± 0.0013	376			
			0.0233 ± 0.0008	475			
			0.0382 ± 0.0013	566			
0.0846 ± 0.0006	670						

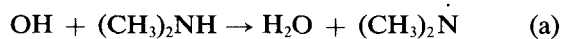
a. Aliphatic Amines

Only for 2-(dimethylamino)ethanol and N-nitrosodimethylamine have more than one study been carried out. For 2-(dimethylamino)ethanol the room temperature rate constants determined by Harris and Pitts⁴ and Anderson and Stephens,⁵ both using flash photolysis-resonance fluorescence methods, disagree by a factor of ~ 2 . As discussed by Anderson and Stephens,⁵ the rate constant measured by Harris and Pitts⁴ may have been low due to adsorption of the 2-(dimethylamino)ethanol onto the reaction vessel walls [the 2-(dimethylamino)ethanol concentrations were measured before and after the reaction vessel in the study of Anderson and Stephens⁵]. Consequently, while no firm recommendation is made concerning the rate constant for this OH radical reaction, in the absence of further data the data of Anderson and Stephens⁵ are preferred.

For N-nitrosodimethylamine, the room temperature rate constants of Tuazon *et al.*⁶ and Zabarnick *et al.*⁷ exhibit a discrepancy of a factor of ~ 1.4 . However, since the rate constants measured by the laser photolysis-laser induced fluorescence technique of Zabarnick *et al.*⁷ were observed to be dependent on the laser fluence, it is possible that the rate constant determined by Zabarnick *et al.*⁷ is still an upper limit. Clearly, further kinetic data are needed for this reaction.

As shown in Table 15, the OH radical reactions with methyl amine, ethyl amine, dimethyl amine and trimethyl amine are rapid, with room temperature rate constants in the range $(2-6) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and with negative temperature dependencies equivalent to $B \approx -230 \text{ K}$. For the methyl-substituted amines, the trend of the room temperature rate constants suggests that these reactions proceed via abstraction from the C—H bonds and, where possible, the N—H bonds. From the rate constants measured by Atkinson *et al.*¹² and the bond dissociation energies for the C—H (93.3 ± 2 , 87 ± 2 and $84 \pm 2 \text{ kcal mol}^{-1}$ in CH_3NH_2 , $(\text{CH}_3)_2\text{NH}$ and $(\text{CH}_3)_3\text{N}$, respectively⁴⁶) and N—H (100.0 ± 2.5 and $91.5 \pm 2 \text{ kcal mol}^{-1}$ in CH_3NH_2 and $(\text{CH}_3)_2\text{NH}$, respectively⁴⁶) bonds, it is expected that for CH_3NH_2 (and probably also $\text{C}_2\text{H}_5\text{NH}_2$) H-atom abstraction from the C—H bonds predominates, while for $(\text{CH}_3)_2\text{NH}$ H-atom abstraction from the N—H bond is competitive with H-atom abstraction from the C—H bonds.²

Indeed, from a product study of irradiated HONO— $(\text{CH}_3)_2\text{NH}$ —air mixtures, utilizing long pathlength FT-IR absorption spectroscopy, Lindley *et al.*⁴⁷ determined that at room temperature $k_a/(k_a + k_b) = 0.37 \pm 0.05$, where k_a and k_b are the rate constants for reaction pathways (a) and (b), respectively.



However, the observations of negative temperature dependencies for these reactions¹² suggest that these OH radical reactions may proceed via the initial formation of

an addition complex, which then rapidly decomposes to the observed products. Clearly, further experimental work concerning the reaction dynamics of these systems is needed.

The OH radical reactions with the substituted amines diethyl hydroxylamine, 2-(dimethylamino)ethanol, 2-amino-2-methyl-1-propanol, N-nitrosodimethylamine, dimethylnitramine and aziridine also almost certainly proceed via overall H-atom abstraction. However, the position of the H-atom abstracted cannot be predicted in all cases, since the C—H and N—H bond strengths are not known. Obviously, for N-nitrosodimethylamine and dimethylnitramine any H-atom abstraction must occur from the C—H bonds.

b. Hydrazines

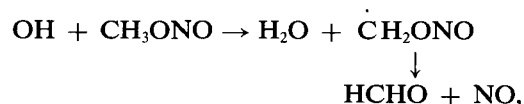
To date, only for hydrazine and methylhydrazine are kinetic data available for the OH radical reactions (Table 15), and no unambiguous product data are available. The reactions of OH radicals with hydrazine and methylhydrazine are expected to occur via overall H-atom abstraction from the N—H bonds (of bond strength $87.5 \text{ kcal mol}^{-1}$ in N_2H_4 ⁴⁸). This is consistent with the magnitude of the rate constants observed,⁹ although it is possible that the reaction proceeds via initial formation of an addition complex followed by rapid decomposition to the RNHNH or RNNH_2 radical and H_2O .

c. Nitrites

The available kinetic data, all obtained at room temperature, are given in Table 15. The relative rate studies of Campbell and co-workers,^{10,11} using the dark heterogeneous reaction of H_2O_2 with NO_2 to generate OH radicals, are in excellent agreement with the discharge flow-resonance fluorescence data of Baulch *et al.*¹³ for methyl nitrite, 1-propyl nitrite and 1-butyl nitrite. However, the rate constants obtained for methyl nitrite in the relative rate study of Tuazon *et al.*¹² (employing the dark reaction of N_2H_4 with O_3 to generate OH radicals) are lower by a factor of ~ 7 . Jenkin *et al.*⁴⁹ have concluded that the products formed, and their yields, from the photolysis of CH_3ONO in $\text{CH}_3\text{ONO—NO—N}_2$ and $\text{CH}_3\text{ONO—O}_2$ mixtures at 298 K are consistent with the lower rate constant of Tuazon *et al.*¹² of $\sim 1.2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. While the reasons for these discrepancies are not known at present, it should be noted that the room temperature rate constant derived from the relative rate method of Campbell and Goodman¹⁰ for nitromethane (CH_3NO_2) is 10 and 60 times higher than the absolute rate constants of Nielsen *et al.*⁴⁰ and Zabarnick *et al.*,³⁹ respectively. These observations suggest that fundamental problems are associated with the relative rate method of Campbell *et al.*^{10,11} employing the dark heterogeneous reaction of H_2O_2 with NO_2 as a source of OH radicals.

Until the kinetics of these OH radical reactions with the alkyl nitrites are more fully understood and product studies carried out, the reaction mechanisms remain un-

certain. These reactions may proceed via H-atom abstraction from the C—H bonds,



and this is expected to be the major, if not only, reaction pathway if the room temperature rate constant for CH_3ONO is $\sim 1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

d. Nitrates

The available kinetic data for the reactions of the OH radical with alkyl nitrates are given in Table 15. Data are available only at room temperature, and only for the C_1 – C_4 alkyl nitrates have more than one kinetic study been carried out. For methyl nitrate the room temperature rate constants obtained by Gaffney *et al.*¹⁴ and Kerr and Stocker¹⁵ disagree by a factor of ~ 11 . The recent rate constants of Atkinson and Aschmann,¹⁶ employing a 6400-liter reaction chamber, supersedes the earlier data of Atkinson *et al.*¹⁷ for the propyl and butyl nitrates. The room temperature rate constants obtained by Kerr and Stocker¹⁵ and Atkinson and Aschmann¹⁶ for 1-propyl nitrate are in good agreement. However, the room temperature rate constant recently determined by Atkinson and Aschmann¹⁶ for 2-propyl nitrate is a factor of 2.3 higher than that of Atkinson *et al.*,¹⁷ at least partially due to the slowness of this reaction and the presumably erroneous conclusion of Atkinson *et al.*¹⁷ that wall losses of the alkyl nitrates, accounting for a significant fraction of the observed 2-propyl nitrate decays, were occurring in the ~ 60 liter reaction chamber used.¹⁷

As expected from the decreasing fractions of the overall alkyl nitrate decay rates attributed to wall losses in the study of Atkinson *et al.*¹⁷ for the faster reacting alkyl nitrates, the room temperature rate constants of Atkinson and Aschmann¹⁶ for 1- and 2-butyl nitrate are higher by only ~ 25 – 35% than those reported of Atkinson *et al.*¹⁷ For the remaining C_5 – C_8 alkyl nitrates studied by Atkinson *et al.*,¹⁷ the reported rate constants are hence expected to be affected to an extent of $\lesssim 20\%$ by this assumption that wall losses were occurring. Based upon the estimation method developed by Atkinson,^{50,51} the room temperature rate constant obtained by Kerr and Stocker¹⁵ for ethyl nitrate is not consistent with those measured for the higher alkyl nitrates by Atkinson and Aschmann¹⁶ and Atkinson *et al.*^{17,18} This suggests that the rate constants obtained by Kerr and Stocker¹⁵ for methyl and ethyl nitrate are systematically high, and that the absolute rate constant of Gaffney *et al.*¹⁴ for methyl nitrate of $3.4 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K is to be preferred.

Since no direct product or mechanistic data are available for these compounds, mechanistic information can only be based upon the available kinetic data. Hydrogen atom abstraction from the C—H bonds appears to be the likely reaction pathway, with the $-\text{ONO}_2$ group

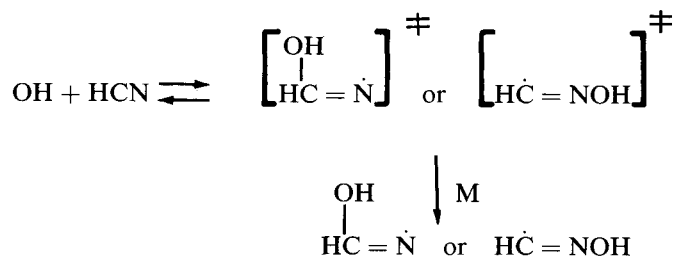
markedly decreasing the rate constant for H-atom abstraction from $>\text{CH}-$ or $-\text{CH}_2-$ groups bonded to the $-\text{ONO}_2$ group, and decreasing those for the β $>\text{CH}-$, $-\text{CH}_2-$ or $-\text{CH}_3$ groups.^{50,51} The distribution of nitroalkyl radicals formed can be approximately calculated using the estimation method of Atkinson.⁵¹

e. Nitriles

The available rate constant data obtained at, or close to, the high-pressure second-order limit are given in Table 15. These kinetic data are discussed for the individual nitriles below.

(1) Hydrogen Cyanide

Rate constants have been derived at elevated temperatures (~ 1300 – 2400 K) by Haynes,¹⁹ Fenimore²⁰ and Morley,²¹ and at temperatures below ~ 850 K by Phillips^{44,45} and Fritz *et al.*^{22,23} At temperatures between 296 and 433 K the rate constants are in the fall-off region between second- and third-order kinetics at total pressures of N_2 below ~ 300 Torr,^{22,23} with bimolecular rate constants (at 373 K) which extrapolate to zero as the total pressure approaches zero.⁴⁴ Thus, at temperatures $\lesssim 433$ K the OH radical reaction with HCN must proceed by initial OH radical addition to form an initially energy-rich adduct which can decompose back to reactants or be collisionally stabilized.



Fritz *et al.*^{22,23} also observed that the rate constants measured at total pressures of N_2 of 10–40 Torr (which are in the fall-off region for temperatures ≤ 433 K) over the temperature range 298–850 K showed marked non-Arrhenius behavior. These rate constants increased rapidly with increasing temperature for temperatures $\gtrsim 500$ K, and had an extrapolated temperature dependence of $B \sim 4500$ K for temperatures $\gtrsim 850$ K. Fritz *et al.*²³ attributed this increase in rate constant at temperatures $\gtrsim 500$ K to the occurrence of either the H-atom abstraction process



or a “transfer” process



The rate constants obtained by Haynes¹⁹ were derived on the assumption that the reaction of OH radicals with

HCN proceeds by channel (b) and not by channel (a) [which would be in equilibrium with the reverse reaction under the conditions employed]. As discussed in detail by Miller and Melius,⁵² reaction pathway (b) involves initial OH radical addition,



and hence the rate constant k_b must be less or equal to the high-pressure OH radical addition rate constant k_{∞} . However, as shown in Fig. 91, in which the rate constant data of Haynes,¹⁹ Fenimore,²⁰ Morley²¹ and Fritz *et al.*^{22,23} are plotted in Arrhenius form, the limiting high pressure rate constant k_{∞} reported by Fritz *et al.*^{22,23} does not extrapolate linearly to the reported rate constants at flame temperatures.¹⁹⁻²¹

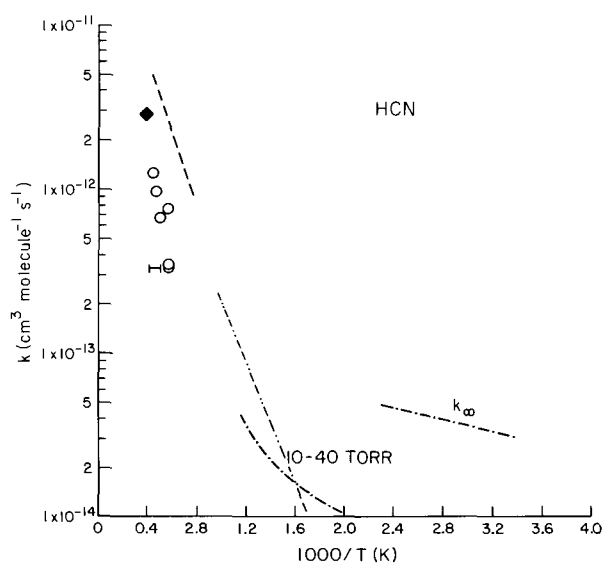
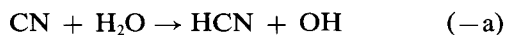


FIG. 91. Arrhenius plot of rate constants for the reaction of the OH radical with HCN. (—) Haynes;¹⁹ (---) Fenimore;²⁰ (○) Morley;²¹ (····) Fritz *et al.*;^{22,23} (◆) calculated by Szekely *et al.*⁵³ from the reverse reaction (—) calculated by Jacobs *et al.*⁵⁴ from the reverse reaction.

It is possible, however, that the limiting high-pressure rate constant k_{∞} exhibits non-Arrhenius behavior and/or that the reported values of k_{∞} of Fritz *et al.*^{22,23} were still in the fall-off regime, with k_{∞} having a steeper temperature dependence than reported.

From shock tube and LP-LIF studies of the kinetics of the reaction,



Szekely *et al.*⁵³ and Jacobs *et al.*⁵⁴ calculated the rate of the reverse reaction (a) to be

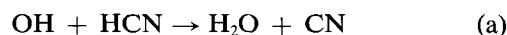
$$k_a = (2.9 \pm 1.4) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 2460–2840 K⁵³ and

$$k_a = (1.28 \pm 0.17) \times 10^{-11} e^{-4162/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 518–1027 K,⁵⁴ and these calculated rate constants are also plotted in Fig. 91. These calculated values of k_a ^{53,54} are in reasonably good agreement with extrapolation of the rate constants obtained by Fritz *et al.*^{22,23} at total pressures of 10–40 Torr and 298–850 K to higher temperatures.

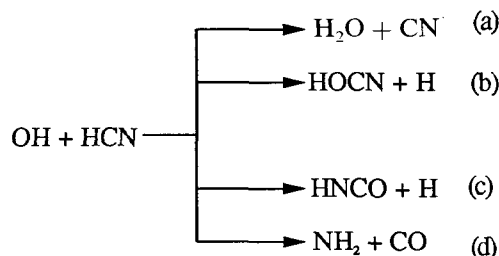
Thus, in the absence of kinetic and product data carried out as a function of total pressure at temperatures >400 K, no firm recommendations can be made. However, it is clear that at temperatures $\lesssim 500$ K the reaction of the OH radical with HCN proceeds by addition to form an adduct which can back dissociate or be collisionally stabilized. At elevated temperatures characteristic of flame conditions this addition reaction will be of no importance because of fall-off effects and thermal decomposition of the OH–HCN adduct, as for the OH radical reaction with C_2H_2 . The kinetic data of Fenimore²⁰ and Morley²¹ are reasonably consistent with the reaction proceeding by H-atom abstraction at these elevated temperatures of ≥ 1300 K,



with a rate constant of^{53,54}

$$k_a = 1.3 \times 10^{-11} e^{-4160/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

For recent theoretical calculations of the rate constants for the four channels



and their comparison with experimental data, the article of Miller and Melius⁵² should be consulted.

(2) Acetonitrile (CH_3CN)

The available rate constant data of Harris *et al.*,²⁶ Fritz *et al.*,²² Zetzsch,^{27,28} Kurylo and Knable²⁹ and Poulet *et al.*³⁰ are given in Table 15 and are plotted in Arrhenius form in Fig. 92. In the flash photolysis-resonance fluorescence study of Zetzsch,²⁸ the room temperature rate constant was observed to be pressure dependent, increasing from $\sim 8 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at ~ 5 Torr total pressure of argon to $\sim 1.1 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 10 Torr total pressure of argon to $1.8 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 100–300 Torr total pressure of argon.

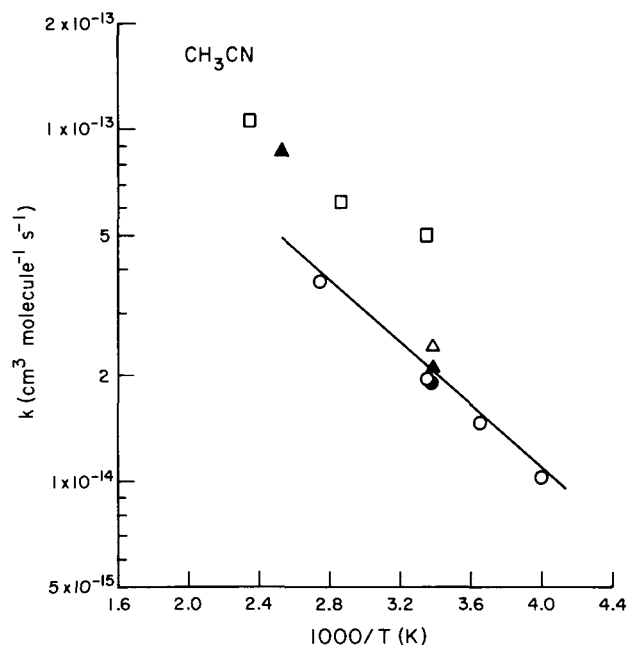


FIG. 92. Arrhenius plot of rate constants for the reaction of the OH radical with CH_3CN . (□) Harris *et al.*;²⁶ (Δ) Fritz *et al.*;²² (●) Zetzsch;^{27,28} (○) Kurylo and Knable;²⁹ (▲) Poulet *et al.*;³⁰ (—) recommendation (see text).

However, the absolute room temperature rate constants of Poulet *et al.*,³⁰ Fritz *et al.*²² and Kurylo and Knable,²⁹ obtained at total pressures of 1.2 Torr, 7 Torr and 20–50 Torr, respectively, are in good agreement, suggesting that the lower pressure data of Zetzsch²⁸ may be in error.

From a comparison of the room temperature rate constants, it is clear (Fig. 92) that the rate constants of Fritz *et al.*,²² Kurylo and Knable²⁹ and Poulet *et al.*³⁰ and the 100–300 Torr total pressure rate constant of Zetzsch²⁸ are in good agreement, but that these rate constants are a factor of ~2–2.5 lower than that of Harris *et al.*²⁶ This observation suggests that the rate constants of Harris *et al.*²⁶ were erroneously high due to the occurrence of secondary reactions or the presence of a reactive impurity. Neglecting these data of Harris *et al.*,²⁶ the only temperature-dependent data then arise from the study of Kurylo and Knable²⁹ and rate constants measured by Poulet *et al.*³⁰ at 393 K (cited as a footnote in their publication) and 295 K. Unfortunately, the temperature dependencies obtained from these data of Kurylo and Knable²⁹ and Poulet *et al.*³⁰ do not agree. Since Le Bras and co-workers have experienced problems associated with heterogeneous wall reactions in previous studies,⁵⁵ the flash photolysis data of Kurylo and Knable²⁹ are used to derive the temperature dependence of this reaction.

A unit-weighted average of the room temperature rate constants of Fritz *et al.*,²² Zetzsch,^{27,28} Kurylo and Knable²⁹ and Poulet *et al.*,³⁰ combined with the temperature dependence of Kurylo and Knable,³⁰ leads to the recommended Arrhenius expression of

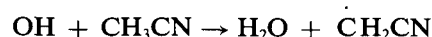
$$k(\text{CH}_3\text{CN}) = 6.77 \times 10^{-13} e^{-1030/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 250–363 K, and

$$k(\text{CH}_3\text{CN}) = 2.14 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

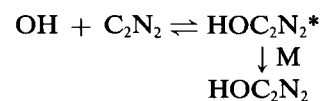
at 298 K, with an estimated overall uncertainty of $\pm 40\%$ at 298 K, with the uncertainties increasing at both lower and higher temperatures. Although an Arrhenius expression has been recommended, non-Arrhenius behavior is expected at higher and lower temperatures. Clearly, further kinetic studies are necessary, especially at higher temperatures (≈ 350 K) and as a function of pressure to resolve the above-mentioned discrepancies.

Based upon the apparent lack of a pressure dependence over the range ~1–50 Torr at room temperature (but see above discussion) and the (qualitative) observation that the room temperature rate constants increase by a factor of ~4–10 in going from acetonitrile to propionitrile (Table 15), it is expected that the OH radical reaction with acetonitrile proceeds mainly by H-atom abstraction from the $-\text{CH}_3$ group:



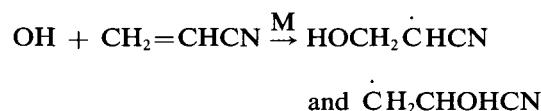
(3) Other Nitriles

The available kinetic data are given in Table 15. For cyanogen, the rate constants are pressure dependent over the temperature range 300–555 K,²⁵ with the rate constants extrapolating to zero at zero pressure.²⁵ Thus the OH radical reaction with C_2N_2 proceeds by initial addition over this temperature range:



It is also possible that the limiting high pressure rate constants were not attained at the highest total pressures employed by Phillips²⁵ of ~15 Torr, and hence that the Arrhenius expression cited in Table 15 is still in the fall-off region.

For acrylonitrile, Harris *et al.*²⁶ observed that the measured rate constants were pressure dependent at room temperature, increasing from $(4.06 \pm 0.41) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 50 Torr total pressure of argon to $(4.80 \pm 0.50) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 500 Torr total pressure of argon. At 50 Torr total pressure of argon, the rate constant was independent of temperature over the range 299–423 K.²⁶ These data, together with the product data of Hashimoto *et al.*,⁵⁶ show that the OH radical reaction with $\text{CH}_2=\text{CHCN}$ proceeds by initial OH radical addition to the $>\text{C}=\text{C}<$ bond.



f. Nitrogen-Containing Heterocycles

The available kinetic data are given in Table 15.

(1) Pyrrole

The rate constants of Atkinson *et al.*,³² Wallington³³ and Witte and Zetzsch³⁴ are given in Table 15 and are plotted in Arrhenius form in Fig. 93.

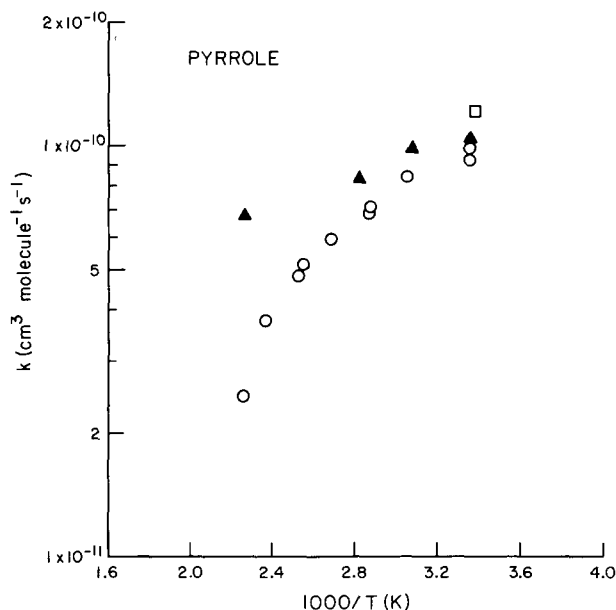


FIG. 93. Arrhenius plot of rate constants for the reaction of the OH radical with pyrrole. (□) Atkinson *et al.*,³² (▲) Wallington,³³ (○) Witte and Zetzsch.³⁴

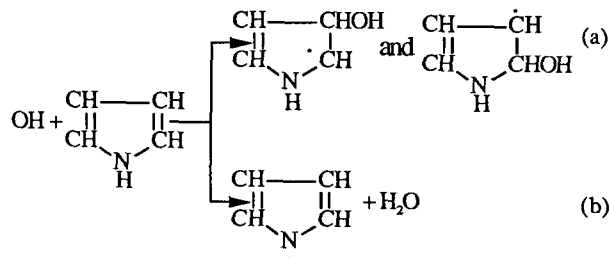
There are substantial disagreements concerning the temperature and pressure effects on the rate constants for this reaction. At 298 K, Witte and Zetzsch³⁴ observed that the rate constants were pressure dependent, increasing from $6.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 22 Torr total pressure of argon to $(9.3\text{--}10.1) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 100–500 Torr total pressure of argon. In contrast, Wallington³³ observed no pressure dependence of the rate constant at $298 \pm 2 \text{ K}$ over the range 25–100 Torr total pressure (of argon diluent). Furthermore, at 100 Torr total pressure, distinct fall-off behavior was observed by Witte and Zetzsch³⁴ for temperatures $\geq 392 \text{ K}$.

