

Evaluated Kinetic Data for High-Temperature Reactions. Volume 5. Part 1. Homogeneous Gas Phase Reactions of the Hydroxyl Radical with Alkanes

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D. L. Baulch, M. Bowers, D. G. Malcolm, and R. T. Tuckerman



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Evaluated Kinetic Data for High-Temperature Reactions

Volume 5. Part 1. Homogeneous Gas Phase Reactions of the Hydroxyl Radical with Alkanes

D. L. Baulch, M. Bowers, D. G. Malcolm, and R. T. Tuckerman

Department of Physical Chemistry, University of Leeds, Leeds, LS2 9JT, England

The available kinetic data for the homogeneous gas phase reactions of the hydroxyl radical with alkanes have been compiled and critically evaluated. For each reaction, relevant thermodynamic data, a table of measured rate constants, a discussion of the data, and a comprehensive bibliography are presented. Wherever possible the preferred rate parameters are given with their associated error limits and temperature ranges.

Key words: chemical kinetics; critical evaluation; gas phase; hydroxyl radical; alkanes; rate constant.

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1. Introduction

The work presented here is output from the kinetics data evaluation project in the Department of Physical Chemistry, University of Leeds. The aims of this project are to (a) select specific homogeneous reactions of importance in high-temperature systems, (b) prepare for each reaction a comprehensive tabulation of the available reaction rate data, (c) evaluate critically the existing data and, wherever possible, recommend reliable values for the rate parameters, and

(d) produce the material in a format convenient for use by both specialist and nonspecialist.

High-temperature systems of greatest practical importance involve reactions of atoms, small radicals, and molecules, composed of the elements hydrogen, carbon, nitrogen, oxygen, sulphur, fluorine, and chlorine. Even restricting our interest to the homogeneous gas phase reactions of these leaves a formidable number of possible reactions; selection is unavoidable. We have concentrated our attention on those reactions for which sufficient rate data exist to allow some critical assessment. However, we have included other reactions which are related to those critically assessed or which may be important in either high-temperature processes or related low-temperature systems. No doubt some reactions of interest will have been overlooked and we hope that users

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of these tables will not hesitate to inform us of such omissions.

The present work is the first part of Vol. 5 in a series planned to cover all the major areas of high-temperature gas phase kinetics. The previous four volumes in the series deal with the systems $\text{H}_2\text{-O}_2$ (Vol. 1, Butterworth and Co., 1972), $\text{N}_2\text{-N}_2\text{-O}_2$ (Vol. 2, Butterworth and Co., 1974), $\text{O}_2\text{-O}_3$, $\text{CO-O}_2\text{-H}_2$, and sulphur-containing species (Vol. 3, Butterworth and Co., 1976), halogen- and cyanide-containing species (Vol. 4, J. Phys. Chem. Ref. Data 10, Suppl. 1, 1981), and were all published as separate books. The decision to fragment Vol. 5 and publish the parts separately was taken because the material being evaluated in this volume (reactions of H, OH, O, and HO_2 with alkanes) is complex, the rate of evaluation is relatively slow, and some of the evaluated material is likely to date more rapidly than many of our previous evaluations. All of these factors point out the need for a more rapid form of publication than could be achieved by accumulating enough material for a complete volume.

In the production of this work we acknowledge the assistance of many associated with the evaluation project, in particular, the Science and Engineering Research Council for the provision of funds.

1.1. Presentation of Material

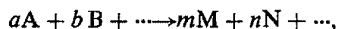
This paper contains critical evaluations of the rate data for elementary reactions between the hydroxyl radical and alkanes. A separate section is devoted to each reaction or group of reactions, and within each section the material is presented in the following order: (a) thermodynamic data, (b) recommended values of the rate parameters and their range of validity, (c) graphical presentation of rate data, (d) table of rate data, (e) discussion, and (f) references.

a. Thermodynamic Data

Thermodynamic data were calculated from a variety of sources.¹⁻⁴ For the reaction between OH and methane, values of ΔH° , ΔS° , and $\log K_p$ are given at intervals over the temperature range 298–5000 K. For other alkanes, ΔH°_{298} is given where thermodynamic data are available.

b. Recommended Values of the Rate Parameters and their Range of Validity

Throughout this paper the rate constant for the elementary reaction,



is defined by the relation

$$\frac{1}{a} \frac{d[\text{A}]}{dt} = -\frac{1}{b} \frac{d[\text{B}]}{dt} = \dots = k[\text{A}]^a[\text{B}]^b \dots$$

$$= \frac{1}{m} \frac{d[\text{M}]}{dt} = \frac{1}{n} \frac{d[\text{N}]}{dt} = \dots,$$

and is given in ($\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$) and ($\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$) units.

The recommended value of the rate constant denotes the value which, in the opinion of the authors, is most consistent with the available experimental rate determinations and the thermodynamic data.

Whenever possible the recommended rate expression is given in the simple Arrhenius form,

$$k = A \exp(C/T), \quad (1)$$

where A (the pre-exponential or “ A ” factor) and C are constants. Alternatively, where the accuracy of the data merits it, they have been expressed as

$$k = A' T^n \exp(C'/T), \quad (2)$$

where A' , n , and C' are constants. In the case of the hydroxyl radical reacting with an alkane, several reaction channels may be operative corresponding to the abstraction of hydrogens from different sites in the molecule. In such cases the overall abstraction rate constant has also been given the form of Eq. (2), but it must be appreciated that the usual physical interpretation of C' in terms of the energy barrier, and the pre-exponential factor in terms of the entropy of activation can no longer simply be made since these constants are now complex composite functions of the physical properties of several channels.

When the data fit Eq. (1), the recommended values of the pre-exponential factor (A) and the activation energy ($E = CR$) for each reaction were obtained from the best straight line which could be drawn through the data plotted on an Arrhenius diagram ($\log k$ vs T^{-1}), taking into account the differing reliabilities of the various experimental determinations. Where it has been necessary to use an expression for k involving a pre-exponential temperature dependence, Eq. (2), values of A' and C' have been obtained from the best straight line drawn through the data on a plot of $\log(kT^{-n})$ vs T^{-1} . The energy of activation (E) is related to C' by the relationship $E = C'R + nRT$. Fitting of a straight line to the data has been purely visual; application of a least-squares calculation involves the assignment of weighting factors, which is difficult to do on a rational basis, and in many cases any attempt to improve the accuracy of the fit is not justified by the quality of the data.

The error limits for A and E were obtained by examining the extreme lines that could reasonably be drawn through the experimental points. There is no simple means of relating the errors in A and E to the error in k when calculated from the recommended expression, and there is a danger of grossly overestimating errors in k by simple substitution of errors in A and E into the expression for k . To avoid this we have chosen to specify errors in $\log k$ estimated from the scatter of data over the entire investigated temperature range. These errors should be used when values of k are calculated from the recommended expression.

Each rate constant expression has been recommended for use in the limited temperature range dependent on the extent of the available data. The recommended expression can be used outside that range, but the error is likely to be large and is difficult to specify.

c. Graphical Presentation of Rate Data

If there are sufficient experimental data on a specific reaction, the available data are presented on a graph usually as $\log k$ vs T^{-1} . Wherever possible the original rate constant data have been recorded as points on the diagram rather than as the rate constant expressions derived from them by

the original authors. In some cases, where the original data are only presented as points on a graph, they have been transferred to our own diagram by measuring the coordinates of each point in the original paper. Only when the experimental results are given solely in the form of a temperature-dependent expression, e.g., Eqs. (1) and (2), do we record it as a line on our diagram.

There have been previous evaluations for many of the reactions in this volume. All such recommendations for k are also presented, sometimes on a separate diagram, so that they may be conveniently compared with those derived here.

Where there is a large body of data to be displayed it has been presented, for clarity, on two diagrams, one recording values of rate constants derived from relative rate measurements, and the other recording absolute values.

d. Table of Rate Data

For each entry in these tables the following features are recorded: (a) measured values of the rate constant; (b) the temperature of each measurement; and (c) a brief outline of the experimental method used and the reference, and any pertinent comments on special features of the work. Whenever necessary the rate constant recorded in the first column has been converted to the system of units used throughout this volume (cm mol s). In a few cases, which are noted in the text, a different definition of k has been used from that in the original paper (see Sec. 1.1.b for definition of k) and the appropriate changes to the values for k have been made. In the third column the intention has been to record sufficient details of the technique for the specialist to be able to understand how the determination was made and pertinent comments on the technique and other aspects of the work. Also recorded are references to all the work in which that particular determination of the rate constant has been subsequently discussed or used. By use of this feature of the tables, in conjunction with the references, it is possible to trace any quoted value of a rate constant to its source.

The entries in the tables are in chronological order but the tables themselves are divided into at least two sections. The first contains details of original experimental and theoretical determinations while the second comprises other work, i.e., recommended expressions from review articles, compilations, and evaluations. A third section has been added in a few cases to record the available data on isotopic reactions.

Our evaluations are based on experimental data with theoretical and empirical estimates being used only for general guidance. No attempt has been made therefore to record all of the theoretical estimates available; the few that have been tabulated have been placed in the tables of experimental values, rather than introduce a separate section for them.

One of the difficulties associated with recording the values of rate constants derived from measurements of rate constant ratios is that the rate constants so obtained depend upon the value of the reference rate constant used. In tabulating such measurements no entry has been placed in column 1 of the table, but in column 3 the measured rate constant ratio is recorded, together with the value of the rate constant derived from it in the original paper, and also the

value derived using the value of the reference rate constant which, in the opinion of the evaluators, is the best value currently available.

e. Discussion

The principal aim of this section is to present concisely the reasons leading to the recommended rate expression. In some cases it is possible to state specifically why some results are rejected in favor of others, but often it is not possible to be so specific. The data are subjected to a variety of comparative tests; their relation to the work of others, to theory, and to the results on other reactions are considered, and as far as is reasonably possible the conclusions from each comparison are recorded. However, in all of this there is an element of personal judgment on the part of the evaluator, which is difficult to record, but which is an essential feature of the evaluation process.

f. References

The bibliographies are largely the result of literature searches by the authors which were terminated in October 1984. There were a number of reviews which were helpful in both the collection of bibliography and the evaluation.⁵⁻¹⁰

1.2. Symbols and Units

A list of symbols used in this work is presented below.

A	Pre-exponential factor in the Arrhenius expression, Eq. (1).
A'	Temperature-independent part of the pre-exponential factor in non-Arrhenius expression, Eq. (2).
C	Constant in the exponential term of the Arrhenius equation $C = E/R$.
C'	Constant in the exponential term of the non-Arrhenius expression $C = (E - nRT)/R$.
E	Activation energy. $E = 2.303R\{\partial \log k / \partial (1/T)\}$.
E'	$E' = E - nRT = C'R$.
T	Temperature in kelvins (K).
k	Rate constant, defined in Sec. 1.1.b.
K_p	Equilibrium constant (standard state 101.325 kPa). $\log K_p = -2.303(\Delta H^\circ - T\Delta S^\circ)/RT$.
n	Constant in non-Arrhenius expression, Eq. (2).
$[X]$	Concentration of X.
R	Ideal gas constant, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ $= 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$ $= 82.05 \text{ cm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$.
ΔH°	Standard enthalpy change (standard state 101.325 kPa).
ΔS°	Standard entropy change (standard state 101.325 kPa).

TABLE 1. Conversion factors

1 cal	= 4.184 J
1 mm Hg	= 133.3 Pa
1 atm	= 101.3 kPa

TABLE 2. Conversion factors for second order reactions

A	$\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$	$\text{L mol}^{-1} \text{s}^{-1}$	$\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$	$\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$	$(\text{mm Hg})^{-1} \text{s}^{-1}$
B					
$\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$		10^3	10^6	6.023×10^{23}	$62.40 \times 10^3 \text{T}$
$\text{L mol}^{-1} \text{s}^{-1}$	10^{-3}		10^3	6.023×10^{20}	62.40 T
$\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$	10^{-6}	10^{-3}		6.023×10^{17}	$62.40 \times 10^{-3} \text{T}$
$\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$	0.1660×10^{-23}	0.1660×10^{-20}	0.1660×10^{-17}		$10.36 \times 10^{-20} \text{T}$
$(\text{mm Hg})^{-1} \text{s}^{-1}$	$16.03 \times 10^{-6} \text{T}^{-1}$	$16.03 \times 10^{-3} \text{T}^{-1}$	16.03 T^{-1}	$96.53 \times 10^{17} \text{T}^{-1}$	

Throughout this work the symbol log refers to logarithm to the base 10.

Mainly, SI units have been used throughout, but for those more familiar with other units, a list of conversion factors is shown in Table 1.

Rate constants have been expressed in (cm mol s) units and, to assist conversion between these and other units, conversion factors are given in Table 2.¹¹

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2. Summary of Rate Data

Evaluated Kinetic Data For High Temperature Reactions, Volume 5.

Part 1. Homogeneous Gas Phase Reactions of the Hydroxyl Radical With Alkanes.

Alkane	k_{298} $\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	$\Delta\log k_{298}$	Temperature dependence of $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temp. range/K	$\Delta\log k$
<u>Normal and Branched Alkanes</u>					
Methane	4.7×10^9	± 0.1	$1.5 \times 10^6 T^{2.13} \exp(-1230/T)$	230-2000	± 0.1 below 500 K rising to ± 0.3 above 1000 K
Ethane	1.8×10^{11}	± 0.1	$1.4 \times 10^{13} \exp(-1340/T)$	250-1200	± 0.1 at 300 K rising to ± 0.3 above 1000 K
Propane	7.9×10^{11}	± 0.12	$1.1 \times 10^4 T^{2.93} \exp(390/T)$	290-1200	± 0.12 at 300 K rising to ± 0.3 above 1000 K
n-Butane	1.6×10^{12}	± 0.11	$1.0 \times 10^9 T^{1.3}$	300-750	± 0.11 at 300 K rising to ± 0.3 at 750 K
Isobutane	1.6×10^{12}	± 0.12	$1.9 \times 10^3 T^{3.1} \exp(860/T)$	290-750	± 0.12 at 300 K rising to ± 0.3 at 750 K
Neopentane	5.4×10^{11}	± 0.12	$4.8 \times 10^6 T^{2.08} \exp(-70/T)$	300-1000	± 0.12 at 300 K rising to ± 0.3 at 1000 K
n-Pentane	2.5×10^{12}	± 0.2	-	-	-
2-Methylbutane	2.4×10^{12}	± 0.2	-	-	-
n-Hexane	3.5×10^{12}	± 0.15	-	-	-
2-Methylpentane	3.4×10^{12}	± 0.2	-	-	-
3-Methylpentane	3.7×10^{12}	± 0.2	-	-	-
2,2-Dimethylbutane	1.6×10^{12}	± 0.2	-	-	-
2,3-Dimethylbutane	3.5×10^{12}	± 0.2	-	-	-
n-Heptane	4.5×10^{12}	± 0.2	-	-	-
2,2,3-Trimethylbutane	2.6×10^{12}	± 0.15	-	-	-
2,4-Dimethylpentane	3.3×10^{12}	± 0.2	-	-	-
n-Octane	5.5×10^{12}	± 0.2	-	-	-
2,2,3,3-Tetramethylbutane	6.6×10^{11}	± 0.15	$1.0 \times 10^7 T^{2.0} \exp(-90/T)$	300-700	± 0.15 at 300 K rising to ± 0.3 at 700 K
2,2,4-Trimethylpentane	2.3×10^{12}	± 0.2	-	-	-
n-Nonane	6.6×10^{12}	± 0.2	-	-	-
n-Decane	7.1×10^{12}	± 0.3	-	-	-
<u>Cycloalkanes</u>					
Cyclobutane	7.0×10^{11}	± 0.3	-	-	-
Cyclopentane	3.0×10^{12}	± 0.2	-	-	-
Cyclohexane	4.5×10^{12}	± 0.15	-	-	-
Methylcyclohexane	6.6×10^{12}	± 0.2	-	-	-

3. $\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O}$

THERMODYNAMIC DATA

T (K)	ΔH° (kJ mol ⁻¹)	ΔS° (J K ⁻¹ mol ⁻¹)	log K
298	-60.982	13.037	11.364
300	-60.969	13.075	11.297
500	-59.794	16.175	7.089
1000	-59.430	16.936	3.989
1500	-61.216	15.518	2.942
2000	-63.467	14.217	2.399
2500	-65.706	13.221	2.064
3000	-67.839	12.447	1.831
3500	-69.864	11.816	1.659
4000	-71.810	11.301	1.528
4500	-73.689	10.862	1.422
5000	-75.521	10.473	1.336

RECOMMENDED RATE CONSTANT

$$k = 1.5 \times 10^6 T^{2.13} \exp(-1230/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$= 2.5 \times 10^{-18} T^{2.13} \exp(-1230/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Temperature Range: 230–2000 K.

Suggested Error Limits for Calculated Rate Constant:

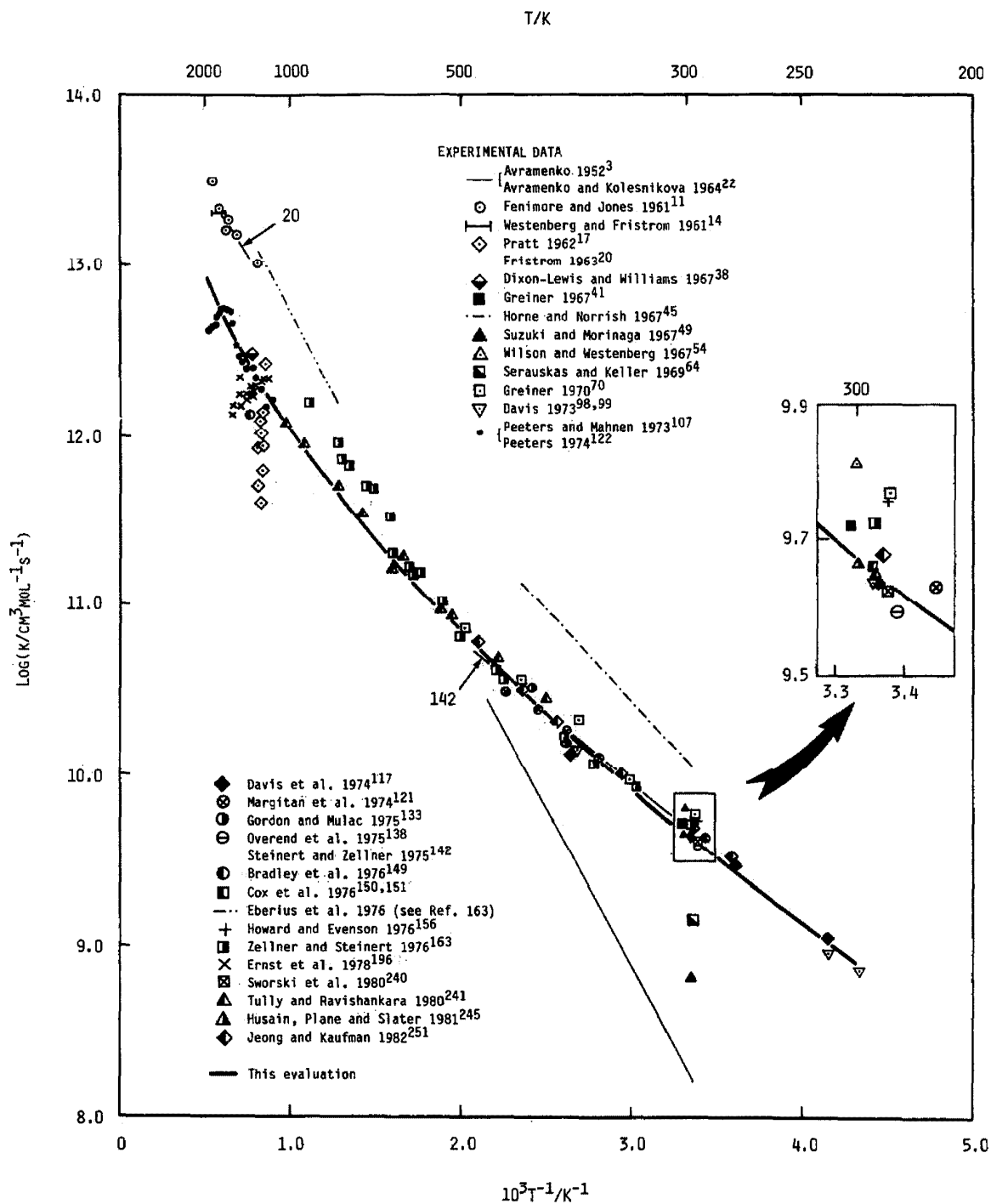
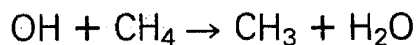
$\Delta \log k = \pm 0.1$ below 500 K, rising to $\Delta \log k = \pm 0.3$ above 1000 K.

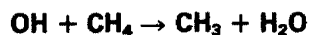
Rate Parameters: $\log(A'/\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = (7.10 + 2.13 \log T) \pm 0.3$

$\log(A'/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = (-16.7 + 2.13 \log T) \pm 0.3$

$E'/\text{J mol}^{-1} = (10\,200 + 17.7 T) \pm 1000$

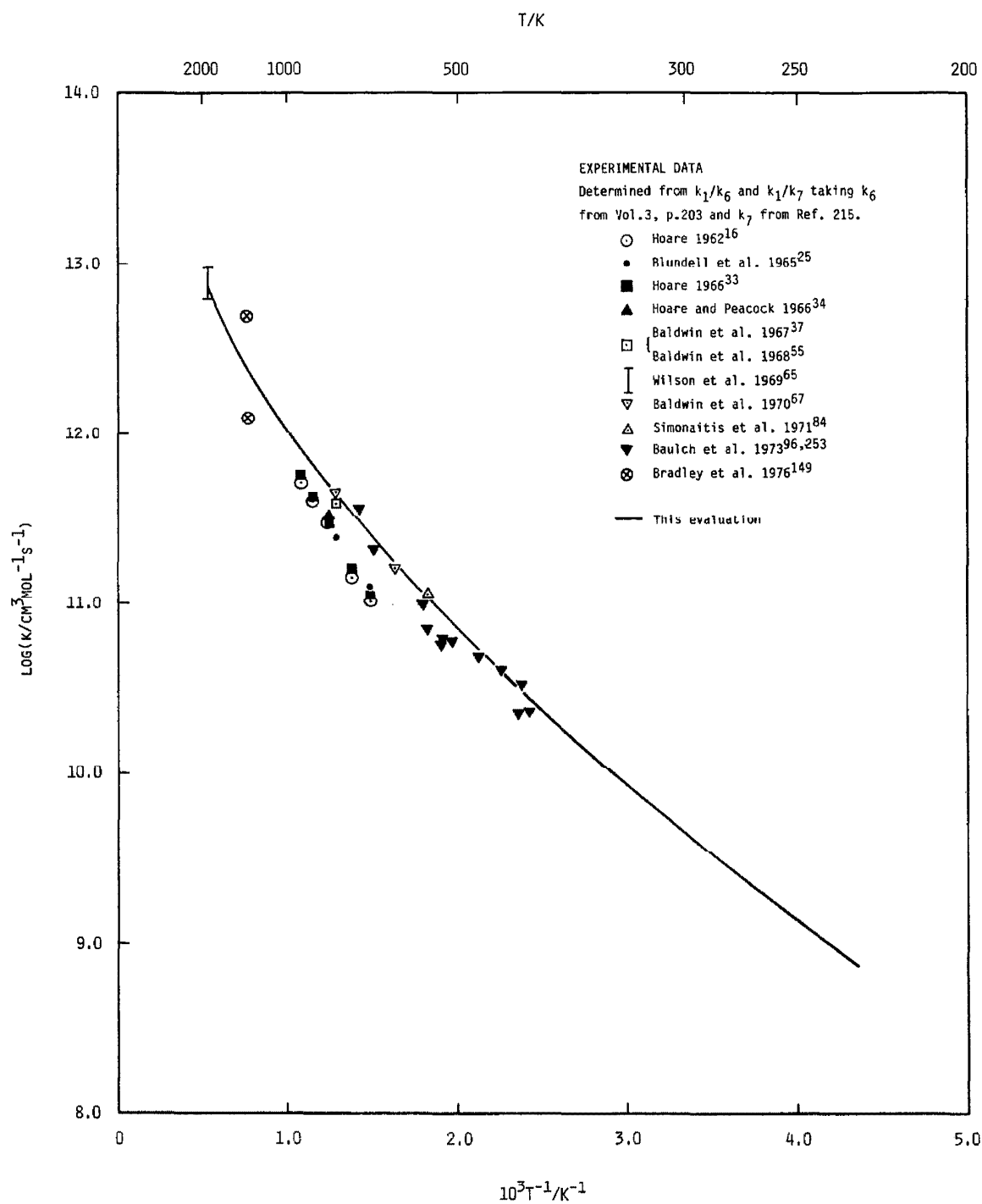
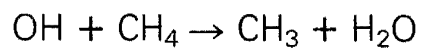
$E'/\text{cal mol}^{-1} = (2\,440 + 4.2 T) \pm 240$

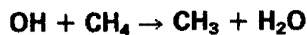




EXPERIMENTAL DATA

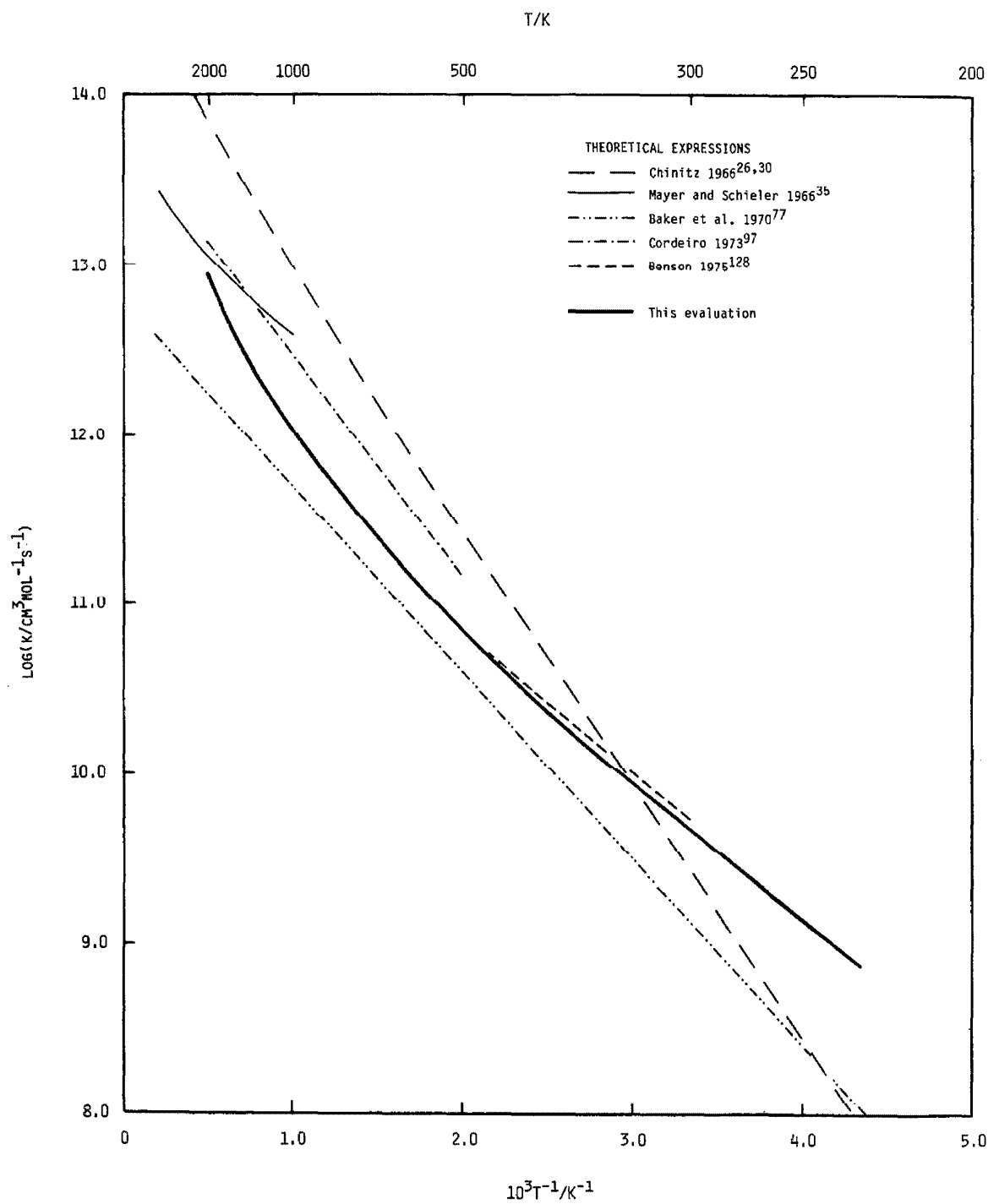
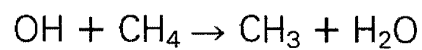
Rate Constant $\text{k/cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
	438-623	<p>VAN TIGGELEN 1942¹</p> <p>Static photolysis of CH_3COCH_3 (4.27-5.65 kPa) in the presence of CH_4 (14.5-20.4 kPa) and O_2 (49.4-70.2 kPa). $[\text{CO}_2]$ determined by absorption on KOH; $[\text{O}_2]$, $[\text{H}_2]$, $[\text{CH}_4]$ and $[\text{CO}]$ by fractionation of the products.</p> <p>Author concluded that reaction 1 was the principal reaction removing CH_4 and was responsible for the observed activation energy $E_1 = 35.6 \text{ kJ mol}^{-1}$ (8.5 kcal mol⁻¹).</p> $\text{OH} + \text{CH}_4 \longrightarrow \text{CH}_3 + \text{H}_2\text{O} \quad (1)$ <p>OH radicals presumed formed by reaction of CH_3 radicals (from acetone photolysis) with O_2.</p> <p>Quoted in Ref. 4, in which doubts expressed as to whether activation energy measured does refer to reaction 1, the system being so complex.</p>
$2.4 \times 10^{14} \exp(-4200/T)$	unspecified	<p>AVRAMENKO 1952³</p> <p>AVRAMENKO and KOLESNIKOVA 1964²²</p> <p>Discharge flow system. H_2O at about 4.0 kPa pressure. CH_4 added downstream. $[\text{OH}]$ measured by u.v. absorption along the axis of the flow reactor.</p> <p>Source of OH suspect.²¹ H and O atoms are also produced in the discharge, giving rise to secondary reactions which generate more OH. Consequently, the apparent rate of removal of OH from the system is much lower than is compatible with reaction 1.</p> <p>Quoted by Refs. 8, 12, 14, 20, 33, 45, 48, 50, 52, 53, 73 and 76.</p> <p>Used by Refs. 28, 78, 79, 85, 127, 147, 148 and 176.</p>
	696-786	<p>ENIKOLOPYAN 1959⁶</p> <p>KARMILOVA, ENIKOLOPYAN, NALBANDYAN and SEMENOV 1960⁹</p> <p>Static system. CH_4 (33.3-66.7%)/O_2 mixtures at total pressures of 13.3-50.0 kPa. Stable products analysed by absorption chromatography.</p> <p>Authors monitored appearance and decay of formaldehyde and proposed a nine step oxidation mechanism to account for this and the rate of methane disappearance. Reproducible results were obtained in aged vessels leading to the ratio,</p> $[\text{HCHO}]_{\text{max}}/[\text{CH}_4] = (k_1 k_2 / k_3 k_4)^{0.5} = \exp(-3900/T)$ <p>over the quoted temperature range.</p> $\text{HO}_2 + \text{CH}_4 \longrightarrow \text{CH}_3 + \text{H}_2\text{O}_2 \quad (2)$ $\text{OH} + \text{HCHO} \longrightarrow \text{CHO} + \text{H}_2\text{O} \quad (3)$ $\text{HO}_2 + \text{HCHO} \longrightarrow \text{CHO} + \text{H}_2\text{O}_2 \quad (4)$ <p>Quoted by Refs. 25 and 58.</p>

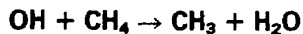




EXPERIMENTAL DATA - CONTINUED

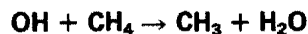
Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
1.0×10^{13}	1225	FENIMORE and JONES 1961 ¹¹
1.5×10^{13}	1445	Flame study. $\text{CH}_4(6.69-19.2\%)/\text{H}_2(0-20.1\%)/\text{N}_2\text{O}(8.19-38.4\%)/\text{O}_2$
1.8×10^{13}	1560	mixtures at total pressures of 0.40-1.87 kPa. $[\text{CH}_4]$, $[\text{CO}_2]$,
1.6×10^{13}	1580	$[\text{N}_2\text{O}]$, $[\text{CO}]$ monitored by mass spectrometry. $[\text{H}]$ estimated from
2.1×10^{13}	1690	$[\text{N}_2\text{O}]$ disappearance, assuming that under the conditions chosen,
3.0×10^{13}	1800	H is lost exclusively through reaction 5.
		$\text{H} + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{OH} \quad (5)$
		$[\text{OH}]$ was estimated from the kinetics of reaction 6, taking k_6 from Ref. 5.
		$\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H} \quad (6)$
		Assuming that in fuel-lean flames CH_4 disappears only through reaction 1, the authors obtained values of k_1 and derived the expression $k_1 = 3.5 \times 10^{14} \exp(-4500/T) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$.
		Quoted by Refs. 19,20,28,30,33,36,37,38,50,51,52,53,54,67,153.
		Used by Refs. 23,48,69,71 and 73.
		E_1 quoted by Ref. 75.
2×10^{13}	1650-1840	WESTENBERG and FRISTROM 1961 ¹⁴
		Flame study. $\text{CH}_4(7.8\%)/\text{O}_2$ mixtures at 5.1-10.1 kPa (0.05-0.1 atm.) pressure. $[\text{CO}]$, $[\text{CO}_2]$, $[\text{CH}_4]$ monitored by mass spectrometry.
		Authors used their own value of k_6 determined in the same study to give $[\text{OH}]$ profiles and thus obtain a value for k_1 , assuming reaction 1 to be the predominant path removing CH_4 . Value of k_1 obtained in 0.1 atm. flame is a factor of three higher than that in 0.05 atm. flame. Value quoted is average.
		Quoted by Refs. 11,15,16,19,20,28,33,50,54,67 and 153.
		Used by Refs. 23,48,71 and 73.
	673-923	HOARE 1962 ¹⁶
		Flow system. H_2O_2 in excess He decomposed in the presence of CO and CH_4 . $[\text{CO}]/[\text{CH}_4]$ varied by factor of 50. Analysis by gas chromatography. No further details.
		Competitive rate k_1/k_6 determined from product analysis. $k_1/k_6 = 0.83(673 \text{ K}), 1.10(723 \text{ K}), 2.1(798 \text{ K}), 2.7(873 \text{ K})$ and $3.4(923 \text{ K})$. Author derives $E_1 - E_6 = 29 \text{ kJ mol}^{-1} (7 \text{ kcal mol}^{-1})$ from which we obtain $k_1/k_6 = 1.5 \times 10^2 \exp(-3500/T)$.
		$\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O} \quad (1)$
		$\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H} \quad (6)$
		Using our expression for k_6 (Vol. 3, p. 203) we obtain $k_1 = 1.03 \times 10^{11}(673 \text{ K}), 1.43 \times 10^{11}(723 \text{ K}), 2.92 \times 10^{11}(798 \text{ K}), 4.03 \times 10^{11}(873 \text{ K})$ and $5.31 \times 10^{11} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}(923 \text{ K})$, giving an expression $k_1 = 4.4 \times 10^{13} \exp(-4100/T) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$.





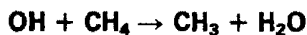
EXPERIMENTAL DATA - CONTINUED

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
		Quoted by Refs. 25,28,44,50,52,53,54 and 71. Author also obtained $k_1/k_3 = 0.030(798\text{ K}), 0.037(873\text{ K})$ and $0.046(923\text{ K})$. $\text{OH} + \text{HCHO} \longrightarrow \text{CHO} + \text{H}_2\text{O} \quad (3)$
2.71×10^{12}	1160	PRATT 1962 ¹⁷
1.41×10^{12}	1175	Flame study. $\text{CH}_4(<0.1\%)/\text{air}$ mixtures at 101.3 kPa
8.7×10^{11}	1180	pressure. $[\text{H}_2]$ analysed by gas chromatography, $[\text{CO}]$, $[\text{CO}_2]$ and
6.3×10^{11}	1184	$[\text{CH}_4]$ by i.r. spectroscopy.
1.05×10^{12}	1191	Author assumed reaction 1 was the principal reaction
4.1×10^{11}	1200	removing CH_4 and deduced a rate constant on the basis of
1.26×10^{12}	1210	species profiles through the flame. $[\text{OH}]$ deduced from reaction
8.6×10^{11}	1220	6 assumed to be the only reaction removing CO. k_6 taken from
5.1×10^{11}	1237	Refs. 2,7 and 10. Mean value of $k_1 = 1 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ given at about 1200 K. $\text{CO} + \text{OH} \longrightarrow \text{CO}_2 + \text{H} \quad (6)$
		In comment following Wilson and Westenberg's paper, ⁵⁴ Pratt suggests his data unreliable.
$1.4 \times 10^{14} \exp(-3300/T)$	1300-1680	FRISTROM 1963 ²⁰ Flame study. $\text{CH}_4(7.8\%)/\text{O}_2$ flames at 5.07 kPa pressure. $[\text{CO}]$ and $[\text{CO}_2]$ determined by mass spectrometry. Author assumed CO converted to CO_2 by reaction 6. $[\text{OH}]$ was derived from $[\text{CO}]$ and $[\text{CO}_2]$, taking k_6 from Ref. 14. Thus k_1 was obtained from $[\text{OH}]$ disappearance. Results for k_1 combined with those from Ref. 14 to give quoted expression. Quoted by Refs. 15,19,25,28,33,39,41,50,52,53,100 and 153. Used by Refs. 48,69,71,163 and 218.
	673	BLUNDELL, COOK, HOARE and MILNE 1965 ²⁵
	773	Static system. CH_4/O_2 mixtures varied from 5:1 to 1:10, at total pressures of 12.0-60.0 kPa. $[\text{CO}]$, $[\text{N}_2]$, $[\text{CH}_4]$, $[\text{O}_2]$, $[\text{CO}_2]$, $[\text{H}_2\text{O}]$, $[\text{HCHO}]$ monitored by gas chromatography. Rate constant ratio k_1/k_6 obtained by comparing rate of removal of CH_4 with the rate of production of CO_2 . Authors deduced $k_1/k_6 = 1$ (673 K) and 1.8 (773 K). Using our expression for k_6 (Vol. 3, p. 203) we obtain $k_1 = 1.25 \times 10^{11}$ (673 K) and $2.45 \times 10^{11} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ (773 K). Quoted by Refs. 37,38,40,50,54,67,71,100,107 and 110. Used by Ref. 48.



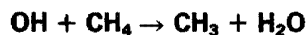
EXPERIMENTAL DATA - CONTINUED

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
$8.51 \times 10^{12} T^{0.5} \exp(-3271/T)$	All	CHINITZ 1965 ²⁶ Theoretical estimate from collision theory. Results used in analysis of non-equilibrium CH_4 /air combustion.
	673-923	HOARE 1966 ³³ Flow system. H_2O_2 decomposed in excess He in the presence of CO (0.01-4.9%) and CH_4 (0.68-13.1%). Total pressure 101.3 kPa. $[\text{CO}]$, $[\text{CO}_2]$, $[\text{O}_2]$, $[\text{CH}_4]$ determined by gas chromatography, $[\text{H}_2\text{O}_2]$ and $[\text{HCHO}]$ by thiosulphate titration. Extension of earlier work. ¹⁶ From the product yields, the ratio k_1/k_6 given as 0.85(673 K), 1.25(723 K), 2.1(798 K), 2.8(873 K) and 3.6(923 K). The activation energy difference $E_1 - E_6$ again given as 29 kJ mol^{-1} (7 kcal mol^{-1}) giving $k_1/k_6 = 1.59 \times 10^2 \exp(-3500/T)$. $\text{OH} + \text{CH}_4 \longrightarrow \text{CH}_3 + \text{H}_2\text{O} \quad (1)$ $\text{CO} + \text{OH} \longrightarrow \text{CO}_2 + \text{H} \quad (6)$ Using our value for k_6 (Vol. 3, p. 203), we obtain $k_1 = 1.07 \times 10^{11}$ (673 K), 1.63×10^{11} (723 K), 2.92×10^{11} (798 K), 4.18×10^{11} (873 K) and $5.62 \times 10^{11} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ (923 K), giving the expression $k_1 = 4.88 \times 10^{13} \exp(-4120/T) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$. Author also obtained $k_1/k_3 = 0.030$ at 798 K. $\text{OH} + \text{HCHO} \longrightarrow \text{CHO} + \text{H}_2\text{O} \quad (3)$ Quoted by Refs. 52, 53, 58, 71, 72 and 110. Used by Ref. 48.
	798	HOARE and PEACOCK 1966 ³⁴ Flow system. Decomposition of H_2O_2 (1.27%) in He or N_2 carrier, in presence of CO (18.0-26.2%) and CH_4 (5.08-15.6%). Total pressures 13.3-101.3 kPa. $[\text{CO}]$, $[\text{CO}_2]$, $[\text{O}_2]$, $[\text{CH}_4]$, $[\text{H}_2]$ determined by gas chromatography, $[\text{HCHO}]$ by thiosulphate titration. Extension of the work in Ref. 33 to pressures <100 kPa. No pressure effect observed, the authors obtaining the ratios $k_1/k_6 = 2.3$ and $k_1/k_3 = 0.036$. Using our expression for k_6 (Vol. 3, p. 203), we obtain $k_1 = 3.21 \times 10^{11} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$. Quoted by Ref. 62. Used by Ref. 48.
$1.1 \times 10^{11} T^{0.675} \exp(-1100/T)$	1000-5000	MAYER and SCHIELER 1966 ³⁵ Theoretical estimate from transition state theory. Quoted by Refs. 51, 52, 53 and 153.



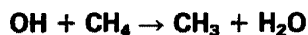
EXPERIMENTAL DATA - CONTINUED

Rate Constant $\text{k}/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
—	773	<p>BALDWIN, NORRIS and WALKER 1967³⁷ BALDWIN, EVERETT, HOPKINS and WALKER 1968⁵⁵ Static system. $\text{H}_2(14-43\%)/\text{O}_2(7-56\%)/\text{CH}_4(\leq 1\%)/\text{N}_2$ mixtures at a total pressure of 66.7 kPa. $[\text{CO}_2]$ determined by gas chromatography; $[\text{H}_2]$ manometrically. Reactions of hydrocarbons in slowly reacting H_2/O_2 mixtures observed. Oxidation products CO and HCHO converted to CO_2 for analysis. From the rates of consumption of CH_4 and H_2, authors obtained $k_1 = k_7$, and taking k_7 from Ref. 21, derived $k_1 = 1.4 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ at 773 K.</p> $\text{OH} + \text{CH}_4 \longrightarrow \text{CH}_3 + \text{H}_2\text{O} \quad (1)$ $\text{H}_2 + \text{OH} \longrightarrow \text{H}_2\text{O} + \text{H} \quad (7)$ <p>Ratio k_1/k_7 rather insensitive to mechanism chosen. Quoted by Refs. 38,52,53,54,89 and 100. Used by Refs. 69,71 and 73. Using value of k_7 from Ref. 215, we get $k_1 = 4.1 \times 10^{11} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$. This point plotted.</p>
3×10^{12}	1285	<p>DIXON-LEWIS and WILLIAMS 1967³⁸ Flame study. $\text{CH}_4(5.03\%)/\text{O}_2(19.94\%)/\text{N}_2$ flames at 101.3 kPa pressure. $[\text{OH}]$ monitored by u.v. absorption spectroscopy. Assuming reaction 1 to be the dominant path for OH removal, authors obtained the quoted rate constant, rejecting any contribution from reaction 8 under O_2 rich conditions and also the slower reaction 9.</p> $\text{H} + \text{CH}_4 \longrightarrow \text{CH}_3 + \text{H}_2 \quad (8)$ $\text{O} + \text{CH}_4 \longrightarrow \text{CH}_3 + \text{OH} \quad (9)$ <p>Quoted by Refs. 40,52,53,67,72,100,153 and 163. Used by Refs. 48,69,71,73 and 218. Taking k_6 from Ref. 31 and combining their value with those of Refs. 17,25,37 and 54, authors obtain $k_1 = 2.6 \times 10^{13} \exp(-2600/T) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$.</p>
5.3×10^9	301	<p>GREINER 1967⁴¹ Flash photolysis of $\text{H}_2\text{O}(1\%)/\text{Ar}$ mixtures in the presence of CH_4. Total pressure 2.67-13.3 kPa. $[\text{OH}]$ monitored by u.v. absorption spectroscopy at 306.4 nm. Because $[\text{CH}_4] \gg [\text{OH}]$, the effect of reaction 10 was assumed to be insignificant.</p> $\text{OH} + \text{OH} \longrightarrow \text{H}_2\text{O} + \text{O} \quad (10)$ <p>Quoted by Refs. 42,45,57,58,63,68,72,76,106 and 153. Used by Refs. 69,71 and 73.</p>



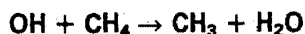
EXPERIMENTAL DATA - CONTINUED

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
$5.0 \times 10^{13} \exp(-2500/T)$	298-423	<p>HORNE and NORRISH 1967⁴⁵</p> <p>Flash photolysis of $\text{H}_2\text{O}(2.5\%)/\text{Ar}$ mixtures at total pressure of 41.1 kPa. Trace amounts of CH_4 added. $[\text{OH}]$ monitored by u.v. absorption spectroscopy at 309 nm.</p> <p>Effect of OH recombination allowed for using an overall rate constant for OH decay determined in the same study. Authors admit to large error in k_1 as few experiments carried out.</p> $\text{OH} + \text{CH}_4 \longrightarrow \text{CH}_3 + \text{H}_2\text{O} \quad (1)$ <p>Quoted by Refs. 57,67,71,72,117,163 and 251.</p> <p>Used by Ref. 69.</p>
6.6×10^8	298	<p>SUZUKI and MORINAGA 1967⁴⁹</p> <p>Static system. Discharge through $\text{CH}_4(15-20\%)/\text{O}_2(30-40\%)/\text{Ar}$ or He mixtures at a total pressure of 33.3 kPa. $[\text{OH}]$ monitored by u.v. emission spectroscopy at 307 nm.</p> <p>Addition of HCHO found to have no effect on the rate of $[\text{OH}]$ decay and so authors concluded reaction 1 was the only one removing CH_4. No attempt was made, however, to consider removal of OH at the vessel wall.</p>
6.5×10^9	300	<p>WILSON and WESTENBERG 1967⁵⁴</p> <p>Discharge flow system. $\text{H}_2(1-2\%)/\text{Ar}$ mixtures at 100-180 Pa total pressure. OH produced by $\text{H} + \text{NO}_2$ titration, CH_4 added downstream so that $[\text{CH}_4] \gg [\text{OH}]$. $[\text{H}]$ and $[\text{OH}]$ monitored by e.s.r. spectroscopy.</p> <p>Mass-spectrometric analysis of the reaction products led the authors to believe that OH reacts further with CH_3 as well as decaying through the fast reaction 10.</p> $\text{OH} + \text{OH} \longrightarrow \text{H}_2\text{O} + \text{O} \quad (10)$ <p>Three separate mechanisms were postulated, giving stoichiometries for OH ranging from 2 to 4. Taking k_{10} from Ref. 27, a value of k_1 was obtained by averaging the results from each mechanism. Taking k_6 from Ref. 27 and combining their data with those of Refs. 11,14,16,17,25 and 37, they give $k_1 = 2.9 \times 10^{13} \exp(-2500/T) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ over the temperature range 300-2000 K.</p> <p>This expression recommended in Ref. 202.</p> <p>Quoted by Refs. 38,41,46,49,52,53,59,62,63,66,67,68,81,84,100,117,123,153,163,189 and 251.</p> <p>Used by Refs. 48,69,71,73 and 159.</p> <p>E_1 quoted by Ref. 75.</p>



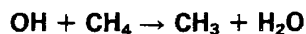
EXPERIMENTAL DATA - CONTINUED

Rate Constant $\text{k}/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
-	773-873	<p>GAILLARD-CUSIN and JAMES 1969⁵⁸</p> <p>Static system. CO/CH_4 mixtures in the range 20:1 - 1000:1 in the presence of O_2. No further details given.</p> <p>Authors state experiments carried out at "high pressures". They obtained $k_1/k_6 = 80$ at 773 K and taking k_6 from Ref. 32, gave $1.9 \times 10^{13} < k_1 < 2.4 \times 10^{13} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ over the temperature range 773-805 K.</p> <p style="text-align: right;">$\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H} \quad (6)$</p> <p>Using our value of k_6 (Vol. 3, p. 203) we obtain $k_1 = 1.1 \times 10^{13} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ at 773 K. Not plotted on Arrhenius diagram.</p>
-	734-798	<p>HOARE and PATEL 1969⁶²</p> <p>Static system. $\text{CH}_4(7.1-31.9\%)/\text{C}_2\text{H}_6(0-16.8\%)/\text{C}_2\text{H}_4(0-15.1\%)/\text{O}_2$ mixtures. Total pressures 9.33-24.7 kPa. $[\text{CO}]$, $[\text{CH}_4]$, $[\text{O}_2]$, $[\text{C}_2\text{H}_6]$, $[\text{CO}_2]$, $[\text{H}_2\text{O}]$, $[\text{C}_2\text{H}_4]$ analysed by gas chromatography.</p> <p>Rate constant ratios obtained: $k_{11}/k_1 = 10.4(734 \text{ K})$, $10.0(773 \text{ K})$, $12.0(798 \text{ K})$.</p> <p style="text-align: right;">$\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O} \quad (1)$</p> <p style="text-align: right;">$\text{OH} + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_5 + \text{H}_2\text{O} \quad (11)$</p> <p>Also $k_{12}/k_1 = 7.4(734 \text{ K})$, $5.8(748 \text{ K})$, $4.9(773 \text{ K})$ and $4.3(798 \text{ K})$. From these results, authors gave $E_1 - E_{12} = 33.6 \text{ kJ mol}^{-1}$ (8 kcal mol^{-1}).</p> <p style="text-align: right;">$\text{OH} + \text{C}_2\text{H}_4 \rightarrow \text{products} \quad (12)$</p> <p>Quoted by Ref. 72.</p>
1.46×10^9	298	<p>SERAUSKAS and KELLER 1969⁶⁴</p> <p>Discharge flow system. OH from $\text{H} + \text{NO}_2$ titration. Reaction followed mass spectrometrically. No further details.</p> <p>Quoted by Ref. 153.</p>
-	1750-2000	<p>WILSON, O'DONOVAN and FRISTROM 1969⁶⁵</p> <p>Flame study. $\text{CH}_4(8.92\%)/\text{O}_2$ flames at 5.05 kPa pressure. $[\text{CH}_4]$, $[\text{CO}]$, $[\text{CO}_2]$, $[\text{H}_2\text{O}]$ monitored by mass spectrometry.</p> <p>$[\text{OH}]$ profiles computed using reaction 6, taking k_6 from Ref. 27.</p> <p style="text-align: right;">$\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H} \quad (6)$</p> <p>Rate constant ratio $k_1/k_6 = 20-25$ derived over given temperature range but no attempt made to derive k_1. Using our expression for k_6 (Vol. 3, p. 203), we obtain $k_1 = (6.4-9.3) \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ at 1875 K.</p> <p>Quoted by Refs. 73 and 100.</p>



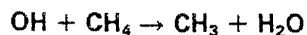
EXPERIMENTAL DATA - CONTINUED

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
-	773	BALDWIN, HOPKINS, NORRIS and WALKER 1970 ⁶⁷ Static system. $\text{H}_2(14-43\%)/\text{O}_2(7-71\%)/\text{CH}_4(<1\%)/\text{N}_2$ mixtures at 33.3 or 66.7 kPa pressure. $[\text{CO}_2]$ determined by gas chromatography. Experimental method the same as in previous work. ³⁷ Authors obtain $k_1/k_7 = 1.1$ at 773 K. Taking k_7 from Ref. 27 they give $k_1 = 8.5 \times 10^{11} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$. Combining this value with those in Refs. 11, 14, 38, 41 and 54 they obtain $k_1 = 2.08 \times 10^{13} \exp(-2450/T) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ over the temperature range 300-2000 K. $\text{H}_2 + \text{OH} \longrightarrow \text{H}_2\text{O} + \text{H} \quad (7)$ Quoted by Refs. 68, 80, 89, 91, 191 and 231. Used by Refs. 29 and 153. Using value of k_7 from Ref. 215 we get $k_1 = 4.5 \times 10^{11} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$. This point plotted.
5.86×10^9	296	GREINER 1970 ⁷⁰
9.26×10^9	333	Flash photolysis of $\text{H}_2\text{O}(1\%)/\text{Ar}$ mixtures in the presence of
2.12×10^{10}	370	CH_4 at 45.5 Pa-12.98 kPa pressure. $[\text{OH}]$ monitored by u.v.
3.68×10^{10}	424	absorption spectroscopy at 306.4 nm.
7.29×10^{10}	493	Method the same as in earlier work. ⁴¹ Author uses data to
7.08×10^{10}	498	derive expression $k_1 = 3.31 \times 10^{12} \exp(-1898/T) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$. $\text{OH} + \text{CH}_4 \longrightarrow \text{CH}_3 + \text{H}_2\text{O} \quad (1)$ An attempt was made to apply transition state theory to the reaction and excellent agreement was obtained. Quoted by Refs. 82, 89, 99, 100, 105, 108, 116, 117, 119, 121, 126, 131, 133, 145, 153, 156, 157, 162, 163, 189 and 251. Used by Refs. 130, 168, 188 and 250. E_1 quoted by Refs. 75 and 95.
$6.3 \times 10^{12} \exp(-2520/T)$	All	BAKER, BALDWIN and WALKER 1971 ⁷⁷ Theoretical value obtained from transition state theory. Incorrect expression used in Ref. 112.
-	548	SIMONAITIS, HEICKLEN, MAGUIRE and BERNHEIM 1971 ⁸⁴ Static photolysis system. Hg-photosensitized decomposition of N_2O in the presence of $\text{CO}(0-24.5\%)/\text{CH}_4(1.2-88.5\%)$ mixtures at total pressures of 17.76-109.6 kPa. $[\text{CO}]$, $[\text{CO}_2]$, $[\text{N}_2]$, $[\text{H}_2]$, $[\text{O}_2]$ analysed by gas chromatography. Under the conditions chosen, CO_2 is also produced by reaction 13 and only an estimate of the ratio $k_1/k_6 = 1.0$ could be made.



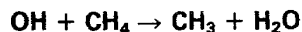
EXPERIMENTAL DATA - CONTINUED

Rate Constant $\text{k/cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
		$\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$ (6) $\text{CO} + \text{O} + \text{M} \rightarrow \text{CO}_2 + \text{M}$ (13) Due to the large scatter in their results, the authors place little reliance on this ratio. Using our expression for k_6 (Vol. 3, p. 203), we obtain $k_1 = 1.11 \times 10^{11} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$. Quoted by Refs. 89 and 105.
-	-	BALDWIN and WALKER 1973 ⁹⁵ Theoretical determination of the activation energy of E_1 using the reaction exothermicity. Authors obtain $E_1 = 13.4 \text{ kJ mol}^{-1}$ ($3.2 \text{ kcal mol}^{-1}$) lower than most experimental values.
-	443-663	BAULCH, DRYSDALE, DIN and RICHARDSON 1973 ⁹⁶ Static photolysis system. Photolysis of H_2O (2.39-3.59 kPa) at 184.9 nm in the presence of CO/CH_4 mixtures. $[\text{CO}_2]$ determined by gas chromatography. Suppression of $[\text{CO}_2]$ by addition of CH_4 to $\text{H}_2\text{O}/\text{CO}$ mixtures measured, hence obtaining the rate constant ratio $k_1/k_6 = 0.39(443 \text{ K}), 0.52(521 \text{ K}), 0.89(553 \text{ K})$ and $1.70(663 \text{ K})$. Using our own expression for k_6 (Vol. 3, p. 203), we obtain $k_1 = 3.94 \times 10^{10}(443 \text{ K}), 5.64 \times 10^{10}(521 \text{ K}), 9.94 \times 10^{10}(553 \text{ K})$ and $2.10 \times 10^{11} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ at 663 K, giving an overall expression $k_1 = 6.1 \times 10^{12} \exp(-2230/T) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$.
$6.03 \times 10^{13} \exp(-3000/T)$	Flame Temperatures	CORDEIRO 1973 ⁹⁷ Theoretical estimate obtained from computer simulation of premixed CH_4/O_2 flames. Expression based on those in Refs. 48, 92 and 107 and modified to fit a 28 reaction scheme.
7.23×10^8	230	DAVIS 1973 ^{98,99}
9.10×10^8	240	Flash photolysis of $\text{H}_2\text{O}(<1.5\%)/\text{CH}_4(1-4.5\%)/\text{He}$ mixtures of total pressures of 2.67-13.3 kPa. $[\text{OH}]$ monitored by resonance fluorescence at 307 nm. A sapphire window was used on the flash lamp with a cut off at about 141 nm to prevent photolysis of CH_4 . Author derives preliminary expression $k_1 = 1.5 \times 10^{12} \exp(-1670/T) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ over the temperature range 240-370 K.
4.34×10^9	298	
1.42×10^{10}	373	
		$\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O}$ (1) Data used in Ref. 119. The expression $k_1 = 1.5 \times 10^{12} \exp(-1160/T) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ is attributed to this source in Ref. 115.



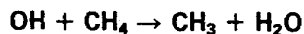
EXPERIMENTAL DATA - CONTINUED

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
1.67×10^{12}	1090	PEETERS and MAHNEN 1973 ¹⁰⁷
1.50×10^{12}	1145	PEETERS 1974 ¹²²
1.90×10^{12}	1190	Flame study. $\text{CH}_4(9.5\%)/\text{O}_2$ flames at a total pressure of
2.20×10^{12}	1242	5.33 kPa. $[\text{CH}_4]$, $[\text{H}_2\text{O}]$, $[\text{O}_2]$, $[\text{CO}]$, $[\text{CO}_2]$, $[\text{CH}_2\text{O}]$, $[\text{CH}_3]$,
2.54×10^{12}	1281	$[\text{CH}_3\text{O}_2]$, $[\text{CH}_3\text{OH}]$, $[\text{O}]$, $[\text{OH}]$, $[\text{H}_2]$, $[\text{H}]$, $[\text{HO}_2]$ determined by
2.49×10^{12}	1330	mass spectrometry.
2.70×10^{12}	1372	Rate constants calculated from the rate of disappearance of
2.96×10^{12}	1415	CH_4 . Under the prevailing conditions, reaction 8 was believed
3.38×10^{12}	1446	to be insignificant while a value of k_9 was taken from Ref. 60.
4.61×10^{12}	1485	$\text{H} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2$ (8)
5.20×10^{12}	1510	$\text{O} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{OH}$ (9)
5.43×10^{12}	1542	Authors derived an overall expression $k_1 = 3 \times 10^{13} \exp(-3000/T)$
5.47×10^{12}	1595	$\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$ over the temperature range 1100-1900 K.
5.44×10^{12}	1644	Quoted by Refs. 97, 119, 120, 134, 153, 163 and 208.
5.15×10^{12}	1683	Used by Refs. 166, 180 and 218.
4.98×10^{12}	1717	
4.48×10^{12}	1750	
4.38×10^{12}	1817	
4.28×10^{12}	1856	
1.11×10^9	240	DAVIS, FISCHER and SCHIFF 1974 ¹¹⁷
2.98×10^9	276	Flash photolysis of $\text{H}_2\text{O}(<1\%)/\text{He}$ mixtures with added
4.39×10^9	298	$\text{CH}_4(<5\%)$. Total pressures 4.00-53.3 kPa. $[\text{OH}]$ monitored by
1.42×10^{10}	373	resonance fluorescence at 307 nm.
		Extension of earlier work ⁹⁹ to higher pressures. Authors
		derive expression $k_1 = 1.42 \times 10^{12} \exp(-1710/T) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ over
		the temperature range 240-373 K.
		Quoted by Refs. 114, 116, 121, 138, 144, 156, 161, 163, 189 and 251.
		Used by Refs. 146, 193, 194, 204, 209, 218 and 250.
		Recommended by Ref. 134. E_1 quoted by Refs. 152, 158 and 177.
4.28×10^9	290	MARGITAN, KAUFMAN and ANDERSON 1974 ¹²¹
1.26×10^{10}	357	Discharge flow system. H_2/Ar mixtures at total pressures of
1.87×10^{10}	380	400-1330 Pa. OH produced by $\text{H} + \text{NO}_2$ titration. CH_4 added
2.47×10^{10}	405	downstream at 3-20 Pa pressure so that $[\text{CH}_4] \gg [\text{OH}]$. $[\text{OH}]$
3.07×10^{10}	440	monitored by resonance fluorescence at 309 nm.
		Authors derive expression $k_1 = 2.31 \times 10^{12} \exp(-1840/T) \text{ cm}^3$
		$\text{mol}^{-1}\text{s}^{-1}$ but note that activation energy may not be constant
		over this temperature range.
		$\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O}$ (1)
		Quoted by Refs. 136, 146, 189 and 251.
		E_1 quoted by Ref. 158.
		Used by Refs. 169, 155 and 218.



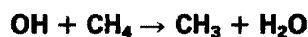
EXPERIMENTAL DATA - CONTINUED

Rate Constant $\text{k/cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
$3.1 \times 10^{12} \exp(-1900/T)$	300-500	BENSON 1975 ¹²⁸ Theoretical value derived from transition state theory. Based on the value of $S^0(\text{CH}_3\text{OH})$ calculated earlier in the same study.
1.6×10^{10}	381	GORDON and MULAC 1975 ¹³³
3.3×10^{10}	416	Pulse radiolysis of H_2O at 101.3 kPa pressure in the presence of CH_4 (3.33-20 kPa). $[\text{OH}]$ monitored by u.v. absorption spectroscopy at 308.7 nm. Quoted by Refs. 128, 134 and 251.
-	653	HUCKNALL, BOOTH and SAMPSON 1975 ¹³⁵ Static system. OH produced by H_2O_2 decomposition in H_2O_2 (3.33%)/ O_2 (20%)/ N_2 mixtures. $\text{C}_2\text{H}_6/\text{CH}_4$ mixtures (1:1, 1:3, 1:9) added in trace amounts (<1%). Total pressure 40 kPa. Experiments performed in boric acid coated vessels. $[\text{CH}_4]$, $[\text{C}_2\text{H}_6]$, $[\text{C}_2\text{H}_4]$ determined by gas chromatography. $[\text{H}_2\text{O}_2]$ by permanganate titration. From the data on consumption of CH_4 and C_2H_6 , authors obtained the ratio $k_{11}/k_1 = 9.6$ at 653 K. $\text{OH} + \text{C}_2\text{H}_6 \longrightarrow \text{C}_2\text{H}_5 + \text{H}_2\text{O} \quad (11)$
3.92×10^9	295	OVEREND, PARASKEVOPOULOS and CVEJANOVIC 1975 ¹³⁸ Flash photolysis of H_2O (about 0.5%)/He mixtures at 66.7 kPa pressure in the presence of CH_4 (0-51.5 kPa). $[\text{OH}]$ monitored by u.v. absorption spectroscopy. Results confirmed using flash photolysis of N_2O in the presence of H_2 to produce OH. $\text{N}_2\text{O} + h\nu \longrightarrow \text{N}_2 + \text{O}(^1\text{D})$ $\text{H}_2 + \text{O}(^1\text{D}) \longrightarrow \text{H} + \text{OH}$ A computer simulation showed the only competing reaction to be reaction 14. Authors assumed k_{14} = gas kinetics collision frequency, possibly accounting for slightly low value of k_1 . $\text{OH} + \text{CH}_3 \longrightarrow \text{products} \quad (14)$ Quoted by Refs. 134, 182, 189, 225, 247 and 251. Preliminary value $k_1 = 5.0 \times 10^9 \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ quoted in Ref. 119.
$2.8 \times 10^{12} \exp(-1900/T)$	300-480	STEINERT and ZELLNER 1975 ¹⁴² Flash photolysis of H_2O (1-2%)/He mixtures at total pressures of 1.33-3.33 kPa in the presence of trace amounts of CH_4 . $[\text{OH}]$ monitored by u.v. absorption spectroscopy at 308.2 nm. Experiments extended to 700 K but above 480 K the value of k_1 appeared to increase more rapidly than described by the



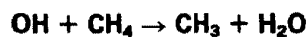
EXPERIMENTAL DATA - CONTINUED

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
		<p>Arrhenius expression. After a correction had been made for the effect of reaction 14 (assuming $k_{14} = 10^{13} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ at 700K) extrapolation of the high temperature results to flame temperatures gave good agreement with the results of Peeters and Mahnen,¹⁰⁷ suggesting non-Arrhenius behaviour.</p> <p style="text-align: right;"> $\text{OH} + \text{CH}_3 \rightarrow \text{products} \quad (14)$ $\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O} \quad (1)$ </p> <p>Used by Ref. 250.</p>
1.34×10^{12}	1300	<p>BRADLEY, CAPEY, FAIR and PRITCHARD 1976¹⁴⁹</p> <p>Shock tube study. H_2O_2 (about 0.1%)/Ar mixtures at about 15 kPa pressure in the presence of CH_4 at 3.86–30.0 Pa pressure. Incident shocks. $[\text{OH}]$ monitored by u.v. absorption spectroscopy at 309.2 nm.</p> <p>Shock tube coated by epoxy resin to avoid catalytic decomposition of H_2O_2. Temperature of 1300 K chosen as being most convenient for measurement of $[\text{OH}]$. A 28 reaction mechanism was formulated and a computer fit made to give the quoted value of k_1. Because of the assumptions necessary regarding the fate of OH and H_2O_2 the authors do not consider this value to be at all accurate, preferring the ratio $k_6:k_{15}:k_7:k_1:k_{12}:k_{11} = 0.18:0.19:0.59:1.00:2.33:2.88$ obtained in the same study using other substrates.</p> <p style="text-align: right;"> $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H} \quad (6)$ $\text{OH} + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_5 + \text{H}_2\text{O} \quad (11)$ $\text{OH} + \text{C}_2\text{H}_4 \rightarrow \text{products} \quad (12)$ $\text{OH} + \text{CF}_3\text{H} \rightarrow \text{CF}_3 + \text{H}_2\text{O} \quad (15)$ </p> <p>Using our value of k_6 (Vol. 3, p. 203), we obtain $k_1 = 1.22 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$. Using Baldwin and Walker's value of k_7,²¹⁵ we obtain $k_1 = 3.3 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$.</p>
4.58×10^9	298	<p>COX, DERWENT and HOLT 1976¹⁵⁰</p> <p>COX, DERWENT, HOLT and KERR 1976¹⁵¹</p> <p>Photolysis flow system. HNO_2 (<0.01%)/N_2 (66%)/O_2 mixtures at 101.3 kPa pressure containing trace quantities of NO and NO_2, photolysed at 330–380 nm. CH_4 added in large excess ($[\text{CH}_4]:[\text{HNO}_2] = 20:1-2 \times 10^5:1$). $[\text{NO}_x]$ determined by NO_x analyser; $[\text{CH}_3\text{ONO}]$, $[\text{CH}_3\text{ONO}_2]$, $[\text{CH}_4]$ by gas chromatography; $[\text{HCHO}]$ colorimetrically.</p> <p>Authors took 20-step mechanism and assuming $[\text{OH}]$ reduced only slightly on addition of CH_4 obtained $k_{16}/k_1 = 906$ from a complex kinetic analysis of the product yield data.</p> <p style="text-align: right;">$\text{OH} + \text{HNO}_2 \rightarrow \text{NO}_2 + \text{H}_2\text{O} \quad (16)$</p>



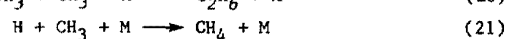
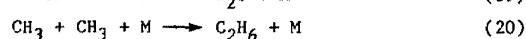
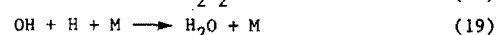
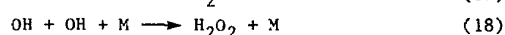
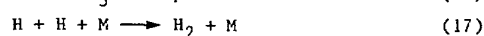
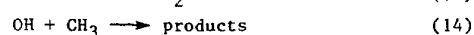
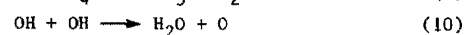
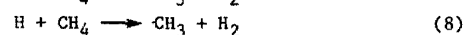
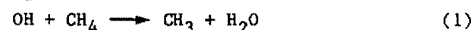
EXPERIMENTAL DATA - CONTINUED

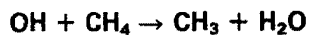
Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
		Using their own value of k_{16}/k_7 determined earlier in the same study, they obtained $k_1/k_7 = 1.04$ at 298 K. They used a consensus value for k_7 , slightly higher than our evaluation to give the quoted value of k_1 .
		$\text{H}_2 + \text{OH} \longrightarrow \text{H}_2\text{O} + \text{H} \quad (7)$
		Quoted by Ref. 197.
$4.5 \times 10^{14} \exp(-4400/T)$	780-1200	EBERIUS, HOYERMANN and WAGNER, quoted by ZELLNER and STEINERT 1976 ¹⁶³ No details available.
5.7×10^9	296	HOWARD and EVENSON 1976 ¹⁵⁶ Discharge flow system. H_2/He mixtures at total pressures of 107-1300 Pa, OH radicals being produced by $\text{H} + \text{NO}_2$ titration. CH_4 added downstream at <8% of total pressure. [OH] monitored by laser magnetic resonance spectroscopy. Very low concentrations of [OH] obtained (about 10^{-15} or 10^{-14} mol cm^{-3}). Authors also derive the theoretical expression $k_1 = 2 \times 10^{12} \exp(-1700/T)$ $\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$ from BEBO theory and from the measurements of Refs. 117 and 121. Quoted by Refs. 146, 163, 222 and 251. Used by Ref. 210.
5.3×10^9	298	ZELLNER and STEINERT 1976 ¹⁶³
8.9×10^9	330	Flash photolysis of $\text{H}_2\text{O}(1.79-100\%)/\text{He}$ mixtures at 18.7 Pa-
1.2×10^{10}	358	4.18 kPa pressure, in the presence of $\text{CH}_4(28.0 \text{ Pa}-5.24 \text{ kPa})$.
1.7×10^{10}	381	[OH] monitored by u.v. absorption spectroscopy at 308.2 nm.
3.7×10^{10}	444	Extension of work in Ref. 142. He added to photolysis cell
4.2×10^{10}	453	above 381 K to suppress flash heating. A 7-step reaction
6.8×10^{10}	498	mechanism was chosen and from a computer fit the authors
1.05×10^{11}	525	concluded that only reactions 1 and 14 were important in OH
1.55×10^{11}	564	removal. Values of k_1 were obtained using the author's own
1.51×10^{11}	576	value of $k_{14} = 2 \times 10^{13}$ $\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$, determined in the same
1.66×10^{11}	584	study. A strongly curved Arrhenius plot was obtained and they
2.02×10^{11}	622	derived the expression $k_1 = 3.47 \times 10^3 T^{3.08} \exp(-1010/T)$ cm^3
3.32×10^{11}	629	$\text{mol}^{-1}\text{s}^{-1}$ over the temperature range 300-900 K.
4.95×10^{11}	671	$\text{OH} + \text{CH}_4 \longrightarrow \text{CH}_3 + \text{H}_2\text{O} \quad (1)$
5.00×10^{11}	680	$\text{OH} + \text{CH}_3 \longrightarrow \text{products} \quad (14)$
6.76×10^{11}	738	Used by Refs. 188, 190, 207, 218, 227, 228, 242 and 243.
7.31×10^{11}	756	Curvature of Arrhenius plot cited by Refs. 140 and 226.
9.11×10^{11}	776	E_a quoted by Refs. 189, 199 and 251.
1.63×10^{12}	892	



EXPERIMENTAL DATA - CONTINUED

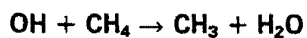
Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
2.12x10 ¹²	1140	ERNST, WAGNER, and ZELLNER 1978 ¹⁹⁶
2.12x10 ¹²	1160	Combined flash photolysis-shock tube study. Ar/H ₂ O(about
2.18x10 ¹²	1165	0.5%) mixtures at a total pressure of about 40 kPa containing
2.09x10 ¹²	1188	0.6-16% CH ₄ . Reflected shock. [OH] monitored by resonance
1.95x10 ¹²	1192	absorption at 308 nm.
1.97x10 ¹²	1203	Absorption by OH found not to obey Beer-Lambert law;
2.01x10 ¹²	1220	$\ln(I_0/I) = \epsilon_{\text{eff}}([\text{OH}]\cdot l)^Y$ used. Calibration using partial
2.06x10 ¹²	1245	equilibrium OH concentrations in heated H ₂ /O ₂ mixtures gave
1.75x10 ¹²	1260	$\gamma = 0.74$ and $\epsilon_{\text{eff}} = 1.6 \times 10^5 \text{ cm}^2\text{mol}^{-1}$. Reaction 1 is only
1.86x10 ¹²	1260	reaction removing OH; first order kinetics obeyed.
1.82x10 ¹²	1265	
1.93x10 ¹²	1270	
1.85x10 ¹²	1270	
1.91x10 ¹²	1275	
1.86x10 ¹²	1275	
1.90x10 ¹²	1303	
1.80x10 ¹²	1313	
1.65x10 ¹²	1335	
1.53x10 ¹²	1404	
2.23x10 ¹²	1410	
1.77x10 ¹²	1415	
1.52x10 ¹²	1500	
1.35x10 ¹²	1505	
4.2x10 ⁹	296	SWORSKI, HOCHANADEL and OGREN 1980 ²⁴⁰
		Flash photolysis of N ₂ /CH ₄ (16-97%) mixtures saturated with
		H ₂ O, at a total pressure of 101 kPa. [CH ₃] monitored by
		absorption at 216 nm.
		[CH ₃] obtained using $\epsilon(\text{CH}_3) = 9 \times 10^6 \text{ cm}^3\text{mol}^{-1} \text{ cm}^{-1}$ at a 0.6
		nm band width. [CH ₃] profiles computer fitted to reaction
		scheme.