However, at room temperature the (supposedly) limiting high-pressure rate constants of Wallington³³ and Witte and Zetzsch³⁴ and that obtained by Atkinson *et al.*³² in the presence of ~ 740 Torr total pressure of air are in good agreement. The mean of the high pressure rate constants of Atkinson *et al.*,³² Wallington³³ and Witte and Zetzsch³⁴ leads to the recommendation of

$$k(\text{pyrrole}) = 1.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty of $\pm 30\%$.

Based upon the observed effects of pressure and temperature on the rate constant for this reaction, it is clear³⁴ that at temperatures $\lesssim 400 \text{ K}$ the reaction proceeds, at least in part, by OH radical addition. This OH radical reaction can proceed by the pathways



with channel (b) also possibly involving initial OH radical addition to the N atom followed by decomposition.

(2) Other Nitrogen-Containing Heterocycles

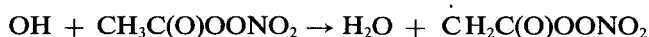
The available kinetic data are given in Table 15. Only for pyridine has more than a single study been carried out, and the room temperature rate constants of Atkinson *et al.*³⁵ and Witte and Zetzsch³⁴ disagree by a factor of ~ 2 . For pyridine, the absolute rate constant data obtained by Witte and Zetzsch³⁴ exhibit non-Arrhenius behavior, with two distinct temperature regimes ($\leq 290 \text{ K}$ and $> 420 \text{ K}$) which suggest predominantly an OH radical addition process in the lower temperature region and an H-atom abstraction (from the aromatic ring C—H bonds) process at the higher temperatures.

As noted above, the OH radical reaction with aziridine is expected to proceed by overall H-atom abstraction from the N—H bond and (less likely) the C—H bonds of the three-membered ring. For imidazole and 1,2,4-triazole, the OH radical reactions are expected to be analogous to that for pyrrole, with the ring N-atom(s) decreasing the reactivity of the ring towards OH radical addition. This is observed.³⁴ Similarly, based upon the relative rate data of Atkinson *et al.*,³⁵ 1,3,5-triazine is less reactive than pyridine towards OH radical addition to the ring, as expected.

g. Miscellaneous

(1) Peroxyacetyl Nitrate

While the room temperature rate constants of Wallington *et al.*³⁷ and Tsalkani *et al.*³⁸ are consistent with the upper limit determined by Winer *et al.*,³⁶ the rate constants of Wallington *et al.*³⁷ and Tsalkani *et al.*³⁸ disagree by a factor of almost 2 (Table 15). The magnitude of this rate constant suggests that the reaction proceeds by H-atom abstraction from the $-\text{CH}_3$ group



(2) Nitromethane

The available rate constant data of Campbell and Goodman,¹⁰ Zabarnick *et al.*³⁹ and Nielsen *et al.*⁴⁰ are given in Table 15 and are plotted in Arrhenius form in Fig. 94. At room temperature, the reported rate constants for CH_3NO_2 span two orders of magnitude.

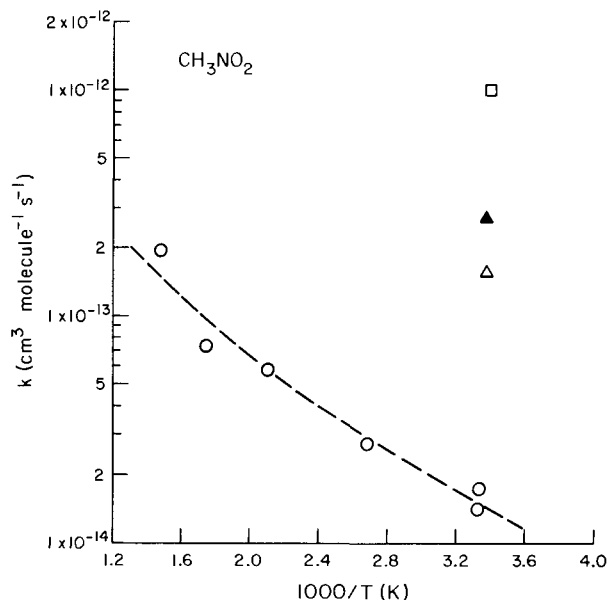
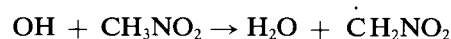


FIG. 94. Arrhenius plot of rate constants for the reaction of the OH radical with CH_3NO_2 . (\square) Campbell and Goodman;¹⁰ (\circ) Zabarnick *et al.*;³⁹ (Δ) Nielsen *et al.*;⁴⁰ absolute rate constant; (\blacktriangle) Nielsen *et al.*;⁴⁰ relative rate constant; (— — —) three-parameter expression fit to the data of Zabarnick *et al.*³⁹

Despite the discrepancies between the absolute and relative rate studies of Zabarnick *et al.*³⁹ and Nielsen *et al.*⁴⁰ (and the factor of 2 disagreement between the absolute and relative rate data of Nielsen *et al.*⁴⁰), it appears that the rate constant derived at 292 ± 2 K by Campbell and Goodman¹⁰ is in error. The study of Zabarnick *et al.*³⁹ utilized the laser photolysis of CH_3NO_2 itself to generate OH radicals, and the measured rate constants were observed to be dependent on the laser photolysis energy (presumably due to secondary reactions involving a photolytically formed species). This dependence of the measured rate constant on the laser fluence necessitated a significant extrapolation to zero laser energy to obtain the supposedly secondary-reaction free rate constant.³⁹ Thus, as the cited error limits indicate, the rate constants obtained by Zabarnick *et al.*³⁹ are subject to significant uncertainties. Zabarnick *et al.*³⁹ observed no effect, within the experimental errors, on the measured rate constant at room temperature when the total pressure was varied from 100–300 Torr of argon, indicating that the rate constant is not pressure-dependent.

However, based upon the rate constants obtained by Nielsen *et al.*⁴¹ and Atkinson and Aschmann¹⁶ for 1-nitrobutane from absolute and relative rate studies (which are in reasonable agreement), it is apparent that the $-\text{NO}_2$ group markedly decreases the reactivity of the α and β $-\text{CH}_2-$ groups [since the observed rate constant¹⁶ is consistent with substituent factors^{50,51} of $F(-\text{NO}_2) \sim 0$ and $F(-\text{CH}_2\text{NO}_2) \lesssim 0.5$ at 298 K]. This implies that the OH radical reaction rate constant for CH_3NO_2 should be $\ll 1.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. The nitroalkanes are expected to photolyze,³⁷ and it is not clear whether photolysis occurred under the experimental conditions of the relative rate study of Nielsen *et al.*,⁴⁰ or whether or not photolysis (if it occurred) was taken into account.

In the absence of further experimental data, the rate constants obtained by Zabarnick *et al.*³⁹ for the reactions of the OH radical with CH_3NO_2 (Table 15) and of the OD radical with CH_3NO_2 and CD_3NO_2 (Table 16) are preferred. The magnitude of these rate constants and the observation of a deuterium isotope effect³⁹ indicates that these reactions proceed by H- or D-atom abstraction from the $-\text{CH}_3$ or $-\text{CD}_3$ groups



A unit-weighted least-squares analysis of the rate constant data of Zabarnick *et al.*³⁹ for the reaction of the OH radical with CH_3NO_2 , using the equation $k = CT^2e^{-D/T}$, leads to

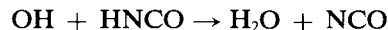
$$k(\text{CH}_3\text{NO}_2) = 5.6$$

$$\times 10^{-19} T^2 e^{-360/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 299–671 K, and this expression is shown in Fig. 94 as the dashed line.

(3) Isocyanic Acid (HNCO)

The only kinetic study carried out to date is that of Tully *et al.*⁴² Attempts to determine rate constants for the reaction of the OH radical with DNCO were rendered difficult by the ready D-atom exchange with the OH radical precursor H_2O . However, the magnitude of the rate constants obtained for HNCO suggests that the reaction proceeds mainly by H-atom abstraction.



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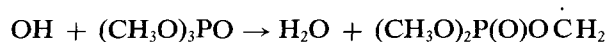
2.9. Phosphorus-Containing Organics

The available kinetic data for the gas-phase reactions of the OH radical with organophosphorus compounds are given in Table 17. In addition, the available data for the OH radical reaction with phosphine (PH₃) are also included. For each of the organophosphorus compounds, as for phosphine, only a single study has been carried out, and hence no recommendations are given.

From a product study carried out at atmospheric pressure of air and room temperature, Tuazon *et al.*² concluded that the reaction of the OH radical with trimethyl phosphate does not proceed by the displacement mechanism,

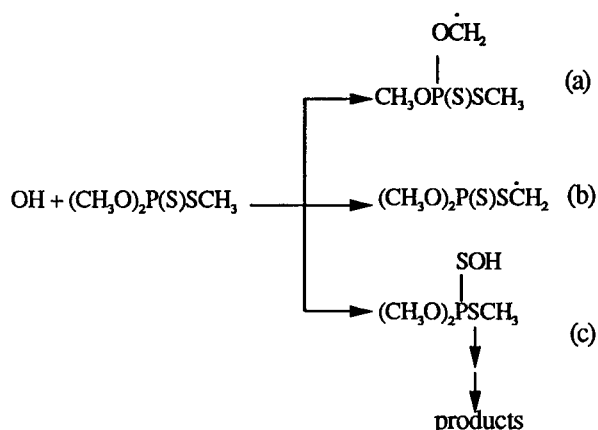


since the expected HCHO product formed from reaction of the CH₃O radical with O₂ was not observed. This observation then suggests that this reaction proceeds by H-atom abstraction from the —OCH₃ groups.



Based upon these product data for trimethyl phosphate² and the kinetic data for triethyl phosphate³ and a series of trimethyl phosphorothioates,⁴ Goodman *et al.*,⁴ Atkinson *et al.*³ and Atkinson⁶ proposed that at room temperature the OH radical reactions with these organophosphorus compounds proceed by H-atom ab-

straction from the $-\text{OCH}_3$ and $-\text{SCH}_3$ groups and by initial OH radical addition to the $-\text{>P=S}$ bond. For example, for $(\text{CH}_3\text{O})_2\text{P(S)SCH}_3$,



with the rate constant for H-atom abstraction from either a $-\text{OCH}_3$ or $-\text{SCH}_3$ group being $\sim 2.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and the rate constant at $\sim 298 \text{ K}$ for addition to the $-\text{>P=S}$ bond being $\sim 5.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The occurrence of reaction pathway (c) is further supported by the observed formation of $(\text{CH}_3\text{O})_3\text{PO}$ and $(\text{CH}_3\text{O})_2\text{P(O)SCH}_3$ from the OH radical-initiated reactions of $(\text{CH}_3\text{O})_3\text{PS}$ and

$(\text{CH}_3\text{O})_2\text{P(S)SCH}_3$, respectively, under simulated atmospheric conditions.⁷

The kinetic data for the dimethyl phosphoroamidates and dimethyl phosphorothioamidates suggest that for these compounds the OH radical reactions also proceed, in part, by reaction with the $-\text{N}(\text{CH}_3)_2$, $-\text{NHCH}_3$ or $-\text{NH}_2$ groups,⁵ presumably by a process involving overall H-atom abstraction from these groups.⁵

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TABLE 17. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with phosphorus-containing organics

Organic	$10^{12} \times A$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	B (K)	$10^{12} \times k$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference
Phosphine [PH_3]			14 ± 3	249	LP-RF	Fritz <i>et al.</i> ¹
			17 ± 3	249		
			13 ± 3	256		
			18 ± 3	296		
			12 ± 3	296		
			13 ± 3	296		
			18 ± 3	370		
		27 ± 6	155	18 ± 3		
Trimethyl phosphate [$(\text{CH}_3\text{O})_3\text{PO}$]			7.37 ± 0.74	296 ± 2	RR [relative to $k(\text{dimethyl ether})$ $= 2.96 \times 10^{-12}]^a$	Tuazon <i>et al.</i> ²
Triethyl phosphate [$(\text{C}_2\text{H}_5\text{O})_3\text{PO}$]			55.3 ± 3.5	296 ± 2	RR [relative to $k(\text{propene}) =$ $2.66 \times 10^{-11}]^a$	Atkinson <i>et al.</i> ³
O,O,S-Trimethyl- phosphorothioate [$(\text{CH}_3\text{O})_2\text{P(O)SCH}_3$]			9.29 ± 0.68	298 ± 2	RR [relative to $k(\text{cyclohexane}) =$ $7.49 \times 10^{-12}]^a$	Goodman <i>et al.</i> ⁴
O,S,S-Trimethyl- phosphorodithioate [$(\text{CH}_3\text{S})_2\text{P(O)OCH}_3$]			9.59 ± 0.75	298 ± 2	RR [relative to $k(\text{cyclohexane}) =$ $7.49 \times 10^{-12}]^a$	Goodman <i>et al.</i> ⁴

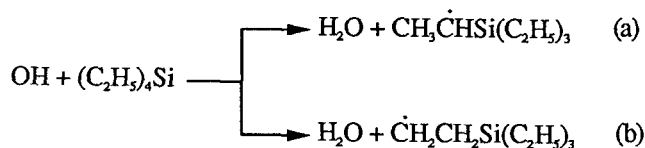
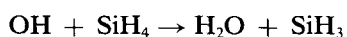
TABLE 17. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with phosphorus-containing organics — Continued

Organic	$10^{12} \times A$ ($\text{cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$)	B (K)	$10^{12} \times k$ ($\text{cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference
O,O,O-Trimethyl-phosphorothioate [(CH ₃ O) ₃ PS]			69.7 ± 3.9	298 ± 2	RR [relative to $k(2\text{-methyl-1,3-butadiene})$ = 1.01×10^{-10}] ^a	Goodman <i>et al.</i> ⁴
O,O,S-Trimethyl-phosphorodithioate [(CH ₃ O) ₂ P(S)SCH ₃]			56.0 ± 1.8	298 ± 2	RR [relative to $k(2\text{-methyl-1,3-butadiene})$ = 1.01×10^{-10}] ^a	Goodman <i>et al.</i> ⁴
(CH ₃ O) ₂ P(O)N(CH ₃) ₂			31.9 ± 2.4	296 ± 2	RR [relative to $k(\text{propene})$ = 2.66×10^{-11}] ^a	Goodman <i>et al.</i> ⁵
(CH ₃ O) ₂ P(S)N(CH ₃) ₂			46.8 ± 1.4	296 ± 2	RR [relative to $k(\text{propene})$ = 2.66×10^{-11}] ^a	Goodman <i>et al.</i> ⁵
(CH ₃ O) ₂ P(S)NHCH ₃			233 ± 15	296 ± 2	RR [relative to $k(\text{propene})$ = 2.66×10^{-11}] ^a	Goodman <i>et al.</i> ⁵
			232 ± 13	296 ± 2	RR [relative to $k(2,3\text{-dimethyl-2-butene})$ = 1.11×10^{-10}] ^a	Goodman <i>et al.</i> ⁵
(CH ₃ O) ₂ P(S)NH ₂			244 ± 9	296 ± 2	RR [relative to $k(2,3\text{-dimethyl-2-butene})$ = 1.11×10^{-10}] ^a	Goodman <i>et al.</i> ⁵
Dimethyl chloro-phosphorothioate [(CH ₃ O) ₂ P(S)Cl]			59.0 ± 3.8	296 ± 2	RR [relative to $k(2\text{-methyl-1,3-butadiene})$ = 1.01×10^{-10}] ^a	Atkinson <i>et al.</i> ³

^aFrom present recommendations (see text).

2.10. Silicon-Containing Compounds

The available kinetic data for the reactions of the OH radical with organosilicon compounds are given in Table 18. The rate constant data for the reaction of the OH radical with silane (SiH₄) are also included for completeness. To date, the only silicon-containing compounds for which OH radical reaction rate data are available are silane¹ and tetraethylsilane.² Both of these reactions have been postulated to occur by overall H-atom abstraction:^{1,2}



with reaction pathway (a) being expected to dominate for the tetraethylsilane reaction since the Si atom must activate the neighboring —CH₂— groups towards reaction if the measured rate constant² at 793 K is correct (although it should be noted that the reported rate constant² was not subsequently revised to take into account the effects of self-heating of the reaction mixtures, as was carried out for a series of alkanes³). Clearly, further kinetic and mechanistic data for this class of compounds are required.

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TABLE 18. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with silicon-containing compounds

Compound	$10^{12} \times A$ ($\text{cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$)	B (K)	$10^{12} \times k$ ($\text{cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered
Silane [SiH ₄]			12.4 ± 1.9	299.6	FP-RF	Atkinson and Pitts ¹	300–426
	14.4	48 ± 201	12.4 ± 1.9	355.6			
			13.0 ± 2.0	425.8			
Tetraethylsilane [(C ₂ H ₅) ₄ Si]			75	793	RR [relative to $k(\text{H}_2)$ $= 1.02 \times 10^{-12}$] ^a	Baldwin <i>et al.</i> ²	

^aSee Introduction.

2.11. Aromatic Compounds

a. Kinetics

The available kinetic data are listed in Table 19. In general, these rate constant data, obtained from both absolute and rate constant studies, are in reasonably good agreement. Room temperature rate constants are available for a wide variety of aromatic hydrocarbons and substituted aromatics. Additionally, temperature dependence studies have been carried out for benzene,^{4,6,8,9,13,14,16} benzene- d_6 ,^{6,8} toluene,^{4,6} toluene- d_3 ,⁶ toluene- d_5 ,⁶ toluene- d_8 ,^{4,6} the xylene isomers,^{4,21} the trimethylbenzene isomers,⁴ phenol,^{29,30} methoxybenzene,³¹ o-cresol,³¹ fluorobenzene,¹⁶ chlorobenzene,¹⁶ bromobenzene,^{14,16} iodobenzene,¹⁶ aniline,^{14,40} N,N-dimethylaniline,⁴⁰ nitrobenzene,¹⁴ o-nitrophenol,³⁶ 1,2,4-trichlorobenzene,¹¹ hexafluorobenzene,¹⁶ naphthalene^{8,9} and phenanthrene.^{9,48}

For a number of the aromatic compounds, three distinct temperature regimes have been observed with the flash or laser photolysis techniques employed to date:^{4,6,8,9,14,16,21,29,31,40} (a) at low temperatures, i.e., $\lesssim 325$ K for the monocyclic aromatic hydrocarbons and $\lesssim 410$ K for naphthalene and phenanthrene, exponential OH radical decays are observed, and the rate constants change only slightly with temperature, with negative temperature dependencies being obtained in many cases; (b) at elevated temperatures, $\gtrsim 400$ –450 K for the monocyclic aromatic hydrocarbons and $\gtrsim 600$ K for naphthalene and phenanthrene, exponential OH radical decays are also observed. For the aromatic hydrocarbons, at elevated temperatures the measured rate constants increase rapidly with increasing temperature, with the rate constants at ~ 400 –450 K (or ~ 600 K for naphthalene and phenanthrene) being typically a factor of 5–10 lower than those at ~ 325 K; and (c) at intermediate temperatures of ~ 325 –400 K for the monocyclic aromatics, and ~ 410 –600 K for naphthalene and phenanthrene, non-exponential decays of OH radicals are observed,^{4,6,10,14,21} with the decay rate decreasing with the reaction time. In this temperature regime any rate data obtained are a combination of the forward and reverse reaction steps (see below) and are dependent on the experimental conditions (for example, the observation time) employed.

As discussed below, for the aromatic hydrocarbons, phenol, methoxybenzene, o-cresol, fluorobenzene, chlorobenzene, bromobenzene, iodobenzene, aniline and N,N-dimethylaniline, the available kinetic and mechanistic data show that in the low temperature regime OH radical addition to the aromatic ring is the dominant reaction pathway, while at elevated temperatures H-atom abstraction occurs. The intermediate temperature regime where non-exponential OH radical decays occur is characterized by formation and redissociation of the OH-aromatic adducts. Furthermore, this precise intermediate temperature range where non-exponential decays are observed is dependent to some extent on the time-resolution of the experimental technique. For these reasons the reported kinetic data in this intermediate temperature regime are not discussed, apart from tabulating these data, as reported, in Table 19.

Furthermore, although exponential OH radical decays were observed by Perry *et al.*⁴ for the monocyclic aromatics and by Wallington *et al.*¹⁶ for benzene for temperature $\gtrsim 380$ K, Tully *et al.*⁶ report that the OH radical addition process continues to contribute to the high temperature reaction pathway up to ~ 450 K. Hence in the discussion and derivation of temperature dependent rate constants for the individual aromatic hydrocarbons in the sections below, only rate constants in the temperature regimes ≤ 325 K and ≥ 450 K for the monocyclic aromatic hydrocarbons, and ≤ 410 K and ≥ 600 K for naphthalene and phenanthrene, have been utilized. The kinetic data for the individual compounds are discussed below.

(1) Benzene

The available rate constant data obtained at, or close to, the high pressure limit are listed in Table 19. The kinetic data of Davis *et al.*,¹ Lorenz and Zellner,⁸ Wahner and Zetzsch,¹⁰ Witte *et al.*,¹⁴ Baulch *et al.*⁵² and Bourmada *et al.*⁵³ show that at around room temperature the rate constant is in the fall-off regime between second and third-order kinetics below ~ 25 –50 Torr total pressure of argon or helium diluent, with the room temperature rate constant being essentially independent of total pressure above this pressure range^{3,6,8,10,11,14} (although Davis *et al.*¹ observed a pressure-dependence extending to ≥ 100 Torr

total pressure of helium, in contrast to more recent studies⁶). Based upon the room temperature pressure-dependent data of Lorenz and Zellner⁸ and Witte *et al.*,¹⁴ the limiting low pressure third-order rate constant k_0 for argon diluent is

$$k_0^{\text{Ar}}(\text{benzene}) = 3 \times 10^{-29} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

at 298 K, with a lower value (by a factor of ~ 2) for helium diluent.⁵² With a value of $F = 0.6^{14}$ in the Troe fall-off expression and $k_\infty \approx 1.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K, this shows that at 298 K and 760 and 100 Torr total pressure of argon diluent the measured rate constant is $\sim 5\text{--}6\%$ and $\sim 12\%$, respectively, below the high pressure limiting value, k_∞ .

TABLE 19. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with aromatic compounds at, or close to, the high pressure limit

Aromatic	$10^{12} \times A$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{molecule}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
Benzene			1.59 ± 0.12	298	FP-RF	Davis <i>et al.</i> ¹	
			≤ 2.6	304 ± 1	RR [relative to $k(n\text{-butane}) =$ $2.61 \times 10^{-12}]^a$	Doyle <i>et al.</i> ²	
			1.24 ± 0.12	298	FP-RF	Hansen <i>et al.</i> ³	
			1.20 ± 0.15	297.6	FP-RF	Perry <i>et al.</i> ⁴	298–422
			1.32 ± 0.30	304.4			
			1.33 ± 0.25	305.8			
			1.66 ± 0.25	322.7			
			1.37 ± 0.20^b	331.9			
			1.66^b	333.2			
			1.04^b	350.6			
			0.63^b	354.7			
			1.00^b	355.2			
			1.00^b	361.2			
			0.31^b	364.8			
			0.31^b	380.8			
			0.26 ± 0.15	396.2			
			0.34 ± 0.07	396.4			
			0.34 ± 0.12	405.8			
			0.45 ± 0.07	422.0			
				0.84	300	RR [relative to $k(\text{ethene}) =$ $8.44 \times 10^{-12}]^a$	Cox <i>et al.</i> ⁵
			1.04 ± 0.08	250	FP-RF	Tully <i>et al.</i> ⁶	250–1017
			1.20 ± 0.09	270			
	3.1 ± 2.6	270 ± 220 (250–298 K)	1.24 ± 0.09	298			
			0.7^b	352			
			0.3^b	390			
			0.4^b	442			
			0.543 ± 0.023	542			
			0.639 ± 0.029	621			
			0.682 ± 0.074	630			
			0.606 ± 0.034	653			
			1.02 ± 0.04	715			
			1.20 ± 0.16	742			
			1.59 ± 0.09	817			
			1.90 ± 0.20	895			
			2.26 ± 0.13	917			
			2.35 ± 0.23	981			
	24 ± 9	2260 ± 300 (621–1017 K)	2.20 ± 0.34	1017			

TABLE 19. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with aromatic compounds at, or close to, the high pressure limit — Continued

Aromatic	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)	
			0.93	300	RR [relative to $k(\text{ethene}) =$ $8.44 \times 10^{-12}]^a$	Barnes <i>et al.</i> ⁷		
	6.3 ± 1.7	500 ± 50 (244–298 K)	0.76 ± 0.15 1.15 ± 0.25	244 298 ± 2	LP-RF	Lorenz and Zellner ^{8,9}	244–870	
			1.26 ± 0.25 0.83 ± 0.17 0.50 ± 0.10 0.40 ± 0.09 0.48 ± 0.16 0.43 ± 0.09 0.75 ± 0.20 0.46 ± 0.10 0.76 ± 0.25 1.28 ± 0.16 1.13 ± 0.25	336 373 384 453 522 523 567 604 665 720 803				
	20 ± 10	2100 ± 400 (522–870 K)	2.16 ± 0.50	870				
			0.88 ± 0.04	295	FP-RF	Wahner and Zetzsch ¹⁰		
			1.02 ± 0.2	296	FP-RF	Rinke and Zetzsch ¹¹		
			1.46 ± 0.06	c	RR [relative to $k(n\text{-hexane}) =$ $5.61 \times 10^{-12}]^a$	Ohta and Ohyama ¹²		
			2.09 ± 0.06 1.78 ± 0.06 2.67 ± 0.18 3.04 ± 0.29 3.52 ± 0.25 6.66 ± 0.23	787 805 865 1019 1196 1309	FP-RF	Madronich and Felder ¹³	787–1409	
	35 ± 3	2300 ± 100	7.36 ± 1.12	1409				
			1.00 ± 0.04 1.11 ± 0.12 1.04 ± 0.03 1.06 ± 0.03 1.13 ± 0.04 1.04 ± 0.05 1.11 ± 0.02 1.12 ± 0.08 1.11 ± 0.04 1.05 ± 0.05 1.18 ± 0.17 1.23 ± 0.09 1.37 ± 0.09 1.21 ± 0.12 1.28 ± 0.05 1.26 ± 0.08 1.39 ± 0.22 1.48 ± 0.12 1.50 ± 0.29 1.25 ± 0.22	239 239 245 253 253 259 274 274 283 299 299 312 312 325 328 331 331 334 342 352		FP-RF	Witte <i>et al.</i> ¹⁴	239–354
	2.3	190 ± 60	1.33 ± 0.36	354				
			1.22 ± 0.45	296	RR [relative to $k(\text{propane}) =$ $1.13 \times 10^{-12}]^a$	Edney <i>et al.</i> ¹⁵		

TABLE 19. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with aromatic compounds at, or close to, the high pressure limit — Continued

Aromatic	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$) at T (K)	Technique	Reference	Temperature range covered (K)					
			1.40 ± 0.23	234	FP-RF	Wallington <i>et al.</i> ¹⁶	234–438				
			1.30 ± 0.19	263							
			1.29 ± 0.14	296							
			0.193 ± 0.037	393							
			0.258 ± 0.034	438							
Benzene- d_6	13 ± 6	2300 ± 340 (568–1150 K)	1.08 ± 0.05	250	FP-RF	Tully <i>et al.</i> ⁶	250–1150				
			1.19 ± 0.05	298							
			0.4 ^b	498							
			0.227 ± 0.03	568							
			0.424 ± 0.045	630							
			0.300 ± 0.032	653							
			0.430 ± 0.023	675							
			0.481 ± 0.019	734							
			0.720 ± 0.046	830							
			1.04 ± 0.03	917							
			1.08 ± 0.10	981							
			1.47 ± 0.07	1002							
			1.91 ± 0.28	1150							
			1.10 ± 0.22	298	LP-RF	Lorenz and Zellner ⁸	298–524				
			1.00 ± 0.20	336							
			0.76 ± 0.15	380							
			0.48 ± 0.10	398							
			0.28 ± 0.05	436							
Toluene			6.11 ± 0.40	298	FP-RF	Davis <i>et al.</i> ¹					
			3.7 ± 1.6	304 ± 1				RR [relative to $k(n\text{-butane}) =$ $2.61 \times 10^{-12}]^a$	Doyle <i>et al.</i> ²		
			5.78 ± 0.58	298				FP-RF		Hansen <i>et al.</i> ³	
			6.40 ± 0.64	297.9				FP-RF		Perry <i>et al.</i> ⁴	298–473
			4.90 ± 0.6	323.7							
			4.99 ± 0.6 ^b	325.3							
			4.04 ^b	334.6							
			5.36 ± 0.9 ^b	338.5							
			1.51 ^b	339.7							
			1.66 ± 0.25 ^b	352.6							
			1.19 ^b	354.2							
			1.38 ± 0.17 ^b	364.0							
			1.35 ^b	366.0							
			1.22 ± 0.14 ^b	378.4							
			1.49 ± 0.22	379.3							
			1.58 ± 0.24	394.2							
			1.69 ± 0.25	408.7							
			1.76 ± 0.18	424.4							
			1.71 ± 0.20	472.7							
7.6	300	RR [relative to $k(\text{ethene}) =$ $8.44 \times 10^{-12}]^a$	Cox <i>et al.</i> ⁵								
8.20 ± 0.54	213	FP-RF	Tully <i>et al.</i> ⁶	213–1046							
8.73 ± 0.39	231										
7.97 ± 0.56	250										
8.53 ± 0.37	260										
7.44 ± 0.55	270										

TABLE 19. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with aromatic compounds at, or close to, the high pressure limit — Continued

Aromatic	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
	3.8 ± 2.5	-180 ± 170 (213–298 K)	6.36 ± 0.69	298			
			6.3 ± 0.6^b	320			
			5.4 ± 1.1^b	332			
			3.6^b	352			
			1.4^b	397			
			1.7^b	442			
			2.16 ± 0.08	504			
			2.45 ± 0.05	568			
			2.49 ± 0.12	568			
			3.26 ± 0.29	666			
			3.58 ± 0.16	694			
			4.67 ± 0.19	793			
			5.54 ± 0.27	868			
			6.87 ± 0.23	958			
			9.5 ± 1.0	1046			
			6.06 ± 0.17	c	RR [relative to $k(n\text{-hexane}) =$ $5.61 \times 10^{-12}]^a$	Ohta and Ohyama ¹²	
			5.44 ± 0.55	297	RR [relative to $k(\text{cyclohexane}) =$ $7.47 \times 10^{-12}]^a$	Edney <i>et al.</i> ¹⁵	
			6.45 ± 0.74	773	RR [relative to $k(\text{H}_2)$ $= 9.22 \times 10^{-13}]^d$	Baldwin <i>et al.</i> ¹⁷	
			5.48 ± 0.16	296 ± 2	RR [relative to $k(\text{propene}) =$ $2.66 \times 10^{-11}]^a$	Atkinson and Aschmann ¹⁸	
Toluene- d_3 [$\text{C}_6\text{H}_5\text{CD}_3$]			5.62 ± 0.52	250	FP-RF	Tully <i>et al.</i> ⁶	250–1002
			5.97 ± 0.17	270			
			5.63 ± 0.30	298			
			0.8^b	383			
			1.23 ± 0.09	518			
			1.32 ± 0.08	568			
			1.41 ± 0.06	568			
			1.46 ± 0.09	568			
			1.40 ± 0.08	568			
			2.10 ± 0.07	653			
			3.01 ± 0.10	742			
			3.59 ± 0.13	817			
			4.55 ± 0.34	895			
			5.92 ± 0.42	966			
			8.54 ± 1.21	1002			
Toluene- d_5 [$\text{C}_6\text{D}_5\text{CH}_3$]			6.11 ± 0.40	250	FP-RF	Tully <i>et al.</i> ⁶	250–1002
			6.02 ± 1.68	270			
			6.47 ± 0.65	298			
			3.0^b	358			
			1.1^b	412			
			1.66 ± 0.10	470			
			2.04 ± 0.14	518			
			2.52 ± 0.14	568			
			2.69 ± 0.28	630			
			3.29 ± 0.25	653			
			4.53 ± 0.52	742			
			5.08 ± 0.32	793			
			6.48 ± 0.41	895			
			6.52 ± 0.91	996			

TABLE 19. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with aromatic compounds at, or close to, the high pressure limit — Continued

Aromatic	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$) at T (K)	Technique	Reference	Temperature range covered (K)	
			7.97 \pm 0.73				
Toluene- d_8 [C ₆ D ₅ CD ₃]			6.13 \pm 0.63	298.1	FP-RF	Perry <i>et al.</i> ⁴	298–432
			4.78 ^b	323.6			
			3.56 ^b	324.2			
			0.38 \pm 0.06	385.2			
			0.51 \pm 0.07	397.0			
			0.70 \pm 0.07	432.2			
			6.04 \pm 0.48	250	FP-RF	Tully <i>et al.</i> ⁶	250–1150
			6.36 \pm 0.52	270			
			6.40 \pm 0.20	298			
			0.5 ^b	390			
			0.73 \pm 0.07	470			
			1.17 \pm 0.09	498			
			1.27 \pm 0.03	542			
			1.15 \pm 0.05	568			
			1.97 \pm 0.12	621			
			2.35 \pm 0.16	700			
			2.18 \pm 0.10	715			
			3.53 \pm 0.28	793			
			2.76 \pm 0.14	842			
			3.18 \pm 0.30	842			
			4.05 \pm 0.30	868			
			4.52 \pm 0.25	966			
			6.91 \pm 1.32	1017			
			6.51 \pm 1.50	1150			
Ethylbenzene			6.94 \pm 1.39	305 \pm 2	RR [relative to $k(n\text{-butane}) =$ $2.62 \times 10^{-12}]^a$	Lloyd <i>et al.</i> ¹⁹	
			7.95 \pm 0.50 ^c	298	FP-RF	Ravishankara <i>et al.</i> ²⁰	
			6.51 \pm 0.29	c	RR [relative to $k(n\text{-hexane}) =$ $5.61 \times 10^{-12}]^a$	Ohta and Ohyama ¹²	
<i>o</i> -Xylene			11.2 \pm 3.4	304 \pm 1	RR [relative to $k(n\text{-butane}) =$ $2.61 \times 10^{-12}]^a$	Doyle <i>et al.</i> ²	
			15.3 \pm 1.5	298.0	FP-RF	Hansen <i>et al.</i> ³	
			14.3 \pm 1.5	298.5	FP-RF	Perry <i>et al.</i> ⁴	298–432
			12.9 ^b	313.5			
			14.0 \pm 2.0	319.0			
			12.3 ^b	332.1			
			9.27 ^b	348.2			
			4.98 ^b	367.7			
			3.76 ^b	372.8			
			3.25 \pm 0.45	379.5			
			3.35 \pm 0.46	395.6			
			3.27 \pm 0.46	414.6			
			3.63 \pm 0.43	425.3			
			3.34 \pm 0.35	432.4			
			12.4 \pm 1.2 ^c	298	FP-RF	Ravishankara <i>et al.</i> ²⁰	
			14.0	300	RR [relative to $k(\text{ethene}) =$ $8.44 \times 10^{-12}]^a$	Cox <i>et al.</i> ⁵	

TABLE 19. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with aromatic compounds at, or close to, the high pressure limit — Continued

Aromatic	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)		
	65 ± 11	1420 ± 120 (508–970 K)	14.2 ± 1.7	298	FP-RF	Nicovich <i>et al.</i> ²¹	298–970		
			15.8 ± 1.8	320					
			5.1^b	357					
			2.39 ± 0.20	400					
			4.19 ± 0.48	508					
			5.42 ± 0.45	576					
			6.87 ± 0.91	647					
			10.20 ± 0.91	757					
			12.8 ± 1.1	886					
			15.7 ± 1.3	970					
			12.6 ± 0.6	c				RR [relative to $k(n\text{-hexane}) =$ $5.61 \times 10^{-12}]^a$	Ohta and Ohyama ¹²
			13.6	300				RR [relative to $k(1,3,5\text{-trimethylbenzene}) =$ $5.75 \times 10^{-11}]^a$	Klöpffer <i>et al.</i> ²²
			12.6	297				RR [relative to $k(\text{cyclohexane}) =$ $7.47 \times 10^{-12}]^a$	Edney <i>et al.</i> ¹⁵
12.2 ± 0.6	296 ± 2	RR [relative to $k(\text{propene}) =$ $2.66 \times 10^{-11}]^a$	Atkinson and Aschmann ¹⁸						
19.6 ± 1.4	304 ± 1	RR [relative to $k(n\text{-butane}) =$ $2.61 \times 10^{-12}]^a$	Doyle <i>et al.</i> ²						
23.6 ± 2.4	297.3	FP-RF	Hansen <i>et al.</i> ³						
18.8 ± 3.8	305 ± 2	RR [relative to $k(n\text{-butane}) =$ $2.62 \times 10^{-12}]^a$	Lloyd <i>et al.</i> ¹⁹						
24.0 ± 2.5	298.3	FP-RF	Perry <i>et al.</i> ⁴	298–427					
24.4 ± 3.6	314.5								
20.5^b	320.0								
13.1^b	327.8								
2.81^b	354.9								
1.68^b	365.2								
2.19^b	373.8								
2.21 ± 0.33	379.1								
2.23 ± 0.33	390.9								
2.49 ± 0.36	403.5								
2.86 ± 0.38	414.0								
3.02 ± 0.30	427.0								
20.6 ± 1.3^c	298	FP-RF	Ravishankara <i>et al.</i> ²⁰						
19.6	300	RR [relative to $k(\text{ethene}) =$ $8.44 \times 10^{-12}]^a$	Cox <i>et al.</i> ⁵						
26.5 ± 2.5	250	FP-RF	Nicovich <i>et al.</i> ²¹	250–960					
25.6 ± 4.3	269								
25.4 ± 3.5	298								
5.2^b	330								
2.47 ± 0.41	400								

TABLE 19. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with aromatic compounds at, or close to, the high pressure limit — Continued

Aromatic	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Tempera- ture range covered (K)
	68 ± 23	1540 ± 240 (508–960 K)	3.44 ± 0.34	508			
			4.60 ± 0.54	576			
			6.2 ± 1.1	684			
			9.3 ± 1.1	757			
			10.1 ± 1.5	875			
			14.6 ± 3.1	960			
			21.4 ± 1.4	299 ± 2	RR [relative to $k(\text{cyclohexane}) =$ $7.51 \times 10^{-12}]^a$	Atkinson <i>et al.</i> ²³	
			22.3 ± 0.7	c	RR [relative to $k(n\text{-hexane}) =$ $5.61 \times 10^{-12}]^a$	Ohta and Ohyama ¹²	
			23.1	297	RR [relative to $k(\text{cyclohexane}) =$ $7.47 \times 10^{-12}]^a$	Edney <i>et al.</i> ¹⁵	
			23.0 ± 0.6	296 ± 2	RR [relative to $k(\text{propene}) =$ $2.66 \times 10^{-11}]^a$	Atkinson and Aschmann ¹⁸	
<i>p</i> -Xylene			10.7 ± 2.4	304 ± 1	RR [relative to $k(n\text{-butane}) =$ $2.61 \times 10^{-12}]^a$	Doyle <i>et al.</i> ²	
			12.2 ± 1.2	297.3	FP-RF	Hansen <i>et al.</i> ³	
			15.3 ± 1.7	298.0	FP-RF	Perry <i>et al.</i> ⁴	298–428
			18.2 ± 2.2	306.3			
			18.2 ± 2.2	310.7			
			17.3 ± 2.2	313.2			
			16.7^b	315.0			
			14.9 ± 2.0	324.2			
			15.3^b	330.2			
			11.7^b	352.7			
			5.49^b	358.7			
			3.39^b	369.6			
			2.50^b	372.1			
			2.66 ± 0.40	383.8			
			2.43 ± 0.32	385.3			
			2.67 ± 0.36	387.1			
			2.96 ± 0.40	392.8			
			3.17 ± 0.43	400.0			
			3.29 ± 0.40	404.3			
			3.68 ± 0.45	412.6			
			3.56 ± 0.55	422.4			
			3.29 ± 0.33	428.4			
			10.5 ± 1.0^c	298	FP-RF	Ravishankara <i>et al.</i> ²⁰	
			13.5 ± 1.4	298	FP-RF	Nicovich <i>et al.</i> ²¹	298–960
			13.8 ± 1.1	320			
			12.5 ± 1.3	335			
			4.3^b	357			
1.71 ± 0.28	400						
3.70 ± 0.64	484						
3.40 ± 0.48	526						
5.03 ± 0.88	576						
6.01 ± 0.59	647						

TABLE 19. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with aromatic compounds at, or close to, the high pressure limit — Continued

Aromatic	$10^{12} \times A$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{molecule}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference	Tempera- ture range covered (K)
			9.66 ± 0.85	757			
			11.6 ± 1.6	886			
	64 ± 24	1440 ± 250 (526–960 K)	14.6 ± 1.9	960			
			13.0 ± 0.6	c	RR [relative to $k(n\text{-hexane}) =$ $5.61 \times 10^{-12}]^a$	Ohta and Ohyama ¹²	
			13.6	300	RR [relative to $k(1,3,5\text{-trimethylbenzene})$ $= 5.75 \times 10^{-11}]^a$	Klöppfer <i>et al.</i> ²²	
			13.9	296	RR [relative to $k(\text{cyclohexane}) =$ $7.45 \times 10^{-12}]^a$	Edney <i>et al.</i> ¹⁵	
			14.2 ± 4.1	298 ± 2	RR [relative to $k(\text{cyclohexane}) =$ $7.49 \times 10^{-12}]^a$	Becker and Klein ²⁴	
			13.0 ± 0.5	296 ± 2	RR [relative to $k(\text{propene}) =$ $2.66 \times 10^{-11}]^a$	Atkinson and Aschmann ¹⁸	
Xylenes (mixture of isomers)			18.7	298	DF-MS	Morris and Niki ²⁵	
<i>n</i> -Propyl- benzene			5.42 ± 1.09	305 ± 2	RR [relative to $k(n\text{-butane}) =$ $2.62 \times 10^{-12}]^a$	Lloyd <i>et al.</i> ¹⁹	
			5.86 ± 0.50^c	298	FP-RF	Ravishankara <i>et al.</i> ²⁰	
			6.62 ± 0.23	c	RR [relative to $k(n\text{-hexane}) =$ $5.61 \times 10^{-12}]^a$	Ohta and Ohyama ¹²	
Isopropyl- benzene			5.32 ± 1.07	305 ± 2	RR [relative to $k(n\text{-butane}) =$ $2.62 \times 10^{-12}]^a$	Lloyd <i>et al.</i> ¹⁹	
			7.79 ± 0.50	298	FP-RF	Ravishankara <i>et al.</i> ²⁰	
			6.28 ± 0.34	c	RR [relative to $k(n\text{-hexane}) =$ $5.61 \times 10^{-12}]^a$	Ohta and Ohyama ¹²	
<i>o</i> -Ethyl- toluene			12.0 ± 2.4	305 ± 2	RR [relative to $k(n\text{-butane}) =$ $2.62 \times 10^{-12}]^a$	Lloyd <i>et al.</i> ¹⁹	
			12.5 ± 1.3	c	RR [relative to $k(n\text{-hexane}) =$ $5.61 \times 10^{-12}]^a$	Ohta and Ohyama ¹²	
<i>m</i> -Ethyl- toluene			17.0 ± 3.4	305 ± 2	RR [relative to $k(n\text{-butane}) =$ $2.62 \times 10^{-12}]^a$	Lloyd <i>et al.</i> ¹⁹	

TABLE 19. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with aromatic compounds at, or close to, the high pressure limit — Continued

Aromatic	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{molecule}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Tempera- ture range covered (K)
			21.3 ± 1.1	c	RR [relative to $k(n\text{-hexane}) =$ $5.61 \times 10^{-12}]^a$	Ohta and Ohyama ¹²	
<i>p</i> -Ethyl- toluene			11.3 ± 2.3	305 ± 2	RR [relative to $k(n\text{-butane}) =$ $2.62 \times 10^{-12}]^a$	Lloyd <i>et al.</i> ¹⁹	
			12.9 ± 1.3	c	RR [relative to $k(n\text{-hexane}) =$ $5.61 \times 10^{-12}]^a$	Ohta and Ohyama ¹²	
<i>t</i> -Butyl- benzene			4.60 ± 0.45	c	RR [relative to $k(n\text{-hexane}) =$ $5.61 \times 10^{-12}]^a$	Ohta and Ohyama ¹²	
1,2,3-Tri- methylbenzene			19.8 ± 4.2	304 ± 1	RR [relative to $k(n\text{-butane}) =$ $2.61 \times 10^{-12}]^a$	Doyle <i>et al.</i> ²	
			26.4 ± 2.6	297.1	FP-RF	Hansen <i>et al.</i> ³	
			33.3 ± 4.5	296.9	FP-RF	Perry <i>et al.</i> ⁴	297–421
			27.6 ^b	317.5			
			24.5 ± 3.7	325.1			
			19.4 ^b	338.6			
			4.32 ^b	374.4			
			3.54 ^b	377.4			
			4.28 ± 0.64	388.6			
			4.89 ± 0.74	396.8			
			6.00 ± 0.80	420.7			
			29.7 ± 4.1	c	RR [relative to $k(n\text{-hexane}) =$ $5.61 \times 10^{-12}]^a$	Ohta and Ohyama ¹²	
			32.7 ± 1.9	296 ± 2	RR [relative to $k(\text{propene}) =$ $2.66 \times 10^{-11}]^a$	Atkinson and Aschmann ¹⁸	
1,2,4-Tri- methylbenzene			28.7 ± 5.3	304 ± 1	RR [relative to $k(n\text{-butane}) =$ $2.61 \times 10^{-12}]^a$	Doyle <i>et al.</i> ²	
			33.5 ± 3.4	296.9	FP-RF	Hansen <i>et al.</i> ³	
			40.0 ± 4.5	298.2	FP-RF	Perry <i>et al.</i> ⁴	298–430
			37.3 ± 4.8	314.3			
			32.4 ± 4.8	323.4			
			15.2 ^b	340.2			
			4.56 ^b	370.9			
			2.47 ^b	374.1			
			3.34 ± 0.44	383.7			
			4.82 ± 0.63	397.7			
			4.75 ± 0.62	400.3			
			5.31 ± 0.69	423.5			
			5.24 ± 0.60	429.5			
			31.7 ± 1.3	c	RR [relative to $k(n\text{-hexane}) =$ $5.61 \times 10^{-12}]^a$	Ohta and Ohyama ¹²	

TABLE 19. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with aromatic compounds at, or close to, the high pressure limit — Continued

Aromatic	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Tempera- ture range covered (K)
			32.5 ± 1.1	296 ± 2	RR [relative to $k(\text{propene}) =$ $2.66 \times 10^{-11}]^a$	Atkinson and Aschmann ¹⁸	
1,3,5-Tri- methylbenzene			44.4 ± 5.3	304 ± 1	RR [relative to $k(n\text{-butane}) =$ $2.61 \times 10^{-12}]^a$	Doyle <i>et al.</i> ²	
			47.2 ± 4.8	297.1	FP-RF	Hansen <i>et al.</i> ³	
			62.4 ± 7.5	298.3	FP-RF	Perry <i>et al.</i> ⁴	298-420
			51.9 ± 6.3	318.4			
			52.1 ^b	322.5			
			3.16 ^b	368.0			
			3.38 ± 0.45	372.4			
			3.45 ± 0.45	381.0			
			3.82 ± 0.50	390.1			
			5.03 ± 0.60	420.1			
			38.9 ± 5.3	c	RR [relative to $k(n\text{-hexane}) =$ $5.61 \times 10^{-12}]^a$	Ohta and Ohyama ¹²	
			57.5 ± 3.0	296 ± 2	RR [relative to $k(\text{propene}) =$ $2.66 \times 10^{-11}]^a$	Atkinson and Aschmann ¹⁸	
Styrene [$\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$]			52 ± 5	298 ± 2	RR [relative to $k(2,2,4\text{-trimethyl-}$ $\text{pentane}) = 3.68 \times 10^{-12}]^a$	Bignozzi <i>et al.</i> ²⁶	
			58.1 ± 1.5	296 ± 2	RR [relative to $k(2\text{-methyl-1,3-buta-}$ $\text{diene}) = 1.01 \times 10^{-10}]^a$	Atkinson and Aschmann ²⁷	
α -Methylstyrene [$\text{C}_6\text{H}_5\text{C}(\text{CH}_3)=\text{CH}_2$]			52 ± 6	298 ± 2	RR [relative to $k(2,2,4\text{-trimethylpentane})$ $= 3.68 \times 10^{-12}]^a$	Bignozzi <i>et al.</i> ²⁶	
β -Methylstyrene [$\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_3$]			59 ± 6	298 ± 2	RR [relative to $k(2,2,4\text{-trimethylpentane})$ $= 3.68 \times 10^{-12}]^a$	Bignozzi <i>et al.</i> ²⁶	
β -Dimethylstyrene [$\text{C}_6\text{H}_5\text{CH}=\text{C}(\text{CH}_3)_2$]			33 ± 5	298	RR [relative to $k(2,2,4\text{-trimethylpentane})$ $= 3.68 \times 10^{-12}]^a$	Chiorboli <i>et al.</i> ²⁸	
Phenol			28.3 ± 5.7	296	FP-RF	Rinke and Zetzsch ¹¹	
			35.2 ± 1.7	245	FP-RF	Witte and Zetzsch ²⁹	245-470
			33.2 ± 1.0	257			
			29.4 ± 2.9	272			
			27.7 ± 0.9	286			
			26.0 ± 1.8	296			
	5.3 ± 0.9	-470 ± 50 (245-296 K)	25.7 ± 0.9	296			
			22.0 ± 0.8	310			
			20.5 ± 0.6	319			
			19.8 ± 0.5	320			
			17.6 ± 0.9	324			
			17.0 ± 0.3	330			
			14.4 ± 0.5	335			

TABLE 19. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with aromatic compounds at, or close to, the high pressure limit — Continued

Aromatic	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
			14.8 ± 0.7	339			
			13.7 ± 0.5	343			
			10.6 ± 0.6	346			
			10.6 ± 1.0	349			
			10.3 ± 0.6	351			
			7.85 ± 1.00	356			
			6.98 ± 0.74	359			
			3.23 ± 0.19	393			
			3.56 ± 0.39	394			
			3.08 ± 0.16	394			
			3.46 ± 0.11	423			
			3.23 ± 0.07	445			
			2.90 ± 0.23	466			
			3.10 ± 0.17	470			
			9.5	1000-1150	RR [relative to $k(\text{CO}) = 1.12 \times 10^{-13}$ $e^{0.0009077T} \text{]}^d$	He <i>et al.</i> ³⁰	1000-1150
Methoxybenzene [C ₆ H ₅ OCH ₃]			19.6 ± 2.4	299.9	FP-RF	Perry <i>et al.</i> ³¹	300-435
			17.3 ± 2.6	309.0			
			17.5 ± 2.6	309.7			
			17.5 ± 2.6	318.5			
3.7		-403 (300-322 K)	17.8 ± 2.7	321.7			
			12.7 ^b	329.5			
			6.7 ^b	357.4			
			3.0 ^b	370.4			
			3.33 ± 0.50	385.5			
			3.25 ± 0.50	392.3			
			3.31 ± 0.50	404.1			
			3.90 ± 0.56	413.2			
			2.85 ± 0.43	417.9			
			3.30 ± 0.40	422.0			
			2.76 ± 0.41	428.7			
1.7		-252 (386-435 K)	2.72 ± 0.41	435.3			
			14.1 ± 0.6	c	RR [relative to $k(n\text{-hexane}) =$ $5.61 \times 10^{-12}]^a$	Ohta and Ohyama ¹²	
<i>o</i> -Cresol			34.1 ± 6.8	299.4	FP-RF	Perry <i>et al.</i> ³¹	299-423
			29.3 ± 5.9	310.6			
			29.8 ± 6.0	322.0			
			26.8 ± 5.4	330.7			
1.6		-906 (299-335 K)	25.5 ± 5.1	335.4			
			18.5 ^b	344.4			
			15.0 ^b	356.5			
			6.4 ^b	385.8			
			6.0 ^b	392.8			
			5.6 ± 1.1	400.6			
			5.4 ± 1.1	407.8			
50		906 (401-423 K)	6.2 ± 1.2	423.1			
			42.5 ± 3.7	300 ± 1	RR [relative to $k(n\text{-butane}) -$ $k(\text{neopentane}) =$ $1.70 \times 10^{-12}]^a$	Atkinson <i>et al.</i> ³²	