EXPERIMENTAL DATA - CONTINUED

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
		Values of k_8 , k_{10} , k_{17} , k_{18} , k_{19} and k_{20} assumed, values of k_1 , k_{14} , k_{21} obtained. Sensitivity to assumed values tested and incorporated in error limits of $\pm 10\%$. Used by Ref. 236.
4.51x10 ⁹	298	TULLY and RAVISHANKARA 1980 ²⁴¹
2.84x10 ¹⁰	398	Flash photolysis of Ar(6.7 kPa)/CH ₄ (0-0.13 kPa)/H ₂ O(20 Pa)
4.87x10 ¹⁰	448	mixtures. [OH] monitored by resonance fluorescence and photon
8.73x10 ¹⁰	511	counting.
1.01x10 ¹¹	529	Static system. First order decay of OH. Authors derive
1.89x10 ¹¹	600	expression $k_1 = 7.95 \times 10^6 T^{1.32} \exp(-1355/T) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ which is
1.66x10 ¹¹	619	barely distinguishable from the expression suggested by
3.48x10 ¹¹	696	Zellner. ²²⁹
5.06x10 ¹¹	772	Quoted by Ref. 251.
9.03x10 ¹¹	915	Used by Ref. 250.
1.20x10 ¹²	1020	
4.61x10 ⁹	300	HUSAIN, PLANE and SLATER 1981 ²⁴⁵ Flash photolysis study. [OH] monitored by time-resolved resonance fluorescence at 307 nm. OH radicals generated by vacuum u.v. photolysis of water vapour in He/CH ₄ mixture at a total pressure of about 3.2 kPa. Flow system, kinetically equivalent to a static system used. Using observed first-order rate coefficients for decay of OH, the absolute second-order rate constant k_1 was determined. Variation of [H ₂ O] by a factor of 5 did not significantly affect k_1 . Reactions of OH with both CH ₄ and CO were investigated in order to test the kinetic system. Experimental rate constants in good agreement with those given in Refs. 117 and 230.
3.35x10 ⁹	269	JEONG and KAUFMAN 1981 ²⁵¹
4.75x10 ⁹	297	Discharge flow system. [OH] monitored by resonance
1.07x10 ¹⁰	339	fluorescence. Experiments carried out under pseudo-first-order
2.09x10 ¹⁰	389	conditions [RH]>>[OH].
3.30x10 ¹⁰	419	Two Arrhenius expressions derived, $k_1 = 3.37 \times 10^{12} \exp$
6.14x10 ¹⁰	473	$(-1970/T) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ and $k_1 = 3.77 \times 10^6 T^{2.00} \exp(-1260/T)$ $\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$. Fitting procedure used to give latter expression faulty. Later corrected to $k_1 = 0.77 T^{4.32} \exp(-455/T)$ $\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$. ²⁵⁴ Used by Ref. 250.

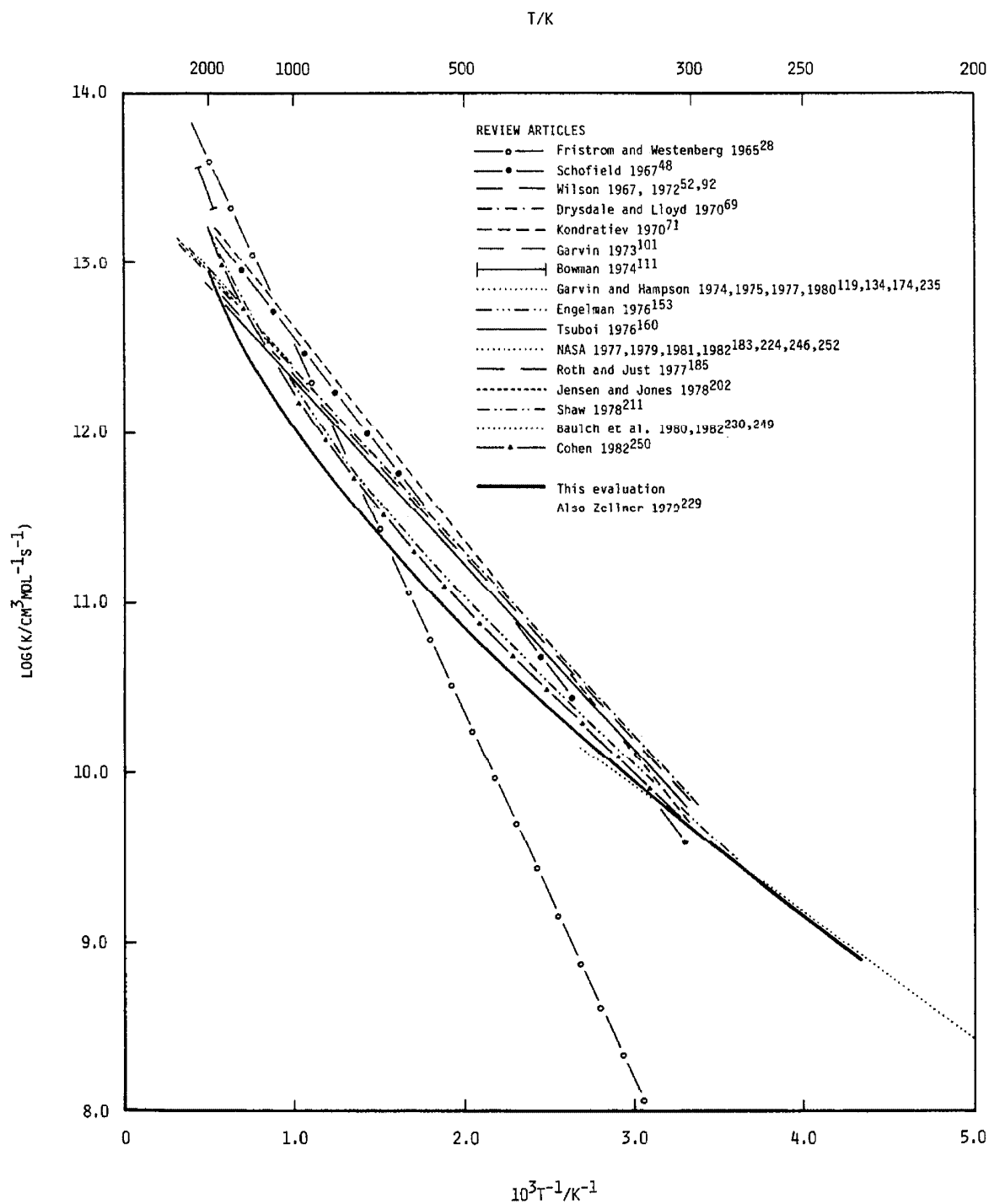
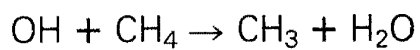


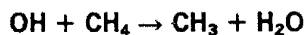
EXPERIMENTAL DATA - CONTINUED

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
$9.1 \times 10^{5} T^{2.3} \exp(-1370/T)$	300-2000	COHEN 1982 ²⁵⁰ Theoretical expression derived using transition state theory and experimental data of Refs. 70,117,142,241 and 251.
-	413-693	BAULCH, CRAVEN, DIN, DRYSDALE, GRANT, RICHARDSON, WALKER and WATLING 1983 ²⁵³ Static photolysis system. Photolysis of H_2O (2.85-12.6 kPa) at 184.9 nm in the presence of CO/CH_4 mixtures. $[\text{CO}_2]$ determined by gas chromatography. Extension of previous work. ⁹⁶ Obtained rate constant ratios, $k_1/k_6 = 0.24(413 \text{ K}), 0.34(417 \text{ K}), 0.22(422 \text{ K}), 0.46(471 \text{ K}), 0.55(505 \text{ K}), 0.58(517 \text{ K}), 0.61(546 \text{ K}), 1.38(603 \text{ K}), 2.80(693 \text{ K})$. $\text{CO} + \text{OH} \longrightarrow \text{CO}_2 + \text{H} \quad (6)$ Using our expression for k_6 (Vol. 3, p. 206) we obtain $k_1 \times 10^{-11}/\text{cm}^3\text{mol}^{-1}\text{s}^{-1} = 0.236(413 \text{ K}), 0.334(417 \text{ K}), 0.222(422 \text{ K}), 0.477(471 \text{ K}), 0.591(505 \text{ K}), 0.623(517 \text{ K}), 0.675(546 \text{ K}), 1.61(603 \text{ K}), 3.55(693 \text{ K})$.

REVIEW ARTICLES

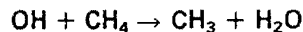
$1-2 \times 10^{13}$	1750	FENIMORE 1964 ²³ Consensus value. Value based on k_1/k_6 ratios from Refs. 11 and 14, combined with author's own value for k_6 evaluated in the same work. Author suspects that E_1 as determined in Ref. 11 is probably too high. $\text{OH} + \text{CH}_4 \longrightarrow \text{CH}_3 + \text{H}_2\text{O} \quad (1)$ $\text{CO} + \text{OH} \longrightarrow \text{CO}_2 + \text{H} \quad (6)$
$5.0 \times 10^{14} \exp(-5000/T)$	300-2500	FRISTROM and WESTENBERG 1965 ²⁸ Evaluation. Based on data from Refs. 3,11 and 14. Also reported are the results of Pratt ¹⁷ (considered too low) and the ratio given by Hoare. ¹⁶ Quoted by Refs. 35,43 and 69. Used by Ref. 47.





REVIEW ARTICLES - CONTINUED

Rate Constant $\text{k}/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
$7.2 \times 10^{13} \exp(-2970/T)$	300-1850	SCHOFIELD 1967 ⁴⁸ Evaluation. Least-squares fit based on data from Refs. 11, 14, 20, 25, 33, 34, 38, 54. Also quotes Ref. 3 but notes criticism of H_2O discharge method by Kaufman et al. ¹³ Quoted by Refs. 61, 113, 146, 153 and 202. Used by Ref. 179.
$2.8 \times 10^{13} \exp(-2500/T)$	300-2000	WILSON 1967 ^{52,53} Suggested value. Quotes Refs. 20, 35, 38, 41 and 54. The expression $k_1/k_6 = 5.6 \times 10^{-2} \exp[2200(0.0033 - T^{-1})]$ derived using the ratio k_1/k_6 from Refs. 11, 14 and 37. The quoted expression for k_1 obtained from the expressions for k_1/k_6 and k_6 (evaluated in the same study). The intermediate temperature work of Hoare ^{33,34} is rejected on the grounds of high $[\text{HO}_2]$ in his system. $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H} \quad (6)$ Quoted by Ref. 153. Used by Ref. 195.
-	-	KAUFMAN 1969 ⁶³ Review of elementary gas reactions. Quotes Refs. 41, 54 and 57. Also mentions the ratios determined in Ref. 62.
$2.9 \times 10^{13} \exp(-2500/T)$	300-3000	DRYSDALE and LLOYD 1970 ⁶⁹ Evaluation. Based on data from Refs. 37, 38, 41, 45, 52, 54 and 65. Also quoted are Refs. 3 and 17 but authors note criticism of H_2O discharge method by Kaufman et al. ¹³ Quoted by Refs. 88, 100 and 124. Used by Ref. 153. Misquoted by Refs. 83 and 102.
$7.94 \times 10^{13} \exp(-2910/T)$	300-1800	KONDRATIEV 1970 ⁷¹ Evaluation. Least-squares fit to data of Refs. 11, 14, 20, 37, 38, 41 and 54. Also quoted are Refs. 1, 3, 16, 17, 25, 33 and 45. Notes doubts of Steacie ⁴ that the activation energy E_1 given in Ref. 1 may not be accurate. Quoted by Refs. 90, 153, 202 and 216. Used by Ref. 173.



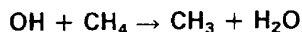
REVIEW ARTICLES - CONTINUED

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
$(1.08 \pm 0.38) \times 10^{14} \exp(-2980/T)$	300-1800	SINGH and SAWYER 1970 ⁷³ Evaluation. Least-squares fit to data of Refs. 11,14,37,38, 41 and 54. The expression is suspect and is not plotted because the value of k_1 calculated using k_1/k_6 from Ref. 37, and k_6 from Ref. 56 is in error by one order of magnitude. $\text{OH} + \text{CH}_4 \longrightarrow \text{CH}_3 + \text{H}_2\text{O} \quad (1)$ $\text{CO} + \text{OH} \longrightarrow \text{CO}_2 + \text{H} \quad (6)$ Author also misquotes but does not use Ref. 3, noting the objection of Kaufman et al. ²¹ to the source of OH used and quotes but does not use the ratio k_1/k_6 from Ref. 65.
-	-	WILSON 1970 ⁷⁵ Review of activation energies of OH radical reactions. Quotes Refs. 11,54 and 70. Author notes steady reduction in value of E_1 with progressively more recent determinations. Suggests possible non-Arrhenius behaviour to explain discrepancies between values measured at high and low temperatures.
6.6×10^9	298	ZAFONTE 1970 ⁷⁶ Preferred value. Quotes Refs. 3,54 and 70. Notes that results from Ref. 3 may be suspect due to use of discharge in H_2O as OH source. Preferred value is that of Greiner. ⁷⁰
-	-	CAMPBELL and BAULCH 1972 ⁸⁷ Review of atomic and bimolecular reactions. Quotes general expression determined by Baker et al. ⁶⁶ Also refers to work in Refs. 69 and 70.
$2.8 \times 10^{13} \exp(-2500/T)$	300-2000	WILSON 1972 ⁹² Evaluation. Updating of Refs. 52 and 53. Author also recommends the ratio $k_1/k_6 = 92 \exp(2200/T)$ between 300-2000 K. Quoted by Refs. 86,97,101,116,117,118,119,125,132,134,138,139 146 and 152. Used by Refs. 104,153,159,187,201 and 217.
$2.9 \times 10^{13} \exp(-2500/T)$	300-2000	GARVIN 1973 ¹⁰¹ Recommended expression. Expression is taken from Ref. 92. Recommendation superseded by Refs. 119 and 134. Quoted by Ref. 141.



REVIEW ARTICLES - CONTINUED

Rate Constant $\text{k}/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
-	443-923	BAULCH and DRYSDALE 1974 ¹¹⁰ Review of rate data for the $\text{CO} + \text{OH}$ reaction. Quotes k_1/k_6 from Refs. 25,33,58,84 and 96. Good agreement noted between these ratios and those derived from the work of Greiner. ⁷⁰ No attempt made to deduce k_1 or k_6 from these ratios. $\text{OH} + \text{CH}_4 \longrightarrow \text{CH}_3 + \text{H}_2\text{O} \quad (1)$ $\text{CO} + \text{OH} \longrightarrow \text{CO}_2 + \text{H} \quad (6)$
$6 \times 10^{14} \exp(-6290/T)$	1875-2240	BOWMAN 1974 ¹¹¹ Evaluation for use in the high temperature CH_4/O_2 reaction. No further details given. Quoted by Refs. 129 and 137. Used by Refs. 165,167 and 212.
-	-	DAVIS 1974 ¹¹⁶ Review of OH reactions in the atmosphere. Quotes Refs. 92 and 117. Notes the work of Greiner ⁷⁰ not reviewed by Wilson ⁹² and points out that the activation energy is probably lower than the 21 kJ mol^{-1} (5 kcal mol^{-1}) given by the latter.
$1.77 \times 10^{12} \exp(-1770/T)$	240-370	GARVIN and HAMPSON 1974 ¹¹⁹ Recommended expression. Expression calculated from data by Davis. ⁹⁹ Also quoted are Refs. 70,92 and 107, and preliminary work by Paraskevopoulos. Recommendation superceded by Ref. 134. Quoted by Refs. 103,116,143 and 153.
$1.42 \times 10^{12} \exp(-1710/T)$	240-373	HAMPSON and GARVIN 1975 ¹³⁴ Recommended expression is that of Davis. ¹¹⁷ Also quoted are Refs. 70,92,107,133 and 138. Updates earlier work. ¹¹⁹ Used by Refs. 154,170,171,175,186,200,203,213 and 221. Quoted by Ref. 202. E_1 quoted by Ref. 177. Recommended by Ref. 183.
-	-	KAUFMAN 1975 ¹³⁶ Review of hydrogen chemistry in the atmosphere. Quotes Refs. 70 and 121; also the activation energy E_1 given by Wilson. ⁹²
4.5×10^9	298	ANDERSON 1976 ¹⁴⁶ Selected value for use in atmospheric studies is that of Davis. ¹¹⁷ Also quotes Refs. 48,92,121 and 156. Criteria for selection not given.



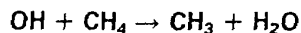
REVIEW ARTICLES - CONTINUED

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
$3.1 \times 10^{13} \exp(-2500/T)$	1500-2500	ENGELMAN 1976 ¹⁵³ Evaluation. Based on data of Refs. 67,69 and 92. Also listed are Refs. 3,11,14,20,26,35,38,41,48,52,54,64,70,71,107 and 119. No details given as to how evaluation was arrived at. Quoted by Ref. 164.
-	-	KERR 1976 ¹⁵⁷ Review of H atom transfer reactions. Quotes Greiner. ⁷⁰
$2.5 \times 10^{13} \exp(-2500/T)$	300-2000	TSUBOI 1976 ¹⁶⁰ Evaluation for use in the CH_4/O_2 system at high temperatures. Used in modeling shock tube studies of $\text{CH}_4/\text{O}_2/\text{Ar}$ mixtures. Based on work in Refs. 11,14,21,22,25,38 and 54.
$1.42 \times 10^{12} \exp(-1710/T)$	240-373	HAMPSON and GARVIN 1977 ¹⁷⁴ Recommended value is that of Davis. ¹¹⁷ Considers also Refs. 70,107,121,133 and 138. Used by Ref. 239.
$2.8 \times 10^{13} \exp(-2500/T)$	1500-2250	ROTH and JUST 1977 ¹⁸⁵ Review. Used in shock tube study of $\text{CH}_4/\text{N}_2\text{O}/\text{Ar}$ system. Based on expressions in Refs. 67,107 and 112 in the temperature range quoted, this expression gives values of k_1 15-35% higher than those given by the parent expressions.
$1.42 \times 10^{12} \exp(-1710/T)$	240-373	NASA 1977 ¹⁸³ NASA 1979 ²²⁴ NASA 1981 ²⁴⁶ Evaluation. This is a continuing series of evaluations by NASA Evaluation Panel. The value given by Davis ¹¹⁷ is accepted over the temperature range quoted in each of the evaluations. Experimental results deviate from this expression at higher temperatures. Quoted by Ref. 251. Used by Refs. 178,192,198,205,206,220,223,232,234 and 244.
$3 \times 10^{13} \exp(-2500/T)$	1000-3000	JENSEN and JONES 1978 ²⁰² Recommended expression is that of Wilson. ⁵⁴ Also quotes Refs. 48,71 and 134.



REVIEW ARTICLES - CONTINUED

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
$8.5 \times 10^6 T^2 \exp(-1485/T)$	250-2000	SHAW 1978 ²¹¹ Evaluation subject to certain constraints of transition state theory. Data better fitted using $\Delta C_p^{\ddagger} = 0$ rather than $\Delta C_p^{\ddagger} = \text{constant}$. Uses data of Refs. 11,14,20,25,33,37,38,45, 54,55,65,70,107,117,121,133,138,149,150,156 and 163.
-	-	ATKINSON, DARNALL, LLOYD, WINER, and PITTS 1979 ²¹⁴ Review of kinetics of hydroxyl radical reactions with organic compounds. No recommendation given. Lists work of Refs. 54,70,117,121,133,138,156 and 163. Quoted by Ref. 219.
$1.5 \times 10^6 T^{2.13} \exp(-1233/T)$	250-2000	ZELLNER 1979 ²²⁹ Evaluation. Based on data from Refs. 20,38,67,70,107,117, 121,142,149 and 196, and data at 300 K from other unquoted authors. Used by Ref. 233.
$1.42 \times 10^{12} \exp(-1710/T)$	240-373	HAMPSON 1980 ²³⁵ Recommended value. Lists Refs. 70,107,117,121,133,138,150, 156,163,224 and 230. Accepts expression in Refs. 224 and 230.
$1.42 \times 10^{12} \exp(-1710/T)$	200-300	CODATA 1 1980 ²³⁰ CODATA 2 1982 ²⁴⁹ Evaluation for atmospheric modeling. Value of Davis ¹¹⁷ accepted for temperature range of interest in atmospheric chemistry. Quoted by Ref. 251.
-	-	WESTLEY 1981 ²⁴⁸ Compilation. Lists Refs. 107,117,121,133,138,142,150,151,156 and 163.
$1.42 \times 10^{12} \exp(-1710/T)$	240-373	NASA 1982 ²⁵² Evaluation. New data of Tully et al. ²⁴¹ are in good agreement with previously recommended expression. ^{224,246}
$1.9 \times 10^5 T^{2.4} \exp(-1060/T)$	300-2000	COHEN and WESTBERG 1983 ²⁵⁵ Evaluation. Based on data of Refs. 54,70,117,121,133,138, 149,151,156,163,196,241 and 251.



REVIEW ARTICLES - CONTINUED

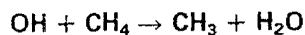
Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
$1.6 \times 10^6 T^{2.1} \exp(-1240/T)$	300-2200	WARNATZ 1985 ²⁵⁶ Evaluation. Considers data of Refs. 70,117,133,138,149,151, 156,196,240 and 241. Recommended expression is that of Tully and Ravishankara. ²⁴¹

ISOTOPIC REACTION $\text{OD} + \text{CH}_4$

4.8×10^9	300	GREINER 1968 ⁵⁷ Flash photolysis of D_2O in the presence of 13.0 kPa CH_4 . No further details given. Method reported to be the same as that used in other work. ⁴¹ No isotope effect observed. Quoted by Refs. 63,69,72 and 106.
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ISOTOPIC REACTIONS $\text{OH} + \text{CDH}_3$, CD_2H_2 , CD_3H AND CD_4

2.2×10^{10} (D1)	416	GORDON and MULAC 1975 ¹³³
1.8×10^{10} (D2)	416	Pulse radiolysis of H_2O at 101.3 kPa in the presence of CDH_3
6.7×10^9 (D3)	416	(6.67-23.3 kPa), CD_2H_2 (6.67-26.7 kPa), CD_3H (6.67-22.7 kPa) or
3.0×10^9 (D4)	416	CD_4 (6.67-26.7 kPa). $[\text{OH}]$ monitored by u.v. absorption spectroscopy at 308.7 nm. From the steady decrease in rate constant with increasing deuterium content, the authors concluded that there is a marked primary isotope effect.
		$\text{OH} + \text{CDH}_3 \rightarrow \text{Products}$ (D1)
		$\text{OH} + \text{CD}_2\text{H}_2 \rightarrow \text{Products}$ (D2)
		$\text{OH} + \text{CD}_3\text{H} \rightarrow \text{Products}$ (D3)
		$\text{OH} + \text{CD}_4 \rightarrow \text{CD}_3 + \text{HDO}$ (D4)



ISOTOPIC REACTIONS - CONTINUED

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
ISOTOPIC REACTION $\text{OH} + {}^{13}\text{CH}_4$		
-	Unspecified	<p>RUST and STEVENS 1980²³⁸</p> <p>Static system. OH from photolysis of H_2O_2 (<1.0%) in the presence of CH_4 (<0.1%)/O_2 (about 3.5%) mixtures, made up to total pressures of 80-90 kPa with He. Samples irradiated by filtered high pressure Hg lamp from 20-40 hours.</p> <p>The carbon kinetic isotope effect, ${}^{12}\text{k}/{}^{13}\text{k}$ was calculated from both the yield of photolytic oxidation products and yield of CO_2 after combustion of unreacted CH_4. An average value of ${}^{12}\text{k}/{}^{13}\text{k} = 1.003$ was measured.</p>

Discussion

Hydroxyl radicals abstract hydrogen from alkanes according to the general reaction (A)

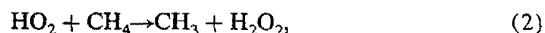


where R is an alkyl radical. This reaction is of fundamental importance in hydrocarbon combustion systems where it is generally accepted to constitute the principal attack on the alkane molecule.^{11,28,69} The reaction of OH with methane has received the most attention, but many of the details discussed here with reference to reaction (1) are relevant to other alkanes and will be referred to when considering their reactions with OH:



In addition, reaction (1) plays a significant role in atmospheric chemistry¹⁶² and in air pollution.^{118,139} It is therefore important that its rate constant be known accurately over a wide temperature range. In recent times reaction (1) has received added attention because sufficient good quality data are now available to demonstrate that the rate constant does not conform to a simple Arrhenius expression.

In combustion systems three possible alternatives to reaction (1) have been considered for the removal of methane in the presence of oxygen:



Of these, reaction (9) is slower than reaction (1) at all temperatures; reaction (2) has received little study, but evidence shows it to be too slow,²⁵ while reaction (8), of comparable speed to reaction (1) at flame temperatures, is unimportant in oxygen-rich conditions.

Until recently, reaction (1) had been investigated mainly in the low- and high-temperature regions with little data existing in between. New work, particularly that of Tully and Ravishankara,²⁴¹ has now bridged the gap.

Below 500 K there is very good agreement among the bulk of the low-temperature data, involving flow discharge,^{3,22,54,64,121,156,251} flash photolysis,^{41,45,70,99,117,138,142,163,240,241,245} static photolysis,⁸⁴ discharge,⁴⁹ photolysis flow,^{150,151} and pulse radiolysis¹³³ methods. There are a few notable exceptions. We reject the data of Avramenko,³ who used a discharge through H_2O as his source of OH. This has since been shown¹³ to produce H and O atoms and molecular and radical species as well as OH, which may lead to anomalies in the observed rate for OH removal. Of the low values at room temperature we have insufficient information to comment on the flow system of Serauskas and Keller⁶⁴ while we reject the data of Suzuki and Morinaga,⁴⁹ who made no attempt to correct for wall loss of OH. Horne and Norrish⁴⁵ carried out very few experiments and admit to the possibility of a large error in their results.

In the remaining studies care was taken in discharge flow work to reduce OH wall recombination to a minimum by coating flow tube surfaces, and all of the flash photolysis

studies used sufficiently low OH concentrations to ensure first-order kinetics without interference from competitive reactions. Steinert and Zellner^{142,163} considered the fast reaction (14) but concluded that the OH and CH₃ concentrations were too low for it to have any significant effect:



Many of the studies in the low-temperature region have been made at or close to 298 K. On the basis of the absolute rate measurements in Refs. 41, 54, 70, 99, 117, 121, 138, 156, 163, 240, 241, 245, and 251 and a relative measurement from Ref. 151 which are all in good agreement, we recommend a value of

$$k_1 = 4.7 \times 10^9 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

at 298 K with error limits of $\Delta \log k = \pm 0.1$.

It is clear from the data over the whole temperature range that the Arrhenius plot is curved but over the restricted temperature range 230–500 K, the results can be fitted within the experimental scatter to a simple Arrhenius expression given by

$$k_1 = 3.4 \times 10^{12} \exp(-1950/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1},$$

with error limits of $\pm 40\%$. A number of recent evaluations concerned with supplying data for atmospheric modeling^{134,183,230,235,249,252} recommend the expression,

$$k_1 = 1.42 \times 10^{12} \exp(-1710/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1},$$

for the range 240–373 K first suggested by Davis *et al.*¹¹⁷ The small differences between this and our recommended expression merely reflect the effect of the curvature of the Arrhenius plot for the different ranges of temperature to which the two expressions apply.

There is less agreement among the high-temperature data. A number of these results were obtained from CH₄/O₂ or air flames, in which determination of [OH] presents the major problem. Fristrom^{14,20} and Fenimore and Jones¹¹ determined concentration profiles for stable species from mass spectrometry and then [OH] from the equilibrium in reaction (6) assuming OH in equilibrium at the hot boundary. We agree with Wilson⁹² that this assumption is likely to be incorrect and to lead to high values of k_1 ; [OH] in the post-flame cases of many flames has been found to be higher than the equilibrium concentration. The value of Dixon-Lewis and Williams,³⁸ with [OH] monitored spectroscopically, is more likely to be correct. Pratt¹⁷ resolves the scatter on his data by quoting an average k_1 at 1200 K to within an order of magnitude.

Peeters and Mahnen^{107,122} also used mass spectrometry to measure concentration profiles in a low-pressure CH₄/O₂ flame, but were able to monitor a much greater range of species than previous workers, including atoms and radicals. This increased amount of information provides a much better basis for understanding the reaction mechanism and hence to correct for minor pathways in competition with reaction (1) for removal of OH and CH₄. There is a fairly large scatter in the results, reflecting the difficulty of such measurements at these temperatures, but we feel that in essence the results are reliable. They agree well with the more recent shock-tube work of Ernst *et al.*,¹⁹⁸ in which OH radi-

cals were produced by flash photolysis rather than by using the high temperatures generated by the shock wave as is usual. The preparation of OH in this way makes the measurement of k_1 much more direct. The values of k_1 so obtained over the range 1140–1505 K appear to decrease with increase in temperature by about 35% over this range but this is considered to be a measure of the experimental precision rather than indicative of a genuine negative temperature coefficient.

There are two sets of direct determinations of k_1 covering the intermediate temperature range 1000 K $> T >$ 500 K,^{163,241} and both extend to $T <$ 500 K, where they agree well with other measurements. Both employ flash photolysis. The results from these studies are identical within experimental error up to about 650 K but diverge slightly above that temperature. We prefer the results of Tully and Ravishankara,²⁴¹ since they extrapolate extremely well to the most reliable data at higher temperatures. This view is shared by the senior author of the other study.²²⁹

A considerable number of data are available in the form of rate constant ratios, especially in the intermediate temperature range.^{16,25,33,34,37,65,67,84,96,149,253} The reference reaction has usually been (6) or (7):



For values of k_6 , we have used our own evaluation (Vol. 3, p. 203) but for k_7 , data which have been produced since our original evaluation (Vol. 1, p. 77) suggest that k_7 would better be fitted to a curved Arrhenius plot and we have used the expression,

$$k_7 = 1.28 \times 10^5 T^{1.5} \exp(-1480/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1},$$

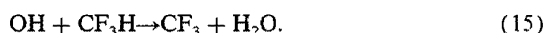
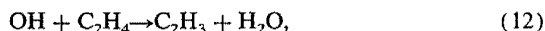
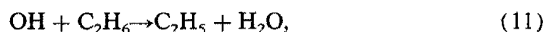
for the range 300–900 K as recommended by Baldwin and Walker.²¹⁵

In the various studies of Baldwin *et al.*,^{37,55,67} traces of CH₄ were added to slowly reacting H₂/O₂ mixtures. This is a complex system but is now well understood and successive refinements to the mechanism have brought the values of k_1 calculated from the measurements of k_1/k_7 into good agreement with the more direct studies. Hoare *et al.* used two systems to obtain values of k_1/k_6 , a flow system producing OH from H₂O₂ decomposition,^{16,33,34} and a static thermal system for CH₄ oxidation.²⁵ Despite some mechanistic uncertainties, the values of k_1 derived are in reasonable agreement with other work at these temperatures, but appear to give too large a temperature coefficient for k_1 . Values of k_1/k_6 were also obtained by Baulch *et al.* but using photolysis of H₂O as the OH source. In this case the values of k_1 agree closely with the work of Zellner and Steinert¹⁶³ and Tully and Ravishankara,²⁴¹ but slightly favoring the latter.

At high temperatures a shock tube study¹⁴⁰ gave values of k_1/k_6 and k_1/k_7 , and a flame study⁶⁵ gave an approximate value of k_1 . At the temperature of the shock tube work (1300 K) values of k_1 derived from relative rate measurements suffer from the added uncertainty in their reference rate constants and it is not surprising that the values of k_1 derived differ by a factor of more than 2; nevertheless, they are close to other measurements in this region.

The only other relative rate measurement considered is that of Cox *et al.* at 298 K.^{150,151} From the value of k_1/k_7 measured, a value of k_1 in good agreement with absolute data at 298 K is obtained.

Values are also available for the ratios k_1/k_3 , k_1/k_{11} , k_1/k_{12} , and k_1/k_{15} , but we make no use of them because of lack of reliable data for the reference reactions:



From the experimental data it is clear that k_1 does not follow a simple Arrhenius expression over a wide temperature range, although as mentioned earlier, a good fit can be obtained over a limited range. Using all the data we have indicated as reliable but giving particular weight to that of Tully and Ravishankara²⁴¹ at intermediate temperatures and that of Peeters and Mahnen,^{107,122} Ernst *et al.*,¹⁹⁶ and Dixon-Lewis and Williams³⁸ at high temperatures, we recommend

$$k_1 = 1.5 \times 10^6 T^{2.13} \exp(-1230/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1},$$

over the temperature range 230–2000 K, with error limits of $\Delta \log k = \pm 0.1$ up to 500 K, increasing to an error in $\log k$ of ± 0.3 above 1000 K.

Rate of the Reverse Reaction

There are no experimental data available on the reverse reaction (–1):



Kondratiev^{24,71} and Skinner *et al.*⁹¹ have calculated expressions using data on reaction (1) and the equilibrium constant.

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4. OH + C₂H₆ → C₂H₅ + H₂O

THERMODYNAMIC DATA

$$\Delta H_{298}^0 = -89.50 \text{ kJ mol}^{-1} \text{ } (-21.39 \text{ kcal mol}^{-1})$$

RECOMMENDED RATE CONSTANT

$$k_1 = 1.4 \times 10^{13} \exp(-1340/T) \text{ cm}^2 \text{ mol}^{-1} \text{ s}^{-1}$$

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

Temperature Range: 250–1200 K.

Suggested Error Limits for Calculated Rate Constant:

$\Delta \log k = \pm 0.1$ at 300 K, rising to $\Delta \log k = \pm 0.3$ above 1000 K.

Rate Parameters: $\log(A/\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = 13.15 \pm 0.30$

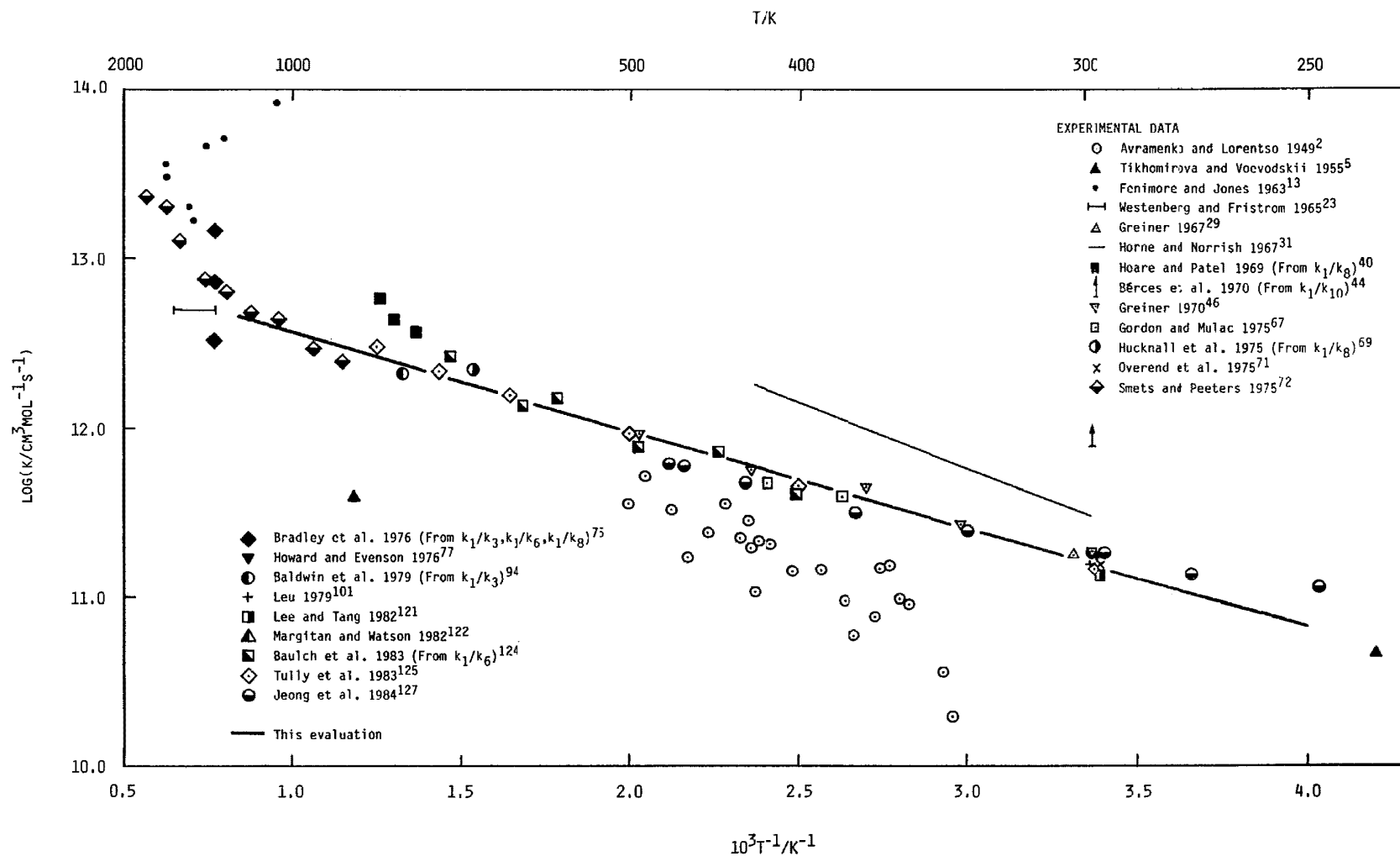
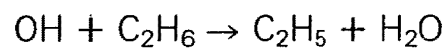
$\log(A/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = -10.64 \pm 0.30$

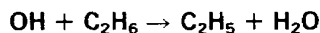
$E/\text{J mol}^{-1} = 11\,100 \pm 2000$

$E/\text{cal mol}^{-1} = 2\,660 \pm 500$

EXPERIMENTAL DATA

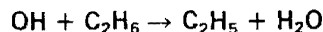
Rate Constant $k/\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	Temperature T/K	Reference and Comments
1.99×10^{10}	338	AVRAMENKO and LORENTSO' 1949 ²
3.61×10^{10}	341	Discharge flow system. 100% H ₂ O at 293–573 Pa pressure.
9.34×10^{10}	354	C ₂ H ₆ added downstream at about 0.5 Pa pressure. [OH] monitored
1.01×10^{11}	357	by u.v. absorption spectroscopy.
1.54×10^{11}	361	Source of OH now known to be suspect. ^{10,15} H and O atoms
1.51×10^{11}	365	are also produced in the discharge, giving rise to secondary
7.83×10^{10}	367	reactions which generate more OH. Consequently, the apparent
6.02×10^{10}	375	rate of removal of OH from the system is much lower than is
9.46×10^{10}	379	compatible with reaction 1.
1.48×10^{11}	390	$\text{OH} + \text{C}_2\text{H}_6 \longrightarrow \text{C}_2\text{H}_5 + \text{H}_2\text{O} \quad (1)$
1.47×10^{11}	403	Authors derive expression $k_1 = 6 \times 10^{12} T^{0.5} \exp(-2800/T) \text{ cm}^3$
2.10×10^{11}	414	$\text{mol}^{-1} \text{ s}^{-1}$. Restated in Arrhenius form as $k_1 = 1.3 \times 10^{14} \exp$
2.17×10^{11}	421	$(-2800/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ in Ref. 16 and as $k_1 = 2.4 \times 10^{14} \exp$
1.09×10^{11}	423	$(-3000/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ in Ref. 22.
1.99×10^{11}	425	Quoted by Refs. 31,32,33,34,43,45,47 and 48.
2.93×10^{11}	427	Used by Refs. 30,49,73 and 82.
2.35×10^{11}	431	
3.63×10^{11}	439	
2.47×10^{11}	449	
1.75×10^{11}	461	
3.28×10^{11}	471	
5.24×10^{11}	490	
3.61×10^{11}	501	





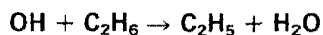
EXPERIMENTAL DATA - CONTINUED

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
-	813	<p>BALDWIN and SIMMONS 1955⁴ BALDWIN, JACKSON, WALKER and WEBSTER 1965¹⁹</p> <p>Static system. $\text{H}_2(7-56\%)/\text{O}_2(7-56\%)/\text{N}_2$ mixtures at a total pressure of 5.33-16.0 kPa in KCl-coated vessels. $\text{C}_2\text{H}_6(0.4-0.8\%)$ added. Products estimated by a vacuum condensation method.¹ Reaction followed manometrically.</p> <p>Effect of C_2H_6 on the second explosion limit of the H_2/O_2 reaction investigated. Assuming that C_2H_6 interferes by removing H atoms and OH radicals by reactions 1 and 2, authors were able to derive a complex expression involving k_1 and k_2 and used this in the later work to give $k_1/k_3 = 12$ at 813 K, assuming reaction 4 to have no effect.</p> $\text{H} + \text{C}_2\text{H}_6 \longrightarrow \text{C}_2\text{H}_5 + \text{H}_2 \quad (2)$ $\text{H}_2 + \text{OH} \longrightarrow \text{H}_2\text{O} + \text{H} \quad (3)$ $\text{O} + \text{C}_2\text{H}_6 \longrightarrow \text{C}_2\text{H}_5 + \text{OH} \quad (4)$ <p>Using his own value for k_3,³³ Schofield gives $k_1 = 1.5 \times 10^{13} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$. Using a value of k_3 from Ref. 94 we get $k_1 = 4.86 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$.</p> <p>Quoted by Ref. 34. Used by Refs. 40, 43 and 60.</p>
3.9×10^{11}	843	<p>TIKHOMIROVA and VOEVODSKII 1955⁵</p> <p>Capacity flow system. $\text{H}_2(10 \text{ or } 80\%)/\text{O}_2(90 \text{ or } 20\%)$ mixtures at total pressures of 3.33-33.3 kPa. $\text{C}_2\text{H}_6(0.3-0.7\%)$ added to reaction vessel. Reaction followed manometrically.</p> <p>Inhibition of upper explosion limit of H_2/O_2 reaction studied over temperature range 773-923 K. k_2 obtained from H_2-rich mixtures, where reaction 1 assumed absent, then used in formula for lean mixtures to obtain k_1.</p> <p>Quoted by Ref. 45.</p>
-	793	<p>BALDWIN and SIMMONS 1957⁶ BALDWIN and WALKER 1964¹⁷</p> <p>Static system. $\text{H}_2(7-56\%)/\text{O}_2(14-56\%)/\text{N}_2$ mixtures at total pressures of 0.53-2.67 kPa. C_2H_6 added up to 1.3%. KCl-coated vessels. Other experimental details as in Ref. 4.</p> <p>Effect of C_2H_6 on first explosion limit of the H_2/O_2 reaction studied. Results found to be compatible with those in Ref. 4 and a number of expressions for k_1 put forward, dependent on reaction mechanism.</p> $\text{OH} + \text{C}_2\text{H}_6 \longrightarrow \text{C}_2\text{H}_5 + \text{H}_2\text{O} \quad (1)$



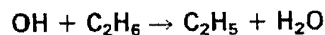
EXPERIMENTAL DATA - CONTINUED

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
		<p>In the later study, authors determined rate constants on the basis that all C_2H_5 radicals formed underwent chain termination reactions. They give $k_1/k_3 = 13$ at 793 K and take k_3 from Refs. 9 and 15 to derive k_1. Using our value of k_3 (Vol. 1 p. 77) we obtain $k_1 = 1.09 \times 10^{13} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ at 793 K.</p> $\text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H} \quad (3)$ <p>However, authors warn that the ratio k_1/k_3 may include a contribution from k_4/k_5.</p> $\text{O} + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_5 + \text{OH} \quad (4)$ $\text{O} + \text{H}_2 \rightarrow \text{H} + \text{OH} \quad (5)$ <p>Quoted by Ref. 34. Used by Refs. 20,38,45 and 47. Superseded by later work (Refs. 43,52,84,94) - not plotted on graph.</p>
8.4×10^{13}	1050	FENIMORE and JONES 1963 ¹³
5.1×10^{13}	1260	Flame study. $\text{H}_2(0-70\%)/\text{O}_2(18.0-58.0\%)/\text{C}_2\text{H}_6(1.50-11.4\%)/\text{Ar}$
4.7×10^{13}	1350	flames at 267-667 Pa pressure. Stable species monitored by
1.7×10^{13}	1420	mass spectrometry.
2.0×10^{13}	1440	[H] estimated from O_2 consumption in the early stages of the
3.0×10^{13}	1600	flame (before the equilibrium in reaction 5 was established)
3.6×10^{13}	1610	and [OH] from the equilibrium in reaction 6.
		$\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H} \quad (6)$ <p>Authors used their own values of k_5^9 and k_6^7. The four highest temperature values of k_1 were determined in the absence of H_2 and are considered by the authors to be more reliable. Having insufficient information on activation energies they gave an approximate value of $k_1 = 3 \times 10^{13} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ over the temperature range 1400-1600 K.</p> <p>Quoted by Refs. 12,14,18,22,23,27,33,34,45,47 and 72. Used by Refs. 30,60 and 64.</p>
about 5×10^{12}	1300-1550	WESTENBERG and FRISTROM 1965 ²³
		<p>Flame study. $\text{C}_2\text{H}_6(5\%)/\text{O}_2$ flames at 10.1 kPa pressure. [H] and [O] monitored by e.s.r. spectroscopy, stable species by mass spectrometry.</p> <p>[OH] profiles determined from the equilibrium of reaction 6, using k_6 determined in the same study. Assuming reaction 1 to represent the initial attack on C_2H_6, authors obtained values of k_1 ranging from 1.3×10^{12} to $1.2 \times 10^{13} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ over the quoted temperature range.</p> <p>Quoted by Refs. 27,33,34 and 45. Used by Ref. 60.</p>



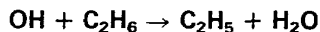
EXPERIMENTAL DATA - CONTINUED

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
$8.9 \times 10^{10} T^{0.5} \exp(-2800/T)$	-	CHINITZ and BAURER 1966 ²⁴ Theoretical estimate based on gas kinetic and SEMENOV theories. Activation energy taken from Ref. 3. A factor obtained by similar method to that adopted in earlier work. ²¹ Quoted by Ref. 47.
-	798	HOARE and PEACOCK 1966 ²⁶ Flow system. Decomposition of H_2O_2 (1.27%) in He or N_2 carrier, in presence of CH_4 (0.56-6.38 kPa) and O_2 (344-813 Pa) at total pressures of 13.3-101 kPa. $[\text{CO}]$, $[\text{CO}_2]$, $[\text{C}_2\text{H}_4]$, $[\text{CH}_4]$, $[\text{C}_2\text{H}_6]$ determined by gas chromatography, $[\text{HCHO}]$ by thiosulphate titration. Authors assumed C_2H_4 produced by oxidation of C_2H_5 radicals produced in reaction 1 and CO and CO_2 by oxidation of the CHO radical produced in reaction 7. Hence a value of $k_7/k_1 = 2.8$ was determined at 798 K. $\text{OH} + \text{C}_2\text{H}_6 \longrightarrow \text{C}_2\text{H}_5 + \text{H}_2\text{O} \quad (1)$ $\text{OH} + \text{HCHO} \longrightarrow \text{CHO} + \text{H}_2\text{O} \quad (7)$ They admit that such assumptions must give only an approximate value for the ratio but note agreement with data calculated from Refs. 6 and 11. Quoted by Ref. 48. Used by Ref. 40. k_7/k_1 given as 3.8 in Ref. 20.
1.76×10^{11}	302	GREINER 1967 ²⁹ Flash photolysis of H_2O (1-2%)/Ar mixtures in the presence of C_2H_6 (0.5-4%) at a total pressure of 13.3 kPa. $[\text{OH}]$ monitored by u.v. absorption spectroscopy at 306.4 nm. Method and apparatus as described in Ref. 28. Author also obtained the following activation energy using Evans-Polanyi theory: $E_1 = 25.5 \text{ kJ mol}^{-1}$ (6.1 kcal mol ⁻¹), leading to the ratio $A_1/A_8 = 3.8$. $\text{OH} + \text{CH}_4 \longrightarrow \text{CH}_3 + \text{H}_2\text{O} \quad (8)$ Quoted by Refs. 31, 41, 43, 48, 51 and 92. Used by Refs. 45, 47, 60 and 120.
$1.3 \times 10^{14} \exp(-1800/T)$	298-423	HORNE and NORRISH 1967 ³¹ Flash photolysis of H_2O (2.5%)/Ar mixtures in the presence of C_2H_6 (<0.3%) at a total pressure of 41.1 kPa. $[\text{OH}]$ monitored by u.v. absorption spectroscopy at 309 nm.



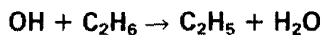
EXPERIMENTAL DATA - CONTINUED

Rate Constant $\text{k}/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
-	300	<p>Effect of OH recombination allowed for by using an overall rate constant for [OH] decay determined in the same study. Quoted by Refs. 43,48,90,103 and 104. Used by Refs. 45 and 60.</p> <p>WILSON and WESTENBERG 1967³⁵</p> <p>Discharge flow system. $\text{H}_2(1-2\%)/\text{Ar}$ mixtures at 100-180 Pa total pressure. OH produced by $\text{H} + \text{NO}_2$ titration. C_2H_6 added downstream so that $[\text{C}_2\text{H}_6] \gg [\text{OH}]$. [H], [OH] monitored by e.s.r. spectroscopy.</p> <p>Authors unable to obtain any information on secondary reactions and hence on stoichiometry. They were thus only able to quote an apparent rate constant $n\text{k}_1 = 6 \times 10^{11} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ at 300 K, where n is the stoichiometry.</p> $\text{OH} + \text{C}_2\text{H}_6 \longrightarrow \text{C}_2\text{H}_5 + \text{H}_2\text{O} \quad (1)$ <p>Used by Ref. 60.</p>
-	753-773	<p>BALDWIN, EVERETT, HOPKINS and WALKER 1968³⁶</p> <p>Static system. $\text{H}_2(28\%)/\text{O}_2(14\%)/\text{N}_2$ mixture at a total pressure of 66.7 kPa. $\text{C}_2\text{H}_6(0.1\%)$ added. Aged boric acid-coated vessels. $[\text{H}_2]$ monitored manometrically, $[\text{HCHO}]$ colorimetrically; other carbon-containing compounds by gas chromatography.</p> <p>Effect of C_2H_6 addition on the slow H_2/O_2 reaction studied. C_2H_6 found to have a marked effect and thus could only be added in small quantities. Assuming that all C_2H_5 radicals are converted to oxidation products, the authors were able to obtain a value for the ratio $k_1/k_3 = 8.5$ at 773 K.</p> $\text{H}_2 + \text{OH} \longrightarrow \text{H}_2\text{O} + \text{H} \quad (3)$ <p>Using our expression for k_3 (Vol. 1, p. 77), we obtain $k_1 = 6.56 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ at this temperature. Not plotted on graph - see Ref. 84.</p> <p>Used by Ref. 45.</p>
-	734-798	<p>HOARE and PATEL 1969⁴⁰</p> <p>Static system. $\text{CH}_4(7.1-31.9\%)/\text{C}_2\text{H}_6(9.4-16.8\%)/\text{C}_2\text{H}_4(0-8.7\%)/\text{O}_2$ mixtures at total pressures of 9.33-24.7 kPa. All stable species analysed by gas chromatography.</p> <p>From the product ratios, authors obtained the following values for the ratio k_1/k_8: 10.4(734 K), 10.0(773 K) and 12.0(798 K).</p> $\text{OH} + \text{CH}_4 \longrightarrow \text{CH}_3 + \text{H}_2\text{O} \quad (8)$



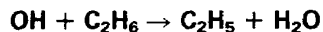
EXPERIMENTAL DATA - CONTINUED

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
		<p>Using our expression for k_8 (this paper) we obtain $k_1 = 3.71 \times 10^{12}$ (734 K), 4.33×10^{12} (773 K) and $5.85 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ (798 K). On account of the apparent temperature independence of k_1/k_8, authors assumed that E_1 is approximately equal to E_8. Quoted by Ref. 48.</p> <p>Used by Ref. 45.</p>
2.3×10^{12}	773	<p>BALDWIN, HOPKINS and WALKER 1970⁴³ BAKER, BALDWIN and WALKER 1971⁵² BALDWIN, BENNET and WALKER 1977⁸⁴ BALDWIN and WALKER 1979⁹⁴</p> <p>Static system. H_2 (14–86%)/O_2 (7–72%)/N_2 mixtures at a total pressure of 66.7 kPa. 0.1% C_2H_6 added. Aged boric-acid coated vessels. $[\text{H}_2]$ monitored manometrically, $[\text{HCHO}]$ colorimetrically, other carbon-containing species by gas chromatography.</p> <p>Extension of work first quoted in Ref. 36, giving details of inhibition by C_2H_6 of the slow H_2/O_2 reaction over a wide concentration range. Assuming reaction 4 to be a minor reaction removing C_2H_6, authors obtained $k_1/k_3 = 10.5$ (753 K) and 10.9 (773 K). If reaction 9 also removes C_2H_6, a value of 9.5 is obtained at 773 K but authors believe reaction 4 to be more important.</p> $\text{OH} + \text{C}_2\text{H}_6 \longrightarrow \text{C}_2\text{H}_5 + \text{H}_2\text{O} \quad (1)$ $\text{H}_2 + \text{OH} \longrightarrow \text{H}_2\text{O} + \text{H} \quad (3)$ $\text{O} + \text{C}_2\text{H}_6 \longrightarrow \text{C}_2\text{H}_5 + \text{OH} \quad (4)$ $\text{HO}_2 + \text{C}_2\text{H}_6 \longrightarrow \text{C}_2\text{H}_5 + \text{H}_2\text{O}_2 \quad (9)$ <p>Authors took k_3 from Ref. 25 to give $k_1 = 8.5 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ at 773 K. Combining this result with those in Refs. 29 and 31, authors obtained $k_1 = 8.7 \times 10^{13} \exp(-1770/T) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$. Quoted by Refs. 54, 59, 65, 66, 72 and 96.</p> <p>Used by Refs. 42, 45, 60, 81, 93, 108 and 111.</p> <p>After allowance for self-heating, authors obtained revised estimate $k_1/k_3 = 5.7$ at 773 K.^{84, 94} Using k_3 from Ref. 94 we get $k_1 = 2.3 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$. This value plotted on graph.</p>
—	298	<p>BERGES, FORGETEG and MARTA 1970⁴⁴</p> <p>Static photolysis of HNO_3 at 265 nm at total pressures of about 0.7–5.5 kPa, in the presence of C_2H_6. $[\text{NO}_2]$ monitored by absorption of light at 440 nm.</p> <p>Authors suggested the following mechanism for NO_2 production in the absence of additive:</p>



EXPERIMENTAL DATA - CONTINUED

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
		$\text{HNO}_3 + h\nu \rightarrow \text{NO}_2 + \text{OH}$ $\text{OH} + \text{HNO}_3 \rightarrow \text{NO}_3 + \text{H}_2\text{O} \quad (10)$ $\text{NO}_3 + \text{M} \rightarrow \text{NO} + \text{O}_2 + \text{M}$ $\text{NO}_3 + \text{NO} \rightarrow 2\text{NO}_2$ <p>In the presence of C_2H_6, enhancement of the initial rate observed. Degree of enhancement approached a limit when $[\text{C}_2\text{H}_6]/[\text{HNO}_3]$ is about 2. Authors were unable to propose a detailed mechanism in the presence of additive but suggested that under conditions of maximum rate enhancement at least 95% of OH radicals attack C_2H_6, according to reaction 1. Thus they deduced $k_{10}/k_1 \leq 0.1$. Using our value for k_{10} (Vol. 2, p. 439) we obtain $k_1 \geq 8 \times 10^{11} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ at 298 K. Quoted by Ref. 59.</p>
1.87×10^{11}	297	GREINER 1970 ⁴⁶
2.75×10^{11}	335	Flash photolysis of $\text{H}_2\text{O}(1\%)/\text{Ar}$ mixtures in the presence of C_2H_6 at 109–132 Pa pressure. [OH] monitored by u.v. absorption spectroscopy at 306.4 nm.
4.52×10^{11}	369	
5.64×10^{11}	424	
9.35×10^{11}	493	Rate constants determined from [OH] decay and corrected for the effect of reaction 11 using a computer simulation.
		$\text{OH} + \text{C}_2\text{H}_5 \rightarrow \text{products} \quad (11)$ <p>Author derived the expression $k_1 = 1.12 \times 10^{13} \exp(-1232/T) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ over the temperature range 300–500 K after combining these data with corrected data from Ref. 29. Data calculated from transition state theory agree well with this. Quoted by Refs. 59, 67, 68, 69, 77, 78, 89, 97, 100, 103, 104, 117, 122. E_1 quoted by Refs. 61 and 83. Used by Refs. 60, 85, 91, 106, 111, 112, 113 and 115. Used in altered form in Ref. 105.</p>
-	-	BALDWIN and WALKER 1973 ⁶¹
		Theoretical determination of the activation energy E_1 using the reaction exothermicity.
		Used in Ref. 86 but attributed to the reaction of C_2H_6 with Cl atoms. Authors obtain $E_1 = 8.4 \text{ kJ mol}^{-1}$ lower than most experimental values.
$1.26 \times 10^{13} \exp(-1300/T)$	300–500	BENSON 1975 ⁶⁵
		Theoretical value, derived from transition state theory. Based on the value of $S^\ddagger(\text{C}_2\text{H}_5\text{OH})$ calculated earlier in the same study. A non-linear complex would have an A factor an order of magnitude higher.



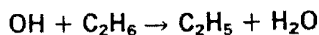
EXPERIMENTAL DATA - CONTINUED

Rate Constant $\text{k}/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
4.0×10^{11}	381	GORDON and MULAC 1975 ⁶⁷
4.8×10^{11}	416	Pulse radiolysis of H_2O at 101.3 kPa pressure in the presence of C_2H_6 (0.27–2.40 kPa). [OH] monitored by u.v. absorption spectroscopy at 308.7 nm.
-	653	HUCKNALL, BOOTH and SAMPSON 1975 ⁶⁹ <p>Static system. OH produced by decomposition of 1.33 kPa H_2O_2 in O_2/N_2 mixtures to a total pressure of 5.33–66.7 kPa. (a) $\text{C}_2\text{H}_6/\text{CH}_4$ mixtures (1:1, 1:3, 1:9) added in trace amounts (<1%) and (b) $\text{C}_2\text{H}_6/\text{C}_3\text{H}_8$ mixtures (1:1, 1:4, 4:1) added up to 667 Pa pressure. Aged boric acid coated vessels. [H_2O_2] determined by permanganate titration, other stable species by gas chromatography.</p> <p>From the $\text{CH}_4/\text{C}_2\text{H}_6$ co-oxidation, authors obtained $k_1/k_8 = 9.6$ at 653 K. Using our expression for k_8 (this paper) we obtain, $k_1 = 2.16 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ at this temperature.</p> $\text{OH} + \text{CH}_4 \longrightarrow \text{CH}_3 + \text{H}_2\text{O} \quad (8)$ <p>The $\text{C}_2\text{H}_6/\text{C}_3\text{H}_8$ system was studied more extensively over a wide range of conditions. $k_{12}/k_1 = 2.18$ at 653 K obtained.</p> $\text{OH} + \text{C}_3\text{H}_8 \longrightarrow \text{C}_3\text{H}_7 + \text{H}_2\text{O} \quad (12)$ <p>No evidence found for interference by HO_2 reactions, but see Discussion.</p>
1.59×10^{11}	295	OVEREND, PARASKEVOPOULOS and CVETANOVIC 1975 ⁷¹ <p>Flash photolysis of H_2O (about 0.5%)/He mixtures at 66.7 kPa pressure in the presence of C_2H_6 (0–589 Pa). [OH] monitored by u.v. absorption spectroscopy.</p> <p>Results confirmed using flash photolysis of N_2O in the presence of H_2 to produce OH.</p> $\text{N}_2\text{O} + h\nu \longrightarrow \text{N}_2 + \text{O}(^1\text{D})$ $\text{H}_2 + \text{O}(^1\text{D}) \longrightarrow \text{H} + \text{OH}$ <p>A computer simulation showed the only competing reaction to be reaction 11. Authors assumed k_{11} = collision frequency.</p> $\text{OH} + \text{C}_2\text{H}_5 \longrightarrow \text{products} \quad (11)$ <p>Quoted by Refs. 68, 77, 97, 102, 103, 104, 114 and 117. Used by Ref. 120. Preliminary value of $k_1 = 1.8 \times 10^{11} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$. Quoted by Ref. 64.</p>
2.46×10^{12}	870	SMETS and PEETERS 1975 ⁷²
2.95×10^{12}	940	Flame study. C_2H_6 (6.3%)/ O_2 flames at 4 kPa total pressure.
4.37×10^{12}	1040	Stable species followed by mass spectrometry.



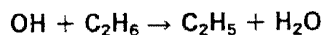
EXPERIMENTAL DATA - CONTINUED

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
4.79x10 ¹²	1140	Rate constants determined from the disappearance of C ₂ H ₆ , assuming reaction 1 to be the principal means of attack on C ₂ H ₆ . $\text{OH} + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_5 + \text{H}_2\text{O}$ (1) Authors derived the overall expression $k_1 = 6.5 \times 10^{13} \exp(-2800/T) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$. Quoted by Ref. 80.
6.46x10 ¹²	1240	
7.50x10 ¹²	1340	
1.26x10 ¹³	1500	
2.04x10 ¹³	1600	
2.34x10 ¹³	1770	
-	1300	BRADLEY, CAPEY, FAIR and PRITCHARD 1976 ⁷⁵ Shock tube study. H ₂ O ₂ (about 0.1%)/Ar mixtures at about 15 kPa pressure in the presence of C ₂ H ₆ at 7.78-15.4 Pa pressure. Incident shocks. [OH] monitored by u.v. absorption spectroscopy at 309.2 nm. Shock tube coated by epoxy resin to avoid catalytic decomposition of H ₂ O ₂ . Temperature of 1300 K chosen as being most convenient for measurement of [OH]. A 28-reaction mechanism (almost certainly incomplete) was formulated and using data obtained in the same study from other substrates, authors gave the ratio $k_6:k_{13}:k_3:k_8:k_{14}:k_1 = 0.18:0.19:0.59:1.00:2.33:2.88$. $\text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H}$ (3) $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$ (6) $\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O}$ (8) $\text{OH} + \text{CF}_3\text{H} \rightarrow \text{CF}_3 + \text{H}_2\text{O}$ (13) $\text{OH} + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_3 + \text{H}_2\text{O}$ (14) Using our value of k_3 (Vol. 1, p. 77), we obtain $k_1 = 1.47 \times 10^{13} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$; using our value of k_6 (vol. 3, p. 203), we obtain $k_1 = 3.33 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$; using our value of k_8 (this paper) we obtain $k_1 = 7.2 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$, all at 1300 K. Quoted by Refs. 103 and 104. Used by Ref. 105.
1.74x10 ¹¹	296	HOWARD and EVENSON 1976 ⁷⁷ Discharge flow system. H ₂ /He mixtures at total pressures of 0.1-1.0 kPa, NO ₂ added downstream. C ₂ H ₆ added further downstream in large excess. [OH] monitored by laser magnetic resonance spectroscopy. Very low [OH] used, about $10^{-14} \text{ mol cm}^{-3}$. Otherwise details as given in Ref. 76. Quoted by Refs. 74,87,97,99,117 and 118. Used by Ref. 120.



EXPERIMENTAL DATA - CONTINUED

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
1.6×10^{11}	298	LEU 1979 ¹⁰¹ Fast flow-discharge system. OH prepared by reaction of NO_2 with H atoms produced in H_2/He discharge (about 0.4 kPa). C_2H_6 in large excess added downstream. OH detected by resonance fluorescence at 309 nm. Concentration of OH about 10^9 molecules cm^{-3} . Rate constant determined from pseudo-first-order decay of OH. Quoted by Ref. 117.
$7.8 \times 10^6 T^{2.0} \exp(-430/T)$	300-2000	COHEN 1982 ¹²⁰ Theoretical expression derived using transition state theory and experimental data of Refs. 29, 71 and 77.
1.39×10^{11}	295	LEE and TANG 1982 ¹²¹ Fast flow discharge system. OH generated by reaction of NO_2 with H atoms produced in H_2/He discharge. C_2H_6 added in excess downstream. OH detected by resonance fluorescence. Rate constant measured under pseudo-first-order conditions with $[\text{C}_2\text{H}_6] \gg [\text{OH}]$.
4.82×10^{10}	238	MARGITAN and WATSON 1982 ¹²² Flash photolysis of mixtures of HNO_3 (7.3 Pa) / C_2H_6 (4.0-53 Pa) / He (2.6-13.3 kPa). OH monitored by resonance fluorescence. OH generated by u.v. photolysis of HNO_3 . Rate constant determined from pseudo-first-order decay of OH.
-	403-683	BAULCH, CRAVEN, DIN, DRYSDALE, GRANT, RICHARDSON, WALKER and WATLING 1983 ¹²⁴ Static photolysis system. Photolysis of H_2O (about 3.3 kPa) at 184.9 nm in the presence of $\text{CO}/\text{C}_2\text{H}_6$ mixtures. CO_2 yield measured by gas chromatography. Measurement of CO_2 yield as a function of $[\text{CO}]/[\text{C}_2\text{H}_6]$ gives $k_1/k_6 = 4.2(403 \text{ K}), 7.2(443 \text{ K}), 7.4(493 \text{ K}), 13.4(561 \text{ K}), 11.7(595 \text{ K})$ and $21.4(683 \text{ K})$. $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H} \quad (6)$ Using our expression for k_6 (vol. 3, p. 23) we obtain $k_1 \times 10^{-11}/\text{cm}^3\text{mol}^{-1}\text{s}^{-1} = 4.09(403 \text{ K}), 7.28(443 \text{ K}), 7.82(493 \text{ K}), 15.1(561 \text{ K}), 13.6(595 \text{ K})$ and $26.9(683 \text{ K})$.

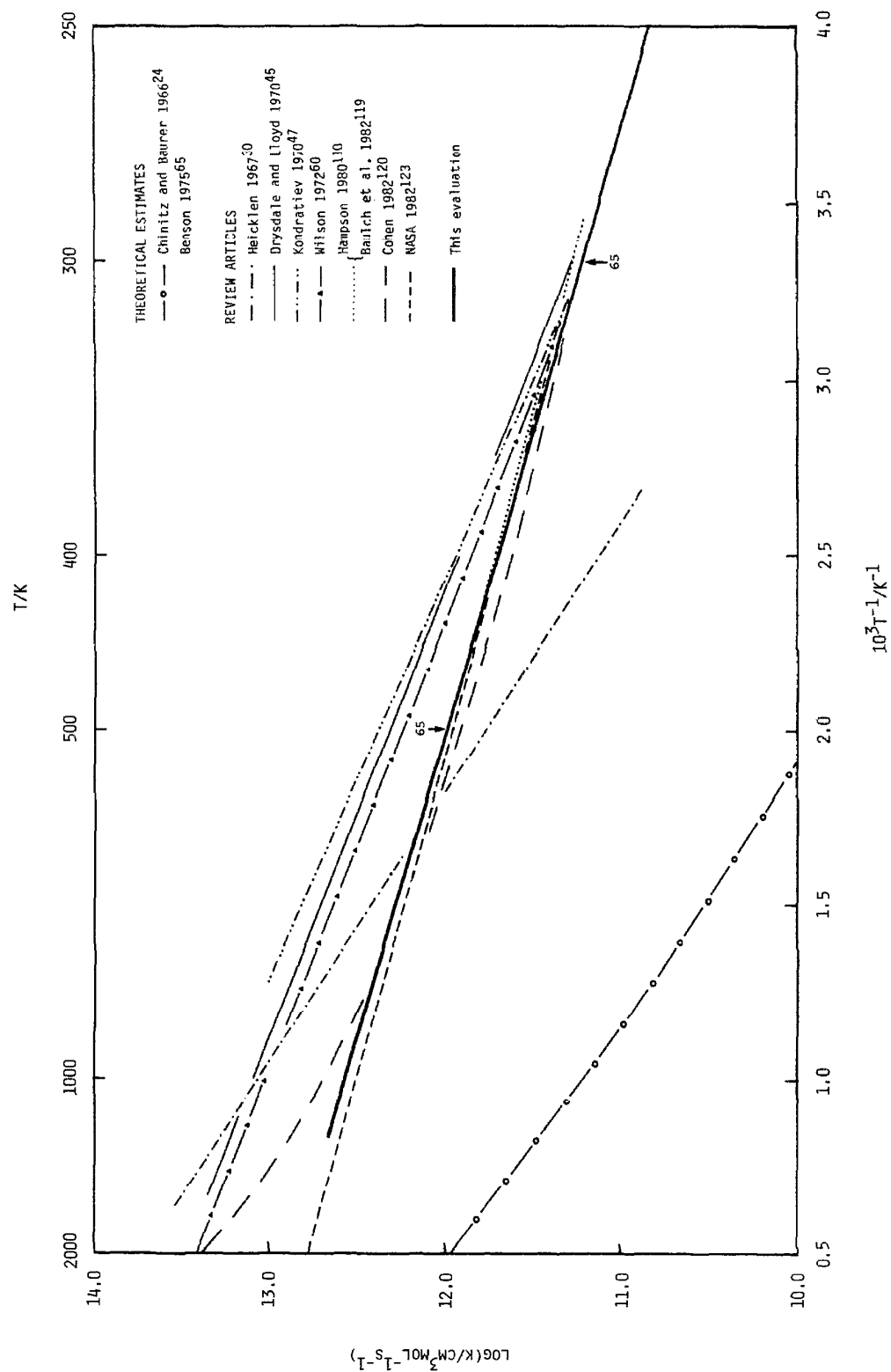


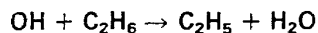
EXPERIMENTAL DATA - CONTINUED

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
1.56×10^{11}	297	TULLY, RAVISHANKARA and CARR 1983 ¹²⁵
4.64×10^{11}	400	Flash photolysis of mixtures of $\text{H}_2\text{O}/\text{C}_2\text{H}_6/\text{Ar}$ in static
9.51×10^{11}	499	reactor. All experiments at 13 kPa pressure Ar and
1.57×10^{12}	609	$[\text{C}_2\text{H}_6] \gg [\text{OH}]$. $[\text{OH}]$ monitored by resonance fluorescence.
2.20×10^{12}	697	Rate constants determined from pseudo-first-order decay of
3.05×10^{12}	800	OH. The expression, $k_1 = 8.61 \times 10^9 T^{1.05} \exp(-911/T)$ was derived from the rate coefficient data.
1.18×10^{11}	248	JEONG, HSU, JEFFRIES and KAUFMAN 1984 ¹²⁷
1.37×10^{11}	273	Discharge flow system. NO_2 added to $[\text{H}]$ produced upstream
1.87×10^{11}	294	in He/H_2 microwave discharge. $[\text{OH}]$ monitored by resonance
1.84×10^{11}	298	fluorescence.
2.50×10^{11}	333	Pseudo-first-order conditions, $[\text{RH}] \gg [\text{OH}]$. Initial $[\text{OH}]$
3.21×10^{11}	375	about 5×10^{11} molecules cm^{-3} .
4.81×10^{11}	428	
4.64×10^{11}	429	
5.98×10^{11}	464	
6.20×10^{11}	472	

REVIEW ARTICLES

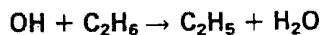
-	-	FRISTROM and WESTENBERG 1965 ²²
		Review of elementary flame reactions. Quotes Ref. 13 and restates data from Ref. 2 in Arrhenius form, with warning as to their reliability given in Ref. 15.
-	-	FRANKLIN 1967 ²⁷
		Review of kinetics of hydrocarbon combustion. Quotes Refs. 13 and 23.
$2.4 \times 10^{14} \exp(-3000/T)$	373-1573	HEICKLEN 1967 ³⁰
		Review of gas phase chemistry. Selected value based on Refs. 2 and 13. No comments made.
-	-	KAUFMAN 1969 ⁴¹
		Review of elementary gas reactions. Quotes Ref. 29. Also refers to the work of Ref. 26.





REVIEW ARTICLES - CONTINUED

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
$7.7 \times 10^{13} \exp(-1800/T)$	300-1500	<p>DRYSDALE and LLOYD 1970⁴⁵</p> <p>Evaluation. Based on data in Refs. 29 and 43, assuming the activation energy given in Ref. 31. Also quotes Refs. 2,5,6,13,35 and 37, and authors derive values of k_1 from Refs. 19,26 and 36 using k_3 and k_8 derived in the same review.</p> $\text{OH} + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_5 + \text{H}_2\text{O} \quad (1)$ $\text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H} \quad (3)$ $\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O} \quad (8)$ <p>Used by Refs. 57 and 70.</p>
$1.29 \times 10^{14} \exp(-2000/T)$	302-793	<p>KONDRATIEV 1970⁴⁷</p> <p>Evaluation. Based on data from Refs. 17 and 29. Also quotes Refs. 2,19,23 and 26. Author uses his own value of k_3 to derive k_1 from Ref. 17.</p> <p>Used by Refs. 53,56 and 79.</p>
1.82×10^{11}	298	<p>ZAFONTE 1970⁵⁰</p> <p>Preferred value. Quotes Refs. 2,46 and 60. Preferred value is that of Greiner.⁴⁶</p>
-	-	<p>CAMPBELL and BAULCH 1972⁵⁸</p> <p>Review of atomic and bimolecular reactions. Quotes general expression for $k(\text{OH} + \text{alkane})$ determined by Baker et al.,⁴² which gives $k_1 = 9.0 \times 10^{13} \exp(-1770/T) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$. Also refers to work from Refs. 29,46 and 52.</p>
$6.5 \times 10^{13} \exp(-1800/T)$	300-2000	<p>WILSON 1972⁶⁰</p> <p>Evaluation. Based on data from Refs. 13,23,26,29 and 46. Author also derives values of k_1 from Refs. 19 and 43, taking k_3 both from his own evaluation in the same review and Ref. 39. A value of $k_1 = 2.3 \times 10^{11} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ is derived from data in Ref. 35, assuming a stoichiometry of 2-3.</p> <p>Used by Refs. 63 and 74.</p>
1.5×10^{11}	298	<p>ANDERSON 1976⁷⁴</p> <p>Selected value for use in atmospheric chemistry is that of Wilson.⁶⁰ Also quotes Ref. 77. No criteria for selection given.</p>
-	-	<p>KERR 1976⁷⁸</p> <p>Review of H atom transfer reactions. Quotes Ref. 46. Quoted by Ref. 109.</p>



REVIEW ARTICLES - CONTINUED

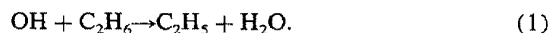
Rate Constant $\text{k}/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
-	-	HAMPSON and GARVIN 1978 ⁸⁸ Compilation of data for atmospheric chemistry. Quotes Refs. 46,71 and 77.
-	-	ATKINSON, DARNALL, LLOYD, WINER and PITTS 1979 ⁹³ Review of gas phase reactions of OH with organic compounds. Quotes Refs. 46,67,71 and 77. Quoted by Refs. 98 and 107.
$1.12 \times 10^{13} \exp(-1230/T)$	300-500	HAMPSON 1980 ¹¹⁰ Compilation of data for atmospheric chemistry. Quotes Refs. 46,71 and 77. Recommends expression of Ref. 46.
-	-	WESTLEY 1981 ¹¹⁶ Compilation of data for combustion reactions. Quotes Refs. 69,71,75 and 77.
$1.14 \times 10^{13} \exp(-1230/T)$	290-500	CODATA 1982 ¹¹⁹ Evaluation for use in atmospheric chemistry. Considers Refs. 46,67,71 and 77. Recommends expression of Ref. 46.
$2.2 \times 10^7 T^{1.9} \exp(-570/T)$	300-2000	COHEN and WESTBERG 1983 ¹²⁸ Evaluation. Considers data in Refs. 29,67,69,71,75,77 and 94.
$1.15 \times 10^{13} \exp(-1260/T)$	-	NASA 1982, 1983 ^{123,126} Evaluation for use in stratospheric modeling. Based on Refs. 46,71,77 and 125.
$6.3 \times 10^6 T^{2.0} \exp(-325/T)$	300-2000	WARNATZ 1985 ¹²⁹ Evaluation. Considers data of Refs. 13,43,46,67,71,72,75 and 76.