TABLE 19. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with aromatic compounds at, or close to, the high pressure limit — Continued

Aromatic	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{molecule}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Tempera- ture range covered (K)
			42.6 ± 2.2	296 ± 2	RR [relative to $k(\text{propene}) =$ $2.66 \times 10^{-11}]^a$	Atkinson and Aschmann ³³	
<i>m</i> -Cresol			59.6 ± 3.4	300 ± 1	RR [relative to $k(o\text{-cresol}) =$ $4.2 \times 10^{-11}]^a$	Atkinson <i>et al.</i> ³²	
			67.8 ± 4.0	296 ± 2	RR [relative to $k(\text{propene}) =$ $2.66 \times 10^{-11}]^a$	Atkinson and Aschmann ³³	
<i>p</i> -Cresol			46.2 ± 2.1	300 ± 1	RR [relative to $k(o\text{-cresol}) =$ $4.2 \times 10^{-11}]^a$	Atkinson <i>et al.</i> ³²	
			48.4 ± 5.1	296 ± 2	RR [relative to $k(\text{propene}) =$ $2.66 \times 10^{-11}]^a$	Atkinson and Aschmann ³³	
Thiophenol [C ₆ H ₅ SH]			11.2 ± 1.4	300	RR [relative to $k(n\text{-hexane}) =$ $5.64 \times 10^{-12}]^a$	Barnes <i>et al.</i> ³⁴	
Acetophenone [C ₆ H ₅ COCH ₃]			2.74 ± 0.15	298	FP-RF	Nolting <i>et al.</i> ³⁵	
Fluoro- benzene			0.54 ± 0.05	296	FP-RF	Zetzsch ³⁶	
			0.90 ± 0.12	c	RR [relative to $k(n\text{-hexane}) =$ $5.61 \times 10^{-12}]^a$	Ohta and Ohyama ¹²	
			0.524 ± 0.088	234	FP-RF	Wallington <i>et al.</i> ¹⁶	234–438
			0.632 ± 0.103	253			
			0.649 ± 0.099	263			
			0.610 ± 0.080	277			
			0.631 ± 0.081	296			
			0.656 ± 0.074	303			
			0.196 ± 0.047	393			
			0.209 ± 0.038	438			
Chloro- benzene			0.67 ± 0.05	296	FP-RF	Zetzsch ^{36,37}	
			0.91 ± 0.12	299 ± 2	RR [relative to $k(\text{benzene}) =$ $1.24 \times 10^{-12}]^a$	Atkinson <i>et al.</i> ³⁸	
			0.55 ± 0.44	297	RR [relative to $k(n\text{-butane}) =$ $2.53 \times 10^{-12}]^a$	Edney <i>et al.</i> ¹⁵	
			0.707 ± 0.084	234	FP-RF	Wallington <i>et al.</i> ¹⁶	234–438
			0.624 ± 0.062	263			
			0.741 ± 0.094	296			
			0.214 ± 0.046	393			
			0.191 ± 0.033	438			
Bromobenzene			0.70 ± 0.07	296	FP-RF	Zetzsch ³⁶	
			0.57 ± 0.07	245	FP-RF	Witte <i>et al.</i> ¹⁴	245–362
			0.64 ± 0.04	253			

TABLE 19. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with aromatic compounds at, or close to, the high pressure limit — Continued

Aromatic	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Tempera- ture range covered (K)
			0.68 ± 0.06	259			
			0.72 ± 0.04	265			
			0.71 ± 0.04	274			
			0.66 ± 0.05	283			
			0.71 ± 0.04	299			
			0.72 ± 0.03	312			
			0.69 ± 0.04	316			
			0.76 ± 0.02	316			
			0.75 ± 0.04	325			
			0.77 ± 0.03	334			
			0.92 ± 0.12	339			
			0.79 ± 0.06	343			
			0.76 ± 0.07	343			
			0.78 ± 0.10	346			
			0.92 ± 0.15	354			
	1.3	180 ± 60	0.91 ± 0.19	362			
			0.915 ± 0.187	234	FP-RF	Wallington <i>et al.</i> ¹⁶	234-438
			1.02 ± 0.16	263			
			0.915 ± 0.097	296			
			0.763 ± 0.053	353			
			0.219 ± 0.039	438			
Iodobenzene			0.93 ± 0.05	296	FP-RF	Zetzsch ³⁶	
			1.25 ± 0.15	263	FP-RF	Wallington <i>et al.</i> ¹⁶	263-438
			1.32 ± 0.16	296			
			1.32 ± 0.19	353			
			1.03 ± 0.12	393			
Benzyl chloride			2.97 ± 0.16	298	RR [relative to $k(\text{n-butane}) =$ $2.54 \times 10^{-12}]^a$	Edney <i>et al.</i> ¹⁵	
			2.80 ± 0.19	298 ± 2	RR [relative to $k(\text{dimethyl ether}) =$ $2.98 \times 10^{-12}]^a$	Tuazon <i>et al.</i> ³⁹	
Benzyl alcohol			22.9 ± 2.5	298	FP-RF	Nolting <i>et al.</i> ³⁵	
Benzotri- fluoride [$\text{C}_6\text{H}_5\text{CF}_3$]			0.46 ± 0.12	299 ± 2	RR [relative to $k(\text{benzene}) =$ $= 1.24 \times 10^{-12}]^a$	Atkinson <i>et al.</i> ³⁸	
Aniline			119 ± 24	296	FP-RF	Rinke and Zetzsch ¹¹	
			173 ± 8	239	FP-RF	Witte <i>et al.</i> ¹⁴	239-359
			164 ± 11	245			
			158 ± 4	253			
			133 ± 9	265			
			136 ± 7	274			
			128 ± 10	283			
			114 ± 3	299			
			106 ± 3	312			
			98 ± 6	316			
			93 ± 3	325			
			92 ± 7	336			
			86 ± 6	342			
			86 ± 3	346			
			83 ± 28	352			
	17	-560 ± 30	83 ± 15	359			

TABLE 19. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with aromatic compounds at, or close to, the high pressure limit — Continued

Aromatic	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Tempera- ture range covered (K)
			112 ± 12	265	FP-RF	Atkinson <i>et al.</i> ⁴⁰	265–455
			118 ± 10	283			
			118 ± 11	298			
			92 ^b	310			
			67 ^b	325			
			47.8 ± 5.3	342			
			36.3 ± 6.1	382			
			39.6 ± 7.5	391			
			29.7 ± 1.2	426			
			29.7 ± 5.4	455			
N,N-Dimethyl- aniline			151 ± 31	278	FP-RF	Atkinson <i>et al.</i> ⁴⁰	278–464
			148 ± 11	298			
			119 ± 6	303			
			57 ^b	318			
			29 ^b	329			
			5.8 ^b	361			
			1.71 ± 0.25	421			
			2.20 ± 0.51	425			
			2.09 ± 0.30	437			
			2.85 ± 0.24	460			
		3.12 ± 0.34	464				
Benzonitrile			0.33 ± 0.03	296	FP-RF	Zetzsch ^{36,37}	
Nitrobenzene			0.16 ± 0.05	296	FP-RF	Zetzsch ^{14,36,37}	
			<0.9	296 ± 2	RR [relative to $k(\text{dimethyl ether})$ $= 2.96 \times 10^{-12}]^a$	Atkinson <i>et al.</i> ⁴⁰	
			<0.7	296 ± 2	RR [relative to $k(\text{benzene}) =$ $1.23 \times 10^{-12}]^a$	Atkinson <i>et al.</i> ⁴⁰	
			0.120 ± 0.007	259	FP-RF	Witte <i>et al.</i> ¹⁴	259–362
			0.110 ± 0.012	265			
			0.119 ± 0.007	274			
			0.126 ± 0.009	283			
			0.132 ± 0.007	288			
			0.137 ± 0.014	299			
			0.146 ± 0.015	312			
			0.169 ± 0.022	316			
			0.137 ± 0.025	316			
			0.181 ± 0.028	331			
			0.154 ± 0.021	339			
			0.169 ± 0.011	342			
			0.163 ± 0.065	352			
			0.136 ± 0.013	358			
			0.133 ± 0.021	358			
	0.6	440 ± 80 (259–342 K)	0.158 ± 0.040	362			
4-Chloro- benzotri- fluoride			0.24 ± 0.08	299 ± 2	RR [relative to $k(\text{benzene}) =$ $1.24 \times 10^{-12}]^a$	Atkinson <i>et al.</i> ³⁸	
<i>o</i> -Dichloro- benzene			0.42 ± 0.02	295	FP-RF	Wahner and Zetzsch ¹⁰	
<i>m</i> -Dichloro- benzene			0.72 ± 0.02	295	FP-RF	Wahner and Zetzsch ¹⁰	

TABLE 19. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with aromatic compounds at, or close to, the high pressure limit — Continued

Aromatic	$10^{12} \times A$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{molecule}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
<i>p</i> -Dichloro- benzene			0.32 ± 0.02	295	FP-RF	Wahner and Zetzsch ¹⁰	
			0.52	300	RR [relative to $k(\text{ethene}) =$ $8.44 \times 10^{-12}]^a$	Klöpffer <i>et al.</i> ²²	
<i>p</i> -Chloro- aniline			83.0 ± 4.2	295	FP-RF	Wahner and Zetzsch ¹⁰	
			~ 43	296 ± 5	RR [relative to $k(\text{ethene}) =$ $8.61 \times 10^{-12}]^a$	Klöpffer <i>et al.</i> ²²	
<i>o</i> -Nitro- phenol	0.42 ± 0.05	-217 ± 60	0.90 ± 0.02	294	FP-RF	Zetzsch ³⁶	273–353
2,3-Dimethyl- phenol			80.2 ± 3.0	296 ± 2	RR [relative to $k(2\text{-methyl-1,3-butadiene})$ $= 1.01 \times 10^{-10}]^a$	Atkinson and Aschmann ³³	
2,4-Dimethyl- phenol			71.5 ± 4.1	296 ± 2	RR [relative to $k(2\text{-methyl-1,3-butadiene})$ $= 1.01 \times 10^{-10}]^a$	Atkinson and Aschmann ³³	
2,5-Dimethyl- phenol			80.0 ± 11.0	296 ± 2	RR [relative to $k(2\text{-methyl-1,3-butadiene})$ $= 1.01 \times 10^{-10}]^a$	Atkinson and Aschmann ³³	
2,6-Dimethyl- phenol			65.9 ± 5.0	296 ± 2	RR [relative to $k(2\text{-methyl-1,3-butadiene})$ $= 1.01 \times 10^{-10}]^a$	Atkinson and Aschmann ³³	
3,4-Dimethyl- phenol			81.4 ± 5.8	296 ± 2	RR [relative to $k(2\text{-methyl-1,3-butadiene})$ $= 1.01 \times 10^{-10}]^a$	Atkinson and Aschmann ³³	
3,5-Dimethyl- phenol			113 ± 8	296 ± 2	RR [relative to $k(2\text{-methyl-1,3-butadiene})$ $= 1.01 \times 10^{-10}]^a$	Atkinson and Aschmann ³³	
1,2,4-Tri- chloro- benzene			0.497 ± 0.036	273	FP-RF	Rinke and Zetzsch ¹¹	273–368
			0.532 ± 0.050	296			
			0.631 ± 0.082	323			
			0.706 ± 0.054	348			
			0.712 ± 0.083	368			
	2.3 ± 1.0	429 ± 125	0.58	300	RR [relative to $k(\text{toluene}) =$ $5.91 \times 10^{-12}]^a$	Klöpffer <i>et al.</i> ²²	
2,3-Dichloro- phenol			1.66 ± 0.15	298	FP-RF	Nolting <i>et al.</i> ³⁵	
2,4-Dichloro- phenol			1.06 ± 0.06	298	FP-RF	Nolting <i>et al.</i> ³⁵	
2,4- + 2,6- Toluene diisocyanate			7.09 ± 0.24	298 ± 2	RR [relative to $k(\text{toluene}) =$ $5.96 \times 10^{-12}]^a$	Becker <i>et al.</i> ⁴¹	
2,4-Toluene- diamine			192 ± 71	298 ± 2	RR [relative to $k(\text{cyclohexene}) =$ $6.77 \times 10^{-11}]^a$	Becker <i>et al.</i> ⁴¹	

TABLE 19. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with aromatic compounds at, or close to, the high pressure limit — Continued

Aromatic	$10^{12} \times A$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{molecule}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference	Temperature range covered (K)
2,6-Toluene-diamine			≥ 101	298 ± 2	RR [relative to $k(\text{cyclohexene}) =$ $6.77 \times 10^{-11}]^a$	Becker <i>et al.</i> ⁴¹	
Hexafluorobenzene			0.219 ± 0.016^c	298	FP-RF	Ravishankara <i>et al.</i> ²⁰	
			0.093 ± 0.013	234	FP-RF	Wallington <i>et al.</i> ¹⁶	234–438
			0.122 ± 0.013	263			
			0.161 ± 0.024	296			
			0.222 ± 0.029	353			
			0.266 ± 0.030	393			
	1.3 ± 0.3	610 ± 80	0.358 ± 0.059	438			
<i>o</i> -Nitrotoluene			0.70 ± 0.05	298	FP-RF	Nolting <i>et al.</i> ³⁵	
<i>m</i> -Nitrotoluene			0.95 ± 0.05	298	FP-RF	Nolting <i>et al.</i> ³⁵	
			1.3 ± 0.9	298 ± 2	RR [relative to $k(\text{benzene}) =$ $1.23 \times 10^{-12}]^a$	Atkinson <i>et al.</i> ⁴²	
<i>n</i> -Propylpentafluorobenzene			3.06 ± 0.24^c	298	FP-RF	Ravishankara <i>et al.</i> ²⁰	
Biphenyl			5.8 ± 0.8	296	FP-RF	Zetzsch ^{36,37}	
			7.61 ± 0.67	294 ± 1	RR [relative to $k(n\text{-nonane}) =$ $1.01 \times 10^{-11}]^a$	Atkinson <i>et al.</i> ⁴³	
			8.32 ± 0.75	295 ± 1	RR [relative to $k(\text{cyclohexane}) =$ $7.43 \times 10^{-12}]^a$	Atkinson and Aschmann ⁴⁴	
			8.0	300	RR [relative to $k(\text{ethene}) =$ $8.44 \times 10^{-12}]^a$	Klöpffer <i>et al.</i> ²²	
2-Chlorobiphenyl			2.82 ± 0.38	295 ± 1	RR [relative to $k(\text{cyclohexane}) =$ $7.43 \times 10^{-12}]^a$	Atkinson and Aschmann ⁴⁴	
3-Chlorobiphenyl			5.28 ± 0.82	295 ± 1	RR [relative to $k(\text{cyclohexane}) =$ $7.43 \times 10^{-12}]^a$	Atkinson and Aschmann ⁴⁴	
4-Chlorobiphenyl			3.86 ± 0.67	295 ± 1	RR [relative to $k(\text{cyclohexane}) =$ $7.43 \times 10^{-12}]^a$	Atkinson and Aschmann ⁴⁴	
Methylene-dianiline			30 ± 10	298 ± 2	RR [relative to $k(\text{cyclohexene}) =$ $6.77 \times 10^{-11}]^a$	Becker <i>et al.</i> ⁴¹	
1,4-Naphthoquinone			3.1 ± 1.2	298 ± 2	RR [relative to $k(\text{cyclohexane}) =$ $7.49 \times 10^{-12}]^a$	Atkinson <i>et al.</i> ⁴⁵	
Tetralin ^f			34.3 ± 0.6	296 ± 2	RR [relative to $k(\text{propene}) =$ $2.66 \times 10^{-11}]^a$	Atkinson and Aschmann ²⁷	

TABLE 19. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with aromatic compounds at, or close to, the high pressure limit — Continued

Aromatic	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{molecule}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Tempera- ture range covered (K)
Indane ^f			9.2	295	DF-RF	Baulch <i>et al.</i> ⁴⁶	
Indene ^f			>51	295	DF-RF	Baulch <i>et al.</i> ⁴⁶	
2,3-Dihydro- benzofuran ^f			36.6 ± 1.1	298 ± 2	RR [relative to $k(\text{propene}) =$ $2.63 \times 10^{-11}]^a$	Atkinson <i>et al.</i> ⁴⁷	
1,4-Benzo- dioxan ^f			25.2 ± 0.4	298 ± 2	RR [relative to $k(\text{propene}) =$ $2.63 \times 10^{-11}]^a$	Atkinson <i>et al.</i> ⁴⁷	
2,3-Benzo- furan ^f			37.3 ± 4.8	298 ± 2	RR [relative to $k(\text{propene}) =$ $2.63 \times 10^{-11}]^a$	Atkinson <i>et al.</i> ⁴⁷	
Fluorene ^f			13.0	300	RR [relative to $k(\text{ethene}) =$ $8.44 \times 10^{-12}]^a$	Klöpffer <i>et al.</i> ²²	
Naphthalene	2.3 ± 1.5	-640 ± 300 (300–407 K)	18.6 ± 1.0	300	LP-RF	Lorenz and Zellner ^{8,9}	300–873
			14.6 ± 5.0	337			
			11.0 ± 4.4	358			
			10.1 ± 4.0	378 ± 2			
			11.6 ± 3.0	404			
			10.5 ± 4.0	407			
			6.3 ± 2.0	452			
			4.3 ± 1.5	476			
			1.3 ± 0.5	502			
			1.2 ± 0.4	525 ± 1			
			0.7 ± 0.2	528			
			0.6 ± 0.1	531			
			1.1 ± 0.1	636			
			1.1 ± 0.2	665			
			1.4 ± 0.2	727			
			50	2500 (636–873 K)			
		22.8 ± 1.6	294 ± 1	RR [relative to $k(n\text{-nonane}) =$ $1.01 \times 10^{-11}]^a$	Atkinson <i>et al.</i> ⁴³		
		23.5 ± 0.6	298 ± 1	RR [relative to $k(\text{propene}) =$ $2.63 \times 10^{-11}]^a$	Biermann <i>et al.</i> ⁴⁸		
		25.9 ± 2.4	295 ± 1	RR [relative to $k(2\text{-methyl-1,3-butadiene})$ $= 1.02 \times 10^{-10}]^a$	Atkinson and Aschmann ⁴⁹		
		21.6	300	RR [relative to $k(\text{ethene}) =$ $8.44 \times 10^{-12}]^a$	Klöpffer <i>et al.</i> ²²		
1-Methyl- naphthalene			53.0 ± 4.8	298 ± 2	RR [relative to $k(2\text{-methyl-1,3-butadiene})$ $= 1.01 \times 10^{-10}]^a$	Atkinson and Aschmann ⁵⁰	
2-Methyl- naphthalene			52.3 ± 4.2	295 ± 1	RR [relative to $k(2\text{-methyl-1,3-butadiene})$ $= 1.02 \times 10^{-10}]^a$	Atkinson and Aschmann ⁴⁹	

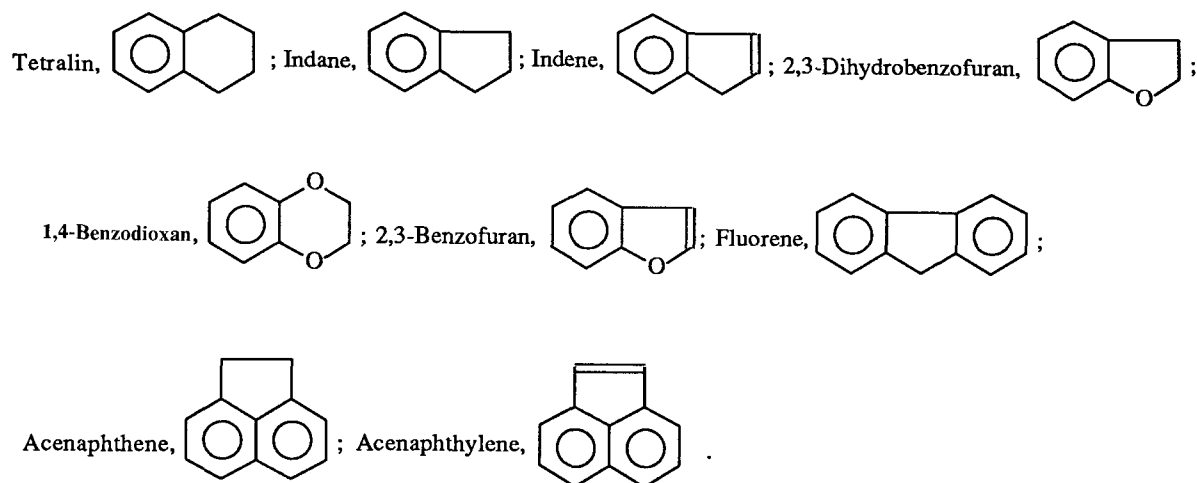
TABLE 19. Rate constants k and temperature-dependent parameters for the gas-phase reactions of the OH radical with aromatic compounds at, or close to, the high pressure limit — Continued

Aromatic	$10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$)	B (K)	$10^{12} \times k$ (cm^3 $\text{mole}^{-1} \text{s}^{-1}$)	at T (K)	Technique	Reference	Tempera- ture range covered (K)
1-Nitro- naphthalene			5.4 ± 1.8^c	298 ± 2	RR [relative to $k(\text{cyclohexane}) =$ $7.49 \times 10^{-12}]^a$	Atkinson <i>et al.</i> ⁴⁵	
2-Nitro- naphthalene			5.6 ± 0.9	298 ± 2	RR [relative to $k(\text{cyclohexane}) =$ $7.49 \times 10^{-12}]^a$	Atkinson <i>et al.</i> ⁴⁵	
2,3-Dimethyl- naphthalene			76.8 ± 4.8	295 ± 1	RR [relative to $k(2\text{-methyl-1,3-butadiene}) =$ $1.02 \times 10^{-10}]^a$	Atkinson and Aschmann ⁴⁹	
2-Methyl-1- nitronaphthalene			< 8.3	298 ± 2	RR [relative to $k(\text{cyclohexane}) =$ $7.49 \times 10^{-12}]^a$	Arey <i>et al.</i> ⁵¹	
1,4-Dichloro- naphthalene			5.8	300	RR [relative to $k(\text{toluene}) =$ $5.91 \times 10^{-12}]^a$	Klöpffer <i>et al.</i> ²²	
Acenaphthene ^f			58.4	300	RR [relative to $k(\text{ethene}) =$ $8.44 \times 10^{-12}]^a$	Klöpffer <i>et al.</i> ²²	
			103 ± 13	296 ± 2	RR [relative to $k(2,3\text{-dimethyl-2-butene}) =$ $1.11 \times 10^{-10}]^a$	Atkinson and Aschmann ²⁷	
Acenaph- thylene ^f			110 ± 11	296 ± 2	RR [relative to $k(2,3\text{-dimethyl-2-butene}) =$ $1.11 \times 10^{-10}]^a$	Atkinson and Aschmann ²⁷	
Phenan- threne			15.6 ± 2.0	338	LP-RF	Lorenz and Zellner ⁹	338-748
			16.1 ± 2.0	355			
			19.1 ± 2.5	387			
			12.0 ± 1.7	399			
			8.3 ± 0.8	431			
			4.0 ± 0.7	492			
			2.8 ± 0.7	526			
			1.2 ± 0.2	597			
			1.2 ± 0.4	648			
			2.2 ± 0.5	748			
			34 ± 12	298 ± 1	RR [relative to $k(\text{propene}) =$ $4.85 \times 10^{-12} e^{504/T}]^a$	Biermann <i>et al.</i> ⁴⁸	298-319
			28 ± 6	319 ± 1			
Anthracene			112 ± 9	325 ± 1	RR [relative to $k(\text{propene}) =$ $2.29 \times 10^{-11}]^a$	Biermann <i>et al.</i> ⁴⁸	

^aFrom the present recommendations (see text).^bNon-exponential OH radical decays observed (see text).^cRoom temperature, not specified.^dSee Introduction.^eAt 200 Torr total pressure of helium diluent, data also obtained at other total pressures.