ISOTOPIC REACTION $\text{OD} + \text{C}_2\text{H}_6$

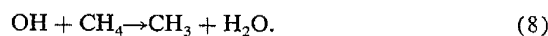
1.65×10^{11}	300	GREINER 1968 ³⁷ Flash photolysis of $\text{D}_2\text{O}/\text{Ar}$ mixtures at a total pressure of 13 kPa in the presence of C_2H_6 (4%). No further details given. Method reported to be the same as that used in Ref. 29. No isotope effect observed. Quoted by Refs. 45 and 48.
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Discussion

The reaction between hydroxyl radicals and ethane has much in common with the analogous methane reaction. It has been studied by similar techniques and frequent referral will be made to points dealt with in the discussion of the methane case:



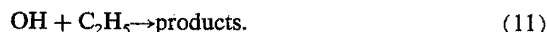
Reaction (1) is of less importance in atmospheric chemistry than the analogous reaction of methane and consequently it has received less study at low temperatures than reaction (8):



As with reaction (8), there is more agreement among the low-temperature data than among those obtained above 1000 K which for ethane are widely scattered and difficult to evaluate.

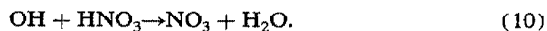
Below 500 K, reaction (1) has been studied by flash photolysis,^{29,31,46,71,122,125} discharge flow,^{2,77,101,121,127} and pulse radiolysis⁶⁷ methods. For the reasons given when considering reaction (8) we reject the data of Avramenko and Lorentso² and accept those of Greiner⁴⁶ with which good agreement is shown by other work.^{67,71,77,101,121,125,127} As for reaction (8), the results of Horne and Norrish³¹ are higher than others. There are obviously errors in their method. For example, the rate constant chosen by them for [OH] decay in the absence of hydrocarbon is low when compared with our values taken from Vol. 1, p. 425. This would account for their high k_1 and k_8 , while giving reasonable values for E_1 and E_8 .

The result of Wilson and Westenberg³⁵ has not been plotted since the rate of [OH] decay was too fast and they were unable to deduce the stoichiometry. There are no data on the secondary reaction (11), assumed to proceed at a rate equal to the collision frequency by Overend *et al.*⁷¹ Greiner⁴⁶ made a correction of about 10% to his observed rate constant to allow for this:



At the lowest end of the temperature range, Margitan and Watson¹²² obtained an absolute value of $k_1 = 4.82 \times 10^{10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 238 K. Our recommended expression, given at the end of this discussion, extrapolates very closely to this value.

Turning to the relative measurements below 500 K, we reject the lower limit for the ratio k_1/k_{10} obtained by Bérces *et al.*⁴⁴:



In the absence of a detailed reaction mechanism the authors were forced to use a very approximate method to treat their results. It is probably fortuitous that use of their value of k_{10} , measured in the same work and an order of magnitude lower than our recommended value (Vol. 2, p. 439), brings the value of k_1 into agreement with the other data at this temperature.

The range of high-temperature values covers two orders of magnitude. For the reasons given in the discussion of reaction (8), however, we can dismiss the flame data of Fen-

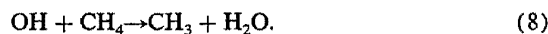
imore and Jones¹³ and Westenberg and Fristrom,²³ where [OH] is calculated assuming it to be in equilibrium in the hot boundary. We have little information on the static pyrolysis system of Tikhomirova and Voevodskii,⁵ except that it was designed to measure the rate of reaction (2) and the authors admit that the k_1 values determined are at best only order of magnitude estimates:



Bradley *et al.*⁷⁵ give three possible values of k_1 at 1300 K, depending on which of the ratios k_1/k_3 , k_1/k_6 , or k_1/k_8 is used. In view of the corresponding wide spread of results we make no use of their work. That leaves only the flame work of Smets and Peeters,⁷² whose lower temperature values extrapolate well to Greiner's data. The apparent increase in activation energy at the very highest temperatures suggests possible non-Arrhenius behavior, though to a much smaller extent than with CH_4 , but clearly before reaching such a conclusion more data are required on reaction (1) above 1000 K and in the intermediate temperature range 500–1000 K.

In the intermediate temperature range the only absolute data are those of Tully, Ravishankara, and Carr.¹²⁵ The flash photolysis method used has no obvious kinetic complications and has proved reliable in analogous work on reaction (8). We therefore accept its findings. There is good agreement below 500 K and at the high-temperature end the results extrapolate to fit values of k_1 given by Smets and Peeters.⁷² The results of Tully *et al.* give no indication of curvature in the Arrhenius plot below 1000 K.

The remaining results in the range 500–1000 K have been obtained from measurements of the ratios k_1/k_3 , k_1/k_6 , k_1/k_8 , and combination with the relevant values of the reference rate constants:



Values of k_6 and k_8 have been taken from our own evaluations (Vol. 3, p. 203; and this paper) but recent data suggest that in parts of the temperature range, our evaluation of k_3 (Vol. 1, p. 71) is slightly high. We have therefore used the expression suggested by Baldwin and Walker⁹⁴ for k_3 .

Baldwin *et al.*^{4,6,17,19,36,43,52} have studied the addition of C_2H_6 to H_2/O_2 mixtures under a wide range of conditions obtaining values of k_1/k_3 . In their most recent work these values have been corrected for the effects of self-heating and other minor refinements in the mechanism of the H_2/O_2 reaction.⁹⁴ The value of k_1 thus obtained at 773 K is in excellent agreement with an extrapolation from the most reliable low-temperature data. Hoare and Patel⁴⁰ obtained values of k_1/k_8 over a narrow temperature range from analysis of products from $\text{CH}_4/\text{C}_2\text{H}_6/\text{C}_2\text{H}_4/\text{O}_2$ system. Although the results appear high and do not agree with results by either Smets and Peeters⁷² or Tully *et al.*,¹²⁵ they may be evidence for curvature of the Arrhenius plot at high temperatures. Hucknall *et al.*⁶⁹ also measured k_1/k_8 producing OH from H_2O_2 . Although their result leads to a value of k_1 which appears reasonable, their system contained high concentra-

tions of HO_2 , reactions of which may have affected their results and for this reason we make no use of their data. The most reliable data in the intermediate temperature range appear to be those of Baulch *et al.*¹²⁴ using a simple photolytic technique to obtain values of k_1/k_6 . The values of k_1 derived are essentially in agreement with the more precise results of Tully *et al.*¹²⁵

A value of

$$k_1 = 1.8 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

at 298 K seems well established.^{29,46,71,77,101,121,125} From 298 K up to about 1000 K we base our evaluation on six sets of data.^{46,67,94,124,125,127} Beyond 1000 K the data of Smets and Peeters seem the most reliable, being consistent with other results in the 1000 K region but complete acceptance of their data would require the Arrhenius plot to curve more sharply above 1000 K than for methane. In a recent theoretical study, Cohen¹²⁰ accepts strong curvature setting in at a slightly lower temperature partly on the basis of a transition state calculation. While we agree that there may be curvature we see little compelling experimental evidence for it below 1000 K and we do not believe the higher temperature data to be sufficiently well established to recommend such an expression with any confidence. Until the status of the high-temperature data is clarified, we recommend the expression

$$k_1 = 1.4 \times 10^{13} \exp(-1340/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1},$$

over the temperature range 250–1200 K, with error limits of $\Delta \log k = \pm 0.1$ at 300 K, rising to an error in $\log k$ of ± 0.3 at 1200 K.

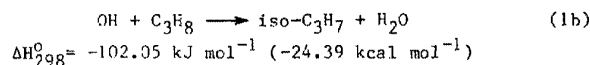
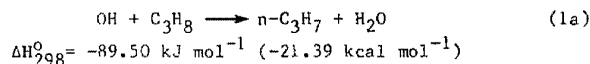
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5. OH + C₃H₈ → C₃H₇ + H₂O

THERMODYNAMIC DATA



RECOMMENDED RATE CONSTANT

$$k = k_{1a} + k_{1b} = 1.1 \times 10^4 T^{2.93} \exp(390/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

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

Temperature range: 290–1200 K

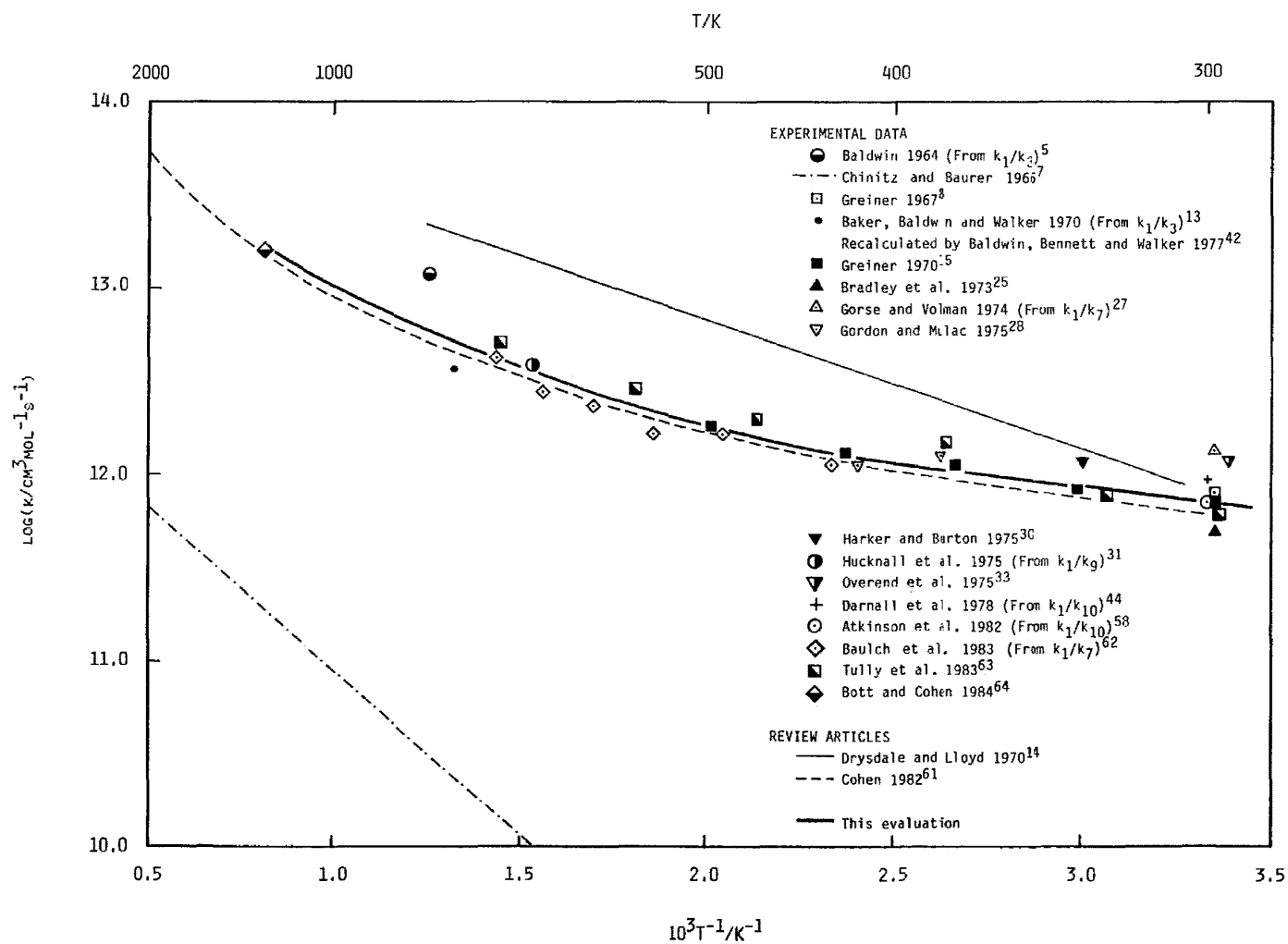
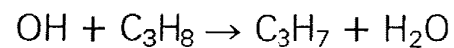
Suggested Error Limits for Calculated Rate Constant:

$\Delta \log k = \pm 0.12$ at 300 K, rising to $\Delta \log k = \pm 0.3$ above 1000 K.

Rate Parameters: See Discussion.

EXPERIMENTAL DATA

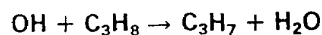
Rate Constant $\text{k/cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	Temperature T/K	Reference and Comments
4.3×10^{13}	793	<p>BALDWIN 1964⁴</p> <p>BALDWIN and WALKER 1964⁵</p> <p>Static system. H₂ (7–56%)/O₂ (7–72%)/N₂ mixtures at total pressures of about 12 kPa. <0.1% C₃H₈ added. KCl-coated vessels. Reaction followed manometrically, products estimated by separation with various freezing mixtures.</p> <p>Inhibition by C₃H₈ of 2nd limit of H₂-O₂ reaction. Authors found reaction 2 to be main source of removal of C₃H₈, and assumed reaction 1 important secondary source by analogy with work on other alkanes, e.g. Ref. 1.</p> $\text{OH} + \text{C}_3\text{H}_8 \longrightarrow \text{C}_3\text{H}_7 + \text{H}_2\text{O} \quad (1)$ $\text{H} + \text{C}_3\text{H}_8 \longrightarrow \text{C}_3\text{H}_7 + \text{H}_2 \quad (2)$ <p>Assuming all C₃H₇ radicals undergo termination reactions, authors obtain $k_1/k_3 = 27.0$. Taking k_3 from Refs. 2 and 3 they give the value of k_1 quoted. Using our value of k_3 (Vol. 1, p. 77), we obtain $k_1 = 2.27 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 793 K. Using k_3 from Ref. 49 we get $k_1 = 1.19 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. This point plotted.</p> $\text{H}_2 + \text{OH} \longrightarrow \text{H}_2\text{O} + \text{H} \quad (3)$ <p>Quoted by Refs. 6,9,16,32 and 62.</p> <p>Used by Ref. 14.</p>





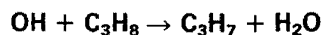
EXPERIMENTAL DATA - CONTINUED

Rate Constant $\text{k/cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
$10^{11}T^{0.5}\exp(-3600/T)$	-	CHINITZ and BAURER 1966 ⁷ Theoretical estimate. E_1 based on unpublished work by Fristrom et al. A_1 derived from kinetic theory.
8.2×10^{11}	298	GREINER 1967 ⁸ Flash photolysis of H_2O (1-2%)/Ar mixtures at 13.3 kPa pressure in the presence of C_3H_8 (27.0-150 Pa). [OH] monitored by u.v. absorption spectroscopy at 306.4 nm. Effect of secondary reactions considered insignificant. Author unable to distinguish between n- C_3H_7 and iso- C_3H_7 products using theoretical values for activation energy differences. Quoted by Refs. 14,15,16,17,19 and 62. Used in Ref. 61.
1.5×10^{13} Revised to 3.7×10^{12}	753	BAKER, BALDWIN and WALKER 1970 ^{12,13} BALDWIN, BENNETT and WALKER 1977 ⁴² BALDWIN and WALKER 1979 ⁴⁹ Static system. H_2 (7-85%)/ O_2 (7-92%)/ N_2 mixtures at total pressures of 33.3-89.1 kPa. <0.1% C_3H_8 added. Aged boric acid coated vessels. [HCHO] determined colorimetrically, other products by gas chromatography. Investigation of the effect of C_3H_8 on the slow H_2/O_2 reaction. Evidence from gas chromatography showed reaction 2 to be more important than reaction 4, and authors were able to give the ratio $k_1/k_3 = 21.5$ at 753 K. $\text{HO}_2 + \text{C}_3\text{H}_8 \longrightarrow \text{C}_3\text{H}_7 + \text{H}_2\text{O}_2 \quad (4)$ Taking k_3 from Ref. 10 authors obtain first quoted value of k_1 . Combining this with k_1 from Ref. 8 they obtain the expression $k_1 = 1.02 \times 10^{14} \exp(-1440/T) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$. Quoted by Refs. 20,22,23,31,52 and 62. The authors later corrected their ratio for the effects of self-heating, ⁴² obtaining $k_1/k_3 = 9.9$ at 753 K. Using k_3 from Ref. 49, $k_1 = 3.7 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$. Assuming that (i) C_2H_4 was produced only by decomposing n- C_3H_7 radicals; (ii) C_3H_7 radicals give C_3H_6 by reaction 5; (iii) k_b/k_a is the same for H atoms and OH radicals, authors applied a computer analysis to [C_2H_4] and [C_3H_6] production to give $k_{1b}/k_{1a} = 1.2$ at 753 K, compared with an empirical value of 1.05 derived in the same study. They believe, however, that assumption (iii) is doubtful and do not recommend the ratio obtained.



EXPERIMENTAL DATA - CONTINUED

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
		$\text{C}_3\text{H}_7 + \text{O}_2 \rightarrow \text{C}_3\text{H}_6 + \text{HO}_2$ (5) $\text{X} + \text{C}_3\text{H}_8 \rightarrow \text{n-C}_3\text{H}_7 + \text{HX}$ (a) $\text{X} + \text{C}_3\text{H}_8 \rightarrow \text{iso-C}_3\text{H}_7 + \text{HX}$ (b) (where X = H, OH)
7.64x10 ¹¹	298	GREINER 1970 ¹⁵
8.67x10 ¹¹	335	Flash photolysis of H ₂ O(1%)/Ar mixtures in the presence of
1.15x10 ¹²	375	C ₃ H ₈ at 5.5-106 Pa pressure. [OH] monitored by absorption
1.32x10 ¹²	423	spectroscopy at 306.4 nm.
1.88x10 ¹²	497	Extension of previous work. ⁸ A 10-15% correction was made for the effect of secondary reaction 6.
		$\text{OH} + \text{C}_3\text{H}_7 \rightarrow \text{products}$ (6) Author derived the expression $k_1 = 7.24 \times 10^{12} \exp(-679/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ over the temperature range 300-500 K after combining these data with corrected data from Ref. 8. Quoted by Refs. 21,23,27,29,30,36,62 and 63. Used by Refs. 43,46,47,56 and 61. E ₁ quoted by Refs. 40 and 53.
-	-	BALDWIN and WALKER 1973 ²⁴
		Theoretical determination of activation energy using exothermicity of reaction.
		Authors obtain E ₁ = 5.9 kJ mol ⁻¹ (1.4 kcal mol ⁻¹).
5.0x10 ¹¹	298	BRADLEY, HACK, HOYERMAN and WAGNER 1973 ²⁵
		Discharge flow system. H ₂ (<1%)/He mixtures at 200-413 Pa pressure. NO ₂ added downstream, C ₃ H ₈ further downstream so that [C ₃ H ₈]:[OH] varied from 1.8:1 to 10.1:1. [OH] monitored by e.s.r. spectroscopy, [H ₂ O], [CH ₃ OH], [C ₃ H ₇ OH], [C ₃ H ₈], [C ₂ H ₅ OH], [C ₂ H ₃ CHO] by t.o.f. mass spectrometry.
		Mass spectrometry results used to establish stoichiometry of the reaction, the t.o.f. instrument being preferred as it minimised effects of adsorption of species at the wall. An observed rate constant $k_{\text{obs}} = 2.56 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ was obtained, with a stoichiometry of 5.3, giving the quoted value of k_1 .
		Quoted by Refs. 34,62 and 63.
1.33x10 ¹²	298	GORSE and VOLMAN 1974 ²⁷
		VOLMAN 1975 ³⁵
		Photolysis of H ₂ O ₂ (5.9%) in the presence of O ₂ (34.4%)/CO mixtures at a total pressure of 2.10 kPa. C ₃ H ₈ added at 21.3-206 Pa. [CO ₂] measured by gas chromatography.



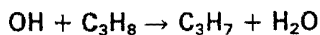
EXPERIMENTAL DATA - CONTINUED

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
		<p>Suppression of $[\text{CO}_2]$ yield observed when C_3H_8 added, giving the ratio $k_1/k_7 = 14.3$ at 298 K. Taking a value of k_7 from the literature (no reference given) they obtained the quoted value of k_1.</p> $\text{CO} + \text{OH} \longrightarrow \text{CO}_2 + \text{H} \quad (7)$ $\text{OH} + \text{C}_3\text{H}_8 \longrightarrow \text{C}_3\text{H}_7 + \text{H}_2\text{O} \quad (1)$ <p>Quoted by Refs. 38,45,62 and 63. Used by Ref. 54. Using our expression for k_7 (Vol.3, p.203), we obtain $k_1 = 1.27 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$.</p>
1.33×10^{12}	381	GORDON and MULAC 1975 ²⁸
1.15×10^{12}	416	<p>Pulse radiolysis of H_2O at 101.3 kPa (1 atm.) pressure in the presence of C_3H_8 (132–1080 Pa). $[\text{OH}]$ monitored by u.v. absorption spectroscopy at 308.7 nm.</p> <p>Correction made for disappearance of $[\text{OH}]$ in the absence of C_3H_8 from authors' own experiments. Quoted by Ref. 62.</p>
1.19×10^{12}	329	<p>HARKER and BURTON 1975³⁰</p> <p>Photolysis flow system. Hg photosensitisation of N_2O (5.7–100%)/He or N_2 mixtures at 253.7 nm at total pressures of (13.3–46.7 kPa) in the presence of C_3H_8 (13.3–533 Pa). $[\text{OH}]$ monitored by u.v. absorption spectroscopy at 308.2 and 309.0 nm.</p> <p>Experiments conducted at 313 K, but localised heating in the flow tube caused the average temperature to be raised to 329 K. O atoms produced by Hg photosensitisation of N_2O, which then react with C_3H_8.</p> $\text{Hg}(6^3\text{P}_1) + \text{N}_2\text{O} \longrightarrow \text{Hg} + \text{O} + \text{N}_2$ $\text{O} + \text{C}_3\text{H}_8 \longrightarrow \text{C}_3\text{H}_7 + \text{OH} \quad (8)$ $\text{OH} + \text{C}_3\text{H}_8 \longrightarrow \text{C}_3\text{H}_7 + \text{H}_2\text{O} \quad (1)$ <p>From $[\text{OH}]$ decay along the flow tube, authors were able to calculate k_1 and k_8. No evidence was found for the occurrence of reaction 6.</p> $\text{OH} + \text{C}_3\text{H}_7 \longrightarrow \text{products} \quad (6)$ <p>Quoted by Ref. 62.</p>
-	653	<p>HUCKNALL, BOOTH and SAMPSON 1975³¹</p> <p>Static system. OH produced by decomposition of 1.33 kPa H_2O_2 in (a) O_2/N_2 mixtures at a total pressure of 5.33–66.7 kPa; (b,c) O_2(20%)/N_2 mixtures at a total pressure of 40 kPa. (a) $\text{C}_2\text{H}_6/\text{C}_3\text{H}_8$ mixtures (1:1, 4:1, 1:4) added up to 667 Pa</p>



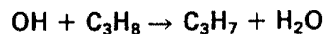
EXPERIMENTAL DATA - CONTINUED

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
		<p>pressure; (b) $\text{C}_3\text{H}_8/\text{n-C}_4\text{H}_{10}$ mixtures (1:1) added up to 267 Pa pressure; (c) $\text{C}_3\text{H}_8/\text{iso-C}_4\text{H}_{10}$ mixtures added up to 225 Pa pressure. Aged boric acid coated vessels. $[\text{H}_2\text{O}_2]$ monitored by permanganate titration, stable products by gas chromatography.</p> <p>The $\text{C}_2\text{H}_6/\text{C}_3\text{H}_8$ co-oxidation was the most extensively studied, over a wide range of pressures. $k_1/k_9 = 2.18$ at 653 K obtained. Using our expression for k_9 (this paper) we obtain, $k_1 = 3.92 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$.</p> $\text{OH} + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_5 + \text{H}_2\text{O} \quad (9)$ <p>From the $\text{C}_3\text{H}_8/\text{C}_4\text{H}_{10}$ co-oxidation, authors obtained $k_{10}/k_1 = 1.54$ and $k_{11}/k_1 = 1.28$ at 653 K.</p> $\text{OH} + \text{n-C}_4\text{H}_{10} \rightarrow \text{n-C}_4\text{H}_9 + \text{H}_2\text{O} \quad (10)$ $\text{OH} + \text{iso-C}_4\text{H}_{10} \rightarrow \text{iso-C}_4\text{H}_9 + \text{H}_2\text{O} \quad (11)$ <p>Interference by HO_2 reactions discussed.</p> <p>Quoted by Ref. 62.</p>
1.22×10^{12}	295	<p>OVEREND, PARASKEVOPOULOS and CVETANOVIC 1975³³</p> <p>Flash photolysis of $\text{H}_2\text{O}(0.5\%)/\text{He}$ mixtures at 66.7 kPa pressure in the presence of $\text{C}_3\text{H}_8(0-253 \text{ Pa})$. $[\text{OH}]$ monitored by u.v. absorption spectroscopy.</p> <p>Results confirmed using flash photolysis of N_2O in the presence of H_2 to produce OH.</p> $\text{N}_2\text{O} + h\nu \rightarrow \text{N}_2 + \text{O}(^1\text{D}) \quad (12)$ $\text{H}_2 + \text{O}(^1\text{D}) \rightarrow \text{H} + \text{OH} \quad (13)$ <p>A computer simulation showed the only competing reaction to be reaction 6. Authors assumed $k_6 =$ collision frequency.</p> $\text{OH} + \text{C}_3\text{H}_7 \rightarrow \text{products} \quad (6)$ <p>Quoted by Refs. 55, 60, 62 and 63.</p>
-	300	<p>DARNALL, ATKINSON AND PITTS 1978⁴⁴</p> <p>Static system. $\text{NO}_x/\text{air}/\text{C}_3\text{H}_8/\text{n-C}_4\text{H}_{10}$ mixture irradiated at atmospheric pressure. Concentration of alkanes measured by gas chromatography.</p> <p>Previous work^{39,50} has shown that alkane loss in this system is due solely to the reaction,</p> $\text{OH} + \text{RH} \rightarrow \text{H}_2\text{O} + \text{products}$ <p>and relative alkane concentrations at various times reflect the relative rates of these reactions. $k_1/k_{10} = 0.58$.</p> $\text{OH} + \text{C}_3\text{H}_8 \rightarrow \text{C}_3\text{H}_7 + \text{H}_2\text{O} \quad (1)$ $\text{OH} + \text{n-C}_4\text{H}_{10} \rightarrow \text{n-C}_4\text{H}_9 + \text{H}_2\text{O} \quad (10)$



EXPERIMENTAL DATA - CONTINUED

Rate Constant $\text{k}/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
		Using $k_{10} = 1.64 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ from Ref. 37, authors obtain $k_1 = (9.6 \pm 1.3) \times 10^{11} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$. Quoted by Ref. 63.
-	299	ATKINSON, ASCHMANN, CARTER, WINER and PITTS 1982 ⁵⁸ Static system. Mixture of $\text{CH}_3\text{ONO}/\text{NO}/\text{air}/\text{C}_3\text{H}_8/\text{n-C}_4\text{H}_{10}$ irradiated at $\geq 290 \text{ nm}$. Reactants monitored by gas chromatography. NO added to reaction mixture to minimize formation of O_3 . $k_1/k_{10} = 0.47$. Using k_{10} from Ref. 59, a value of $k_1 = (7.3 \pm 0.2) \times 10^{11} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ is obtained at 299 K.
$2.6 \times 10^4 T^{2.8} \exp(310/T)$	300-2000	COHEN 1982 ⁶¹ Theoretical expression derived using transition state theory and experimental data of Refs. 8 and 15.
-	428-696	BAULCH, CRAVEN, DIN, DRYSDALE, GRANT, RICHARDSON, WALKER and WATLING 1983 ⁶² Static system. Photolysis of H_2O (1.6-3.8 kPa) in the presence of $\text{C}_3\text{H}_8/\text{CO}$ where $[\text{C}_3\text{H}_8]/[\text{CO}]$ in the range 0.021-2.4. Total pressure < 13 kPa. CO_2 yields measured by gas chromatography. Formation of CO_2 from reaction 7 was found to be constant and independent of $[\text{CO}]/[\text{H}_2\text{O}]$ above a ratio of about 0.2 using fixed photolysis times and constant $[\text{H}_2\text{O}]$. $\text{CO} + \text{OH} \longrightarrow \text{CO}_2 + \text{H} \quad (7)$ $\text{OH} + \text{C}_3\text{H}_8 \longrightarrow \text{C}_3\text{H}_7 + \text{H}_2\text{O} \quad (1)$ A small amount of CO_2 obtained in the absence of photolysing light was assumed to be thermal in origin. Taking k_7 from Ref. 26 we obtain $k_1 \times 10^{-12}/\text{cm}^3\text{mol}^{-1}\text{s}^{-1} = 1.15(428 \text{ K}), 1.69(489 \text{ K}), 1.71(538 \text{ K}), 2.42(589 \text{ K}), 2.87(641 \text{ K}), 4.28(696 \text{ K})$.
6.3×10^{11}	297	TULLY, RAVISHANKARA and CARR 1983 ⁶³
8.9×10^{11}	326	Flash photolysis of $\text{H}_2\text{O}/\text{C}_3\text{H}_8/\text{Ar}$ mixtures in slow flow reactor. All experiments at 13 kPa pressure of Ar and $[\text{C}_3\text{H}_8] \gg [\text{OH}]$. $[\text{OH}]$ monitored by resonance fluorescence.
1.5×10^{12}	378	
2.0×10^{12}	469	
2.9×10^{12}	554	The expression, $k_1 = 9.57 \times 10^8 T^{1.40} \exp(-428/T) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$
5.3×10^{12}	690	was derived from the experimental Arrhenius points. Separation of OH-propane reactivity into primary and secondary H-abstraction channels obtained approximately using results for C_2H_6 in same study.

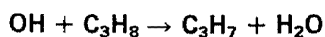


EXPERIMENTAL DATA - CONTINUED

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
1.58×10^{13}	1220	BOTT and COHEN, 1984 ⁶⁴ Shock tube study. T-butyl hydroperoxide (40 ppm)/C ₃ H ₈ (0-360 ppm)/Ar mixtures at total pressure of 6.67 kPa shock heated to temperatures between 1193-1250 K. T-butyl hydroperoxide chosen as OH source because of rapid dissociation in this temperature region. [OH] monitored by absorption spectroscopy. The quoted value of k_1 is in good agreement with a calculated value of $1.53 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 1220 K, derived from an expression by Cohen ⁶¹ which is based on other experimental results and transition state calculations.

REVIEW ARTICLES

-	-	KAUFMAN 1969 ¹¹ Review of elementary gas reactions. Quotes Ref. 8.
$1.6 \times 10^{14} \exp(-1580/T)$	300-800	DRYSDALE and LLOYD 1970 ¹⁴ Evaluation. Based on Refs. 4 and 8. Authors note that both n-C ₃ H ₇ and iso-C ₃ H ₇ are formed in reaction 1. $\text{OH} + \text{C}_3\text{H}_8 \longrightarrow \text{C}_3\text{H}_7 + \text{H}_2\text{O} \quad (1)$ In view of the dearth of data, they place no confidence in their expression. Used by Ref. 41.
7.41×10^{11}	298	ZAFONTE 1970 ¹⁸ Preferred value. Quotes Ref. 15. No other values compared. CAMPBELL and BAULCH 1972 ²² Review of atomic and bimolecular reactions. Quotes Ref. 12. Authors also discuss the data from Refs. 8 and 15.
-	-	KERR 1976 ³⁶ Review of H atom transfer reactions. Quotes Ref. 15.

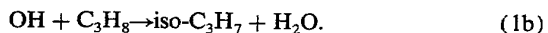
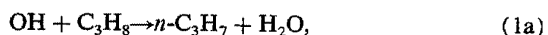


REVIEW ARTICLES - CONTINUED

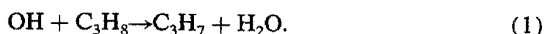
Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
-	-	ATKINSON, DARNALL, LLOYD, WINER and PITTS 1979 ⁴⁸ Review of gas phase reactions of OH with organic compounds. Quotes Refs. 15,25,27,28,30,33 and 44. Quoted by Ref. 51.
-	-	WESTLEY 1981 ⁵⁷ Compilation of data for combustion reactions. Quotes Refs. 25,27,28,30,31 and 33.
$0.4\text{T}^{3.4}\exp(590/T)$	300-2000	COHEN and WESTBERG 1983 ⁶⁵ Evaluation. Based on Refs. 15,25,28,30,31,33,35,44 and 49.
$6.3 \times 10^{12}\exp(-590/T)$	300-1000	WARNATZ 1985 ⁶⁶ Evaluation. Considers data of Refs. 15,25,28,30,33 and 44. Recommended expression based on specific rates of attack on the various types of C-H bond in the molecule. ⁶⁷

Discussion

Although there are fewer data available on the reaction between hydroxyl radicals and propane than on the corresponding reactions with methane and ethane, the agreement between experimental rate constant values is generally good. Two possible reaction paths are available:



The relative importance of these two channels was investigated by Baker *et al.*,¹³ using a gas chromatographic analysis of the products from their $\text{H}_2/\text{O}_2/\text{C}_3\text{H}_8$ system. Although the ratio $k_{1b}/k_{1a} = 1.2$ was obtained at 753 K, the authors do not recommend this value. All other data are for the overall rate constant $k_1 = (k_{1a} + k_{1b})$ and in this discussion only k_1 is considered:



Absolute rate constants were determined by flash photolysis,^{8,15,33,63} pulse radiolysis,²⁸ discharge flow,²⁵ photolysis flow,³⁰ and shock-tube study.⁶⁴

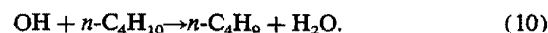
Many of the data points were obtained at or around 300 K. The observed rate constants of Bradley *et al.*²⁵ were corrected for a stoichiometry of 5.3, giving, $k_1 = 5.0 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 298 K. This value is, however, lower than other results measured in this temperature region, and be-

cause of the doubts pertaining to the stoichiometry used, it is rejected. Gorse and Volman²⁷ measured the rate constant ratio k_1/k_7 at 298 K and calculated k_1 using a literature value of k_7 :



Although their value of k_1 is in good agreement with the flash photolysis work of Overend *et al.*³³ at 295 K, both are considerably higher than other rate constant data for reaction (1) at ambient temperatures.

The values of k_1 proposed by Darnall *et al.*⁴⁴ at 300 K and Atkinson *et al.*⁵⁸ at 299 K were both determined from the measured ratios of k_1/k_{10} using k_{10} from Refs. 37 and 59, respectively:



Their values of k_1 are consistent with the flash photolysis results given by both Greiner^{8,15} at 298 K and Tully *et al.*⁶³ at 297 K. On the basis of the data in Refs. 8, 15, 44, 58, 63 we recommend a value of

$$k_1 = 7.9 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

at 298 K with error limits of $\Delta \log k = \pm 0.12$.

In the intermediate temperature region, Greiner^{8,15} derived the expression $k_1 = 7.2 \times 10^{12} \exp(-679/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ over the temperature range 300-500 K, using results obtained from flash photolysis experiments. The

secondary reaction (6),



was considered to have a significant effect on the rate constants and a correction of 10%–15% was made for each value of k_1 measured. Harker and Burton³⁰ found no evidence to suggest the occurrence of reaction (6) in their photolysis flow system and their value of k_1 given at 329 K does not agree too closely with that of Greiner. The rate constants determined by Gordon and Mulac²⁸ in pulse radiolysis experiments are in better agreement with those of Greiner, as are the relative rate constant measurements of Baulch *et al.*,⁶² in which k_1 was derived over the temperature range 428–696 K from k_1/k_7 , taking k_7 from Ref. 26.

In a recent flash photolysis study by Tully *et al.*,⁶³ absolute values of k_1 were obtained over the temperature range 297–690 K. Their results are in good agreement with the majority of other data over the same temperature range. The expression $k_1 = 9.6 \times 10^8 T^{1.4} \exp(-428/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ was derived from the experimental Arrhenius points from Ref. 63.

There are few available data at temperatures greater than 700 K. Baldwin^{4,5} measured the rate constant ratio k_1/k_3 at 793 K:



In later work,^{12,13} a value of $k_1/k_3 = 21.5$ at 753 K was obtained and was later corrected for the effects of self-heating to give $k_1/k_3 = 9.9$ at 753 K.⁴² Using k_3 from Ref. 49, $k_1 = 3.7 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

Recent shock-tube work by Bott and Cohen⁶⁴ has produced data at combustion temperatures, giving $k_1 = 1.58 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 1220 K. This is in excellent agreement with Cohen's theoretical value of $k_1 = 1.53 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at the same temperature.⁶¹

In an early attempt to evaluate kinetic data for reaction (1), Drysdale and Lloyd¹⁴ drew a simple Arrhenius plot based on the results from Refs. 4 and 8. Since the high-temperature value given by Baldwin⁴ had not at the time been corrected for the effects of self-heating, their Arrhenius expression is unreliable. With the subsequent availability of more experimental data, it became evident that a two-parameter Arrhenius expression is not sufficient over a wide temperature range. A more recent calculation by Cohen⁶¹ gives

$$k_1 = 2.6 \times 10^4 T^{2.8} \exp(310/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1},$$

over the temperature range 300–2000 K. The corresponding Arrhenius plot shows pronounced curvature, particularly at high temperatures. Near 2000 K, k_1 is an order of magnitude larger than that implied by a linear extrapolation based on data between 300–500 K. Indeed, curvature is not unexpected since the relative contributions of the two reaction paths (1a) and (1b) will change with temperature. Cohen's expression, based on experimental data^{8,15} and transition state calculations, was later revised⁶⁴ by a factor of 1.26³⁰⁰⁷ to incorporate Tully's new data.⁶³

In this evaluation we recommend the expression

$$k_1 = (k_{1a} + k_{1b}) \\ = 1.1 \times 10^4 T^{2.93} \exp(390/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1},$$

over the temperature range 290–1200 K, with error limits of $\Delta \log k = \pm 0.12$ at 300 K, rising to an error in $\log k$ of ± 0.3 above 1000 K. Since the rate equation given is the sum of two Arrhenius expressions, any single value of activation energy or pre-exponential factor derived from this empirical expression will have no physical significance and therefore we do not recommend any rate parameters.

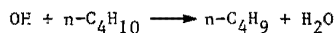
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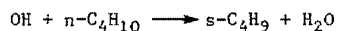
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6. $\text{OH} + \text{n-C}_4\text{H}_{10} \rightarrow \text{C}_4\text{H}_9 + \text{H}_2\text{O}$

THERMODYNAMIC DATA



No thermodynamic data available for $\text{n-C}_4\text{H}_9$



$$\Delta H_{298}^\circ = -102.05 \text{ kJ mol}^{-1} (-24.39 \text{ kcal mol}^{-1})$$

RECOMMENDED RATE CONSTANT

$$k = 1.0 \times 10^9 T^{1.3} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$= 1.7 \times 10^{-15} T^{1.3} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Temperature Range: 300–750 K

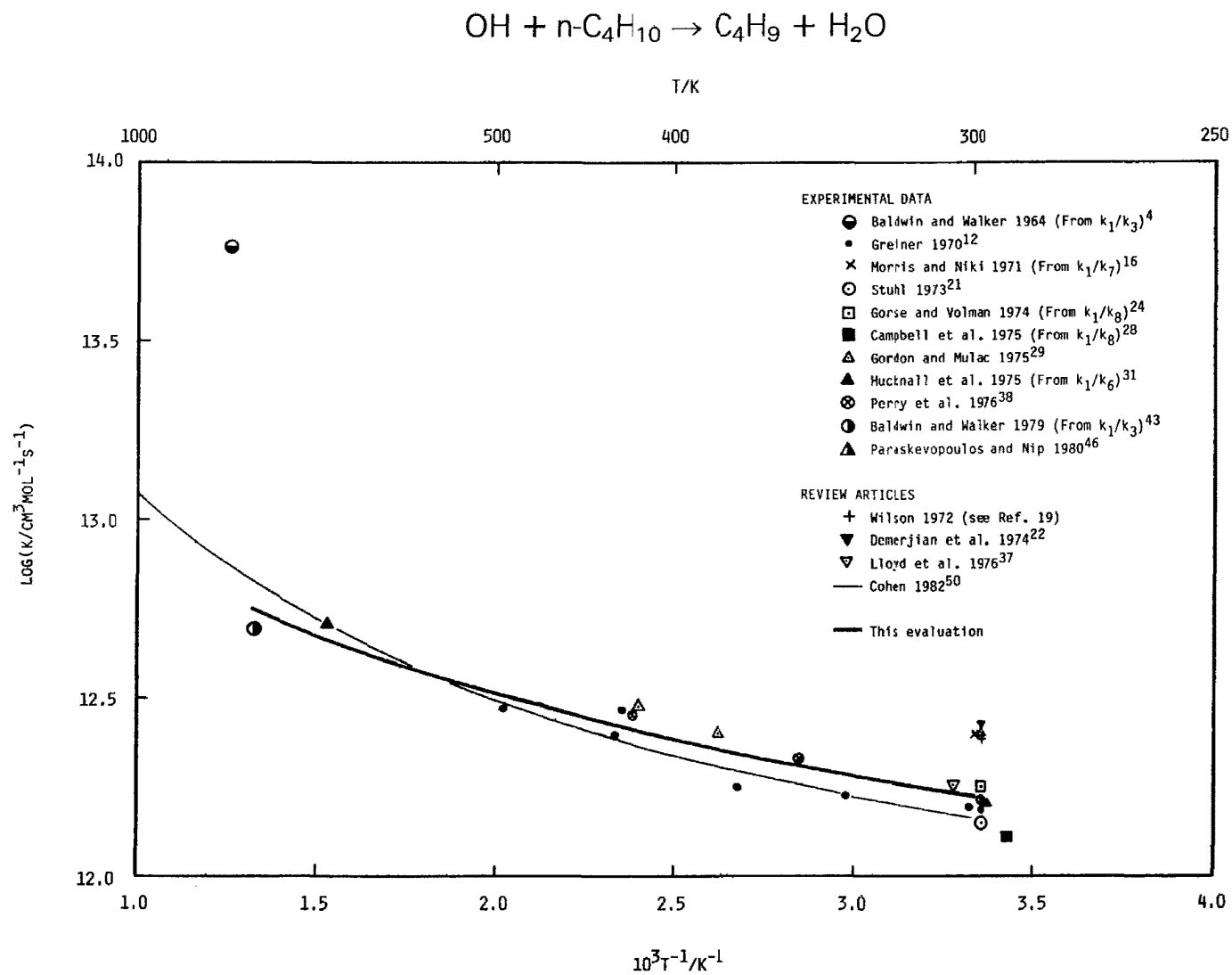
Suggested Error limits for Calculated Rate Constant:

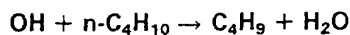
$\Delta \log k = \pm 0.11$ at 300 K, rising to $\Delta \log k = \pm 0.3$ at 750 K

Rate Parameters: See Discussion.

EXPERIMENTAL DATA

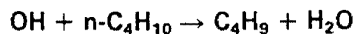
Rate Constant $\text{k/cm}^3 \text{mol}^{-1} \text{s}^{-1}$	Temperature T/K	Reference and Comments
5.8×10^{13}	793	<p>BALDWIN and WALKER 1964⁴</p> <p>Static system. $\text{H}_2(7-56\%)/\text{O}_2(7-56\%)/\text{N}_2$ mixtures at total pressures of approximately 12 kPa. <0.1% $\text{n-C}_4\text{H}_{10}$ added. KCl-coated vessels. Reaction followed manometrically, products estimated by separation with various freezing mixtures.</p> <p>Inhibition by $\text{n-C}_4\text{H}_{10}$ of 2nd limit of H_2/O_2 reaction. Authors found reaction 2 to be main source of removal of $\text{n-C}_4\text{H}_{10}$ and assumed reaction 1 important secondary source by analogy with similar work on propane.³</p> $\text{OH} + \text{n-C}_4\text{H}_{10} \longrightarrow \text{C}_4\text{H}_9 + \text{H}_2\text{O} \quad (1)$ $\text{H} + \text{n-C}_4\text{H}_{10} \longrightarrow \text{C}_4\text{H}_9 + \text{H}_2 \quad (2)$ <p>Assuming all C_4H_9 radicals undergo termination reactions, authors obtain $k_1/k_3 = 36.0$. Taking k_3 from Refs. 1 and 2, they give the value of k_1 quoted. Using our expression for k_3 (Vol. 1, p. 77), we obtain $k_1 = 3.02 \times 10^{13} \text{ cm}^3 \text{mol}^{-1} \text{s}^{-1}$ at 793 K.</p> $\text{H}_2 + \text{OH} \longrightarrow \text{H}_2\text{O} + \text{H} \quad (3)$ <p>Quoted by Refs. 5, 7, 11 and 13.</p>
2.4×10^{13} Revised to 4.9×10^{12}	753	<p>BAKER, BALDWIN and WALKER 1970⁹</p> <p>BALDWIN, BENNETT and WALKER 1977³⁹</p> <p>BALDWIN and WALKER 1979⁴³</p> <p>Static system. $\text{H}_2(7-85\%)/\text{O}_2(7-92\%)/\text{N}_2$ mixtures at total pressures of 33.3–89.1 kPa. <1% $\text{n-C}_4\text{H}_{10}$ added. Aged boric acid coated vessels. $[\text{HCHO}]$ determined colorimetrically, other</p>





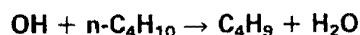
EXPERIMENTAL DATA - CONTINUED

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
		products by gas chromatography.
		Investigation of the effect of $n\text{-C}_4\text{H}_{10}$ on the slow H_2/O_2 reaction. Evidence from gas chromatography showed reaction 2 to be more important than reaction 4 and authors were able to give the ratio $k_1/k_3 = 34.0$ at 753 K.
		$\text{HO}_2 + n\text{-C}_4\text{H}_{10} \rightarrow \text{C}_4\text{H}_9 + \text{H}_2\text{O}_2$ (4)
		Taking k_3 from Ref. 8 authors obtain quoted value of k_1 .
		Quoted by Refs. 15 and 20.
		Used by Ref. 31.
		Authors later made corrections for effects of self-heating, ³⁹ obtaining $k_1/k_3 = 13.2$ at 753 K. Using $k_3 = 1.28 \times 10^8 T^{1.5} \exp(-1480/T) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ derived by Baldwin and Walker, ⁴³ gives revised value of k_1 .
1.54×10^{12}	298	GREINER 1970 ¹²
1.56×10^{12}	301	Flash photolysis of $\text{H}_2\text{O}(1\%)/\text{Ar}$ mixtures in the presence of $n\text{-C}_4\text{H}_{10}$ at 10.6–25.7 Pa pressure. $[\text{OH}]$ monitored by u.v. absorption spectroscopy at 306.4 nm.
1.68×10^{12}	336	
1.78×10^{12}	373	
2.92×10^{12}	425	A correction of 10–15% made to observed rate constants for the effect of reaction 5.
2.48×10^{12}	428	
2.95×10^{12}	495	$\text{OH} + \text{C}_4\text{H}_9 \rightarrow \text{products}$ (5) Author derived the expression $k_1 = 8.51 \times 10^{12} \exp(-523/T) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ over the temperature range 300–500 K. Quoted by Ref. 49. Used by Refs. 42, 45, 47, 48 and 50.
-	300	MORRIS and NIKI 1971 ¹⁶ Discharge flow system. H_2/He mixtures at 133 Pa pressure, NO_2 added downstream, $n\text{-C}_4\text{H}_{10}$ added further downstream so that $[\text{OH}] \gg [n\text{-C}_4\text{H}_{10}]$. $[\text{OH}]$ and $[n\text{-C}_4\text{H}_{10}]$ determined by mass spectrometry. $[\text{OH}]$ and $[n\text{-C}_4\text{H}_{10}]$ measured at various points along the flow tube and compared with similar measurements made in a previous study for reaction 7. ¹⁷ $\text{OH} + \text{C}_3\text{H}_6 \rightarrow \text{products}$ (7) Authors obtain $k_1/k_7 = 0.24$ at 300 K. Stuhl ²¹ uses the value of k_7 from Ref. 17 to obtain $k_1 = 2.5 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$. This value is plotted on the Arrhenius diagram. $\text{OH} + n\text{-C}_4\text{H}_{10} \rightarrow \text{C}_4\text{H}_9 + \text{H}_2\text{O}$ (1) Quoted by Refs. 25 and 38. Used by Ref. 37.



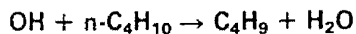
EXPERIMENTAL DATA - CONTINUED

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
1.41×10^{12}	298	STUHL 1973 ²¹ Flash photolysis of $\text{H}_2\text{O}(0.25\%)/\text{He}$ mixtures at a total pressure of 2.67 kPa in the presence of $\text{n-C}_4\text{H}_{10}$ (240–1067 mPa). $[\text{OH}]$ monitored by resonance fluorescence. Quoted by Refs. 23, 30, 32, 34 and 38. Used by Refs. 37, 47, 48 and 50.
1.8×10^{12}	298	GORSE and VOLMAN 1974 ²⁴ VOLMAN 1975 ³³ Static photolysis of $\text{H}_2\text{O}_2(5.9\%)/\text{O}_2(34.4\%)/\text{CO}$ mixtures at a total pressure of 2.10 kPa in the presence of $\text{n-C}_4\text{H}_{10}$ (17.3–827 Pa). $[\text{CO}_2]$ monitored by gas chromatography. Suppression of $[\text{CO}_2]$ yield observed in the presence of $\text{n-C}_4\text{H}_{10}$, giving $k_1/k_8 = 19.4$ at 298 K. Taking a value of k_8 from the literature (no reference given), authors obtained the quoted value of k_1 . $\text{CO} + \text{OH} \longrightarrow \text{CO}_2 + \text{H} \quad (8)$ A value of $k_1 = 1.6 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ is obtained in Ref. 30 using a value of k_8 from that work. Quoted by Refs. 38 and 41. Used by Ref. 37.
-	753	BAKER, BALDWIN, FULLER, and WALKER 1975 ²⁷ Static system. $\text{H}_2(20.9\text{--}85\%)/\text{O}_2(10.5\text{--}71\%)/\text{N}_2$ mixtures at total pressures of 66.7–89.1 kPa. $\text{n-C}_4\text{H}_{10}$ added at a pressure of 667 Pa. Aged boric acid coated vessels. $[\text{HCHO}]$ estimated colorimetrically, other products by gas chromatography. Authors studied product yield from addition of $\text{n-C}_4\text{H}_{10}$ to slowly reacting H_2/O_2 mixtures. Assuming that C_2H_4 was produced only by decomposing $\text{n-C}_4\text{H}_9$ radicals and that k_b/k_a is the same for O or H atoms or OH radicals, authors applied a computer analysis to $[\text{C}_2\text{H}_4]$ production and $[\text{n-C}_4\text{H}_{10}]$ disappearance to give $k_{1b}/k_{1a} = 2.2$ at 753 K. $\text{X} + \text{n-C}_4\text{H}_{10} \longrightarrow \text{n-C}_4\text{H}_9 + \text{HX} \quad (\text{a})$ $\text{X} + \text{n-C}_4\text{H}_{10} \longrightarrow \text{o-C}_4\text{H}_9 + \text{HX} \quad (\text{b})$ (where X = O, H, OH). This compares with $k_{1b}/k_{1a} = 2.25$ derived from empirical calculations in earlier work. ⁹



EXPERIMENTAL DATA - CONTINUED

Rate Constant $\text{k}/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
-	292	<p>CAMPBELL, HANDY and KIRBY 1975²⁸</p> <p>Static system. $\text{H}_2\text{O}_2(0.16\%)/\text{NO}_2(1\%)/\text{CO}/\text{n-C}_4\text{H}_{10}$ mixtures at a total pressure of 13.3 kPa. $[\text{n-C}_4\text{H}_{10}]/[\text{CO}]$ varied between 0.005:1 and 0.08:1. $[\text{CO}_2]$ determined by gas chromatography.</p> <p>OH produced by reaction 9, suppression of $[\text{CO}_2]$ yield by $\text{n-C}_4\text{H}_{10}$ observed.</p> $\text{H}_2\text{O}_2 + \text{NO}_2 \longrightarrow \text{OH} + \text{HNO}_3 \quad (9)$ <p>Authors derive ratio $k_1/k_8 = 14.8$ at 292 K. Using our expression for k_8 (Vol. 3, p. 203), we obtain $k_1 = 1.30 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$. The only other reaction of note in the system is reaction 10, the effect of which was determined in runs in the absence of $\text{n-C}_4\text{H}_{10}$.</p> $\text{OH} + \text{n-C}_4\text{H}_{10} \longrightarrow \text{C}_4\text{H}_9 + \text{H}_2\text{O} \quad (1)$ $\text{CO} + \text{OH} \longrightarrow \text{CO}_2 + \text{H} \quad (8)$ $\text{NO}_2 + \text{OH} + \text{M} \longrightarrow \text{HNO}_3 + \text{M} \quad (10)$ <p>Quoted by Ref. 38.</p>
2.54x10 ¹²	298	<p>GORDON and MULAC 1975²⁹</p> <p>Pulse radiolysis of $\text{H}_2\text{O}(1.39\text{--}100\%)/\text{Ar}$ mixtures at total pressures of 96.0–101.3 kPa in the presence of $\text{n-C}_4\text{H}_{10}$ at 66.7–328 Pa pressure. $[\text{OH}]$ monitored by u.v. absorption spectroscopy at 308.7 nm.</p> <p>The runs at 381 and 416 K were under the standard conditions used for other hydrocarbons viz. 100% H_2O at 101.3 kPa. pressure. For the run at 298 K, the H_2O was diluted with Ar. Quoted by Ref. 38.</p>
2.50x10 ¹²	381	
3.00x10 ¹²	416	
-	653	<p>HUCKNALL, BOOTH and SAMPSON 1975³¹</p> <p>Static system. OH produced by decomposition of $\text{H}_2\text{O}_2(3.33\%)$ in $\text{O}_2(20\%)/\text{N}_2$ mixtures at a total pressure of 40 kPa. 1:1 $\text{C}_3\text{H}_8/\text{n-C}_4\text{H}_{10}$ mixtures added up to 267 Pa pressure. Aged boric acid coated vessels. $[\text{H}_2\text{O}_2]$ determined by permanganate titration, stable products by gas chromatography.</p> <p>Authors obtained $k_1/k_6 = 1.54$ at 653 K. Using our expression for k_6 (this paper) we obtain $k_1 = 5.4 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$.</p> $\text{OH} + \text{n-C}_4\text{H}_{10} \longrightarrow \text{C}_4\text{H}_9 + \text{H}_2\text{O} \quad (1)$ $\text{OH} + \text{C}_3\text{H}_8 \longrightarrow \text{C}_3\text{H}_7 + \text{H}_2\text{O} \quad (6)$

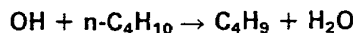


EXPERIMENTAL DATA - CONTINUED

Rate Constant $\text{k}/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
1.63x10 ¹²	298	PERRY, ATKINSON and PITTS 1976 ³⁸
2.12x10 ¹²	351	Flash photolysis of H ₂ O(0.02%)/Ar mixtures at total pressures of 6.7 kPa in the presence of n-C ₄ H ₁₀ . [OH] monitored by resonance fluorescence.
2.81x10 ¹²	420	
		Authors derive the expression $k_1 = 1.06 \times 10^{13} \exp(-560/T)$ cm ³ mol ⁻¹ s ⁻¹ from the data.
		$\text{OH} + n\text{-C}_4\text{H}_{10} \longrightarrow \text{C}_4\text{H}_9 + \text{H}_2\text{O} \quad (1)$
		Quoted by Ref. 44.
		Used by Refs. 40,47,48 and 50.
1.61x10 ¹²	297	PARASKEVOPOULOS and NIP 1980 ⁴⁶
		Flash photolysis of N ₂ O(10%)/H ₂ (1.0%)/He mixtures at total pressure of 6.7 kPa in the presence of n-C ₄ H ₁₀ (<0.5%). [OH] monitored by resonance fluorescence.
		Kinetic isotope effect observed when H replaced by D in the butane. No significant effect if OH replaced by OD.
		Used by Refs. 47,48 and 50.
$2.5 \times 10^5 T^{2.5} \exp(390/T)$	300-2000	COHEN 1982 ⁵⁰
		Theoretical expression derived using transition state theory and experimental results of Refs. 12,21,38 and 46.

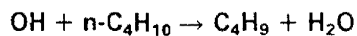
REVIEW ARTICLES

-	-	DRYSDALE and LLOYD 1970 ¹¹
		Review of gas phase OH radical reactions.
		Quotes Ref. 5.
2.34x10 ¹²	298	ZAFONTE 1970 ¹⁴
		Preferred value. Attributed to Greiner. ¹²
		Quoted by Ref. 25.
-	-	CAMPBELL and BAULCH 1972 ¹⁸
		Review of atomic and bimolecular reactions. Quotes Ref. 9.
		Authors also discuss the data from Ref. 12.



REVIEW ARTICLES - CONTINUED

Rate Constant $\text{k/cm}^3 \text{mol}^{-1} \text{s}^{-1}$	Temperature T/K	Reference and Comments
2.45×10^{12}	298	<p>WILSON, quoted by HECHT and SEINFELD 1972¹⁹</p> <p>Selected value for use in smog chamber photo-oxidations. No details available of how k_1 was selected. Chosen value higher than that determined experimentally at room temperature (c.f. Ref. 22).</p> $\text{OH} + \text{n-C}_4\text{H}_{10} \rightarrow \text{C}_4\text{H}_9 + \text{H}_2\text{O} \quad (1)$
2.65×10^{12}	298	<p>DEMERJIAN, KERR and CALVERT 1974²²</p> <p>Selected value for use in smog chamber photo-oxidations. Authors claim value of rate constant refers specifically to reaction 1a, and is about twice the value obtained by Greiner¹² for the overall k_1. This they consider to be within the bounds of experimental error.</p> $\text{OH} + \text{n-C}_4\text{H}_{10} \rightarrow \text{n-C}_4\text{H}_9 + \text{H}_2\text{O} \quad (1a)$ <p>Quoted by Ref. 25.</p>
1.5×10^{12}	298	<p>ANDERSON 1976³⁴</p> <p>Selected value for use in atmospheric chemistry is that of Greiner.¹² Also quotes Ref. 21. No criteria for selection given.</p>
-	-	<p>KERR 1976³⁶</p> <p>Review of H atom transfer reactions.</p> <p>Quotes Ref. 12.</p>
1.8×10^{12}	305	<p>LLOYD, DARNALL, WINER and PITTS 1976³⁷</p> <p>Mean value for use in OH + hydrocarbon studies taken from Refs. 12, 16, 21 and 24.</p> <p>Quoted by Ref. 26.</p>
-	-	<p>ATKINSON, DARNALL, LLOYD, WINER and PITTS 1979⁵¹</p> <p>Review of gas phase reactions of OH with organic compounds.</p> <p>Quotes Refs. 12, 16, 21, 24, 28, 29 and 38.</p>
$2.57 \times 10^5 T^{2.5} \exp(390/T)$	300-2000	<p>COHEN and WESTBERG 1983⁵²</p> <p>Evaluation. Based on data from Refs. 12, 16, 21, 24, 28, 29, 31, 38, 43 and 46.</p>
$9.0 \times 10^{12} \exp(-530/T)$	300-1000	<p>WARNATZ 1985⁵³</p> <p>Evaluation. Considers data of Refs. 12, 21 and 29. Recommended expression based on specific rates of attack on the various types of C-H bond in the molecule.⁵⁴</p>



ISOTOPIC REACTION OD + n-C₄H₁₀

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
1.66×10^{12}	297	<p>PARASKEVOPOULOS and NIP 1980⁴⁶</p> <p>Flash photolysis of N₂O(20%)/D₂(2.0%)/He mixtures at total pressure of 6.7 kPa in the presence of n-C₄H₁₀(<0.5%). [OD] monitored by resonance fluorescence.</p> <p>No significant kinetic isotope effect observed when OH replaced by OD. $k_{\text{OH}}/k_{\text{OD}} = 0.97$.</p>

ISOTOPIC REACTION OH + n-C₄D₁₀

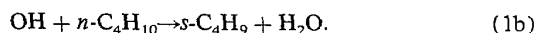
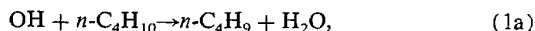
4.20×10^{11}	297	<p>PARASKEVOPOULOS and NIP 1980⁴⁶</p> <p>Flash photolysis of N₂O(10%)/H₂(1.0%)/He mixtures at total pressure of 6.7 kPa in the presence of n-C₄D₁₀(<2.7%). [OH] monitored by resonance fluorescence.</p> <p>Kinetic isotope effect observed when H replaced by D in n-butane. $k_{\text{H}}/k_{\text{D}} = 3.83$.</p>
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ISOTOPIC REACTION OD + n-C₄D₁₀

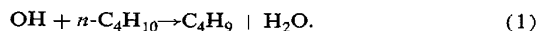
4.84×10^{11}	297	<p>PARASKEVOPOULOS and NIP 1980⁴⁶</p> <p>Flash photolysis of N₂O(20%)/D₂(2.0%)/He mixtures at total pressure of 6.7 kPa in the presence of n-C₄D₁₀(<2.5%). [OD] monitored by resonance fluorescence.</p>
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Discussion

Two reaction paths are available for the reaction between OH and *n*-butane:



The only experimental information on the relative rates of these paths comes from Baker *et al.*,²⁷ who give $k_{1b}/k_{1a} = 2.2$ at 753 K. In deriving this result a number of assumptions are made that require checking. All other data are for the overall rate constant $k_1 = (k_{1a} + k_{1b})$ and in this discussion only k_1 is considered:



At temperatures below 500 K there are absolute studies by flash photolysis^{12,21,38,46} and by pulse radiolysis.²⁹ At room temperature the flash photolysis measurements are in good agreement but the value of k_1 from pulse radiolysis appears much too high. The conditions used in the pulse radiolysis at 300 K were different from those used in similar work at > 400 K, where the results seem more acceptable. It may be that this change in conditions (large excess of inert gas for the 300 K work) has led to less reliable results.

The remaining data at around 300 K come from relative rate measurements.^{16,24,28} Of these, the results of Gorse and Volman²⁴ and Campbell *et al.*²⁸ agree well with the absolute data. In the flow discharge study of Morris and Niki,¹⁶ k_1 is derived from the ratio k_1/k_7 , which, because of doubts concerning the possible pressure dependence of k_7 , must have considerable uncertainty associated with it and is not considered further.

Based on data from Refs. 12, 21, 24, 28, 38, and 46 we recommend a value of

$$k_1 = 1.6 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

at 298 K with error limits of $\Delta \log k = \pm 0.11$:



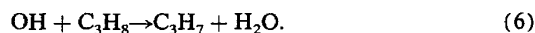
The two sets of flash photolysis results^{12,38} extend to higher temperatures and are generally in good agreement but with one set diverging slightly from the other so that they differ by 20% at 420 K, at which temperature one set finishes, the other extending up to 500 K.

At higher temperatures there are only the results of Hucknall *et al.*³¹ at 653 K and of Baldwin *et al.*^{5,9} at 753 K. Both are relative measurements. The early values of k_1/k_3 obtained by Baldwin *et al.*^{5,9} appeared an order of magnitude higher than might have been expected:



Correction of these results for self-heating and effects of minor reactions lowers the value to an acceptable level.^{39,43} The ratio k_1/k_3 has been combined with the value of k_3 recommended by Baldwin and Walker⁴³ to give the point plotted on the Arrhenius diagram. This procedure when applied to the analogous results for ethane and propane gives rate constant values which compare favorably with absolute results at about 750 K. In the case of *n*-C₄H₁₀ such a comparison is not possible but the value of k_1 obtained can be reconciled with an extrapolation of the results from lower temperatures

and despite the complexity of the reaction system we accept this result from Baldwin *et al.* with the same level of confidence that we assigned to the analogous results for ethane and propane. The work of Hucknall *et al.*³¹ is in a similar category. The value of k_1/k_6 when combined with our recommended value of k_6 (this paper) gives a value for k_1 that must have a considerable uncertainty associated with it but is reasonably consistent with the lower temperature results,



The rate expression for k_1 should consist of the sum of two Arrhenius-type expressions, one for each of the reaction paths (1a) and (1b). We would therefore expect the resulting Arrhenius plot to show a degree of curvature because of the very different activation energies of the two paths. The scatter on the experimental data is such that the extent of curvature is uncertain and the data could just as well be fitted to a straight line. We have, however, chosen to fit the data to an empirical expression of the form $k_1 = AT^n \exp(B/T)$. A computer fit through the best data points gives the empirical expression

$$k_1 = 1.0 \times 10^9 T^{1.3} \exp(-18/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1},$$

between 300 and 750 K. Since the exponential term is small and contributes < 6% to the expression over this temperature range, it may be excluded. Based on rate data from Refs. 12, 21, 24, 28, 38, and 46 at around 300 K and the higher temperature work in Refs. 12, 29, 31, 38, and 43, we therefore recommend the expression

$$k_1 = 1.0 \times 10^9 T^{1.3} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1},$$

over the temperature range 300–750 K with error limits of $\Delta \log k = \pm 0.11$ at 300 K, rising to an error in $\log k$ of ± 0.3 at 750 K. This may be compared with a recent expression given by Cohen,⁵⁰

$$k_1 = 2.6 \times 10^3 T^{2.5} \exp(390/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1},$$

between 300 and 2000 K. Cohen's expression is based on data from Refs. 12, 21, 38, and 46, and transition state calculations.

Because the rate expression is in reality the sum of two Arrhenius expressions, any single value of E_a or pre-exponential factor derived from our empirical expression will have no physical significance and therefore we quote no rate parameters.

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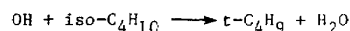
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7. OH + iso-C₄H₁₀ → C₄H₉ + H₂O

THERMODYNAMIC DATA



No thermodynamic data available for iso-C₄H₉



$$\Delta H_{298}^\circ = -114.60 \text{ kJ mol}^{-1} \quad (-27.39 \text{ kcal mol}^{-1})$$

RECOMMENDED RATE CONSTANT

$$k = 1.9 \times 10^3 T^{3.1} \exp(860/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$= 3.2 \times 10^{-21} T^{3.1} \exp(860/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Temperature Range 290–750 K

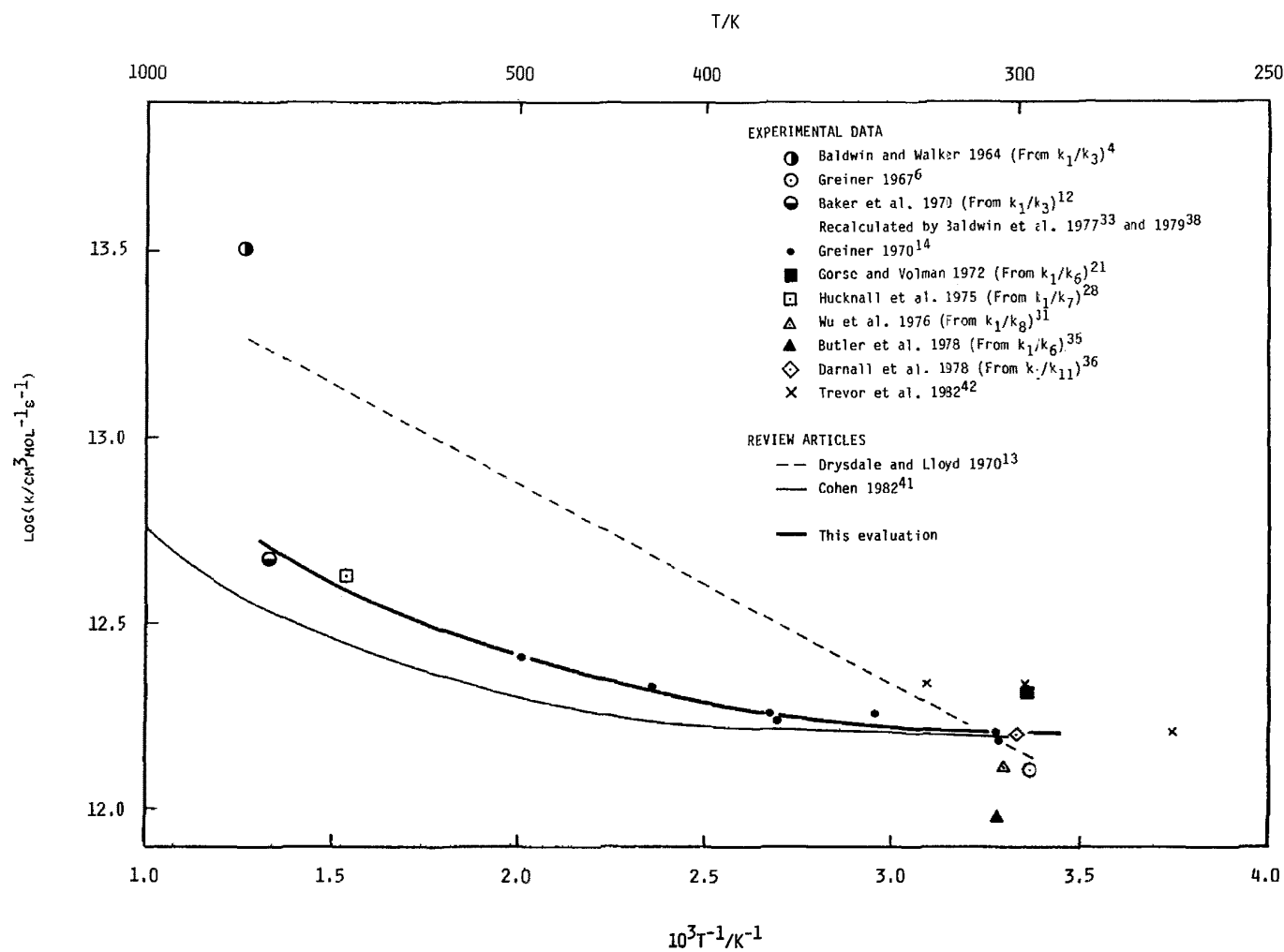
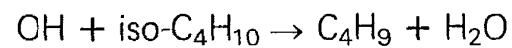
Suggested Error Limits for Calculated Rate Constant:

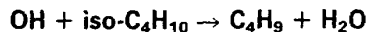
$\Delta \log k = \pm 0.12$ at 300 K, rising to $\Delta \log k = \pm 0.3$ at 750 K.

Rate Parameters: See Discussion.

EXPERIMENTAL DATA

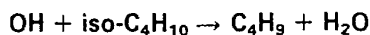
Rate Constant $k/\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	Temperature T/K	Reference and Comments
3.2×10^{13}	793	<p>BALDWIN and WALKER 1964⁴</p> <p>Static system. H₂(7–56%)/O₂(7–56%)/N₂ mixtures at total pressures of about 12 kPa. <0.1% iso-C₄H₁₀ added. KCl coated vessels. Reaction followed manometrically, products estimated by separation with various freezing mixtures.</p> <p>Inhibition by iso-C₄H₁₀ of 2nd explosion limit of H₂/O₂ reaction. Authors found reaction 2 to be main source of removal of hydrocarbon and assumed reaction 1 an important secondary source by analogy with previous work on OH/alkane reactions.¹</p> $\text{OH} + \text{iso-C}_4\text{H}_{10} \longrightarrow \text{C}_4\text{H}_9 + \text{H}_2\text{O} \quad (1)$ $\text{H} + \text{iso-C}_4\text{H}_{10} \longrightarrow \text{C}_4\text{H}_9 + \text{H}_2 \quad (2)$ <p>Assuming all C₄H₉ radicals undergo termination reactions, authors obtain $k_1/k_3 = 20.0$. Taking k_3 from Refs. 2 and 3 they give the value of k_1 quoted. Using our expression for k_3 (Vol. 1, p. 77), we obtain $k_1 = 1.7 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 793 K.</p> $\text{H}_2 + \text{OH} \longrightarrow \text{H}_2\text{O} + \text{H} \quad (3)$ <p>Quoted by Refs. 5, 7, 13 and 15.</p>
1.28×10^{12}	297	<p>GREINER 1967⁶</p> <p>Flash photolysis of H₂O(1%)/Ar mixtures at a total pressure of 13.3 kPa, in the presence of iso-C₄H₁₀ at 33.3–130 Pa pressure. [OH] monitored by u.v. absorption at 306.4 nm.</p>





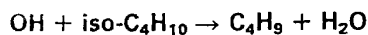
EXPERIMENTAL DATA - CONTINUED

Rate Constant $\text{k/cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
		Effect of secondary reactions considered insignificant, except possibly at very low [iso-C ₄ H ₁₀]. Quoted by Refs. 10,14,15,16,18,37 and 40. Used by Refs. 11,13 and 32.
2.2x10 ¹³ Revised to 4.7x10 ¹²	753	BAKER, BALDWIN and WALKER 1970 ¹² BALDWIN, BENNET and WALKER 1977 ³³ BALDWIN and WALKER 1979 ³⁸ Static system. H ₂ (7-85%)/O ₂ (7-92%)/N ₂ mixtures at total pressures of 33.3-89.1 kPa. <1% iso-C ₄ H ₁₀ added. Aged boric acid coated vessels. [HCHO] determined colorimetrically, other products by gas chromatography. Investigation of the effect of iso-C ₄ H ₁₀ on the slow H ₂ /O ₂ reaction. Evidence from gas chromatography showed reaction 2 to be more important than reaction 4 and authors were able to give the ratio $k_1/k_3 = 31.0$ at 753 K. $\text{HO}_2 + \text{iso-C}_4\text{H}_{10} \longrightarrow \text{C}_4\text{H}_9 + \text{H}_2\text{O}_2 \quad (4)$ Taking k_3 from Ref. 9, authors obtained quoted value of k_1 . Combining this value with that from Ref. 6, they obtain the expression $k_1 = 1.40 \times 10^{14} \exp(-1400/T) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$. Quoted by Refs. 19,20 and 22. Used by Ref. 28. Authors later made corrections for effects of self-heating and refinements to reaction mechanism, ^{33,38} obtaining $k_1/k_3 = 12.6$ at 753 K. Using expression for k_3 derived by Baldwin and Walker ³⁸ gives revised value of k_1 .
1.54x10 ¹²	304	GREINER 1970 ¹⁴
1.62x10 ¹²	305	Flash photolysis of H ₂ O(1%) / Ar mixtures in the presence of iso-C ₄ H ₁₀ at 19.0-49.1 Pa pressure. [OH] monitored by u.v.
1.81x10 ¹²	338	absorption spectroscopy at 306.4 nm.
1.73x10 ¹²	371	A correction of 10-15% made to observed rate constants for the effect of reaction 5.
1.83x10 ¹²	374	
2.15x10 ¹²	425	
2.56x10 ¹²	498	$\text{OH} + \text{C}_4\text{H}_9 \longrightarrow \text{products} \quad (5)$ Author derived the expression $k_1 = 5.25 \times 10^{12} \exp(-387/T) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ over the temperature range 300-500 K, from the experimental results. $\text{OH} + \text{iso-C}_4\text{H}_{10} \longrightarrow \text{C}_4\text{H}_9 + \text{H}_2\text{O} \quad (1)$ Quoted by Refs. 22,27,30 and 34. Used by Refs. 24 and 41.