TABLE 19. Footnotes — Continued

[Structures:



The absolute rate constants obtained at, or close to, the high pressure limit of Davis *et al.*,¹ Perry *et al.*,⁴ Tully *et al.*,⁶ Lorenz and Zellner,^{8,9} Wahner and Zetzsch,¹⁰ Rinke and Zetzsch,¹¹ Madronich and Felder,¹³ Witte *et al.*¹⁴ and Wallington *et al.*¹⁶ are plotted in Arrhenius form in Fig. 95 (the 298 K rate constant of Hansen *et al.*³ is identical to that of Tully *et al.*⁶ and is hence not shown). At room temperature these absolute rate constants exhibit a significant degree of scatter, of a factor of ~ 1.8 . The reasons for these discrepancies are not known, but may, at least in part, be due to the relatively low magnitude of this rate constant. The recommendations are based on the flash and laser photolysis-resonance fluorescence studies of Hansen *et al.*,³ Perry *et al.*,⁴ Tully *et al.*,⁶ Lorenz and Zellner,^{8,9} Madronich and Felder,¹³ Witte *et al.*¹⁴ (which is judged to supersede the earlier room temperature studies of Wahner and Zetzsch¹⁰ and Rinke and Zetzsch¹¹), and Wallington *et al.*¹⁶ For temperatures ≤ 355 K, a unit-weighted least-squares analysis of the rate constants of Hansen *et al.*,³ Perry *et al.*,⁴ Tully *et al.*,⁶ Lorenz and Zellner,^{8,9} Witte *et al.*¹⁴ and Wallington *et al.*¹⁶ yields the Arrhenius expression of

$$k(\text{benzene}; T \leq 355 \text{ K}) = (2.47^{+0.90}_{-0.66}) \times 10^{-12} e^{-(207 \pm 89)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 234–354 K, where the indicated error limits are two least-squares standard deviations, and

$$k(\text{benzene}) = 1.23 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of $\pm 30\%$.

This rate constant and Arrhenius expression are applicable for ~ 100 Torr total pressure of argon diluent and are expected to be somewhat below the limiting high-pressure rate constant k_∞ . Based upon the estimation discussed above, at 298 K the rate constant k_∞ is expected to be:

$$k_\infty(\text{benzene}) = 1.40 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

and hence

$$k_\infty(\text{benzene}) \approx 3.58 \times 10^{-12} e^{-280/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range ~ 235 – 355 K.

The rate constants derived from the relative rate studies of Doyle *et al.*,² Cox *et al.*,⁵ Barnes *et al.*,⁷ Ohta and Ohya¹² and Edney *et al.*¹⁵ are in reasonably good agreement with this recommendation.

At temperatures ≥ 450 K the only reported rate constants are those of Tully *et al.*,⁶ Lorenz and Zellner,^{8,9} Madronich and Felder¹³ and Felder and Madronich⁵⁴ [who extended the study of Madronich and Felder¹³ to obtain $k(\text{benzene}) = (2.5 \pm 0.3) \times 10^{-11} e^{-(2050 \pm 125)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the same temperature range of 787–1409 K, but did not tabulate the additional rate constants measured], and these data are in reasonably good agreement. Consistent with the recommendations for the alkanes, haloalkanes and alkenes, a unit-weighted least-

squares analysis of the data of Tully *et al.*,⁶ Lorenz and Zellner^{8,9} and Madronich and Felder,¹³ using the expression $k = CT^2e^{-D/T}$, yields the recommendation of

$$k(\text{benzene}, T \geq 450 \text{ K}) = (4.67^{+1.73}_{-1.27}) \times 10^{-18} T^2 e^{-(543 \pm 226)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 453–1409 K, where the error limits are two least-squares standard deviations. The rate constants reported by Perry *et al.*⁴ between 396 and 422 K are, as expected,⁶ somewhat higher than predicted from this recommendation, though in agreement within the experimental errors.

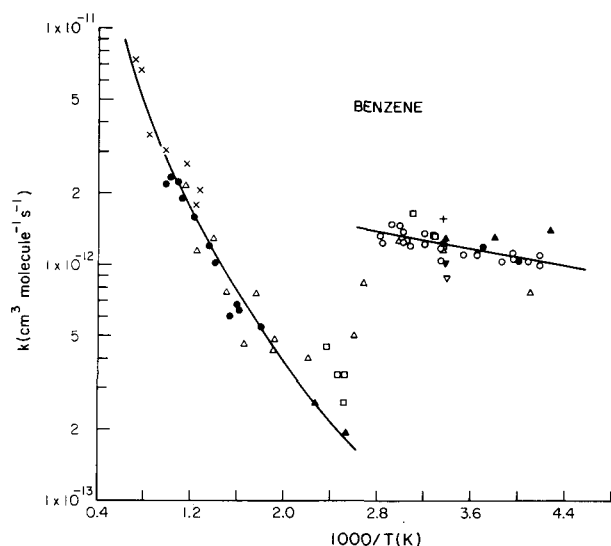


FIG. 95. Arrhenius plot of rate constants obtained at, or close to, the high-pressure limit for the reaction of the OH radical with benzene. (+) Davis *et al.*;¹ (□) Perry *et al.*;⁴ (●) Tully *et al.*;⁶ (Δ) Lorenz and Zellner;^{8,9} (∇) Wahner and Zetzsch;¹⁰ (▼) Rinke and Zetzsch;¹¹ (x) Madronich and Felder;¹³ (○) Witte *et al.*;¹⁴ (▲) Wallington *et al.*;¹⁶ (—) recommendations (see text).

(2) Benzene-*d*₆

The rate constants reported by Tully *et al.*⁶ and Lorenz and Zellner⁸ are listed in Table 19 and are plotted in Arrhenius form in Fig. 96. It can be seen that the rate constants obtained by Lorenz and Zellner⁸ at 298 and 524 K are in excellent agreement with those of Tully *et al.*⁶

For temperatures $\lesssim 325$ K, a unit-weighted least-squares analysis of the rate constants of Tully *et al.*⁶ and Lorenz and Zellner⁸ yields the recommended Arrhenius expression of

$$k(\text{benzene-}d_6; T \leq 325 \text{ K}) = (1.54^{+1.81}_{-0.83}) \times 10^{-12} e^{-(90 \pm 216)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 250–298 K, where the indicated error limits are two least-squares standard deviations, and

$$k(\text{benzene-}d_6) = 1.14 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty at 298 K of $\pm 30\%$. The significant uncertainties in the above Arrhenius parameters are largely due to the small temperature range (250–298 K) covered. Again, this rate expression is applicable for a total pressure of ~ 100 Torr of argon diluent, and is expected to be slightly ($\lesssim 10\%$ at 298 K) below the limiting high-pressure rate constant k_∞ .

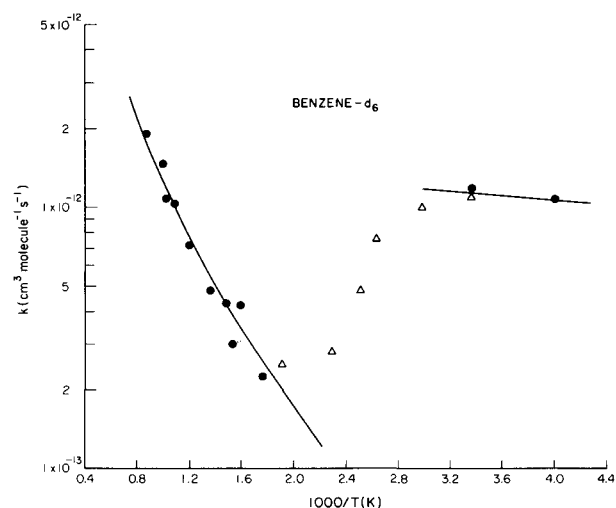


FIG. 96. Arrhenius plot of rate constants for the reaction of the OH radical with benzene-*d*₆. (●) Tully *et al.*;⁶ (Δ) Lorenz and Zellner;⁸ (—) recommendations (see text).

At elevated temperatures, using the criteria discussed above, the recommendation is based on the rate constants obtained at temperatures ≥ 450 K. A unit-weighted least-squares analysis of the data of Tully *et al.*⁶ and Lorenz and Zellner,⁸ using the expression $k = CT^2e^{-D/T}$, yields the recommendation of

$$k(\text{benzene-}d_6; T \geq 450 \text{ K}) = (2.23^{+1.15}_{-0.75}) \times 10^{-18} T^2 e^{-(582 \pm 298)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 524–1150 K, where the indicated error limits are two least-squares standard deviations.

It can be seen from Table 19 and Figs. 95 and 96 that at temperatures $\lesssim 325$ K the rate constants for benzene and benzene-*d*₆ are essentially identical, within the experimental errors. However, for temperatures ≥ 450 K the rate constants for benzene-*d*₆ are significantly lower than

those for benzene- h_6 . As discussed below, these observations are totally consistent with OH radical addition to the aromatic ring dominating for temperatures ≤ 325 K, while H-atom abstraction dominates for temperatures ≥ 450 K (as shown by the study of Madronich and Felder¹³), with the corresponding expected kinetic isotope effect.

(3) Toluene

The available rate constants obtained at, or close to, the high pressure limit are given in Table 19, and those of Davis *et al.*,¹ Hansen *et al.*,³ Perry *et al.*,⁴ Cox *et al.*,⁵ Tully *et al.*,⁶ Edney *et al.*,¹⁵ Baldwin *et al.*¹⁷ and Atkinson and Aschmann¹⁸ are plotted in Arrhenius form in Fig. 97 for the temperature regimes for which exponential OH radical decays have been observed in the two temperature-dependent flash photolysis studies.^{4,6}

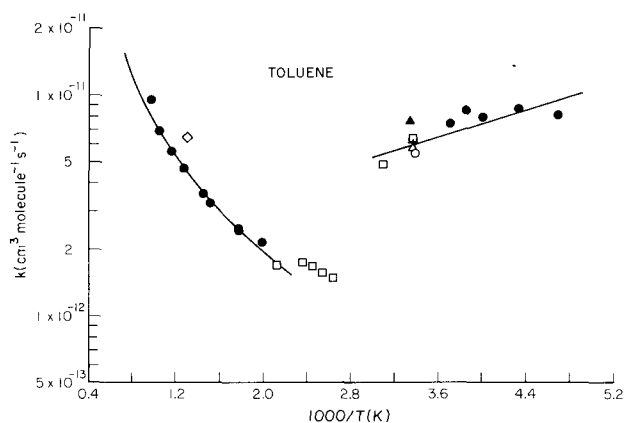


FIG. 97. Arrhenius plot of rate constants obtained at, or close to, the high-pressure limit for the reaction of the OH radical with toluene. (+) Davis *et al.*,¹ (Δ) Hansen *et al.*,³ (□) Perry *et al.*,⁴ (▲) Cox *et al.*,⁵ (●) Tully *et al.*,⁶ (○) Edney *et al.*,¹⁵ Atkinson and Aschmann;¹⁸ (◇) Baldwin *et al.*,¹⁷ (—) recommendations (see text).

Davis *et al.*,¹ Tully *et al.*⁶ and Bourmada *et al.*^{53,55} have reported that at room temperature the rate constant for this reaction is in the fall-off regime between second- and third-order kinetics below ~ 100 Torr total pressure of helium or argon diluent.

Based upon the discharge flow-resonance fluorescence study of Bourmada *et al.*,^{53,55} the limiting low pressure third order rate constant k_0 at 295 ± 2 K for helium diluent is

$$k_0^{\text{He}}(\text{toluene}) = (4.0 \pm 0.5) \times 10^{-28} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

Combined with a limiting high-pressure rate constant of $k_\infty = 6.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ^{53,55} and $F = 0.6$ and assuming $k_0^{\text{Ar}} \geq k_0^{\text{He}}$, this leads to the expectation that at ~ 100 Torr total pressure of argon diluent and

room temperature the measured rate constants are within $\sim 5\%$ of k_∞ .

For temperatures ≤ 325 K, a unit-weighted least-squares analysis of the absolute rate constants of Hansen *et al.*,³ Perry *et al.*,⁴ and Tully *et al.*⁶ (the rate constant of Davis *et al.*¹ has not been included since the corresponding rate constant for benzene appears to be anomalously high; see above) and the relative rate data of Edney *et al.*¹⁵ and Atkinson and Aschmann¹⁸ yields the recommended Arrhenius expression of

$$k(\text{toluene}, T \leq 325) = (1.81_{-0.74}^{+1.27}) \times 10^{-12} e^{(355 \pm 143)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 213–324 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{toluene}) = 5.96 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of $\pm 25\%$.

For temperatures ≥ 450 K, a unit-weighted least-squares analysis of the rate constants obtained by Perry *et al.*⁴ and Tully *et al.*,⁶ using the expression $k = CT^2 e^{-D/T}$, yields the recommendation of

$$k(\text{toluene}, T \geq 450 \text{ K}) = (7.58_{-1.14}^{+1.35}) \times 10^{-18} T^2 e^{(11 \pm 106)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 473–1046 K, where the indicated errors are two least-squares standard deviations. While the rate constant obtained by Perry *et al.*⁴ at 473 K is in good agreement with those of Tully *et al.*,⁶ the rate constants of Perry *et al.*⁴ at temperatures between 378 and 424 K are $\sim 25\%$ higher than those predicted from the above expression. This may well be due to a continuing (but decreasing with increasing temperature) contribution of the addition process to the observed overall rate constant, as discussed by Tully *et al.*⁶

The rate constants obtained from the relative rate studies of Cox *et al.*,⁵ Ohta and Ohyama¹² and Baldwin *et al.*¹⁷ are in good agreement with the above recommendations for the two temperature regions.

(4) Toluene- d_8

Rate constants have been obtained for toluene- d_8 at, or close to, the high pressure limit by Perry *et al.*⁴ and Tully *et al.*⁶ These data are given in Table 19, and the rate constants obtained in the temperature regimes corresponding to exponential OH radical decays are plotted in Arrhenius form in Fig. 98. The rate constants from these two studies^{4,6} are in excellent agreement. At temperatures ≤ 325 K, a unit-weighted least-squares analysis of these rate constants^{4,6} yields the recommended Arrhenius expression of

$$k(\text{toluene-}d_8, T \leq 325 \text{ K}) = (7.31^{+4.25}_{-2.70}) \\ \times 10^{-12} e^{-(44 \pm 127)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 250–298 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{toluene-}d_8) = 6.31 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty of $\pm 20\%$ at 298 K.

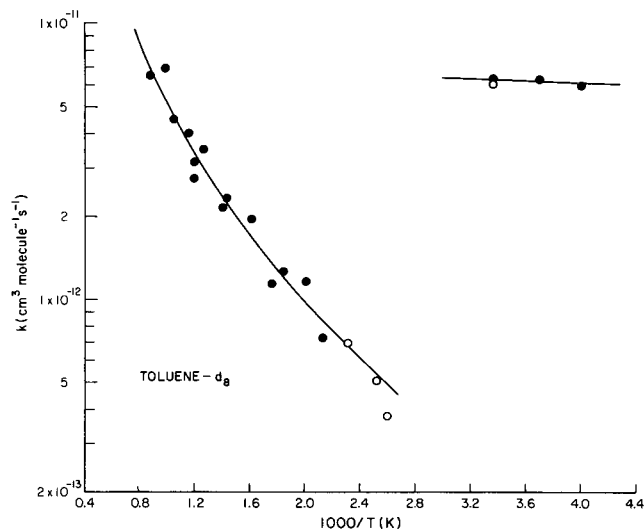


FIG. 98. Arrhenius plot of rate constants for the reaction of the OH radical reaction with toluene- d_8 . (○) Perry *et al.*;⁴ (●) Tully *et al.*;⁶ (—) recommendations (see text).

For temperatures ≥ 450 K, a unit-weighted least-squares analysis of the rate constants of Tully *et al.*,⁶ using the expression $k = CT^2e^{-D/T}$, yields the recommendation of

$$k(\text{toluene-}d_8, T \geq 450 \text{ K}) = (6.85^{+2.55}_{-1.86}) \\ \times 10^{-18} T^2 e^{-(276 \pm 216)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 470–1150 K, where the indicated errors are two least-squares standard deviations. These recommendations are identical to those of Atkinson,⁵⁶ using the same data set.

As for benzene and benzene- d_6 , the rate constants at ≤ 325 K for toluene and toluene- d_8 are very similar, consistent with the dominance of OH radical addition to the aromatic ring. However, for temperatures ≥ 450 K the OH radical rate constant for toluene- d_8 is significantly lower than that for toluene- h_8 . This is also shown in Fig. 99, in which the reported elevated temperature (≥ 450 K) rate constants for toluene,^{4,6} toluene- d_3 ($C_6H_5CD_3$),⁶ toluene- d_5 ($C_6D_5CH_3$),⁶ and toluene- d_8 ⁶ are plotted in Arrhenius form.

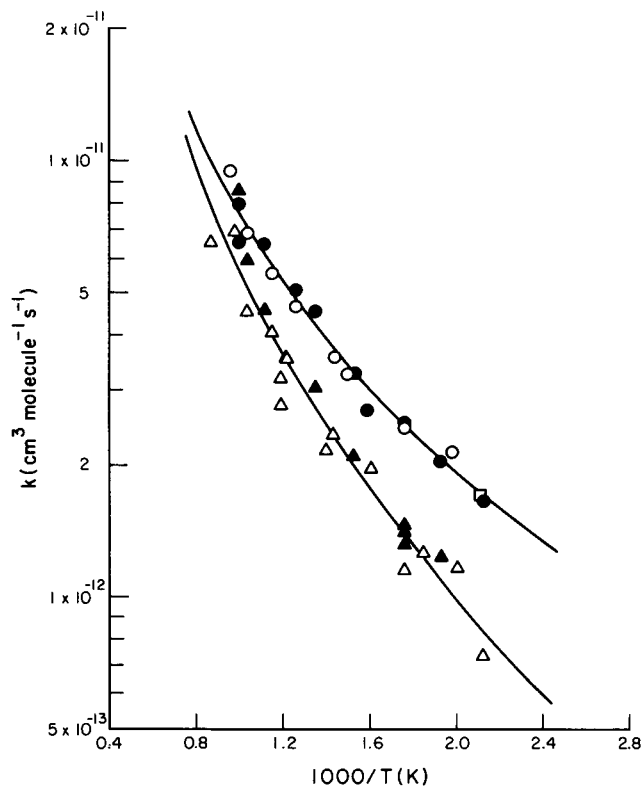


FIG. 99. Arrhenius plot of rate constants at temperatures ≥ 450 K for the reactions of the OH radical with toluene and partially- and fully-deuterated toluenes. Toluene- h_8 : (□) Perry *et al.*;⁴ (○) Tully *et al.*;⁶ Toluene- d_5 ($C_6D_5CH_3$): (●) Tully *et al.*;⁶ Toluene- d_3 ($C_6H_5CD_3$): (▲) Tully *et al.*;⁶ Toluene- d_8 : (Δ) Tully *et al.*;⁶ (—) recommendations (see text).

It can be seen that to a good approximation these data fall into two sets, namely those for $C_6H_5CH_3$ and $C_6D_5CH_3$ and those for $C_6H_5CD_3$ and $C_6D_5CD_3$, with the rate constants for toluene and toluene- d_5 being significantly higher than those for toluene- d_3 and toluene- d_8 (at least up to 1000 K). The lines shown in Fig. 99 are those calculated from unit-weighted least-squares analyses of the data for $C_6H_5CH_3$ ^{4,6} and $C_6D_5CH_3$ ⁶ [$k(C_6X_5CH_3)$] and $C_6H_5CD_3$ ⁶ and $C_6D_5CD_3$ ⁶ [$k(C_6X_5CD_3)$], respectively, with

$$k(C_6X_5CH_3) = (7.63^{+1.01}_{-0.90}) \\ \times 10^{-18} T^2 e^{(3 \pm 82)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

and

$$k(C_6X_5CD_3) = (8.19^{+2.39}_{-1.85}) \\ \times 10^{-18} T^2 e^{-(361 \pm 172)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 470–1150 K, where the indicated errors are two least-squares standard deviations. This leads to a deuterium isotope effect for H- or D-atom abstraction from the $-CH_3$ or $-CD_3$ groups in the

toluenes of $k^D/k^H = 1.07e^{-364/T}$, which is in between the isotope effects observed for primary and secondary C—H bonds in the alkanes (Sec. 2.1). These H- or D-atom abstraction rate constants are significantly higher than those for benzene or benzene- d_6 , again showing that the major process involves H- or D-atom abstraction from the —CH₃ or —CD₃ substituent groups. While there may be consistent differences between the rate constants for toluene and toluene- d_5 , and between those for toluene- d_3 and toluene- d_8 , due to H- or D-atom abstraction from the aromatic ring C—H or C—D bonds, these are minor and are probably within the experimental errors.

(5) Ethylbenzene

The available rate constants of Lloyd *et al.*,¹⁹ Ravishankara *et al.*,²⁰ and Ohta and Ohyama,¹² all obtained at room temperature, are given in Table 19. Within the likely overall experimental error limits, these rate constants are in agreement and, from a unit-weighted average of these data,^{12,19,20} it is recommended that

$$k(\text{ethylbenzene}) = 7.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at ~ 298 K, with an estimated overall uncertainty of $\sim \pm 35\%$. The temperature dependence at temperatures $\lesssim 320$ K is expected to be close to zero.

(6) *o*-Xylene

The available rate constants obtained at, or close to, the high-pressure limit are given in Table 19, and those of Hansen *et al.*,³ Perry *et al.*,⁴ Ravishankara *et al.*,²⁰ Cox *et al.*,⁵ Nicovich *et al.*,²¹ and Atkinson and Aschmann¹⁸ are plotted in Arrhenius form in Fig. 100. In general, the agreement between these studies and those of Doyle *et al.*,² Ohta and Ohyama,¹² Klöpffer *et al.*,²² and Edney *et al.*¹⁵ is good.

For temperatures ≤ 325 K rate constants have been reported only over the very limited temperature range 296–320 K with, within the experimental error limits, no obvious temperature dependence. Hence, a unit-weighted average of the absolute rate constants of Hansen *et al.*,³ Perry *et al.*,⁴ Ravishankara *et al.*,²⁰ and Nicovich *et al.*,²¹ and the recent relative rate data of Ohta and Ohyama,¹² Edney *et al.*¹⁵ and Atkinson and Aschmann¹⁸ (the rate constant of Klöpffer *et al.*²² was not used due to a lack of details) yields the recommendation of

$$k(o\text{-xylene}; T \leq 325 \text{ K}) = 1.37$$

$$\times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

independent of temperature over the range 296–320 K, with an estimated overall uncertainty over this temperature range of $\pm 25\%$. At room temperature, the rate constant for this reaction is close to the limiting high

pressure value for total pressures of helium or argon diluent of ≈ 20 Torr.²⁰

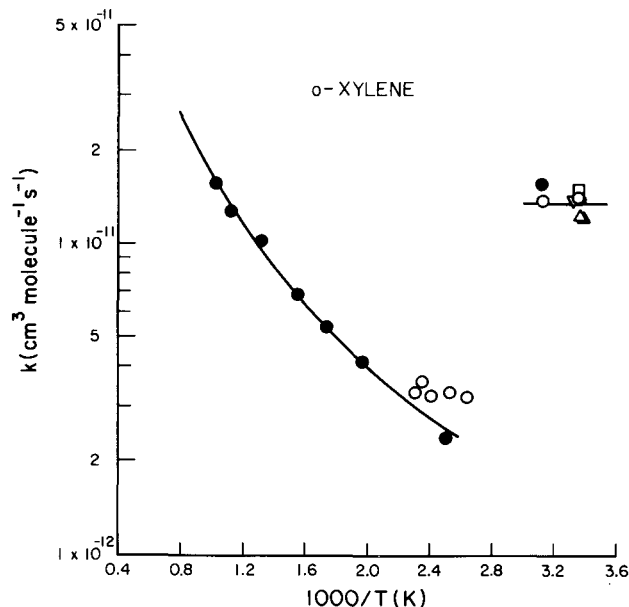


FIG. 100. Arrhenius plot of rate constants for the reaction of the OH radical with *o*-xylene. (□) Hansen *et al.*,³ (○) Perry *et al.*,⁴ (Δ) Ravishankara *et al.*,²⁰ (∇) Cox *et al.*,⁵ (●) Nicovich *et al.*,²¹ (▲) Atkinson and Aschmann;¹⁸ (—) recommendations (see text).

For temperatures ≥ 450 K, a unit-weighted least-squares analysis of the rate constants of Nicovich *et al.*,²¹ using the expression $k = CT^2e^{-D/T}$, yields the recommendation of

$$k(o\text{-xylene}, T \geq 450 \text{ K}) = (1.75^{+0.25}_{-0.23}) \times 10^{-17} T^2 e^{-(35 \pm 90)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 508–970 K, where the indicated errors are two least-squares standard deviations. Again, as is the case for *m*- and *p*-xylene (see below), the rate constants determined by Perry *et al.*⁴ over the small temperature range ~ 379 –432 K are somewhat higher (by up to $\sim 50\%$) than predicted from the recommended ≥ 450 K expression.

(7) *m*-Xylene

The available rate constants obtained at, or close to, the high-pressure limit are given in Table 19, and those of Hansen *et al.*,³ Lloyd *et al.*,¹⁹ Perry *et al.*,⁴ Ravishankara *et al.*,²⁰ Cox *et al.*,⁵ Nicovich *et al.*,²¹ Atkinson *et al.*,²³ Edney *et al.*¹⁵ and Atkinson and Aschmann¹⁸ are plotted in Arrhenius form in Fig. 101. Ravishankara *et al.*²⁰ have shown that at 298 K this reaction is in the

fall-off regime between second- and third-order kinetics at 3 Torr total pressure of argon, with the limiting high pressure value being approached at ~ 20 Torr total pressure of helium or argon.²⁰

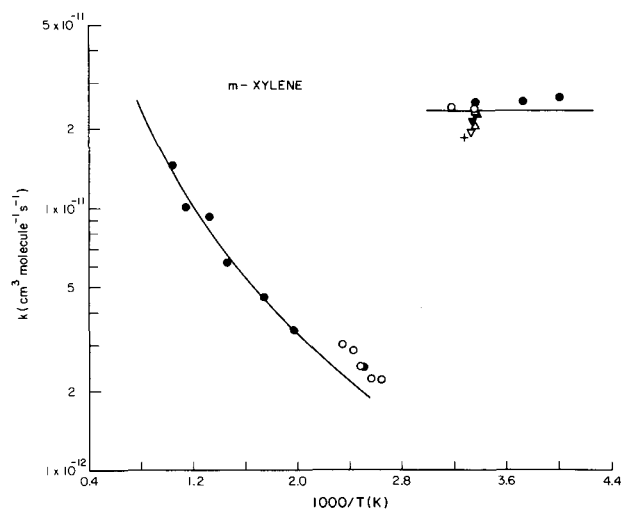


FIG. 101. Arrhenius plot of rate constants for the reaction of the OH radical with *m*-xylene. (□) Hansen *et al.*,³ (+) Lloyd *et al.*,¹⁹ (○) Perry *et al.*,⁴ (Δ) Ravishankara *et al.*,²⁰ (∇) Cox *et al.*,⁵ (●) Nicovich *et al.*,²¹ (▼) Atkinson *et al.*,²³ (▲) Edney *et al.*,¹⁵ Atkinson and Aschmann,¹⁸ (—) recommendations (see text).