EXPERIMENTAL DATA - CONTINUED

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
-	298	CORSE and VOLMAN 1972 ²¹ VOLMAN 1975 ²⁹ Static photolysis of $\text{H}_2\text{O}_2(5.9\%)/\text{O}_2(34\%)/\text{CO}$ mixtures at a total pressure of 2.12 kPa in the presence of iso-C ₄ H ₁₀ (0-625 Pa). [CO ₂] monitored by gas chromatography. Suppression of [CO ₂] yield observed in the presence of iso-C ₄ H ₁₀ , giving $k_1/k_6 = 23.3$ at 298 K. Taking k_6 from Ref. 8 authors obtained $k_1 = 2.1 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$. $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H} \quad (6)$ Quoted by Ref. 25. Used by Refs. 39 and 41.
-	-	BALDWIN and WALKER 1973 ²³ Theoretical determination of activation energy from reaction exothermicity. Authors obtain $E_1 = 4.2 \text{ kJ mol}^{-1}(1.0 \text{ kcal mol}^{-1})$.
-	653	HUCKNALL, BOOTH and SAMPSON 1975 ²⁸ Static system. OH produced by decomposition of $\text{H}_2\text{O}_2(3.33\%)$ in $\text{O}_2(20\%)/\text{N}_2$ mixtures at a total pressure of 40 kPa. 1:1 C ₃ H ₈ /iso-C ₄ H ₁₀ mixtures added up to 225 Pa pressure. Aged boric acid coated vessels. [H ₂ O ₂] determined by permanganate titration, stable products by gas chromatography. Authors obtained $k_1/k_7 = 1.28$ at 653 K. Using our expression for k_7 (this paper) we obtain $k_1 = 4.5 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$. $\text{OH} + \text{C}_3\text{H}_8 \rightarrow \text{C}_3\text{H}_7 + \text{H}_2\text{O} \quad (7)$
-	303	WU, JAPAR and NIKI 1976 ³¹ Photolysis of NO ₂ at ppm level in NO(ppm)/iso-butane(ppm)/air or He/O ₂ (21%) mixtures. NO, NO ₂ , O ₃ concentrations monitored with NO/O ₃ chemiluminescence detectors. Iso-butane concentration measured by gas chromatography. Iso-butane removed by reaction with OH, O and O ₃ but last two contribute <6% to total decay. Decay rate of iso-butane compared with that of cis-2-butene leading to $k_1/k_8 = 0.04$. $\text{OH} + \text{cis-CH}_3\text{CH=CHCH}_3 \rightarrow \text{products} \quad (8)$ Using k_8 from Ref. 26 gives $k_1 = 1.3 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$.

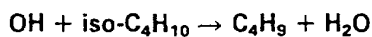


EXPERIMENTAL DATA - CONTINUED

Rate Constant $\text{k/cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
-	305	BUTLER, SOLOMON and SNELSON 1978 ³⁵ Photolysis of $\text{H}_2\text{O}_2(1\%)/\text{H}_2\text{O}(2\%)/\text{CO}(14\%)/\text{iso-C}_4\text{H}_{10}(1\%)/\text{O}_2(33\%)/\text{N}_2(49\%)$ mixtures. CO_2 yield analysed by gas chromatography. Variation of CO_2 yield with $[\text{CO}]/[\text{iso-C}_4\text{H}_{10}]$ attributed to competition between reactions 1 and 6. $\text{OH} + \text{iso-C}_4\text{H}_{10} \rightarrow \text{C}_4\text{H}_9 + \text{H}_2\text{O} \quad (1)$ $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H} \quad (6)$ Analysis of yields gives $k_1/k_6 = 10.6$. Correction made for effects of reaction 9. $\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2 \quad (9)$ Using our value for k_6 (Vol. 3, p. 203) gives value of $k_1 = 9.6 \times 10^{11} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ at 305 K. Used by Ref. 39.
-	300	DARNALL, ATKINSON and PITTS 1978 ³⁶ Photolysis of $\text{NO}_x/\text{air} / \text{iso-C}_4\text{H}_{10}(0.055\text{--}0.058 \text{ ppm})$ at 100 kPa total pressure. $[\text{iso-C}_4\text{H}_{10}]$ monitored by gas chromatography. Rate of $[\text{iso-C}_4\text{H}_{10}]$ decay compared with rate of decay of $[\text{n-C}_4\text{H}_{10}]$ in an analogous experiment; gives $k_1/k_{10} = 0.92$. $\text{OH} + \text{n-C}_4\text{H}_{10} \rightarrow \text{H}_2\text{O} + \text{C}_4\text{H}_9 \quad (10)$ Using our value for k_{10} (this paper) gives $k_1 = 1.5 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ at 300 K. Used by Ref. 41.
$8.9 \times 10^3 T^{2.8} \exp(910/T)$	300-2000	COHEN 1982 ⁴¹ Theoretical expression derived using transition state theory and experimental results of Refs. 14, 25 and 36.
1.62×10^{12}	267	TREVOR, BLACK and BARKER 1982 ⁴²
2.17×10^{12}	298	Flash photolysis. $\text{O}(^1\text{D})$ from the pulsed photolysis of O_3
2.18×10^{12}	324	used to generate OH by reaction with H_2 . Total pressure approximately 1.3 kPa. $[\text{OH}]$ monitored by resonance fluorescence. k_1 determined to test system.

REVIEW ARTICLES

-	-	KAUFMAN 1969 ¹⁰ Review of elementary gas reactions. Quotes Greiner. ⁶
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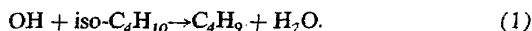


REVIEW ARTICLES - CONTINUED

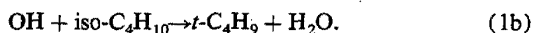
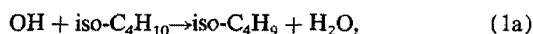
Rate Constant $\text{k/cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
$8.8 \times 10^{13} \exp(-1230/T)$	298-793	DRYSDALE and LLOYD 1970 ¹³ Evaluation. Based on data from Refs. 4 and 6. Noting scarcity of data, authors place little confidence in the expression determined.
1.45×10^{12}	298	ZAFONTE 1970 ¹⁷ Preferred value. Quotes Greiner. ¹⁴ No other value given for comparison.
-	-	CAMPBELL and BAULCH 1972 ²⁰ Review of atomic and bimolecular reactions. Quotes Baker et al., ¹² and also mentions Greiner's work. ^{6,14}
-	-	KERR 1976 ³⁰ Review of H atom transfer reactions. Quotes Greiner. ¹⁴
-	-	ATKINSON, DARNALL, LLOYD, WINER and PITTS 1979 ⁴⁴ Review of gas phase reactions of OH with organic compounds. Quotes Refs. 14, 25, 31 and 35.
$2.6 \times 10^5 T^{2.4} \exp(590/T)$	300-2000	COHEN and WESTBERG 1983 ⁴⁵ Evaluation. Based on data from Refs. 8, 28, 31, 35, 35, 36 and 44.
$5.8 \times 10^{12} \exp(-313/T)$	300-1000	WARNATZ 1985 ⁴⁶ Evaluation. Considers data of Refs. 12, 35 and 36. Recommended expression based on specific rates of attack on the various types of C-H bond in the molecule. ⁴⁷

Discussion

The majority of rate constant data for the reaction between hydroxyl radicals and iso-butane are derived from rate constant ratios. Only the flash photolysis results of Greiner^{6,14} and Trevor *et al.*⁴² give absolute values of k_1 ,



Although no experimental information is available on the relative rates of the two reaction paths (1a) and (1b), both are assumed to be of importance:



Much of the experimental data was obtained at or around 300 K. Greiner's initial value⁶ of k_1 at 297 K did not take into account the effect of reaction (5),



for which a correction of 10%–15% was made on results given in subsequent work.¹⁴

Wu *et al.* determined a rate constant ratio for the reaction of iso-butane and *cis*-2-butene with OH radicals.³¹ Taking the rate constant for the reaction between OH and *cis*-2-butene from Ref. 26, we obtain a value of k_1 that appears low compared with Greiner's absolute result.¹⁴ It must be remembered, however, that k_1 is strongly dependent on the reference rate constant for which there is considerable discrepancy in the literature. Indeed, if we were to take the rate constant for OH + *cis*-2-butene given by Morris and Niki,⁴³ we derive a value of k_1 that compares very favorably with Greiner's value.¹⁴

Darnall *et al.* used a relative method³⁶ to determine k_1 at 300 K, which is in good agreement with Greiner's room-temperature data.¹⁴ Their results are based on the well established rate constant for the reaction between *n*-butane and OH radicals.

Butler *et al.*³⁵ and Gorse and Volman^{21,29} used essentially the same experimental technique but obtained values of k_1 differing by more than a factor of 2. The use of H_2O_2 as a source of OH radicals in these studies may have been the cause of undetected complications. Trevor *et al.*⁴² made three absolute measurements of k_1 between 267 and 324 K. The values given at 298 and 324 K are not in good agreement with other rate constant data for reaction (1) in the same temperature region. Although there are no comparable data below 297 K, an extrapolation of our recommended expression (given at the end of this discussion) would fit their value of k_1 at 267 K.

On the basis of data in Refs. 14, 31, and 36, we recommend a value of

$$k_1 = 1.6 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

at 298 K with error limits of $\Delta \log k = \pm 0.12$. Although we believe Greiner's activation energy of approximately 3.2 kJ mol⁻¹ to be an acceptable value,¹⁴ we make no recommendation for E_1 in the absence of confirmatory data.

The only data in the intermediate temperature region are those of Greiner¹⁴ which extend from ambient temperatures up to 498 K. At higher temperatures, values of k_1 are given by Hucknall *et al.*²⁸ at 653 K and Baldwin *et al.* at 753

K.^{12,33,38} Both are relative rate measurements and consequently there are added uncertainties associated with the values of the reference rate constants. Although there are no comparable absolute measurements of k_1 near 700 K, their methods have produced results in reasonable agreement with absolute measurements for other alkanes, notably ethane and propane. We are therefore reasonably confident of their accuracy.

We base our recommendation on data from Refs. 14, 28, 36, and 38, giving

$$k_1 = 1.9 \times 10^{13} T^{3.1} \exp(860/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

between 290 and 750 K with error limits of $\Delta \log k = \pm 0.12$ at 300 K, rising to an error in $\log k$ of ± 0.3 at 750 K. This may be compared with a recent theoretical expression derived by Cohen,⁴¹ who gives

$$k_1 = 8.9 \times 10^{13} T^{2.8} \exp(910/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

between 300 and 2000 K, based on data from Refs. 14, 25, and 36, and transition state calculations.

Since our rate expression for k_1 is in reality the sum of two Arrhenius expressions, one for each of the reaction paths (1a) and (1b), any single value of activation energy or pre-exponential factor derived from this empirical expression will have no physical significance and therefore we do not recommend any rate parameters.

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8. OH + neo-C₅H₁₂ → C₅H₁₁ + H₂O

THERMODYNAMIC DATA

$$\Delta H_{298}^{\circ} = -79.87 \text{ kJ mol}^{-1} \text{ } (-19.09 \text{ kcal mol}^{-1})$$

RECOMMENDED RATE CONSTANT

$$k_1 = 4.8 \times 10^6 T^{2.08} \exp(-70/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$= 7.5 \times 10^{-18} T^{2.08} \exp(-70/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Temperature Range: 300-1000 K.

Suggested Error Limits for Calculated Rate Constant:

$\Delta \log k = \pm 0.12$ at 300 K, rising to $\Delta \log k = \pm 0.3$ at 1000 K.

Rate Parameters: $\log (A'/\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = (7.58 + 2.08 \log T) \pm 0.3$

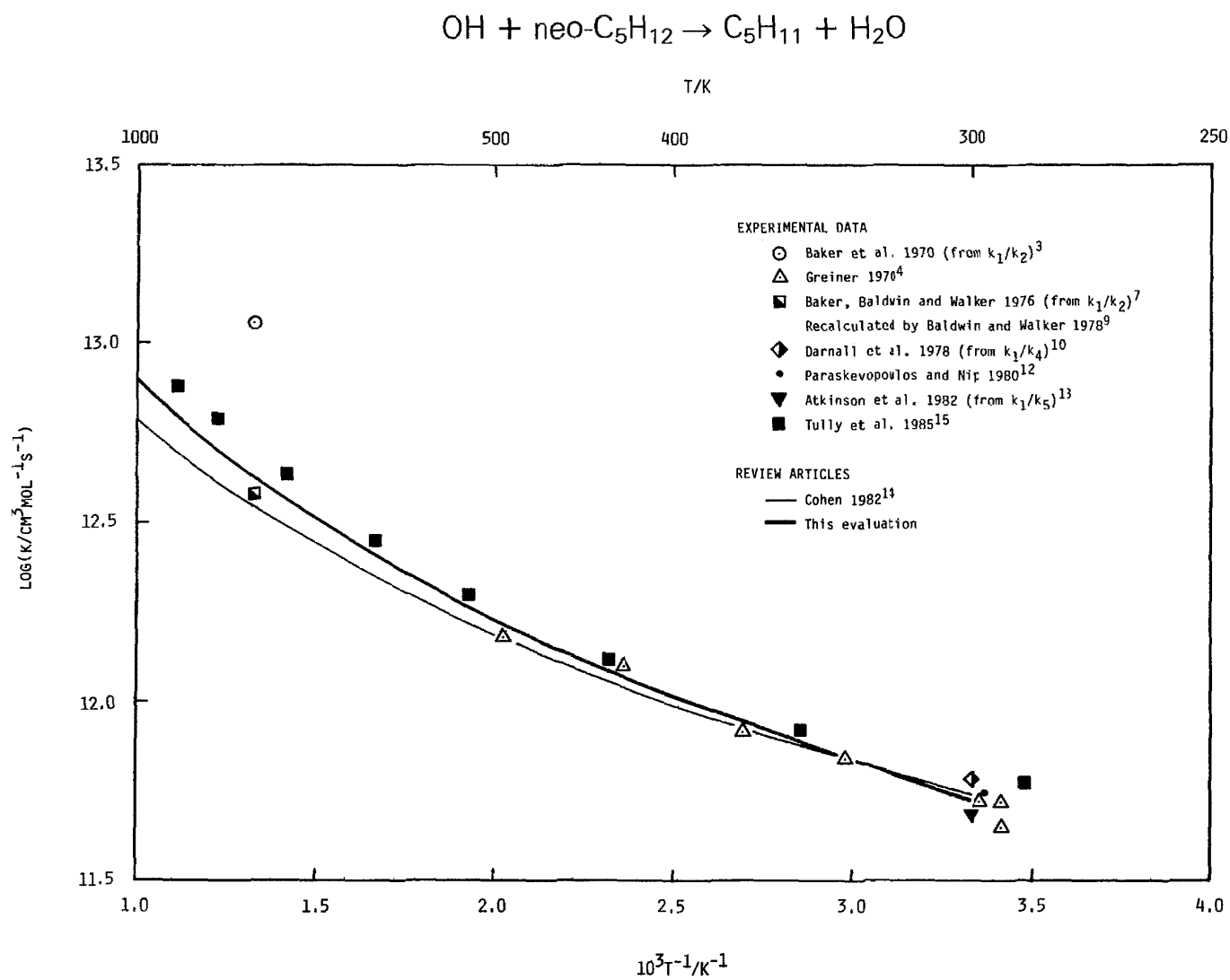
$\log (A'/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = (-16.2 + 2.08 \log T) \pm 0.3$

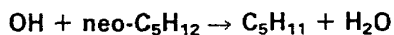
$E'/\text{J mol}^{-1} = (580 + 17.3 T) \pm 1000$

$E'/\text{cal mol}^{-1} = (140 + 4.1 T) \pm 240$

EXPERIMENTAL DATA

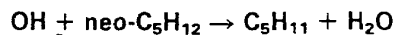
Rate Constant $k/\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	Temperature T/K	Reference and Comments
1.12×10^{13}	753	BAKER, BALDWIN and WALKER 1970 ³ Static system. No experimental details given but presumably analogous to those for OH + propane and butane (this paper). $k_1/k_2 = 16.0$ at 753 K. $\text{OH} + \text{neo-C}_5\text{H}_{12} \longrightarrow \text{neo-C}_5\text{H}_{11} + \text{H}_2\text{O} \quad (1)$ $\text{H}_2 + \text{OH} \longrightarrow \text{H}_2\text{O} + \text{H} \quad (2)$ Taking k_2 from Ref. 1, authors obtain quoted value of k_1 .
4.46×10^{11}	292	GREINER 1970 ⁴
5.17×10^{11}	292	Flash photolysis of H ₂ O(1%)/Ar mixtures in the presence of
5.27×10^{11}	298	neo-C ₅ H ₁₂ at 50.5-149 Pa pressure. [OH] monitored by u.v.
6.96×10^{11}	335	absorption spectroscopy at 306.4 nm.
8.48×10^{11}	370	A correction of 10-15% made to observed values of k_1 for the
1.27×10^{12}	424	effect of reaction 3.
1.53×10^{12}	493	$\text{OH} + \text{C}_5\text{H}_{11} \longrightarrow \text{products} \quad (3)$ The expression, $k_1 = 8.51 \times 10^{12} \exp(-844/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ was derived from experimental results over the temperature range 292-493 K. Used by Refs. 7 and 14. Quoted by Refs. 10, 11, 12 and 13.





EXPERIMENTAL DATA - CONTINUED

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
3.8×10^{12}	753	BAKER, BALDWIN and WALKER 1976 ⁷ BALDWIN and WALKER 1978 ⁹ Static system. $\text{H}_2(28-85\%)/\text{O}_2(14-71\%)/\text{N}_2$ mixtures at total pressure of 66.7 kPa. <1% neo- C_5H_{12} added. Aged boric acid coated vessels. [neo- C_5H_{12}] determined gas chromatographically. $[\text{H}_2]$ followed by measurements of pressure changes due to its reaction with O_2 . $k_1/k_2 = 10.0$ and using k_2 from Refs. 2 and 5 obtain $k_1 = 3.9 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Authors later revised their value of k_1 to take into account effect of self-heating. Using $k_1/k_2 = 10.2$ and $k_2 = 3.7 \times 10^{11}$ gives quoted value of k_1 . $\text{OH} + \text{neo-C}_5\text{H}_{12} \rightarrow \text{neo-C}_5\text{H}_{11} + \text{H}_2\text{O} \quad (1)$ $\text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H} \quad (2)$
-	300	DARNALL, ATKINSON and PITTS 1978 ¹⁰ Photolysis $\text{NO}_x/\text{air}/\text{neo-C}_5\text{H}_{12}(0.053-0.059 \text{ ppm})$ at 101.3 kPa total pressure. [neo- C_5H_{12}] monitored by gas chromatography. Rate of neo- C_5H_{12} decay compared with rate of decay of n- C_4H_{10} in an analogous experiment. $k_1/k_4 = 0.38$. $\text{OH} + \text{neo-C}_5\text{H}_{12} \rightarrow \text{neo-C}_5\text{H}_{11} + \text{H}_2\text{O} \quad (1)$ $\text{OH} + \text{n-C}_4\text{H}_{10} \rightarrow \text{C}_4\text{H}_9 + \text{H}_2\text{O} \quad (4)$ Using our value of k_4 (this paper) gives $k_1 = 6.1 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 300 K. Used by Ref. 14. Quoted by Refs. 11, 12 and 13.
5.48×10^{11}	297	PARASKEVOPOULOS and NIP 1980 ¹² Flash photolysis $\text{H}_2\text{O}(<0.5\%)/\text{neo-C}_5\text{H}_{12}/\text{He}$ mixtures at total pressure of 20 kPa. $[\text{OH}]$ monitored by resonance fluorescence. Used by Ref. 14. Quoted by Ref. 13.
-	300	ATKINSON, ASCHMANN, WINER and PITTS 1982 ¹³ Photolysis $\text{CH}_3\text{ONO}(4-15 \text{ ppm})/\text{NO}(5 \text{ ppm})/\text{air}/\text{neo-C}_5\text{H}_{12}(0.5-1.0 \text{ ppm})/\text{n-hexane}(0.5-1.0 \text{ ppm})$ mixtures at 98 kPa total pressure. Organic reactants monitored chromatographically. Using mean value of k_4 from Refs. 4, 6, 8 and 12, and experimentally determined ratio $k_4/k_5 = 0.453$, authors obtain $k_5 = 3.4 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. k_1 derived using this value of k_5 and the ratio $k_1/k_5 = 0.135$ (from same study) giving, $k_1 = 4.6 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Using our value of k_4 (this paper) gives



EXPERIMENTAL DATA - CONTINUED

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
		$k_1 = 4.8 \times 10^{11} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ at 300 K; this point plotted.
		$\text{OH} + \text{neo-C}_5\text{H}_{12} \rightarrow \text{neo-C}_5\text{H}_{11} + \text{H}_2\text{O} \quad (1)$
		$\text{OH} + \text{n-C}_4\text{H}_{10} \rightarrow \text{C}_4\text{H}_9 + \text{H}_2\text{O} \quad (4)$
		$\text{OH} + \text{n-C}_6\text{H}_{14} \rightarrow \text{C}_6\text{H}_{13} + \text{H}_2\text{O} \quad (5)$
$6.3 \times 10^6 T^{2.0} \exp(-10/T)$	300-2000	COHEN 1982 ¹⁴ Theoretical expression derived using transition state theory and experimental results of Refs. 4, 10 and 12.
5.93×10^{11}	287	TULLY, KOSZYKOWSKI and BINKLEY 1985 ¹⁵
8.25×10^{11}	350	Laser photolysis of $\text{H}_2\text{O}/\text{N}_2\text{O}/\text{neo-pentane}$ mixtures at 53 kPa
1.33×10^{12}	431	helium pressure over the temperature range 287-901 K. Pseudo-
2.00×10^{12}	518	first-order conditions where, $[\text{OH}] = 1 \times 10^{11} \text{ radicals cm}^{-3} \ll$
2.79×10^{12}	600	$[\text{neo-pentane}] \leq 6 \times 10^{14} \text{ molecule cm}^{-3}$. $[\text{OH}]$ monitored by
4.33×10^{12}	705	resonance fluorescence. The data are fitted to the expression,
6.14×10^{12}	812	$k_1 = 6.57 \times 10^3 T^{3.02} \exp(350/T) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$.
7.65×10^{12}	901	$\text{OH} + \text{neo-C}_5\text{H}_{12} \rightarrow \text{neo-C}_5\text{H}_{11} + \text{H}_2\text{O} \quad (1)$

REVIEW ARTICLES

-	-	ATKINSON, DARNALL, LLOYD, WINER and PITTS 1979 ¹¹ Review of gas phase reactions of OH with organic compounds.
$6.3 \times 10^6 T^{2.0} \exp(-10/T)$	300-2000	COHEN and WESTBERG 1983 ¹⁶ Evaluation based on experimental data from Refs. 4, 7, 10 and 12.

ISOTOPIC REACTION OH + NEO-C₅D₁₂

1.08×10^{11}	290	TULLY, KOSZYKOWSKI and BINKLEY 1985 ¹⁵
2.26×10^{11}	352	Laser photolysis of $\text{H}_2\text{O}/\text{N}_2\text{O}/\text{neo-C}_5\text{D}_{12}$ mixtures at 53 kPa
4.38×10^{11}	430	helium pressure over the temperature range 290-903 K. Pseudo-
7.83×10^{11}	508.5	first-order conditions where, $[\text{OH}] \ll [\text{neo-C}_5\text{D}_{12}]$. $[\text{OH}]$
1.32×10^{12}	598	monitored by resonance fluorescence. The data are fitted to
2.37×10^{12}	705	the expression, $k_6 = 6.68 \times 10^4 T^{2.71} \exp(-300/T) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$.
3.38×10^{12}	812	$\text{OH} + \text{neo-C}_5\text{D}_{12} \rightarrow \text{neo-C}_5\text{D}_{11} + \text{H}_2\text{O} \quad (6)$
4.87×10^{12}	903	

Discussion

There are fewer available data on the reaction between hydroxyl radicals and neo-pentane than for the corresponding reactions with methane, ethane and propane,



Below 500 K, absolute data were obtained by flash photolysis/resonance absorption techniques.^{4,12,15} At ambient temperatures the rate constant measurements by Greiner,⁴ Paraskevopoulos and Nip,¹² and Tully *et al.*¹⁵ are in good agreement with each other. The remaining data at 300 K are relative rate measurements by Atkinson and co-workers.^{10,13} Their results are put on an absolute basis using known rate parameters for the reaction between OH and *n*-butane. The rate constants thus obtained are in good agreement with absolute data.

On the basis of data from Refs. 4, 10, 12, 13, and 15, we recommend a value of

$$k_1 = 5.4 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

as 298 K, with error limits of $\Delta \log k = \pm 0.12$.

Greiner's flash photolysis results⁴ extend up to 500 K, while those of Tully *et al.*¹⁵ cover the entire range between 300 and 900 K. Where overlap occurs the two sets of data compare very well. The only other data at temperatures above 500 K are those of Baldwin and co-workers in which neo-pentane was added to slowly reacting mixtures of H₂ and O₂ at 753 K. A rate constant ratio of $k_1/k_2 = 16.0$ was obtained:



This led to a value of k_1 which was an order of magnitude higher than might have been expected. Corrections for self-heating and the effects of minor reactions lower the ratio to give $k_1/k_2 = 10.2$. Combining this ratio with the value of k_2 recommended by Baldwin and Walker⁹ gives $k_1 = 3.8 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 753 K. Treatment of data in a similar way for the analogous reactions of ethane and propane has produced rate constants consistent with values obtained by more direct methods at about 750 K. In the case of neo-pentane such a comparison can only be made with the laser photolysis results of Tully *et al.*¹⁵ The value of k_1 given by Baldwin *et al.* agrees within 25% of that derived from Tully's experimental rate expression at 753 K. Furthermore, their value of k_1 can be reconciled with an extrapolation of Greiner's flash photolysis results from lower temperatures.

In a recent theoretical study using data from Refs. 4, 10, and 12 and transition state calculations, Cohen¹⁴ gives the

rate expression

$$k_1 = 6.3 \times 10^6 T^{2.0} \exp(-10/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1},$$

for temperatures between 300 and 2000 K. Tully *et al.*¹⁵ derive from their experimental data the expression

$$k_1 = 6.6 \times 10^3 T^{3.02} \exp(350/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1},$$

over the temperature range 300–900 K. The latter expression shows a greater degree of curvature in the Arrhenius plot, thereby increasing the magnitudes of rate constants at higher temperatures. Although there are insufficient high-temperature data to precisely determine the degree of curvature in the Arrhenius plots, based on data from Refs. 4, 9, 10, 12, 13, and 15 we have obtained the empirical rate expression

$$k_1 = 4.8 \times 10^6 T^{2.08} \exp(-70/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1},$$

over the temperature range 300–1000 K, which is in good agreement with Cohen's expression below 500 K but with slightly more pronounced curvature at higher temperatures. Error limits for our evaluated expression are $\Delta \log k = \pm 0.12$ at 300 K, rising to an error in $\log k$ of ± 0.3 at 1000 K.

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9. OH + HIGHER ALKANES

THERMODYNAMIC DATA

Thermodynamic data are unavailable for these alkyl radicals.

RECOMMENDED RATE CONSTANTS

OH + n-Pentane: $k = 2.5 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 298 K.

Suggested Error Limits for Evaluated Rate Constant: $\Delta \log k = \pm 0.2$.

OH + 2-Methylbutane: $k = 2.4 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 298 K.

Suggested Error Limits for Evaluated Rate Constant: $\Delta \log k = \pm 0.2$.

OH + n-Hexane: $k = 3.5 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 298 K.

Suggested Error Limits for Evaluated Rate Constant: $\Delta \log k = \pm 0.15$.

OH + 2-Methylpentane: $k = 3.4 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 298 K.

Suggested Error Limits for Evaluated Rate Constant: $\Delta \log k = \pm 0.2$.

OH + 3-Methylpentane: $k = 3.7 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 298 K.

Suggested Error Limits for Evaluated Rate Constant: $\Delta \log k = \pm 0.2$.

OH + 2,2-Dimethylbutane: $k = 1.6 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 298 K.

Suggested Error Limits for Evaluated Rate Constant: $\Delta \log k = \pm 0.2$.

OH + 2,3-Dimethylbutane: $k = 3.5 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 298 K.

Suggested Error Limits for Evaluated Rate Constant: $\Delta \log k = \pm 0.2$.

OH + n-Heptane: $k = 4.5 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 298 K.

Suggested Error Limits for Evaluated Rate Constant: $\Delta \log k = \pm 0.2$.

OH + 2,2,3-Trimethylbutane: $k = 2.6 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 298 K.

Suggested Error Limits for Evaluated Rate Constant: $\Delta \log k = \pm 0.15$.

OH + 2,4-Dimethylpentane: $k = 3.3 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 298 K.

Suggested Error Limits for Evaluated Rate Constant: $\Delta \log k = \pm 0.2$.

OH + n-Octane: $k = 5.5 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 298 K.

Suggested Error Limits for Evaluated Rate Constant: $\Delta \log k = \pm 0.2$.

OH + 2,2,3,3-Tetramethylbutane: $k = 1.02 \times 10^7 T^{2.0} \exp(-90/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

Temperature Range: 300–700 K

Suggested Error Limits for Calculated Rate Constant:

$\Delta \log k = \pm 0.15$ at 300 K, rising to ± 0.3 at 700 K.

OH + HIGHER ALKANES

RECOMMENDED RATE CONSTANTS - CONTINUED

OH + 2,2,4-Trimethylpentane: $k = 2.3 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 298 K.

Suggested Error Limits for Evaluated Rate Constant: $\Delta \log k = \pm 0.2$.

OH + n-Nonane: $k = 6.6 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 298 K.

Suggested Error Limits for Evaluated Rate Constant: $\Delta \log k = \pm 0.2$.

OH + n-Decane: $k = 7.1 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 298 K.

Suggested Error Limits for Evaluated Rate Constant: $\Delta \log k = \pm 0.3$.

EXPERIMENTAL DATA

Rate Constant $k/\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	Temperature T/K	Reference and Comments
OH + n-PENTANE		
-	303	<p>WU, JAPAR and NIKI 1976⁷</p> <p>Photolysis of NO_2 at ppm level in $\text{NO}(\text{ppm})/\text{n-pentane}(\text{ppm})/\text{air}$ or $\text{He}/\text{O}_2(21\%)$ mixtures. NO, NO_2 and O_3 concentrations monitored with NO/O_3 chemiluminescence detectors. [n-pentane] measured by gas chromatography.</p> <p>n-Pentane removed by reaction with OH, O and O_3 but last two contribute <6% to total decay. Decay rate of n-pentane compared with that of cis-2-butene, leading to $k_1/k_2 = 0.12$.</p> $\text{OH} + \text{n-C}_5\text{H}_{12} \longrightarrow \text{C}_5\text{H}_{11} + \text{H}_2\text{O} \quad (1)$ $\text{OH} + \text{cis-CH}_3\text{CH=CHCH}_3 \longrightarrow \text{products} \quad (2)$ <p>Using k_2 derived from the Arrhenius expression given in Ref. 2, $k_1 = 3.8 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 303 K.</p>
-	300	<p>DARNALL, ATKINSON and PITTS 1978⁸</p> <p>Photolysis of $\text{NO}_x/\text{air}/\text{n-pentane}(0.128\text{--}0.137 \text{ ppm})$ at 100 kPa total pressure and 300 K. [n-C₅H₁₂] monitored by gas chromatography. Rate of [n-C₅H₁₂] decay compared with rate of decay of [n-C₄H₁₀] in an analogous experiment.</p> $\text{OH} + \text{n-C}_4\text{H}_{10} \longrightarrow \text{C}_4\text{H}_9 + \text{H}_2\text{O} \quad (3)$ <p>$k_1/k_3 = 1.37$. Using our value of k_3 (this paper) gives $k_1 = 2.2 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 300 K.</p>
-	753	<p>BALDWIN and WALKER 1979¹⁰</p> <p>Static system. n-Pentane added to slowly reacting mixtures of H_2/O_2. Experimental details not available but presumably similar to those for analogous work on 2,2,3,3-tetramethylbutane.¹¹</p>

OH + HIGHER ALKANES

EXPERIMENTAL DATA - CONTINUED

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
-	300	<p>Authors obtain $k_1/k_4 = 18.1$ after allowances were made for self-heating. Using k_4 from an Arrhenius expression given in the same work, $k_1 = 6.7 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ at 753 K.</p> $\text{OH} + \text{H}_2 \longrightarrow \text{H} + \text{H}_2\text{O} \quad (4)$ <p>COX, DERWENT and WILLIAMS 1980¹²</p> <p>Photolysis of HONO(3-20 ppm)/NO(0.3-3 ppm)/NO₂(0.3-3 ppm)/n-pentane/air mixtures at total pressure 100 kPa. [NO_x] monitored by chemiluminescence and [n-C₅H₁₂] by gas chromatography.</p> <p>Decay rate of n-C₅H₁₂ compared with that of ethene giving, $k_1/k_5 = 0.63$ at 300 K.</p> $\text{OH} + \text{n-C}_5\text{H}_{12} \longrightarrow \text{C}_5\text{H}_{11} + \text{H}_2\text{O} \quad (1)$ $\text{OH} + \text{C}_2\text{H}_4 \longrightarrow \text{products} \quad (5)$ <p>Using $k_5 = 4.8 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ from Ref. 19, obtain $k_1 = 3.0 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$.</p>
-	299	<p>ATKINSON, ASCHMANN, CARTER, WINER and PITTS 1982¹⁴</p> <p>Static system. CH₃ONO(9-17 ppm)/NO(5 ppm)/n-pentane(0.5-1.0 ppm)/n-hexane(0.5-1.0 ppm)/air mixtures at total pressure 100 kPa photolysed ≥ 290 nm. Reactants monitored by gas chromatography.</p> $\text{OH} + \text{n-C}_6\text{H}_{14} \longrightarrow \text{C}_6\text{H}_{13} + \text{H}_2\text{O} \quad (6)$ <p>$k_1/k_6 = 0.724$ at 299 K. Using the rate constant ratio $k_3/k_6 = 0.453$,¹⁵ and our value of k_3 (this paper) we obtain $k_1 = 2.6 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$.</p> $\text{OH} + \text{n-C}_4\text{H}_{10} \longrightarrow \text{C}_4\text{H}_9 + \text{H}_2\text{O} \quad (3)$
-	300	<p>BARNES, BASTIAN, BECKER, FINK and ZARFI 1982¹⁶</p> <p>Static system. Two sources of OH;</p> <p>(i) "Photolytic". Photolysis of mixtures of NO₂(2.5 ppm)/n-pentane (15 ppm)/propene(15 ppm)/air at total pressure 100 kPa and 300 K. [n-C₅H₁₂] and [C₃H₆] monitored by gas chromatography.</p> <p>(ii) "Dark". HO₂NO₂(4-20 ppm)/n-pentane(15 ppm)/propene(15 ppm)/air or N₂ mixture at total pressure 100 kPa and 300 K. Excess NO added to produce OH by reactions 7 and 8.</p> $\text{HO}_2\text{NO}_2 \xrightleftharpoons{M} \text{HO}_2 + \text{NO}_2 \quad (7)$ $\text{HO}_2 + \text{NO} \longrightarrow \text{OH} + \text{NO}_2 \quad (8)$ <p>Initial and final hydrocarbon concentrations measured by gas chromatography.</p>

OH + HIGHER ALKANES

EXPERIMENTAL DATA - CONTINUED

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
Decay rate of $n\text{-C}_5\text{H}_{12}$ compared with that of propene and then normalized to ethene giving, (i) $k_1/k_5 = 0.26$ and (ii) $k_1/k_5 = 0.48$ at 300 K.		
		$\text{OH} + n\text{-C}_5\text{H}_{12} \longrightarrow \text{C}_5\text{H}_{11} + \text{H}_2\text{O} \quad (1)$
		$\text{OH} + \text{C}_2\text{H}_4 \longrightarrow \text{products} \quad (5)$
Using $k_5 = 4.8 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ from Ref. 19, we obtain $k_1 \times 10^{-12}/\text{cm}^3\text{mol}^{-1}\text{s}^{-1} = (i) 1.3$ and (ii) 2.3.		