The rate constant data of Perry *et al.*⁴ and Nicovich *et al.*²¹ suggest that the temperature dependence is essentially zero over the range 250–315 K. Thus, for temperatures ≤ 325 K a unit-weighted average of the absolute rate constants of Hansen *et al.*,³ Perry *et al.*,⁴ Ravishankara *et al.*²⁰ and Nicovich *et al.*²¹ and the recent relative rate data of Atkinson *et al.*,²³ Ohta and Ohya,¹² Edney *et al.*¹⁵ and Atkinson and Aschmann¹⁸ yields the recommendation of

$$k(m\text{-xylene}, T \leq 325 \text{ K}) = 2.36 \\ \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 250–315 K, with an estimated overall uncertainty of $\pm 25\%$.

For temperatures ≥ 450 K, a unit-weighted least-squares analysis of the data of Nicovich *et al.*,²¹ using the expression $k = CT^2 e^{-D/T}$, yields the recommendation of

$$k(m\text{-xylene}, T \geq 450 \text{ K}) = (1.71^{+0.71}_{-0.51}) \\ \times 10^{-17} T^2 e^{-(127 \pm 235)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 508–960 K, where the indicated errors are two least-squares standard deviations.

(8) *p*-Xylene

The available rate constants obtained at, or close to, the high pressure limit are listed in Table 19, and those of Hansen *et al.*,³ Perry *et al.*,⁴ Ravishankara *et al.*,²⁰ Nicovich *et al.*,²¹ Edney *et al.*¹⁵ and Atkinson and Aschmann¹⁸ are plotted in Arrhenius form in Fig. 102.

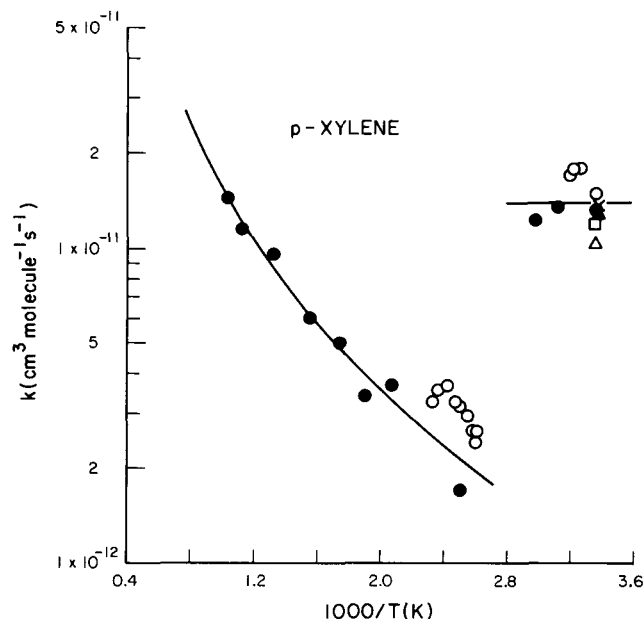


FIG. 102. Arrhenius plot of rate constants for the reaction of the OH radical with *p*-xylene. (□) Hansen *et al.*,³ (○) Perry *et al.*,⁴ (Δ) Ravishankara *et al.*,²⁰ (●) Nicovich *et al.*,²¹ (x) Edney *et al.*,¹⁵ (▲) Atkinson and Aschmann,¹⁸ (—) recommendations (see text).

As for *m*-xylene, Ravishankara²⁰ have reported that at 298 K the rate constant for this reaction is in the fall-off regime between second- and third-order kinetics at 3 Torr total pressure of argon, with the rate constants at 20 Torr total pressure of helium or argon being close to the high-pressure kinetic regime. The rate constants obtained at around room temperature exhibit a significant degree of scatter, and a unit-weighted average of the rate constants determined by Hansen *et al.*,³ Perry *et al.*,⁴ Ravishankara *et al.*,²⁰ Nicovich *et al.*,²¹ Ohta and Ohya,¹² Edney *et al.*¹⁵ and Atkinson and Aschmann¹⁸ at temperatures ≤ 335 K yields the recommendation of

$$k(p\text{-xylene}; T \leq 335 \text{ K}) = 1.43 \\ \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

independent of temperature over the range 296–335 K, with an estimated overall uncertainty of $\pm 40\%$.

At temperatures ≥ 450 K, a unit-weighted least-squares analysis of the rate constants determined by Nicovich *et*

al.,²¹ using the expression $k = CT^2e^{-D/T}$, yields the recommendation of

$$k(p\text{-xylene}; T \geq 450 \text{ K}) = (1.74_{-0.50}^{+0.70}) \times 10^{-17} T^2 e^{-(99 \pm 215)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 484–960 K, where the indicated errors are two least-squares standard deviations.

As noted previously,^{21,56} at any given temperature ≥ 450 K the rate constants for the H-atom abstraction pathway from *o*-, *m*- and *p*-xylene are similar, and are close to a factor of 2 higher than those for toluene and toluene-*d*₅ (C₆D₅CH₃). This suggests that the OH radical reaction rate constant for H-atom abstraction from the —CH₃ groups on the toluenes and xylenes is independent of the aromatic hydrocarbon and depends only on the number of —CH₃ substituent groups. This is shown in Fig. 103, in which the H-atom abstraction rate constants per —CH₃ group are plotted in Arrhenius form for toluene, toluene-*d*₅ and *o*-, *m*- and *p*-xylene for temperatures ≥ 450 K.

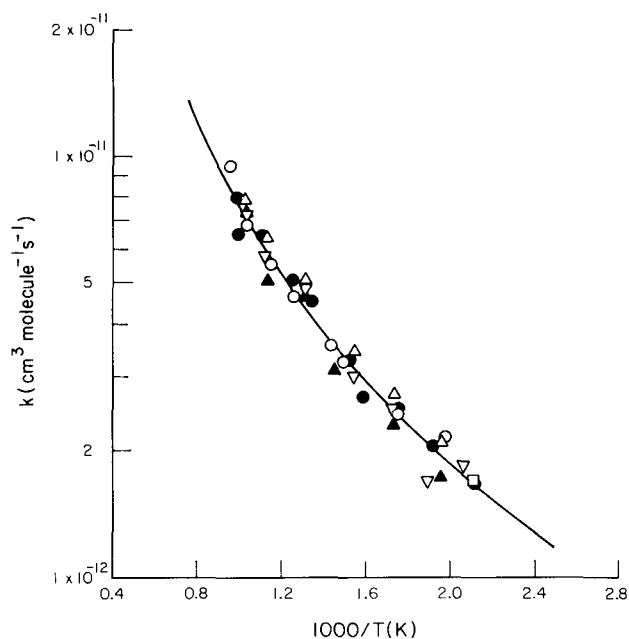


FIG. 103. Arrhenius plot of rate constants at temperatures ≥ 450 K per —CH₃ group for the reaction of the OH radical with toluene, toluene-*d*₅ (C₆D₅CH₃) and *o*-, *m*- and *p*-xylene. Toluene: (□) Perry *et al.*;⁴ (○) Tully *et al.*;⁶ Toluene-*d*₅: (●) Tully *et al.*;⁶ *o*-Xylene: (Δ) Nicovich *et al.*;²¹ *m*-Xylene: (▲) Nicovich *et al.*;²¹ *p*-Xylene: (▽) Nicovich *et al.*;²¹ (—) recommendation (see text).

A unit-weighted least-squares analysis of these data,^{4,6,21} using the expression $k = CT^2e^{-D/T}$, yields

$$k(\text{H-atom abstraction per } -\text{CH}_3 \text{ group}) = (8.07_{-0.88}^{+0.99}) \times 10^{-18} T^2 e^{-(38 \pm 76)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 470–1046 K, where the indicated errors are two least-squares standard deviations. Extrapolation to 298 K yields an H-atom abstraction rate constant per —CH₃ group of $6.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

(9) *n*-Propylbenzene

The available room temperature rate constants of Lloyd *et al.*,¹⁹ Ravishankara *et al.*²⁰ and Ohta and Ohya¹² are in good agreement (Table 19), and a unit-weighted average of these data^{12,19,20} leads to the recommendation of

$$k(n\text{-propylbenzene}) = 6.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at ~ 298 K, with an estimated overall uncertainty of $\pm 30\%$.

(10) Isopropylbenzene

The available rate constants of Lloyd *et al.*,¹⁹ Ravishankara *et al.*²⁰ and Ohta and Ohya¹² all obtained at room temperature, exhibit a spread of $\sim 50\%$ (Table 19). A unit-weighted average of these data^{12,19,20} leads to the recommendation of

$$k(\text{isopropylbenzene}) = 6.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at ~ 298 K, with an estimated overall uncertainty of $\pm 35\%$.

These room temperature rate constants for *n*-propylbenzene and isopropylbenzene (and ethylbenzene) are similar to that for toluene, and indicate that the rate constants for toluene are reasonably applicable to the higher monoalkylbenzenes.

(11) *o*-, *m*- and *p*-Ethyltoluene

Two room temperature relative rate constant studies have been carried out for each of these isomers,^{12,19} with the measured rate constants being in good agreement (Table 19). Unit-weighted averages of these rate data^{12,19} lead to the recommendations of

$$k(o\text{-ethyltoluene}) = 1.23 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

$$k(m\text{-ethyltoluene}) = 1.92 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

and

$$k(p\text{-ethyltoluene}) = 1.21 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

all at ~ 298 K, with estimated overall uncertainties of $\pm 40\%$. These rate constants are similar to those for the corresponding xylene isomers, again showing that the reactions proceed by OH radical addition to the aromatic ring, with the rate constants depending on the number and positions of the alkyl substituents.

(12) 1,2,3-, 1,2,4- and 1,3,5-Trimethylbenzene

The available rate constants of Doyle *et al.*,² Hansen *et al.*,³ Perry *et al.*,⁴ Ohta and Ohyama¹² (carried out at room temperature, which was not specified) and Atkinson and Aschmann¹⁸ are given in Table 19 and are plotted in Arrhenius form in Figs. 104 through 106 (assuming 298 K as the temperature of the Ohta and Ohyama¹² study). In all cases, there is a significant amount of scatter in the reported rate constants for temperatures $\lesssim 325$ K. The rate constants derived from the relative rate study of Doyle *et al.*² are subject to significant uncertainties since dilution, which was of a similar magnitude to the OH radical reaction as a loss process for the *n*-butane reference compound, had to be taken into account.

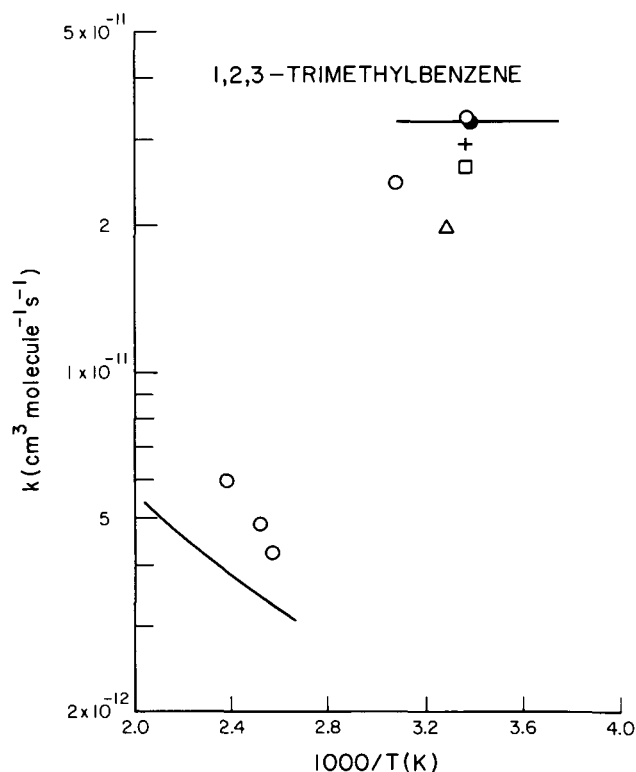


FIG. 104. Arrhenius plot of rate constants for the reaction of the OH radical with 1,2,3-trimethylbenzene. (Δ) Doyle *et al.*,² (\square) Hansen *et al.*,³ (\circ) Perry *et al.*,⁴ (\oplus) Ohta and Ohyama,¹² assuming a temperature of 298 K; (\bullet) Atkinson and Aschmann;¹⁸ (—) recommendations (see text).

The recommendations utilize the room temperature rate constants obtained from the most recent relative rate study of Atkinson and Aschmann,¹⁸ with an assumed zero temperature dependence over the narrow temperature range ~ 295 – 325 K. Thus, it is recommended that

$$k(1,2,3\text{-trimethylbenzene}) = 3.27 \\ \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

$$k(1,2,4\text{-trimethylbenzene}) = 3.25 \\ \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

and

$$k(1,3,5\text{-trimethylbenzene}) = 5.75 \\ \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

all independent of temperature over the range ~ 295 – 325 K and with estimated overall uncertainties of $\pm 35\%$.

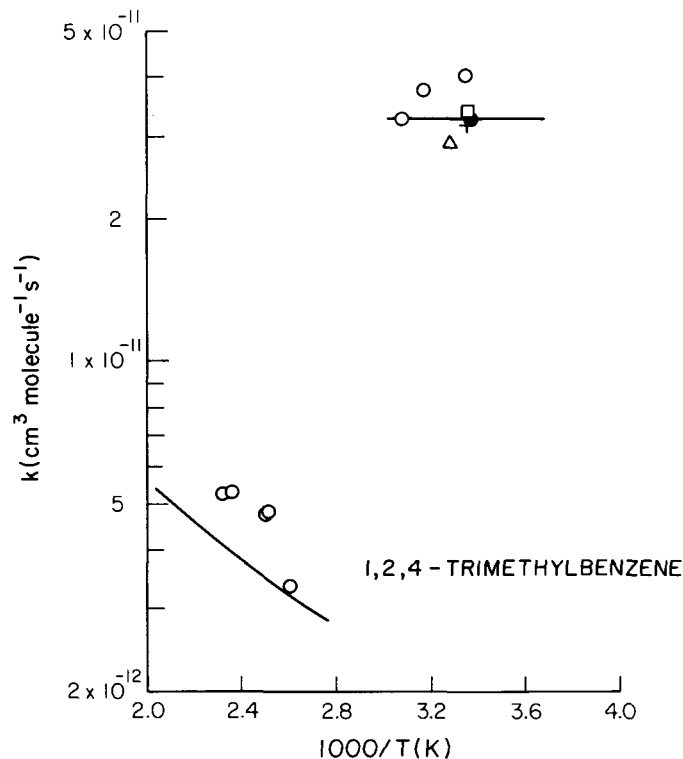


FIG. 105. Arrhenius plot of rate constants for the reaction of the OH radical with 1,2,4-trimethylbenzene. (Δ) Doyle *et al.*,² (\square) Hansen *et al.*,³ (\circ) Perry *et al.*,⁴ (\oplus) Ohta and Ohyama,¹² assuming a temperature of 298 K; (\bullet) Atkinson and Aschmann;¹⁸ (—) recommendations (see text).

At elevated temperatures ($\gtrsim 370$ – 380 K), this OH radical addition process is no longer observed experimentally, and the H-atom abstraction pathway is measured. As noted above and by Tully *et al.*,⁶ at temperatures up to ~ 450 K the OH radical addition process still appears to contribute slightly to the measured rate constants, which are thus greater than those for the abstraction reaction. Since the rate constant for H-atom abstraction from $-\text{CH}_3$ groups in the methyl-substituted benzenes depends only on the number of $-\text{CH}_3$ groups (see above and Fig. 103), for temperatures $\gtrsim 450$ K it is recommended that

$$k(\text{trimethylbenzenes}) = 2.42$$

$$\times 10^{-17} T^2 e^{-38/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

and the lines in Figs. 104 through 106 for this temperature range reflect this recommendation. As anticipated, the rate data of Perry *et al.*⁴ at temperatures ~ 370 – 430 K are somewhat higher than these recommendations.

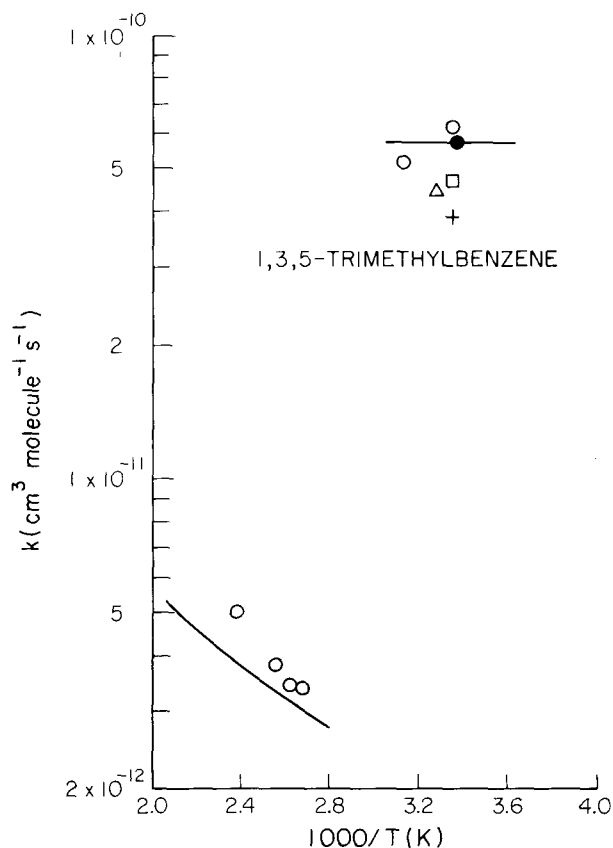


FIG. 106. Arrhenius plot of rate constants for the reaction of the OH radical with 1,3,5-trimethylbenzene. (Δ) Doyle *et al.*;² (\square) Hansen *et al.*;³ (\circ) Perry *et al.*;⁴ (\oplus) Ohta and Ohshima,¹² assuming a temperature of 298 K; (\bullet) Atkinson and Aschmann;¹⁸ (—) recommendations (see text).

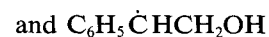
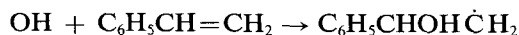
(13) Styrene

The available rate constants of Bignozzi *et al.*²⁶ and Atkinson and Aschmann²⁷ are given in Table 19. Both rate constants were obtained from relative rate studies carried out at room temperature. The agreement is good. Since in the study of Bignozzi *et al.*²⁶ the styrene was a factor of 14 more reactive than the 2,2,4-trimethylpentane reference compound, the rate constant of Atkinson and Aschmann²⁷ is preferred, leading to the recommendation of

$$k(\text{styrene}) = 5.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K},$$

with an estimated overall uncertainty of $\pm 25\%$.

The room temperature product studies of Bignozzi *et al.*²⁶ and Chiorboli *et al.*²⁸ show that the OH radical reactions with styrene and the other aromatic alkenes investigated proceed by OH radical addition to the alkene moiety, for example



At elevated temperatures, ≈ 550 – 650 K, this process is expected to become rapidly reversible, with H-atom abstraction from the various C—H bonds then becoming the important process.

(14) Phenol

The available rate constant data of Rinke and Zetzsch,¹¹ Witte and Zetzsch²⁹ and He *et al.*³⁰ are given in Table 19 and are plotted in Arrhenius form in Fig. 107.

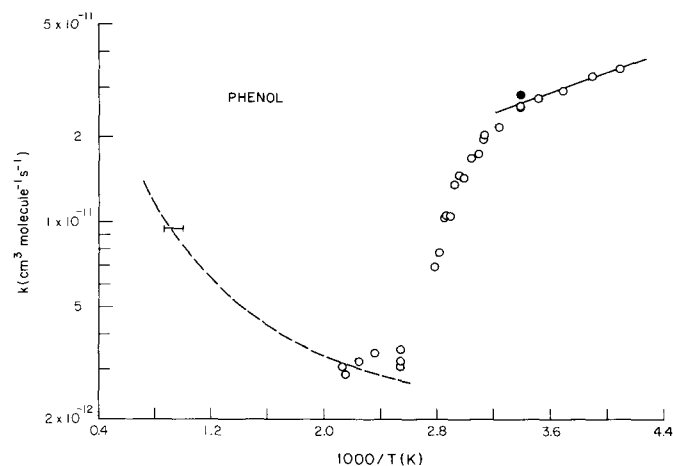


FIG. 107. Arrhenius plot of rate constants obtained at, or close to, the high-pressure limit for the reaction of the OH radical with phenol. (\bullet) Rinke and Zetzsch,¹¹ (\circ) Witte and Zetzsch,²⁹ (\ominus) He *et al.*;³⁰ (—) recommendations (see text).

Rinke and Zetzsch¹¹ observed that at room temperature the rate constant is pressure dependent below ~ 30 Torr total pressure of helium diluent, while Witte and Zetzsch²⁹ observed non-exponential OH radical decays in the temperature range 320–359 K, indicating thermal decomposition of the OH-phenol addition adduct back to reactants over this temperature range.

The room temperature rate constants of Rinke and Zetzsch¹¹ and Witte and Zetzsch²⁹ are in good agreement, and a unit-weighted least-squares analysis of the rate constants of Rinke and Zetzsch¹¹ and Witte and Zetzsch²⁹ for temperatures < 300 K leads to the recommended Arrhenius expression of

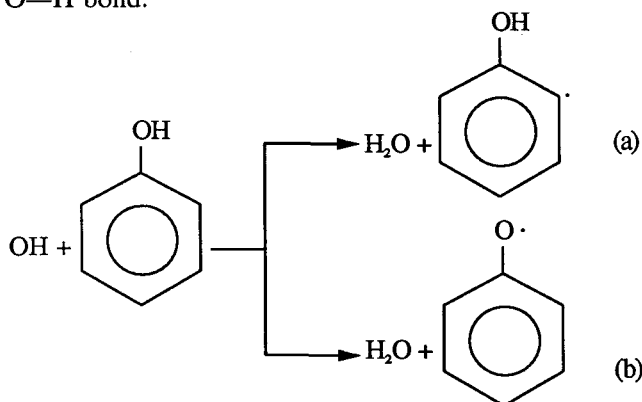
$$k(\text{phenol}; T < 300 \text{ K}) = (6.75^{+2.93}_{-2.04}) \times 10^{-12} e^{(405 \pm 100)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 245–296 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{phenol}) = 2.63 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of $\pm 30\%$.

At temperatures $\gtrsim 390 \text{ K}$, it is expected that the reaction process observed is H-atom abstraction from the C—H bonds of the aromatic ring and/or the substituent O—H bond.



From the recommended rate expression for benzene, and assuming that the rate constant for pathway (a) will be $0.83 k(\text{benzene})$ [$2.26 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 1000 K and $1.6 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 400 K], it appears that H-atom abstraction from the substituent O—H bond to form the phenoxyl radical [reaction pathway (b)] dominates below $\sim 1200 \text{ K}$, as also concluded by He *et al.*³⁰

Assuming the data of Witte and Zetzsch²⁹ and He *et al.*³⁰ at 390–1150 K to be reasonably correct, these data can be fitted by the expression,

$$k(\text{phenol}; T \gtrsim 390 \text{ K}) = 5 \times 10^{-18} T^2 e^{500/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

which is shown as the dashed line in Fig. 107. Clearly, further kinetic data are needed at elevated temperatures, $\gtrsim 400 \text{ K}$, before any firm recommendation can be made.

(15) Methoxybenzene

The available data of Perry *et al.*³¹ and Ohta and Ohyama¹² (carried out at an unspecified room temperature) are given in Table 19 and are plotted in Arrhenius form in Fig. 108 (assuming 298 K for the temperature of the Ohta and Ohyama¹² study). The agreement between these two studies^{12,31} at $\sim 299 \text{ K}$ is reasonable, especially since wall-adsorption of the methoxybenzene would be expected to occur in the static reaction vessel used by Ohta and Ohyama.¹² A unit-weighted average of the rate

constants obtained by Perry *et al.*³¹ and Ohta and Ohyama¹² at temperatures $< 325 \text{ K}$ leads to the recommendation of

$$k(\text{methoxybenzene}; T \leq 325 \text{ K}) = 1.73 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

independent of temperature over the range 298–322 K, with an estimated overall uncertainty of $\pm 35\%$.

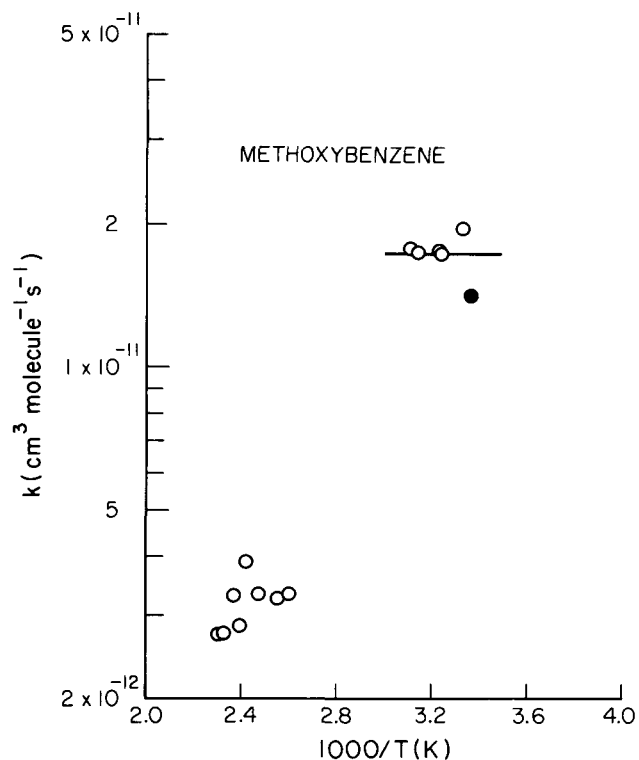


FIG. 108. Arrhenius plot of rate constants for the reaction of the OH radical with methoxybenzene. (○) Perry *et al.*³¹; (●) Ohta and Ohyama,¹² assuming a temperature of 298 K; (—) recommendation (see text).

At temperatures $\gtrsim 325 \text{ K}$, the OH-methoxybenzene addition adduct thermally decomposes³¹ and at temperatures $\gtrsim 380 \text{ K}$ only an H-atom abstraction process is observed. As for phenol, the magnitude of the measured rate constants at $\sim 400 \text{ K}$ indicates that H-atom abstraction from the —OCH₃ group



dominates over H-atom abstraction from the C—H bonds of the aromatic ring.

(16) *o*-, *m*- and *p*-Cresol

The available rate constant data of Perry *et al.*³¹ (for *o*-cresol only), Atkinson *et al.*³² and Atkinson and

Aschmann³³ are given in Table 19. The rate constant data of Perry *et al.*,³¹ Atkinson *et al.*³² and Atkinson and Aschmann³³ for *o*-cresol are plotted in Arrhenius form in Fig. 109.

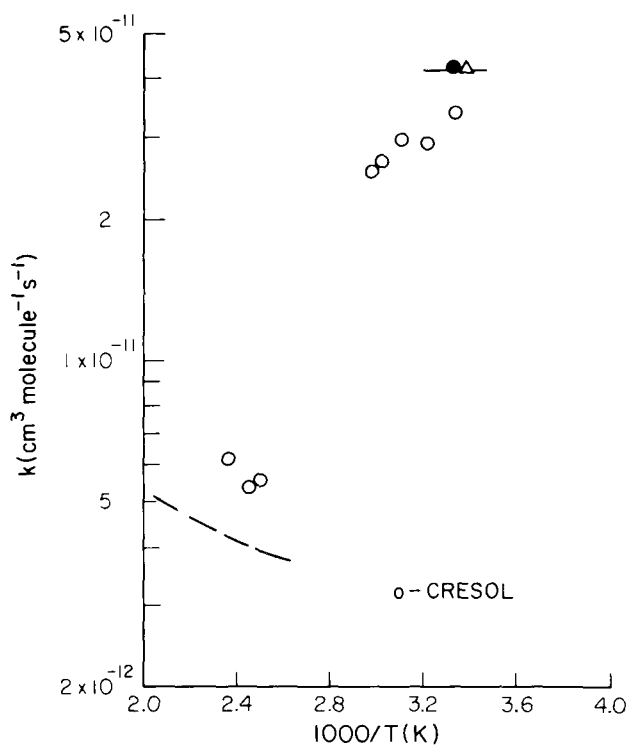


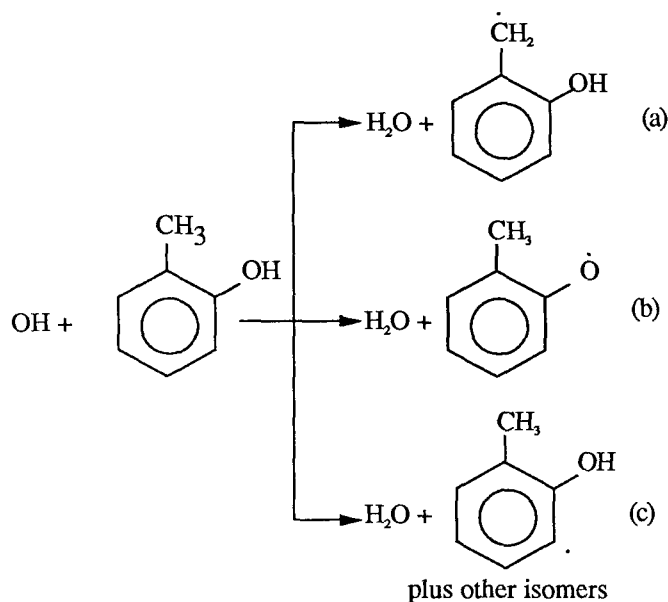
FIG. 109. Arrhenius plot of rate constants for the reaction of the OH radical with *o*-cresol. (○) Perry *et al.*,³¹ (●) Atkinson *et al.*,³² (△) Atkinson and Aschmann,³³ (— — —, —) recommendations (see text).

The room temperature rate constants of Perry *et al.*,³¹ Atkinson *et al.*³² and Atkinson and Aschmann³³ for this isomer show a discrepancy of ~25%, although they agree within the combined experimental error limits. As noted by Atkinson *et al.*,³² the rate constants determined by Perry *et al.*³¹ may have been somewhat low due to wall adsorption problems (especially in the small optical calibration cells used). Since the higher overall error limits assigned by Perry *et al.*³¹ take into account (at least in part) such adsorption problems, a weighted average of these room temperature rate constants³¹⁻³³ yields the recommendation of

$$k(o\text{-cresol}) = 4.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 300 K, with an estimated overall uncertainty of $\pm 30\%$. No recommendation is made concerning the temperature dependence of the rate constant at around room temperature.

The OH-*o*-cresol addition adduct thermally decomposes at temperatures $\gtrsim 335$ K, and at $\gtrsim 400$ K the measured OH radical reaction rate constants reflect H-atom abstraction from the C—H or O—H bonds



The magnitude of the measured rate constants at 400–425 K³¹ shows that H-atom abstraction from the C—H bonds of the aromatic ring [pathway (c)] is of minor (~3%) significance. In fact, the experimental data are consistent with the occurrence of pathways (a) and (b) with rate constants at 400 K (derived from the discussions and/or recommendations for toluene, toluene-*d*₃, the xylenes and phenol) of

$$k_a = 1.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

and

$$k_b \approx 2.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

The rate constant for the sum of pathways (a) and (b)

$$[k_a = 8.07 \times 10^{-18} T^2 e^{-38/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

$$k_b \approx 5 \times 10^{-18} T^2 e^{500/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$$

is shown in Fig. 109 as the dashed line.

From unit-weighted averages of the rate constant data of Atkinson *et al.*³² and Atkinson and Aschmann,³³ the recommended rate constants for *m*- and *p*-cresol at 298 K are then

$$k(m\text{-cresol}) = 6.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

and

$$k(p\text{-cresol}) = 4.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

both with estimated overall uncertainties of $\pm 35\%$.

(17) Fluorobenzene

The available rate constants of Zetzsch,³⁶ Ohta and Ohyama¹² and Wallington *et al.*¹⁶ are given in Table 19 and (assuming a temperature of 298 K for the Ohta and

Ohyama¹² study) are plotted in Arrhenius form in Fig. 110. The room temperature rate constants show a significant degree of scatter. Over the temperature range 234–303 K the data of Wallington *et al.*¹⁶ are, within the experimental errors, independent of temperature. From a unit-weighted average of the room temperature rate constants of Zetzsch,³⁶ Ohta and Ohyama¹² and Wallington *et al.*¹⁶ and assuming a zero temperature dependence over this temperature range, it is recommended that

$$k(\text{fluorobenzene}; T \lesssim 310 \text{ K}) = 6.9 \\ \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

independent of temperature over the range 234–303 K, with an estimated overall uncertainty over this temperature range of \pm a factor of 2.

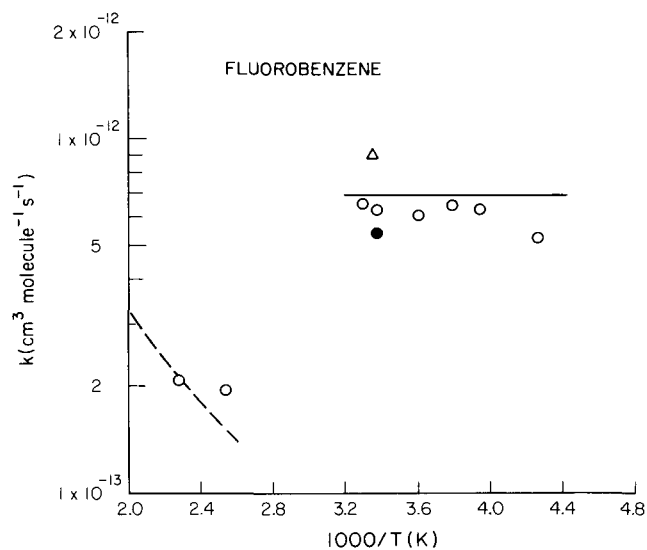


FIG. 110. Arrhenius plot of rate constants for the reaction of the OH radical with fluorobenzene. (●) Zetzsch,³⁶ (Δ) Ohta and Ohyama,¹² assuming a temperature of 298 K; (○) Wallington *et al.*¹⁶ (---, —) recommendations (see text).

Above ~ 310 K the OH-fluorobenzene addition adduct thermally decomposes¹⁶ and above ~ 390 K the measured rate constants presumably reflect an H-atom abstraction process (from the C—H bonds of the aromatic ring). Moreover, as shown in Fig. 110 by the dashed line, the measured rate constants at 393 and 438 K¹⁶ are consistent with the H-atom abstraction rate constant recommended for benzene, scaled by a factor of 0.83 to take into account the fact that fluorobenzene has only five C—H bonds. This leads to

$$k_{\text{abstraction}} \approx 3.9 \times 10^{-18} T^2 e^{-543/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

(18) Chlorobenzene

The available rate constants of Zetzsch,^{36,37} Atkinson *et al.*,³⁸ Edney *et al.*¹⁵ and Wallington *et al.*¹⁶ are given in Table 19, and those of Zetzsch,^{36,37} Atkinson *et al.*³⁸ and Wallington *et al.*¹⁶ are plotted in Arrhenius form in Fig. 111 (the rate constant of Edney *et al.*¹⁵ has a high associated uncertainty which encompasses the other room temperature rate constants,^{16,36–38} and is hence not used in the evaluation).

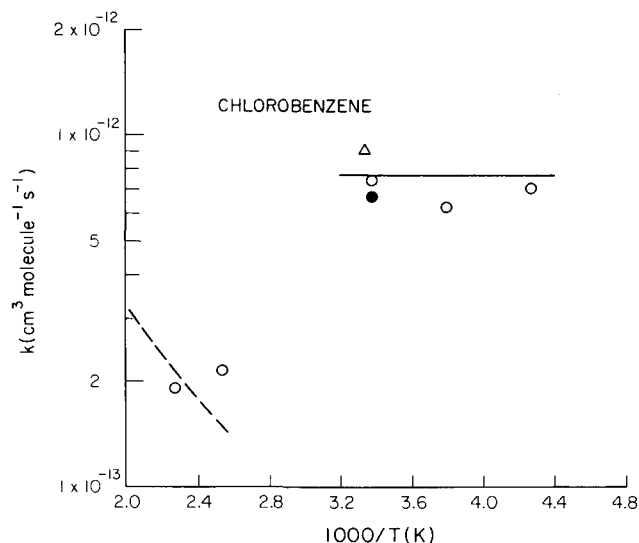


FIG. 111. Arrhenius plot of rate constants for the reaction of the OH radical with chlorobenzene. (●) Zetzsch,^{36,37} (Δ) Atkinson *et al.*,³⁸ (○) Wallington *et al.*¹⁶ (---, —) recommendations (see text).

The only temperature dependent study is that of Wallington *et al.*,¹⁶ which indicates no appreciable temperature dependence over the range 234–296 K, within the experimental error limits. A unit-weighted average of the room temperature rate constants of Zetzsch,^{36,37} Atkinson *et al.*³⁸ and Wallington *et al.*,¹⁶ with an assumed zero temperature dependence below ~ 300 K, leads to the recommendation of

$$k(\text{chlorobenzene}) = 7.7 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 234–299 K, with an estimated overall uncertainty of $\pm 40\%$ over this temperature range. As for fluorobenzene, the OH radical addition adduct thermally decomposes above ~ 300 K,¹⁶ and the measured rate constants at > 390 K presumably reflect H-atom abstraction from the C—H bonds of the aromatic ring. Again, the H-atom abstraction rate constant for benzene, scaled by a factor of 0.83, fits the measurements reasonably well, as shown by the dashed line in Fig. 111.

(19) Bromobenzene

The rate constants of Zetzsch,³⁶ Witte *et al.*¹⁴ and Wallington *et al.*¹⁶ are given in Table 19 and are plotted in Arrhenius form in Fig. 112. The absolute studies of Witte *et al.*¹⁴ and Wallington *et al.*¹⁶ show differences with respect to both the room temperature rate constant and the sign of the temperature dependence. A unit-weighted average of the entire data set^{14,16,36} below 365 K leads to the recommendation of

$$k(\text{bromobenzene}) = 7.7 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

independent of temperature over the range 234–362 K, with an estimated overall uncertainty of $\pm 40\%$ over this temperature range.

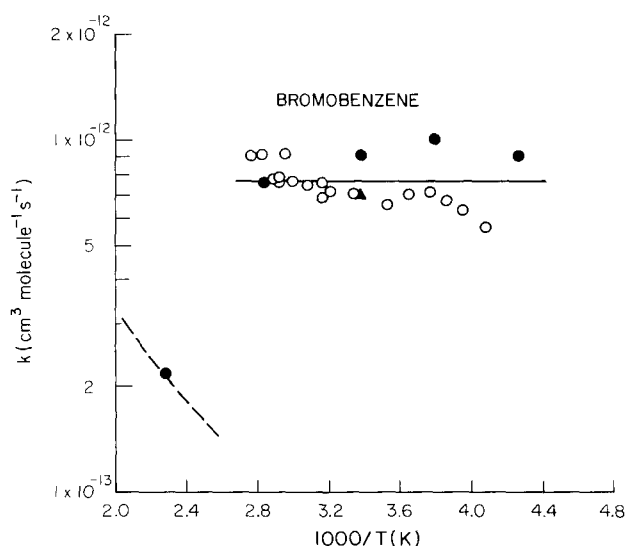


FIG. 112. Arrhenius plot of rate constants for the reaction of the OH radical with bromobenzene. (\blacktriangle) Zetzsch;³⁶ (\circ) Witte *et al.*;¹⁴ (\bullet) Wallington *et al.*;¹⁶ (— — —, —) recommendations (see text).

Thermal decomposition of the OH-bromobenzene addition adduct has been observed to occur at temperatures ≥ 316 K¹⁴ (being rapid above 353 K¹⁶). Hence the rate constant of Wallington *et al.*¹⁶ at 438 K is presumably that for H-atom abstraction from the C—H bonds of the aromatic ring. As for fluorobenzene and chlorobenzene, the magnitude of this rate constant is totally consistent with that derived from the recommendation for benzene, scaled by a factor of 0.83 (which is shown as the dashed line in Fig. 112).

(20) Iodobenzene

The rate constant data of Zetzsch³⁶ and Wallington *et al.*¹⁶ are given in Table 19. At room temperature, the rate constant of Wallington *et al.*¹⁶ is $\sim 50\%$ higher than that of Zetzsch.³⁶ A unit-weighted average of these rate con-

stants, together with the lack of a temperature dependence observed by Wallington *et al.*¹⁶ for $T \leq 393$ K, leads to

$$k(\text{iodobenzene}) = 1.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

independent of temperature over the range 263–393 K. Above ~ 400 K, thermal decomposition of the OH-iodobenzene adduct occurs,¹⁶ and H-atom abstraction is then expected to be the observed reaction pathway for temperatures ≥ 400 –500 K.

(21) Benzyl chloride

The rate constants of Edney *et al.*¹⁵ and Tuazon *et al.*,³⁹ both obtained at room temperature from relative rate studies, are in excellent agreement (Table 19). A unit-weighted average of these data^{15,39} leads to the recommendation of

$$k(\text{benzyl chloride}) = 2.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty of $\pm 30\%$.

(22) Aniline

The available rate constant data of Rinke and Zetzsch,¹¹ Witte *et al.*¹⁴ and Atkinson *et al.*⁴⁰ are given in Table 19 and are plotted in Arrhenius form in Fig. 113.

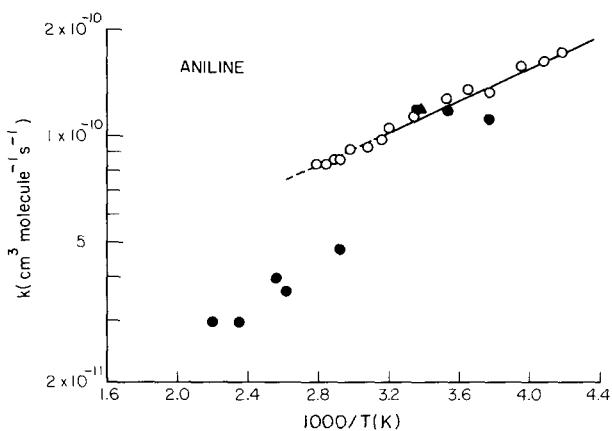


FIG. 113. Arrhenius plot of rate constants for the reaction of the OH radical with aniline. (\blacktriangle) Rinke and Zetzsch;¹¹ (\circ) Witte and Zetzsch;¹⁴ (\bullet) Atkinson *et al.*;⁴⁰ (—) recommendation (see text).

Rinke and Zetzsch¹¹ observed that at room temperature the rate constant was independent of total pressure of helium diluent down to the lowest pressure studied (~ 15 Torr). Witte *et al.*¹⁴ observed biexponential OH radical

decays for temperatures ≥ 336 K, showing that thermal decomposition of the OH-aniline addition adduct was occurring. This observation¹⁴ is in reasonable agreement with the observation by Atkinson *et al.*⁴⁰ of non-exponential OH radical decays at temperatures ≥ 310 K.

The rate constants measured by Atkinson *et al.*⁴⁰ at 265–298 K are in agreement, within the experimental errors, with the much more extensive data set of Witte *et al.*¹⁴ (note that for the temperature regime where the OH-aniline adduct decomposes the OH radical addition rate constants were obtained¹⁴ from the biexponential OH radical decay curves).

Accordingly, for the temperature region $T \leq 360$ K a unit-weighted least-squares analysis of the rate constants of Rinke and Zetzsch,¹¹ Witte *et al.*¹⁴ and the 265, 283 and 298 K data points of Atkinson *et al.*⁴⁰ yields the recommended Arrhenius expression of

$$k(\text{aniline}; T \leq 360 \text{ K}) = (1.94^{+0.52}_{-0.41}) \times 10^{-11} e^{(519 \pm 69)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 239–359 K (but see below), where the indicated errors are two least-squares standard deviations, and

$$k(\text{aniline}) = 1.11 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty at 298 K of $\pm 25\%$. It must be noted, however, that thermal decomposition of the OH-aniline addition adduct begins to occur at ~ 310 – 335 K,^{14,40} and hence the above recommendation is only valid for the temperature range $\lesssim 320$ K unless thermal decomposition of the addition adduct is taken into account.

No recommendation is made concerning the OH radical reaction rate constants at temperatures $\gtrsim 380$ K.

(23) Nitrobenzene

The available kinetic data of Zetzsch,^{14,36,37} Atkinson *et al.*⁴⁰ and Witte *et al.*¹⁴ are given in Table 19. The upper limits to the room temperature rate constants measured by Atkinson *et al.*⁴⁰ are consistent with the data of Zetzsch^{14,36,37} (as revised¹⁴) and Witte *et al.*¹⁴ The sole temperature-dependence study is that of Witte *et al.*¹⁴ who observed non-exponential OH radical decays over the entire temperature range studied, possibly due to regeneration of OH radicals from photolysis fragments.¹⁴

(24) Hexafluorobenzene

The available rate constants of Ravishankara *et al.*²⁰ and Wallington *et al.*¹⁶ are given in Table 19, and are plotted in Arrhenius form in Fig. 114. The room temperature rate constant of Ravishankara *et al.*²⁰ is $\sim 35\%$ higher than that of Wallington *et al.*¹⁶ A unit-weighted least-squares analysis of the rate constants of Ravishankara *et al.*²⁰ and Wallington *et al.*¹⁶ leads to the recommendation of

$$k(\text{hexafluorobenzene}) = (1.46^{+0.91}_{-0.56}) \times 10^{-12} e^{-(638 \pm 148)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 234–438 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{hexafluorobenzene}) = 1.72 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty at 298 K of $\pm 40\%$.

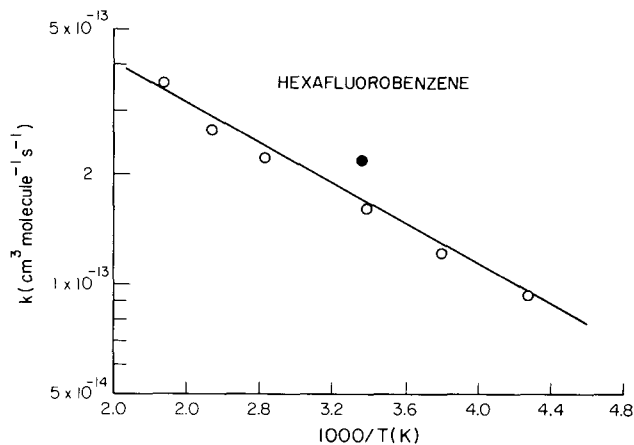


FIG. 114. Arrhenius plot of rate constants for the reaction of the OH radical with hexafluorobenzene. (●) Ravishankara *et al.*;²⁰ (○) Wallington *et al.*;¹⁶ (—) recommendation (see text).

Wallington *et al.*¹⁶ observed no evidence for thermal decomposition of the OH-hexafluorobenzene addition adduct over the temperature range (234–438 K) studied. Clearly, kinetic data are needed at elevated temperatures of $\gtrsim 500$ K.

(25) Biphenyl

The rate constants of Zetzsch,^{36,37} Atkinson *et al.*,⁴³ Atkinson and Aschmann⁴⁴ and Klöpffer *et al.*,²² all obtained at room temperature, are given in Table 19. These studies^{22,36,37,43,44} are in generally good agreement, although the rate constant determined by Zetzsch^{36,37} (which required knowledge of the vapor pressure of biphenyl) is lower by $\sim 25\%$ than the other values. Since no details are available concerning the study of Klöpffer *et al.*,²² the rate constant from that study is not used in the evaluation. A unit-weighted average of the room temperature rate constants of Zetzsch,^{36,37} Atkinson *et al.*⁴³ and Atkinson and Aschmann⁴⁴ leads to the recommendation of

$$k(\text{biphenyl}) = 7.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty of $\pm 30\%$. This rate constant is that for OH radical addition to the aromatic rings. At temperatures ≈ 400 K the OH-biphenyl adduct will rapidly thermally decompose and only H-atom abstraction from the C—H bonds of the aromatic rings will be observed. Based upon the recommendation for benzene at temperatures ≈ 450 K, it is expected that the rate constant for H-atom abstraction from biphenyl will be

$$k_{\text{abstraction}} \approx 7.8 \times 10^{-18} T^2 e^{-543/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

(26) Naphthalene

The available rate constants obtained at, or close to, the high-pressure limit are given in Table 19 and those of Lorenz and Zellner,^{8,9} Atkinson *et al.*,⁴³ Biermann *et al.*⁴⁸ and Atkinson and Aschmann⁴⁹ are plotted in Arrhenius form in Fig. 115. Lorenz and Zellner⁸ have shown that at 378 ± 2 K the rate constant for this reaction is in the fall-off region between second- and third-order kinetics below ~ 50 Torr total pressure of helium, but that no such fall-off behavior is observed at 525 ± 1 K.

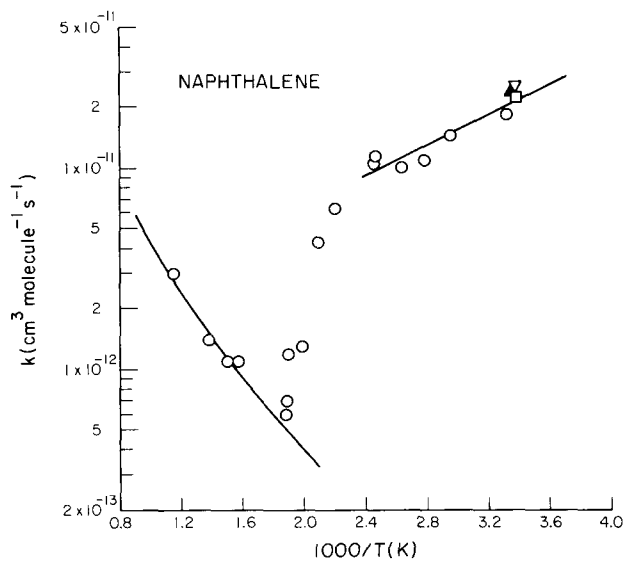


FIG. 115. Arrhenius plot of rate constants obtained at, or close to, the high-pressure limit for the reaction of the OH radical with naphthalene. (○) Lorenz and Zellner;^{8,9} (□) Atkinson *et al.*;⁴³ (▲) Biermann *et al.*;⁴⁸ (▽) Atkinson and Aschmann;⁴⁹ (—) recommendations (see text).

At temperatures ≤ 410 K the rate constants obtained by Lorenz and Zellner,^{8,9} Atkinson and co-workers^{43,48,49} and Klöpffer *et al.*²² are in good agreement (the rate constant of Klöpffer *et al.*²² is not used in the evaluation because of a lack of details). A unit-weighted least-squares analysis of the data of Lorenz and Zellner,^{8,9}

Atkinson *et al.*,⁴³ Biermann *et al.*⁴⁸ and Atkinson and Aschmann⁴⁹ yields the recommended Arrhenius expression of

$$k(\text{naphthalene}, T \leq 410 \text{ K}) = (1.07^{+1.14}_{-0.55}) \times 10^{-12} e^{(895 \pm 239)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 294–407 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{naphthalene}) = 2.16 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty of $\pm 30\%$ at 298 K.

At elevated temperatures, ≥ 600 K for this particular aromatic hydrocarbon,^{8,9} the only rate constants available are those of Lorenz and Zellner.⁹ A unit-weighted least-squares fit of these data,⁹ using the expression $k = CT^2 e^{-D/T}$, yields the recommendation of

$$k(\text{naphthalene}; T \geq 600 \text{ K}) = (1.12^{+2.12}_{-0.73}) \times 10^{-17} T^2 e^{-(969 \pm 752)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 636–873 K, where the indicated errors are two least-squares standard deviations.

(27) Phenanthrene

The available rate constants of Lorenz and Zellner⁹ and Biermann *et al.*⁴⁸ are given in Table 19 and are plotted in Arrhenius form in Fig. 116.

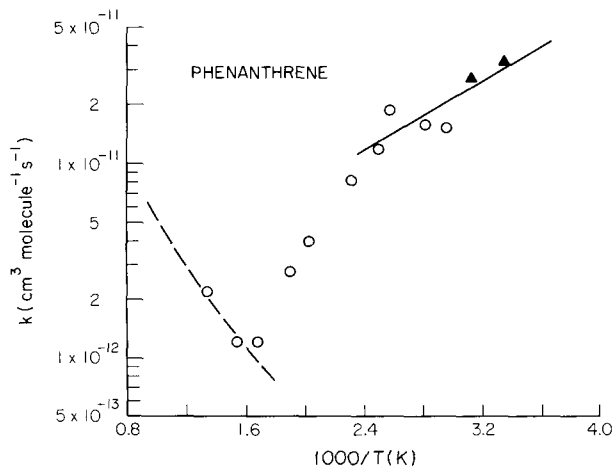


FIG. 116. Arrhenius plot of rate constants for the reaction of the OH radical with phenanthrene. (○) Lorenz and Zellner;⁹ (▲) Biermann *et al.*;⁴⁸ (—, —) recommendations (see text).

The rate constants obtained by Biermann *et al.*⁴⁸ from a relative rate study are consistent with the higher temperature ($T \geq 338$ K) data of Lorenz and Zellner.⁹ For the temperature range ≤ 410 K (the same as for naphthalene) a unit-weighted least-squares analysis of the data of Lorenz and Zellner⁹ and Biermann *et al.*⁴⁸ yields the recommendation of

$$k(\text{phenanthrene}; T \leq 410 \text{ K}) = (1.02^{+5.41}_{-0.86}) \times 10^{-12} e^{(1021 \pm 634)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 298–399 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{phenanthrene}) = 3.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty at 298 K of \pm a factor of 2.

At elevated temperatures, where thermal decomposition of the OH-phenanthrene adduct is sufficiently rapid that only the H-atom abstraction process is observed, data are available only at 648 and 748 K.⁹ Since there are ten aromatic ring C—H bonds on phenanthrene versus eight on naphthalene, it is expected that the H-atom abstraction rate constant for phenanthrene will be 1.25 that for naphthalene,

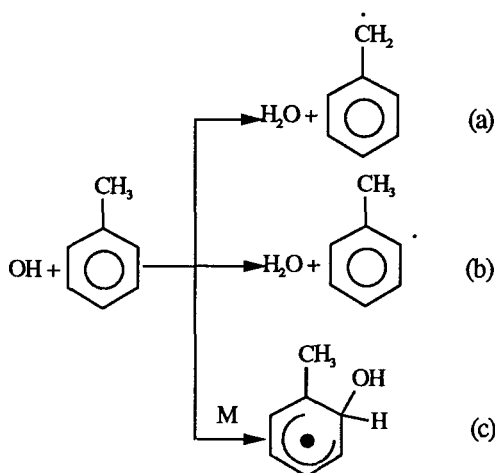
$$k(\text{phenanthrene}; T \geq 600 \text{ K}) = 1.40 \times 10^{-17} T^2 e^{-969/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

and this expression, shown as the dashed line in Fig. 116, is in good agreement with the limited data available in this temperature regime.

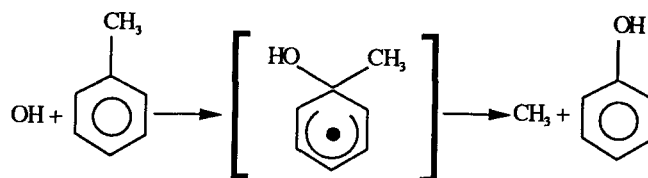
b. Mechanism

The available data discussed above, together with product data,^{42,56-73} show that in general two reaction pathways can occur: a direct reaction involving H-atom abstraction from the aromatic ring C—H bonds or from X—H bonds ($X = \text{C}, \text{O}, \text{N}, \text{S}$) of the substituent group(s), and OH radical addition to the aromatic ring.

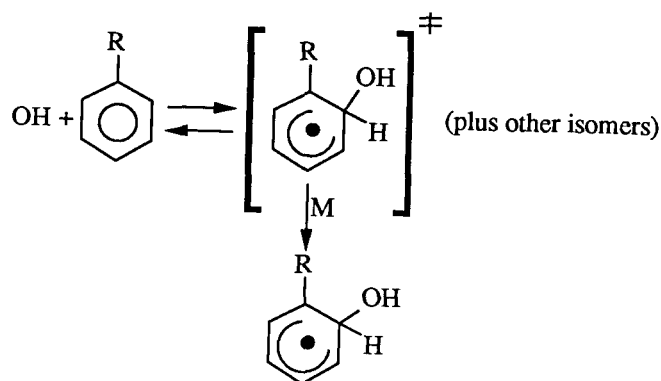
For example, for toluene



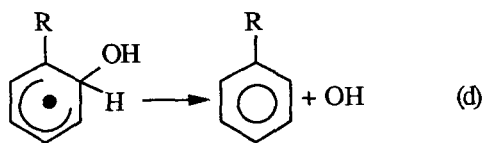
Reaction leading to substituent group (or H-atom) elimination, for example



does not appear to be of any significance.^{13,30} The hydroxycyclohexadienyl radical formed from OH radical addition to benzene has been observed and its reactions with O_2 , NO and NO_2 studied.^{66,70} The initially energy-rich OH radical addition adducts can either decompose back to reactants or be collisionally stabilized.



A further reaction step involves the unimolecular decomposition of this thermalized OH-aromatic adduct back to the reactants



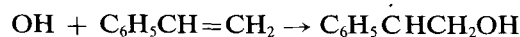
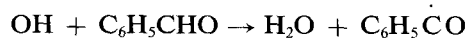
and this reaction pathway obviously becomes more rapid as the temperature increases.

Indeed, it is this thermal back-decomposition of the OH-aromatic adduct which gives rise to the non-exponential OH radical decays observed in the flash or laser photolysis kinetic studies and to the occurrence of distinct temperature regimes with differing kinetic behavior. The thermal decomposition rate constant of the OH-aromatic adduct, k_d , can be estimated from the temperature region over which non-exponential OH radical decays are observed^{4,8,16,31} and, more accurately, from numerical analysis of the time-dependent behavior of the OH radical decays in this temperature region.^{10,14,29} The available data (or estimates) for the Arrhenius parameters of these thermal decomposition rate constants are given in Table 20. (These data, and the recommended Arrhenius expression calculated for the hydroxycyclohexadienyl radical, are assumed to be at, or close to, the high-pressure limit, although it is likely that at temperatures $\gtrsim 350$ K this rate constant k_d will be significantly into the fall-off region at total pressures below approximately one atmosphere.)

For benzene, the available values of k_d are plotted in Arrhenius form in Fig. 117, and the recommended thermal decomposition rate of the hydroxycyclohexadienyl radical, obtained from a unit-weighted least-squares analysis of the data of Wahner and Zetzsch¹⁰ and Witte *et al.*,¹⁴ is given in Table 20. The thermal decomposition rates of the methyl-substituted benzenes and other monocyclic aromatics studied are reasonably similar at ~ 300 – 400 K. Thus, for benzene the thermalized hydroxycyclohexadienyl radical has a lifetime with respect to thermal decomposition of ~ 0.3 sec at 298 K, ~ 0.03 sec at 325 K, ~ 0.6 ms at 380 K and ~ 0.2 ms at 400 K, and these lifetimes are reasonably representative of those for the methyl-substituted benzenes and other monocyclic aromatics. These lifetimes are then totally consistent with the above discussion of the reaction dynamics of these OH radical reactions.

Thus, for most of the aromatic compounds studied, at around room temperature, i.e., ≤ 325 K, OH radical addition to the aromatic ring dominates, while for temperatures $\gtrsim 450$ K ($\gtrsim 600$ K for the OH-naphthalene adduct^{8,9}) back-dissociation of the OH-aromatic adducts becomes so rapid that on the time scale of the flash or laser photolysis studies carried out to date only the direct reaction involving H-atom abstraction is observed.

Apart from benzaldehyde (and presumably other aromatic aldehydes) and the aromatic alkenes such as styrene, where at room temperature the reactions proceed by H-atom abstraction from the $-\text{CHO}$ group and by OH radical addition to the alkene $>\text{C}=\text{C}<$ bond, respectively,



the major fraction of the OH radical reactions with the aromatic compounds studied to date proceeds by OH radical addition to the aromatic ring at around room temperature.

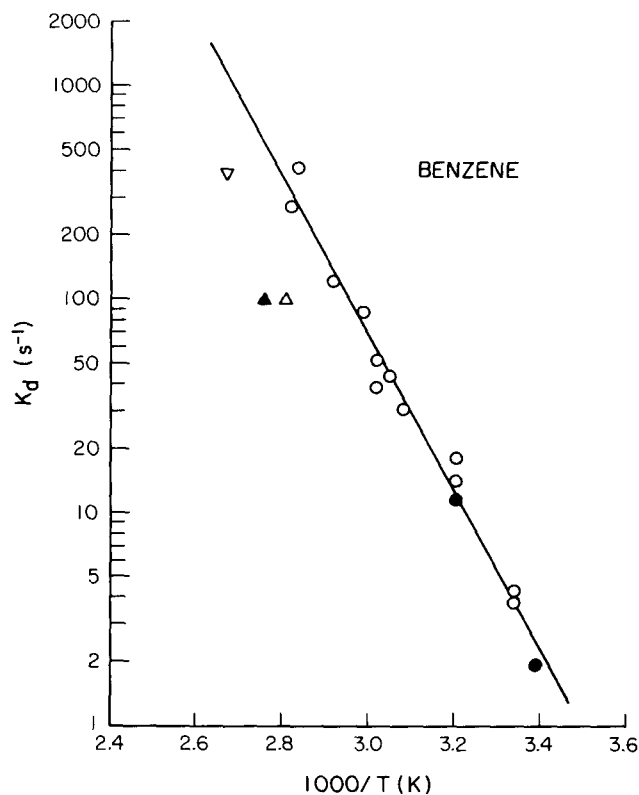


FIG. 117. Arrhenius plot of rate constants k_d for the thermal decomposition of the hydroxycyclohexadienyl radical formed from OH radical addition to benzene. (Δ) Perry *et al.*,⁴ (∇) Lorenz and Zellner,⁸ (\bullet) Wahner and Zetzsch,¹⁰ (\circ) Witte and Zetzsch,¹⁴ (\blacktriangle) Wallington *et al.*,¹⁶ (—) recommendation (see text and Table 20).

The fractions of the overall reactions proceeding by H-atom abstraction from the C—H bonds of the aromatic ring or from X—H bonds of the substituent groups (X = C or O) can be estimated from the kinetic recom-

mendations given above. Table 21 gives estimated rate constant ratios $k_{\text{abs}}/k_{\text{total}}$ at 298 K for benzene, naphthalene and phenanthrene and the substituted benzenes for which estimates can be made, where k_{abs} and k_{total} are the rate constants for the H-atom abstraction reaction

and the overall reaction, respectively. For toluene and the xylenes, these estimates, derived from extrapolations of the elevated temperature (generally ≥ 450 K) rate constants, are in agreement, within the likely uncertainties, with recent product data.^{42,59,60,62,64,65,67-69,72}

TABLE 20. Thermal decomposition rate constants, $k_d = A_d e^{-B_d/T}$, for OH aromatic addition adducts

Aromatic	A_d (s^{-1})	B_d (K)	Reference
Benzene	3×10^{13} ^a	9410 ± 1000	Perry <i>et al.</i> ⁴
	4×10^{13} ^a	9500 ± 720	Lorenz and Zellner ⁸
	3×10^{13} ^a	8960 ± 690	Wahner and Zetzsch ¹⁰
	3×10^{12}	8180 ± 720	Witte <i>et al.</i> ¹⁴
	3×10^{13} ^a	9560	Wallington <i>et al.</i> ¹⁶
	9.4×10^{12}	8540 ± 750	Recommended ^b
Toluene	3×10^{13} ^a	9110 ± 1000	Perry <i>et al.</i> ⁴
<i>o</i> -Xylene	3×10^{13} ^a	9260 ± 1000	Perry <i>et al.</i> ⁴
<i>m</i> -Xylene	3×10^{13} ^a	9010 ± 1000	Perry <i>et al.</i> ⁴
<i>p</i> -Xylene	3×10^{13} ^a	9410 ± 1000	Perry <i>et al.</i> ⁴
1,2,3-Trimethylbenzene	3×10^{13} ^a	9360 ± 1000	Perry <i>et al.</i> ⁴
1,2,4-Trimethylbenzene	3×10^{13} ^a	9210 ± 1000	Perry <i>et al.</i> ⁴
1,3,5-Trimethylbenzene	3×10^{13} ^a	9110 ± 1000	Perry <i>et al.</i> ⁴
Phenol	1×10^{13}	8900 ± 1300	Witte and Zetzsch ²⁹
Methoxybenzene	3×10^{13} ^a	9110 ± 1000	Perry <i>et al.</i> ³¹
<i>o</i> -Cresol	3×10^{13} ^a	9610 ± 1000	Perry <i>et al.</i> ³¹
Fluorobenzene	3×10^{13} ^a	9560	Wallington <i>et al.</i> ¹⁶
Chlorobenzene	3×10^{13} ^a	10070	Wallington <i>et al.</i> ¹⁶
Bromobenzene	2×10^{10}	6740 ± 600	Witte <i>et al.</i> ¹⁴
	3×10^{13} ^a	10570	Wallington <i>et al.</i> ¹⁶
Iodobenzene	3×10^{13} ^a	11580	Wallington <i>et al.</i> ¹⁶
Aniline	6×10^{11}	8420 ± 1080	Witte <i>et al.</i> ¹⁴
Naphthalene	4×10^{13} ^a	11430 ± 720	Lorenz and Zellner ⁸

^aValue of A_d assumed or estimated.

^bCalculated from unit-weighted least-squares analysis of the thermal decomposition rate constants reported by Wahner and Zetzsch¹⁰ and Witte *et al.*¹⁴

TABLE 21. Rate constant ratios $k_{\text{abs}}/k_{\text{total}}$ at 298 K for the gas-phase reactions of the OH radical with a series of aromatic compounds

Aromatic	$k_{\text{abs}}/k_{\text{total}}$ at 298 K ^a
Benzene	0.05
Benzene- <i>d</i> ₆	0.02
Toluene	0.12
Toluene- <i>d</i> ₃	0.04
<i>o</i> -Xylene	0.10
<i>m</i> -Xylene	0.04
<i>p</i> -Xylene	0.08
1,2,3-Trimethylbenzene	0.06
1,2,4-Trimethylbenzene	0.06
1,3,5-Trimethylbenzene	0.03
Phenol	~0.09
Methoxybenzene	~0.14
<i>o</i> -Cresol	~0.07
Naphthalene	0.0018
Phenanthrene	0.0015

^aFrom extrapolation of the elevated temperature rate constant data to 298 K, using the recommendations (see text) for the rate constants k_{abs} and k_{total} . These extrapolated values are expected to be subject to uncertainties of the order of $\pm 50\%$.

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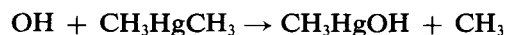
2.12. Organometallic Compounds

a. Kinetics

The available rate constant data are listed in Table 22. Only three organometallic compounds have been studied to date, and for tetramethyl- and tetraethyl lead two kinetic studies have been carried out at room temperature by Harrison and Laxen² and Nielsen *et al.*³ However, the rate constants reported for tetraethyl lead^{2,3} disagree by a factor of ~ 7 . Thus, although the two rate constants for tetramethyl lead^{2,3} (obtained from the same studies as those for tetraethyl lead^{2,3}) are in reasonable agreement, no recommendations are made.

b. Mechanisms

The sole product study carried out concerning the reactions of OH radicals with organometallic compounds under atmospheric conditions is that of Niki *et al.*¹ for CH_3HgCH_3 . It was concluded from this FT-IR absorption spectroscopy study¹ that the initial reaction proceeds via a displacement process,



followed by subsequent oxidation of the CH_3 radical to formaldehyde and other minor products, and by further homogeneous and/or heterogeneous reactions of CH_3HgOH to yield compounds such as $[(\text{CH}_3\text{Hg})_3\text{O}]\text{NO}_3$.¹ The occurrence of such a displacement reaction is consistent with the magnitude of the rate constant observed.¹

For the tetraalkyl lead compounds studied, neither the initial reaction pathways nor the products under atmospheric conditions are known, although again displacement mechanisms leading to the initial formation of $(\text{CH}_3)_3\text{PbOH}$ and $(\text{C}_2\text{H}_5)_3\text{PbOH}$ are possible.

TABLE 22. 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
<i>Organomercury Compounds</i>				
Dimethyl mercury	19.7 ± 1.6	~ 300	RR [relative to $k(\text{ethene}) = 8.44 \times 10^{-12}$] ^a	Niki <i>et al.</i> ¹
	18.4 ± 1.5	~ 300	RR [relative to $k(\text{propene}) = 2.60 \times 10^{-11}$] ^a	Niki <i>et al.</i> ¹
<i>Organolead Compounds</i>				
Tetramethyl lead	9.0	295 ± 3	RR [relative to $k(\text{toluene}) = 6.03 \times 10^{-12}$] ^a	Harrison and Laxen ²
	6.3 ± 1.4	296	PR-RA	Nielsen <i>et al.</i> ³
Tetraethyl lead	80	295 ± 3	RR [relative to $k(m\text{-xylene}) = 2.36 \times 10^{-11}$] ^a	Harrison and Laxen ²
	11.6 ± 1.7	296	PR-RA	Nielsen <i>et al.</i> ³

^aFrom the present recommendations (see text).

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2.13. Organic Radicals

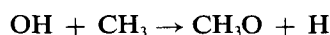
The available kinetic data are given in Table 23. As may be expected, few direct studies have been carried out due to the difficulties of investigating radical-radical reactions.

a. CH_3

In addition to the rate constants given in Table 23, Roth and Just⁸ have derived, from computer modeling of $\text{CH}_4\text{—O}_2$ and $\text{CH}_3\text{—O}_2$ systems, a rate constant of

$$k(\text{CH}_3) = 3.3 \times 10^{-9} e^{-9580/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

for the reaction



over the temperature range 1800–2300 K, with

$$k(\text{CH}_3) = (1.3\text{--}1.8)$$

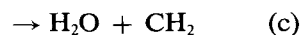
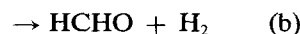
$$\times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 1800 \text{ K}$$

and

$$k(\text{CH}_3) = (4.2\text{--}5.8)$$

$$\times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 2300 \text{ K}.$$

At around room temperature, the reaction of OH radicals with CH_3 radicals probably proceeds mainly by addition.³ However, at elevated temperatures the rate constant for the addition reaction will be far into the fall-off regime and only direct reaction pathways, such as

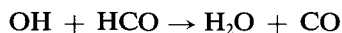


will be observed. Roth and Just⁸ conclude from their computer modeling study that reaction (c) cannot be the sole reaction pathway occurring at $\sim 1800\text{--}2300$ K.

b. HCO

The only reasonably direct measurement is that of Temps and Wagner.⁴ Seery⁹ has inferred a rate constant for this reaction of $(8 \pm 8) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

at 1700–2000 K from induction time measurements. Clearly, this reaction is rapid and proceeds by



The meager data available^{4,9} can be fitted by the expressions

$$k(\text{HCO}) = 7 \times 10^{-11} e^{350/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

or

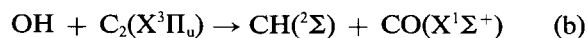
$$k(\text{HCO}) = 2.2 \times 10^{-10} (T/298)^{-0.5} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

c. $\text{C}_2(\text{X}^3\Pi_u)$

The data of Bulewicz *et al.*⁵ refer to the overall rate constant for the reactions



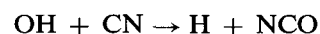
and



From earlier flame studies, Porter *et al.*¹⁰ estimated that $k_b/k_a \sim 0.1$ over the temperature range ~ 900 – 1700 K, and hence it appears that reaction (a) dominates.

d. CN

The rate constants derived by Morley⁶ and Haynes⁷ for the reaction



are in good agreement.

TABLE 23. Rate constants k for the gas-phase reactions of the OH radical with organic radicals

Organic Radical	$10^{12} \times k$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference
CH ₃	4.3 ± 0.5	1970–2185	Flame-MS	Fenimore ¹
	10	1800–1958	Flame-MS	Jones and Fenimore ²
	93 ± 25^a	296	FP-RA; Computer modeling	Sworski <i>et al.</i> ³
HCO	220 ± 80	296	RR [relative to $k(\text{HCHO}) = 9.78 \times 10^{-12}$] ^b	Temps and Wagner ⁴
$\text{C}_2(\text{X}^3\Pi_u)$	8 ± 4	2200	Flame-optical absorption	Bulewicz <i>et al.</i> ⁵
CN	100	2300–2560	Flame-MS	Morley ⁶
	93 ± 12	1950–2380	Flame-product study	Haynes ⁷

^aAt atmospheric pressure.

^bFrom the present recommendation (see text).

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2.14. Addendum

Two 1988 publications^{1,2} which included rate constant data for the gas-phase reactions of the OH radical with

oxygen-containing organic compounds were inadvertently overlooked and the data omitted from Sec. 2.6. Both studies used absolute techniques and the rate constants obtained are given below.

Organic	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference
Acetone- <i>d</i> ₆	0.0358 ± 0.0029	298	FP-RF	Wallington <i>et al.</i> ¹
1,1,1-Trifluoroacetone	0.0151 ± 0.0013	298	FP-RF	Wallington <i>et al.</i> ¹
Methanol	0.88 ± 0.18	298	PR-RA	Pagsberg <i>et al.</i> ²
Methanol- <i>d</i> ₄	0.323 ± 0.002	298	FP-RF	Wallington <i>et al.</i> ¹
Ethanol- <i>d</i> ₆	1.15 ± 0.09	298	FP-RF	Wallington <i>et al.</i> ¹
2-Chloroethanol	1.28 ± 0.09	298	FP-RF	Wallington <i>et al.</i> ¹
2,2,2-Trichloroethanol	0.245 ± 0.024	298	FP-RF	Wallington <i>et al.</i> ¹
2,2,2-Trifluoroethanol	0.0955 ± 0.0071	298	FP-RF	Wallington <i>et al.</i> ¹
1,2-Epoxy-butane	1.91 ± 0.08	298	FP-RF	Wallington <i>et al.</i> ¹

The rate constant of Pagsberg *et al.*² for methanol is in agreement with the recommendation (Sec. 2.6) and those of Wallington *et al.*¹ for 2-chloroethanol and 1,2-epoxybutane are in agreement with the rate constants given in Table 11. However, the rate constant determined by Wallington *et al.*¹ for methanol-*d*₄ is 60% higher than that of McCaulley *et al.*³ (Table 11).

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3. Conclusions

The available (through 1988) kinetic and mechanistic data for the gas-phase reactions of the OH radical with organic compounds have been compiled and evaluated in the above sections. For a large number of compounds, temperature dependent rate expressions have been recommended, often over large temperature ranges which extend from room temperature or below to around 1000 K. However, there is still a paucity of reliable kinetic data at the elevated temperatures characteristic of combustion conditions. Just as important, there is a seri-

ous lack of knowledge concerning the reaction mechanisms and products formed under combustion conditions, and it must be recognized by combustion chemists and modelers that for many organic compounds the reaction mechanisms and products observed at around room temperature are not applicable at temperatures >600 K. This is clearly true for those reactions which proceed by an OH radical addition process at "low" (<300 K) temperatures, since fall-off effects and thermal decomposition of the addition adducts result in the addition reaction pathways being of generally negligible importance at temperatures >1000 K and only direct reactions, often involving H-atom abstraction, are operable. Obvious examples are the OH radical reactions with the alkenes, alkynes and aromatic hydrocarbons, which proceed by OH radical addition at room temperature and atmospheric pressure, but by H-atom abstraction under combustion conditions.

It is also clear that experimental data are only available for a small number of the organic compounds encountered as a result of biogenic and anthropogenic activities. Although not dealt with here in any detailed manner, estimation procedures are available for the calculation of rate constants for the reactions of the OH radical with organic compounds of low-to-moderate complexity,¹⁻⁴ and these references can be consulted for details. Hopefully, future experimental studies will continue to expand the present kinetic and mechanistic data base to more complex organics and to both higher and lower temperatures.

References

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