REVIEW ARTICLE

- - ATKINSON, DARNALL, LLOYD, WINER and PITTS 1979⁹
Review of gas phase reactions of OH with organic compounds.
Quotes Refs. 7 and 8.

OH + 2-METHYLBUTANEEXPERIMENTAL DATA

- 305 LLOYD, DARNALL, WINER and PITTS 1976⁶
Photolysis of $\text{NO}_x/2\text{-methylbutane}/n\text{-butane}/\text{air}$ mixture at 305 K and total pressure of 101.3 kPa. [Hydrocarbon] monitored by gas chromatography.
 $\text{OH} + n\text{-C}_4\text{H}_{10} \longrightarrow \text{C}_4\text{H}_9 + \text{H}_2\text{O} \quad (3)$
 $\text{OH} + \text{iso-C}_5\text{H}_{12} \longrightarrow \text{C}_5\text{H}_{11} + \text{H}_2\text{O} \quad (9)$
 $k_9/k_3 = 1.1$. Using our value of k_3 (this paper) we obtain $k_9 = 1.8 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ at 305 K.
- 300 DARNALL, ATKINSON and PITTS 1978⁸
Photolysis of $\text{NO}_x/2\text{-methylbutane}$ (0.101-0.119 ppm)/ $n\text{-butane}$ (0.073-0.075 ppm)/air mixtures at total pressure 100 kPa and 300 K. [Alkane] monitored by gas chromatography.
 $k_9/k_3 = 1.3$. Using our value of k_3 (this paper) we obtain $k_9 = 2.1 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ at 300 K.

OH + HIGHER ALKANES

EXPERIMENTAL DATA - CONTINUED

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
-	297	<p>ATKINSON, CARTER, ASCHMANN, WINER and PITTS 1984²⁰</p> <p>Photolysis of CH_3ONO(8-27 ppm)/NO(5 ppm)/2-methylbutane (0.5-1.0 ppm)/n-butane(0.5-1.0 ppm)/air mixtures at wavelengths ≥ 290 nm. The reactions were carried out at 297 K and about 97 kPa total pressure. [Alkane] monitored by gas chromatography; $[\text{NO}_x]$ and $[\text{O}_3]$ by chemiluminescence.</p> <p>Rate constant ratio $k_9/k_3 = 1.54$. Using our value of k_3 (this paper) we obtain $k_9 = 2.5 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ at 297 K.</p>

REVIEW ARTICLE

-	-	<p>ATKINSON, DARNALL, LLOYD, WINER and PITTS 1979⁹</p> <p>Review of gas phase reactions of OH with organic compounds. Quotes Refs. 6 and 8.</p>
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OH + N-HEXANE

EXPERIMENTAL DATA

-	292	<p>CAMPBELL, McLAUGHLIN and HANDY 1976⁴</p> <p>Static system. H_2O_2(0.08%)/NO_2(1%)/CO/n-hexane mixtures at a total pressure of 13.3 kPa. $[\text{CO}_2]$ monitored by gas chromatography. Suppression of CO_2 yield by n-C_6H_{14} observed.</p> $\text{OH} + \text{n-C}_6\text{H}_{14} \longrightarrow \text{C}_6\text{H}_{13} + \text{H}_2\text{O} \quad (6)$ $\text{OH} + \text{CO} \longrightarrow \text{CO}_2 + \text{H} \quad (10)$ <p>Decay rate of n-C_6H_{14} compared with that of n-C_4H_{10} in an analogous experiment.</p> $\text{OH} + \text{n-C}_4\text{H}_{10} \longrightarrow \text{C}_4\text{H}_9 + \text{H}_2\text{O} \quad (3)$ <p>$k_6/k_3 = 2.46$. Using a value of k_3 derived from our recommended expression (this paper) gives $k_6 = 3.9 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ at 292 K.</p>
-	305	<p>LLOYD, DARNALL, WINER and PITTS 1976⁶</p> <p>Photolysis of NO_x/n-hexane/n-butane/air mixtures at 305 K and total pressure of 101.3 kPa. Alkane concentrations monitored by gas chromatography.</p> <p>$k_6/k_3 = 2.09$. Using our value of k_3 (this paper) we obtain $k_6 = 3.5 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ at 305 K.</p>

OH + HIGHER ALKANES

EXPERIMENTAL DATA - CONTINUED

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
-	303	<p>WU, JAPAR and NIKI 1976⁷</p> <p>Photolysis of NO_2 at ppm level in $\text{NO}(\text{ppm})/\text{n-hexane}(\text{ppm})/\text{air}$ or $\text{He}/\text{O}_2(21\%)$ mixtures at total pressure 100 kPa. NO, NO_2 and O_3 concentrations monitored with NO/O_3 chemiluminescence detectors. $[\text{n-C}_6\text{H}_{14}]$ monitored by gas chromatography.</p> <p>$\text{n-C}_6\text{H}_{14}$ removed by reaction with OH, O and O_3 but last two contribute <6% to total decay. Decay rate of $\text{n-C}_6\text{H}_{14}$ compared with that of <i>cis</i>-2-butene.</p> <p>$\text{OH} + \text{cis-CH}_3\text{CH=CHCH}_3 \longrightarrow \text{products} \quad (2)$</p> <p>$\text{OH} + \text{n-C}_6\text{H}_{14} \longrightarrow \text{C}_6\text{H}_{13} + \text{H}_2\text{O} \quad (6)$</p> <p>Authors obtain $k_6/k_2 = 0.11$. Using k_2 derived from the Arrhenius expression in Ref. 2, $k_6 = 3.5 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ at 303 K.</p>
-	299	<p>ATKINSON, ASCHMANN, WINER and PITTS 1982¹⁵</p> <p>Static system. $\text{CH}_3\text{ONO}(4\text{--}15 \text{ ppm})/\text{NO}(5 \text{ ppm})/\text{n-hexane}(0.5\text{--}1.0 \text{ ppm})/\text{n-butane}(0.5\text{--}1.0 \text{ ppm})/\text{air}$ mixtures photolysed at 299 K. Organic reactants monitored by gas chromatography.</p> <p>$k_6/k_3 = 2.21$. Using our value of k_3 (this paper) we obtain $k_6 = 3.5 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ at 299 K.</p>

REVIEW ARTICLE

-	-	<p>ATKINSON, DARNALL, LLOYD, WINER and PITTS 1979⁹</p> <p>Review of gas phase reactions of OH with organic compounds. Quotes Refs. 4, 6 and 7.</p>
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OH + 2-METHYLPENTANE

EXPERIMENTAL DATA

-	305	<p>LLOYD, DARNALL, WINER and PITTS 1976⁶</p> <p>Photolysis of $\text{NO}_x/2\text{-methylpentane}/\text{n-butane}/\text{air}$ mixtures at 305 K and 101.3 kPa total pressure. Alkane concentrations monitored by gas chromatography.</p> <p>$\text{OH} + \text{n-C}_4\text{H}_{10} \longrightarrow \text{C}_4\text{H}_9 + \text{H}_2\text{O} \quad (3)$</p> <p>$\text{OH} + \text{CH}_3(\text{CH}_2)_2\text{CH}(\text{CH}_3)_2 \longrightarrow \text{C}_6\text{H}_{13} + \text{H}_2\text{O} \quad (11)$</p> <p>Authors obtain $k_{11}/k_3 = 1.77$. Using our value of k_3 (this paper) gives $k_{11} = 2.9 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ at 305 K.</p>
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OH + HIGHER ALKANES

EXPERIMENTAL DATA - CONTINUED

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
-	300	<p>COX, DERWENT and WILLIAMS 1980¹²</p> <p>Photolysis of HONO(3-20 ppm)/NO(0.3-3 ppm)/NO₂(0.3-3 ppm)/2-methylpentane/air mixtures at total pressure 100 kPa. [NO_x] monitored by chemiluminescence and [2-methylpentane] by gas chromatography.</p> <p>Decay rate of 2-methylpentane compared with that of ethene, giving $k_{11}/k_5 = 0.63$ at 300 K.</p> $\text{OH} + \text{C}_2\text{H}_4 \longrightarrow \text{products} \quad (5)$ $\text{OH} + \text{CH}_3(\text{CH}_2)_2\text{CH}(\text{CH}_3)_2 \longrightarrow \text{C}_6\text{H}_{13} + \text{H}_2\text{O} \quad (11)$ <p>Taking literature value of k_5,^{17,19} we obtain $k_{11} = 3.0 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$.</p>
-	297	<p>ATKINSON, CARTER, ASCHMANN, WINER and PITTS 1984²⁰</p> <p>Photolysis of CH₃ONO(8-27 ppm)/NO(5 ppm)/2-methylpentane(0.5-1.0 ppm)/n-butane(0.5-1.0 ppm)/air mixtures at wavelengths >290 nm. The reactions were carried out at 297 K and about 97 kPa total pressure. [Alkane] monitored by gas chromatography; [NO_x] and [O₃] by chemiluminescence.</p> <p>Rate constant ratio $k_{11}/k_3 = 2.20$. Using our value of k_3 (this paper) we obtain $k_{11} = 3.5 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ at 297 K.</p>

REVIEW ARTICLE

-	-	<p>ATKINSON, DARNALL, LLOYD, WINER and PITTS 1979⁹</p> <p>Review of gas phase reactions of OH with organic compounds. Quotes Ref. 6.</p>
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OH + 3-METHYLPENTANE

EXPERIMENTAL DATA

-	305	<p>LLOYD, DARNALL, WINER and PITTS 1976⁶</p> <p>Photolysis of NO_x/3-methylpentane/n-butane/air mixtures at 305 K and total pressure of 101.3 kPa. Alkane concentrations monitored by gas chromatography.</p> $\text{OH} + \text{n-C}_4\text{H}_{10} \longrightarrow \text{C}_4\text{H}_9 + \text{H}_2\text{O} \quad (3)$ $\text{OH} + (\text{C}_2\text{H}_5)_2\text{CHCH}_3 \longrightarrow \text{C}_6\text{H}_{13} + \text{H}_2\text{O} \quad (12)$ <p>Authors obtain $k_{12}/k_3 = 2.40$. Using our value of k_3 (this paper) gives $k_{12} = 3.9 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ at 305 K.</p>
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OH + HIGHER ALKANES

EXPERIMENTAL DATA - CONTINUED

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
-	297	<p>ATKINSON, CARTER, ASCHMANN, WINER and PITTS 1984²⁰</p> <p>Photolysis of CH_3ONO(8-27 ppm)/NO(5 ppm)/3-methylpentane (0.5-1.0 ppm)/n-butane(0.5-1.0 ppm)/air mixtures at wavelengths ≥ 290 nm. The reactions were carried out at 297 K and about 97 kPa total pressure. [Alkane] monitored by gas chromatography; $[\text{NO}_x]$ and $[\text{O}_3]$ by chemiluminescence.</p> <p>Rate constant ratio $k_{12}/k_3 = 2.24$. Using our value of k_3 (this paper) we obtain $k_{12} = 3.6 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ at 297 K.</p>

REVIEW ARTICLE

-	-	<p>ATKINSON, DARNALL, LLOYD, WINER and PITTS 1979⁹</p> <p>Review of gas phase reactions of OH with organic compounds. Quotes Ref. 6.</p>
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OH + 2,2-DIMETHYLBUTANE

EXPERIMENTAL DATA

-	297	<p>ATKINSON, CARTER, ASCHMANN, WINER and PITTS 1984²⁰</p> <p>Photolysis of CH_3ONO(8-27 ppm)/NO(5 ppm)/2,2-dimethylbutane(0.5-1.0 ppm)/n-butane(0.5-1.0 ppm)/air mixtures at wavelengths ≥ 290 nm. The reactions were carried out at 297 K and about 97 kPa total pressure. [Alkane] monitored by gas chromatography; $[\text{NO}_x]$ and $[\text{O}_3]$ by chemiluminescence.</p> $\text{OH} + n\text{-C}_4\text{H}_{10} \longrightarrow \text{C}_4\text{H}_9 + \text{H}_2\text{O} \quad (3)$ $\text{OH} + (\text{CH}_3)_3\text{CCH}_2\text{CH}_3 \longrightarrow \text{C}_6\text{H}_{13} + \text{H}_2\text{O} \quad (13)$ <p>Rate constant ratio $k_{13}/k_3 = 1.03$. Using our value of k_3 (this paper) we obtain $k_{13} = 1.6 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ at 297 K.</p>
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OH + HIGHER ALKANES

EXPERIMENTAL DATA

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
<u>OH + 2,3-DIMETHYLBUTANE</u>		
4.49x10 ¹²	300	GREINER 1970 ¹
4.04x10 ¹²	336	Flash photolysis of H ₂ O(1%)/Ar mixtures in the presence of 2,3-dimethylbutane at 10.8-18.4 Pa pressure. [OH] monitored by absorption spectroscopy at 306.4 nm. A 10-15% correction was made for the effect of secondary reaction 14. $\text{OH} + \text{C}_6\text{H}_{13} \longrightarrow \text{products} \quad (14)$ Author derived the expression $k_{15} = 2.88 \times 10^{12} \exp(130/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ over the temperature range 300-500 K. $\text{OH} + (\text{CH}_3)_2\text{CHCH}(\text{CH}_3)_2 \longrightarrow \text{C}_6\text{H}_{13} + \text{H}_2\text{O} \quad (15)$ Used by Ref. 18.
4.10x10 ¹²	372	
4.28x10 ¹²	424	
3.58x10 ¹²	498	
-	303	ATKINSON, DARNALL, WINER and PITTS 1976 ³ Decay of 2,3-dimethylbutane compared with that of ethane. $\text{OH} + \text{C}_2\text{H}_6 \longrightarrow \text{C}_2\text{H}_5 + \text{H}_2\text{O} \quad (16)$ $k_{15}/k_{16} = 13.4$ at 303 K. Using our value of k_{16} (this paper) we obtain $k_{15} = 2.4 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.
-	305	DARNALL, WINER, LLOYD and PITTS 1976 ⁵ Photolysis of NO _x (0.61 ppm)/2,3-dimethylbutane(7 ppb)/isobutene/air mixtures at total pressure of 100 kPa. [Alkane] monitored by gas chromatography. [2,3-Dimethylbutane] decay compared with that of [isobutene] giving, $k_{15}/k_{17} = 0.10$ at 305 K. $\text{OH} + \text{CH}_2=\text{C}(\text{CH}_3)_2 \longrightarrow \text{products} \quad (17)$ Using a value of k_{17} derived from an Arrhenius expression in Ref. 2, authors obtain $k_{15} = 3.1 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.
-	300	DARNALL, ATKINSON and PITTS 1978 ⁸ Photolysis of NO _x /2,3-dimethylbutane(0.105-0.114 ppm)/n-butane(0.073-0.075 ppm)/air mixtures at 100 kPa total pressure and 300 K. Alkane concentrations monitored by gas chromatography. $\text{OH} + \text{n-C}_4\text{H}_{10} \longrightarrow \text{C}_4\text{H}_9 + \text{H}_2\text{O} \quad (3)$ $\text{OH} + (\text{CH}_3)_2\text{CHCH}(\text{CH}_3)_2 \longrightarrow \text{C}_6\text{H}_{13} + \text{H}_2\text{O} \quad (15)$ Decay of 2,3-dimethylbutane compared with that of n-butane, giving the rate constant ratio, $k_{15}/k_3 = 2.08$. Using our value of k_3 (this paper) gives $k_{15} = 3.3 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 300 K. Used by Ref. 18.

OH + HIGHER ALKANES

EXPERIMENTAL DATA - CONTINUED

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
-	300	COX, DERWENT and WILLIAMS 1980 ¹² Photolysis of HONO(3.0-20 ppm)/NO(0.3-3 ppm)/NO ₂ (0.3-3 ppm)/2,3-dimethylbutane/air mixtures at total pressure of 100 kPa. [NO _x] monitored by chemiluminescence and [2,3-dimethylbutane] by gas chromatography. Decay rate of 2,3-dimethylbutane compared with that of ethene giving, $k_{15}/k_5 = 0.48$ at 300 K. $\text{OH} + \text{C}_2\text{H}_4 \longrightarrow \text{products} \quad (5)$ Taking k_5 from Refs. 17 and 19, we obtain $k_{15} = 2.3 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$.
-	299	ATKINSON, ASCHMANN, WINER and PITTS 1982 ¹⁵ CH ₃ ONO(4-15 ppm)/NO(5 ppm)/2,3-dimethylbutane(0.5-1.0 ppm)/cyclohexane(0.5-1.0 ppm)/air mixtures photolysed ≥ 290 nm at 299 K. $\text{OH} + \text{C-C}_6\text{H}_{12} \longrightarrow \text{C-C}_6\text{H}_{11} + \text{H}_2\text{O} \quad (18)$ $k_{15}/k_{18} = 0.827$. Using the ratio $k_3/k_{18} = 0.341$ (determined in an analogous experiment in the same work) and our value of k_3 (this paper) we derive, $k_{15} = 3.9 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ at 299 K. $\text{OH} + \text{n-C}_4\text{H}_{10} \longrightarrow \text{C}_4\text{H}_9 + \text{H}_2\text{O} \quad (3)$
$2.5 \times 10^3 T^{3.0} \exp(1200/T)$	300-2000	COHEN 1982 ¹⁸ Theoretical expression derived using transition state theory and experimental data of Refs. 1 and 8.

REVIEW ARTICLES

-	-	ATKINSON, DARNALL, LLOYD, WINER and PITTS 1979 ⁹ Review of gas phase reactions of OH with organic compounds. Quotes Refs. 1,3,5 and 8.
$2.5 \times 10^3 T^{3.0} \exp(1200/T)$	300-2000	COHEN and WESTBERG 1983 ²² Evaluation. Based on experimental data of Refs. 1,5 and 8.

OH + HIGHER ALKANES

EXPERIMENTAL DATA

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
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OH + n-HEPTANE

- 299 ATKINSON, ASCHMANN, CARTER, WINER and PITTS 1982¹⁴
 Photolysis of CH_3ONO (9-17 ppm)/ NO (5 ppm)/n-heptane(0.5-1.0 ppm)/n-hexane(0.5-1.0 ppm)/air mixtures at 299 K. Reactants monitored by gas chromatography.
- $$\text{OH} + \text{n-C}_6\text{H}_{14} \longrightarrow \text{C}_6\text{H}_{13} + \text{H}_2\text{O} \quad (6)$$
- $$\text{OH} + \text{n-C}_7\text{H}_{16} \longrightarrow \text{C}_7\text{H}_{15} + \text{H}_2\text{O} \quad (19)$$
- $k_{19}/k_6 = 1.28$ at 299 K. Using the rate constant ratio $k_3/k_6 = 0.453$ given in other work¹⁵ and our value of k_3 (this paper) we obtain $k_{19} = 4.5 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$.
- $$\text{OH} + \text{n-C}_4\text{H}_{10} \longrightarrow \text{C}_4\text{H}_9 + \text{H}_2\text{O} \quad (3)$$

OH + 2,2,3-TRIMETHYLBUTANE

EXPERIMENTAL DATA

- 3.15x10¹² 296 GREINER 1970¹
 2.93x10¹² 303 Flash photolysis of H_2O (1%)/Ar mixtures in the presence of
 2.71x10¹² 371 2,2,3-trimethylbutane at 8.6-20 Pa pressure. [OH] monitored by
 2.77x10¹² 373 absorption spectroscopy at 306.4 nm.
 3.81x10¹² 497 A 10-15% correction was made for the effect of secondary
 reaction 20.
- $$\text{OH} + \text{C}_7\text{H}_{15} \longrightarrow \text{products} \quad (20)$$
- Author derived the expression $k_{21} = 4.79 \times 10^{12} \exp(-115/T) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ over the temperature range 300-500 K.
- $$\text{OH} + (\text{CH}_3)_3\text{CCH}(\text{CH}_3)_2 \longrightarrow \text{C}_7\text{H}_{15} + \text{H}_2\text{O} \quad (21)$$
- Used by Ref. 18.
- 305 DARNALL, WINER, LLOYD and PITTS 1976⁵
 Photolysis of NO_x (0.61 ppm)/2,2,3-trimethylbutane(14 ppb)/isobutene/air mixtures at 305 K. [Alkane] monitored by gas chromatography.
- [2,2,3-trimethylbutane] decay compared with that of [isobutene] giving, $k_{21}/k_{17} = 0.074$.
- $$\text{OH} + \text{CH}_2=\text{C}(\text{CH}_3)_2 \longrightarrow \text{products} \quad (17)$$
- Using a value of k_{17} derived from an Arrhenius expression in Ref. 2, authors obtain $k_{21} = 2.3 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ at 303 K.

OH + HIGHER ALKANES

EXPERIMENTAL DATA - CONTINUED

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
-	753	BALDWIN, WALKER and WALKER 1981 ¹³ Static system. 2,2,3-Trimethylbutane(0.025%) added to slowly reacting mixtures of H_2 (28-86%)/ O_2 (14%-72%) in N_2 at total pressure of 66.7 kPa and 753 K. [2,2,3-Trimethylbutane] monitored by gas chromatography and $[\text{H}_2]$ by measurement of pressure change. $\text{OH} + \text{H}_2 \longrightarrow \text{H} + \text{H}_2\text{O} \quad (4)$ $\text{OH} + (\text{CH}_3)_3\text{CCH}(\text{CH}_3)_2 \longrightarrow \text{C}_7\text{H}_{15} + \text{H}_2\text{O} \quad (21)$ Allowances were made for the effects of self-heating and for reaction 22. $(\text{CH}_3)_3\text{CCH}(\text{CH}_3)_2 \longrightarrow \text{t-C}_4\text{H}_9 + \text{i-C}_3\text{H}_7 \quad (22)$ Authors obtain $k_{21}/k_4 = 12.2$. Using k_4 derived from an Arrhenius expression ¹⁰ gives, $k_{21} = 4.5 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ at 753 K.
$1.51 \times 10^4 T^{2.8} \exp(925/T)$	300-2000	COHEN 1982 ¹⁸ Theoretical expression derived using transition state theory and experimental data of Refs. 1 and 8.
-	297	ATKINSON, CARTER, ASCHMANN, WINER and PITTS 1984 ²⁰ Photolysis of CH_3ONO (8-27 ppm)/ NO (5 ppm)/2,2,3-trimethylbutane(0.5-1.0 ppm)/n-butane(0.5-1.0 ppm)/air mixtures at wavelengths ≥ 290 nm. The reactions were carried out at 297 K and about 97 kPa total pressure. [Alkane] monitored by gas chromatography; $[\text{NO}_x]$ and $[\text{O}_3]$ by chemiluminescence. $\text{OH} + \text{n-C}_4\text{H}_{10} \longrightarrow \text{C}_4\text{H}_9 + \text{H}_2\text{O} \quad (3)$ Rate constant ratio $k_{21}/k_3 = 1.63$. Using our value of k_3 (this paper) we obtain $k_{21} = 2.6 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ at 297 K.

REVIEW ARTICLES

-	-	ATKINSON, DARNALL, LLOYD, WINER and PITTS 1979 ⁹ Review of gas phase reactions of OH with organic compounds. Quotes Refs. 1 and 5.
$1.5 \times 10^4 T^{2.8} \exp(920/T)$	300-2000	COHEN and WESTBERG 1983 ²² Evaluation. Based on experimental data of Refs. 1, 5 and 13.

OH + HIGHER ALKANES

EXPERIMENTAL DATA

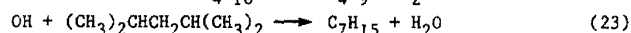
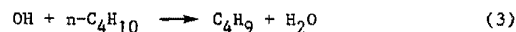
Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
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OH + 2,4-DIMETHYLPENTANE

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297 ATKINSON, CARTER, ASCHMANN, WINER and PITTS 1984²⁰

Photolysis of CH_3ONO (8-27 ppm)/ NO (5 ppm)/2,4-dimethylpentane (0.5-1.0 ppm)/n-butane (0.5-1.0 ppm)/air mixtures at wavelengths ≥ 290 nm. The reactions were carried out at 297 K and about 97 kPa total pressure. [Alkane] monitored by gas chromatography; $[\text{NO}_x]$ and $[\text{O}_3]$ by chemiluminescence.



Rate constant ratio $k_{23}/k_3 = 2.04$. Using our value of k_3 (this paper) we obtain $k_{23} = 3.3 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ at 297 K.

OH + N-OCTANE

EXPERIMENTAL DATA

5.07x10¹²296 GREINER 1970¹7.20x10¹²

371 Flash photolysis of H_2O (1%)/Ar mixtures in the presence of n-octane at 6.9-17.3 Pa pressure. [OH] monitored by absorption spectroscopy at 306.4 nm.

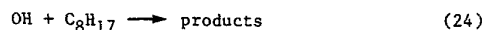
6.50x10¹²

371

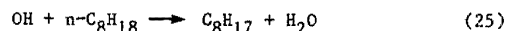
8.62x10¹²

497

A 10-15% correction was made for the effect of secondary reaction 24.



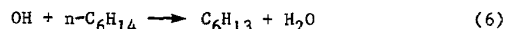
The expression $k_{25} = 1.78 \times 10^{13} \exp(-365/T) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ derived over the temperature range 300-500 K.



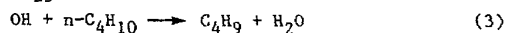
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299 ATKINSON, ASCHMANN, CARTER, WINER and PITTS 1982¹⁴

Photolysis of CH_3ONO (9-17 ppm)/ NO (5 ppm)/n-octane (0.5-1.0 ppm)/n-hexane (0.5-1.0 ppm)/air mixtures at 299 K. Reactants monitored by gas chromatography.



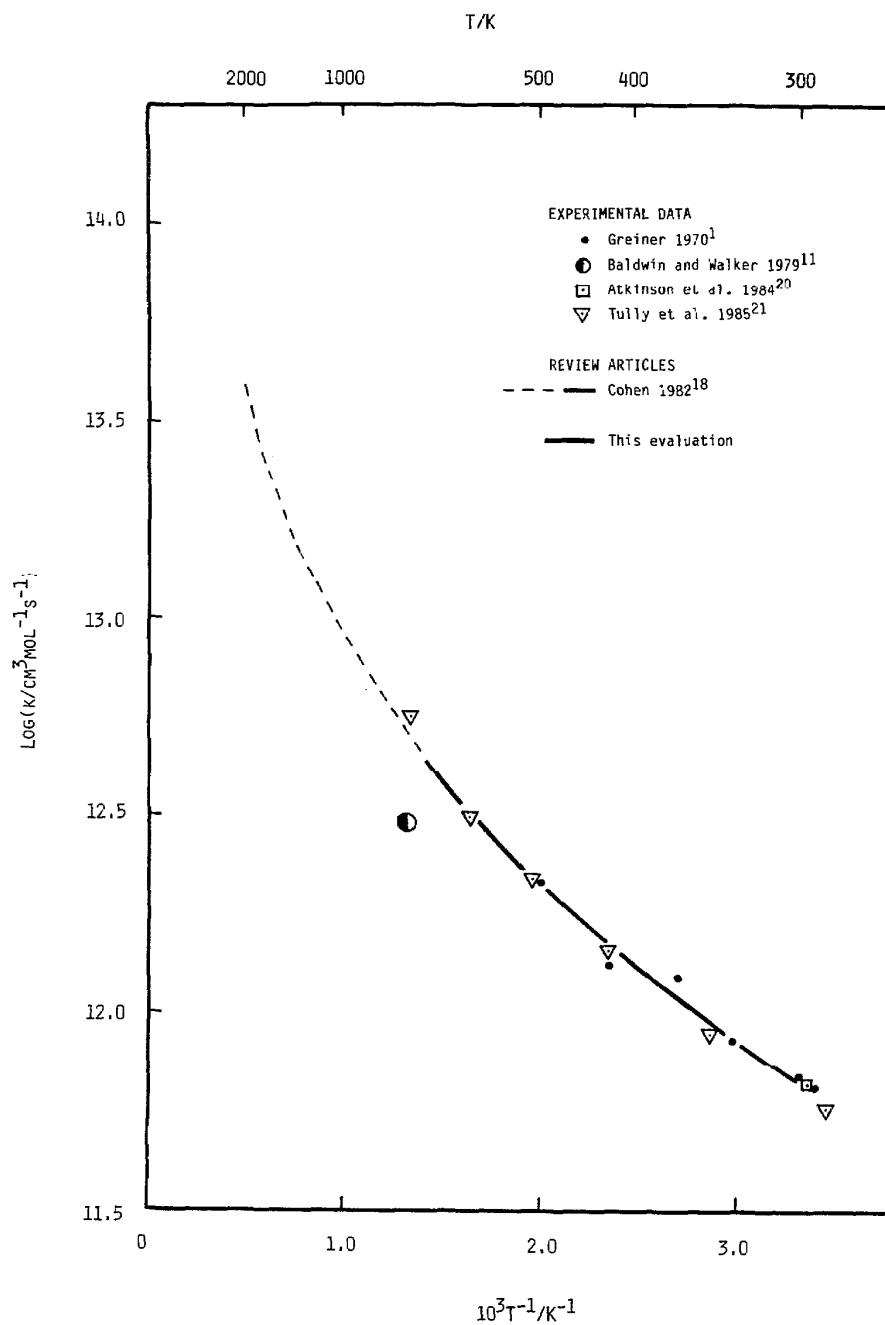
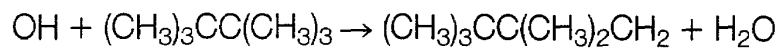
$k_{25}/k_6 = 1.58$ at 299 K. Using the rate constant ratio $k_3/k_6 = 0.453$ determined in other work¹⁵ and our value of k_3 (this paper) we obtain $k_{25} = 5.6 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$.



OH + HIGHER ALKANES

REVIEW ARTICLE

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
-	-	ATKINSON, DARNALL, LLOYD, WINER and PITTS 1979 ⁹ Review of gas phase reactions of OH with organic compounds. Quotes Ref. 1.
<u>OH + 2,2,3,3-TETRAMETHYLBUTANE</u>		
EXPERIMENTAL DATA		
6.52x10 ¹¹	294	GREINER 1970 ¹
6.96x10 ¹¹	301	Flash photolysis of H ₂ O(1%)/Ar mixtures in the presence of
8.57x10 ¹¹	335	2,2,3,3-tetramethylbutane at 19.8-48.9 Pa pressure. [OH]
1.23x10 ¹²	370	monitored by absorption spectroscopy at 306.4 nm.
1.33x10 ¹²	424	A 10-15% correction was made for the effect of the secondary
2.12x10 ¹²	495	reaction
		$\text{OH} + \text{C}_8\text{H}_{17} \longrightarrow \text{products.} \quad (24)$
		Author derived the expression $k_{26} = 9.77 \times 10^{12} \exp(-800/T)$ $\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$ over the temperature range 300-500 K.
		$\text{OH} + (\text{CH}_3)_3\text{CC}(\text{CH}_3)_3 \longrightarrow (\text{CH}_3)_3\text{CC}(\text{CH}_3)_2\text{CH}_2 + \text{H}_2\text{O} \quad (26)$
		Used by Ref. 18.
-	753	BALDWIN, WALKER and WALKER 1979 ¹¹
		Static system. 2,2,3,3-Tetramethylbutane(0.025%) added to slowly reacting mixtures of H ₂ (7-86%)/O ₂ (7-72%) in N ₂ at total pressure of 66.7 kPa and 753 K. [2,2,3,3-Tetramethylbutane] measured by gas chromatography and [H ₂] by measurement of pressure change due to the reaction
		$2\text{H}_2 + \text{O}_2 \longrightarrow 2\text{H}_2\text{O.} \quad (27)$
		Allowances were made for the effects of self-heating and for the unimolecular process (reaction 28) which accounts for about 15% of 2,2,3,3-tetramethylbutane consumption.
		$(\text{CH}_3)_3\text{CC}(\text{CH}_3)_3 \longrightarrow 2\text{t-C}_4\text{H}_9 \quad (28)$
		Authors obtain $k_{26}/k_4 = 8.0$.
		$\text{OH} + \text{H}_2 \longrightarrow \text{H} + \text{H}_2\text{O} \quad (4)$
		Using k_4 derived from an Arrhenius expression ¹⁰ gives, $k_{26} =$ $3.0 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ at 753 K.
$1.02 \times 10^7 T^{2.0} \exp(-90/T)$	300-2000	COHEN 1982 ¹⁸
		Theoretical expression derived using transition state theory and experimental data of Ref. 1.



OH + HIGHER ALKANES

EXPERIMENTAL DATA - CONTINUED

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
-	297	ATKINSON, CARTER, ASCHMANN, WINER and PITTS 1984 ²⁰ Photolysis of CH_3ONO (8-27 ppm)/ NO (5 ppm)/2,2,3,3-tetramethylbutane(0.5-1.0 ppm)/n-butane(0.5-1.0 ppm)/air mixtures at wavelengths >290 nm. The reactions were carried out at 297 K and about 97 kPa total pressure. [Alkane] monitored by gas chromatography; $[\text{NO}_x]$ and $[\text{O}_3]$ by chemiluminescence. $\text{OH} + \text{n-C}_4\text{H}_{10} \longrightarrow \text{C}_4\text{H}_9 + \text{H}_2\text{O} \quad (3)$ $\text{OH} + (\text{CH}_3)_3\text{CC}(\text{CH}_3)_3 \longrightarrow (\text{CH}_3)_3\text{CC}(\text{CH}_3)_2\text{CH}_2 + \text{H}_2\text{O} \quad (26)$ Rate constant ratio $k_{26}/k_3 = 0.41$. Using our value of k_3 (this paper) we obtain $k_{26} = 6.6 \times 10^{11} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ at 297 K.
5.71×10^{11}	290	TULLY, KOSZYKOWSKI and BINKLEY 1985 ²¹
8.91×10^{11}	348.5	Flash photolysis of $\text{H}_2\text{O}/\text{N}_2\text{O}/2,2,3,3$ -tetramethylbutane
1.43×10^{12}	423.5	mixtures at 53 kPa helium pressure over the temperature range
2.16×10^{12}	506	290-738 K. Pseudo-first-order conditions where $[\text{OH}] \ll [2,2,3,3$ -
3.17×10^{12}	606	tetramethylbutane]. $[\text{OH}]$ monitored by resonance fluorescence.
5.64×10^{12}	737.5	Authors fit the data to the expression, $k_{26} = 2.86 \times 10^{16} T^{2.20} \exp(-70/T) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$.

REVIEW ARTICLES

-	-	ATKINSON, DARNALL, LLOYD, WINER and PITTS 1979 ⁹ Review of gas phase reactions of OH with organic compounds. Quotes Ref. 1.
$1.02 \times 10^7 T^{2.0} \exp(-90/T)$	300-2000	COHEN and WESTBERG 1983 ²² Evaluation. Based on Greiner's data. ¹

OH + 2,2,4-TRIMETHYLPENTANE

EXPERIMENTAL DATA

2.35×10^{12}	298	GREINER 1970 ¹
2.14×10^{12}	305	Flash photolysis of H_2O (1%)/Ar mixtures in the presence of
2.63×10^{12}	339	2,2,4-trimethylpentane at 13.3-20.0 Pa pressure. $[\text{OH}]$
3.16×10^{12}	373	monitored by absorption spectroscopy at 306.4 nm.
3.27×10^{12}	423	A 10-15% correction was made for the effect of the secondary
3.99×10^{12}	493	reaction

OH + HIGHER ALKANES

EXPERIMENTAL DATA - CONTINUED

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
		$\text{OH} + \text{C}_8\text{H}_{17} \longrightarrow \text{products.} \quad (24)$ The expression $k_{29} = 9.33 \times 10^{12} \exp(-425/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ was derived over the temperature range 300-500 K. $\text{OH} + (\text{CH}_3)_3\text{CCH}_2\text{CH}(\text{CH}_3)_2 \longrightarrow \text{C}_8\text{H}_{17} + \text{H}_2\text{O} \quad (29)$
-	297	ATKINSON, CARTER, ASCHMANN, WINER and PITTS 1984 ²⁰ Photolysis of $\text{CH}_3\text{ONO}(8-27 \text{ ppm})/\text{NO}(5 \text{ ppm})/2,2,4\text{-trimethylpentane}(0.5-1.0 \text{ ppm})/\text{n-butane}(0.5-1.0 \text{ ppm})/\text{air}$ mixtures at wavelengths $\geq 290 \text{ nm}$. The reactions were carried out at 297 K and about 97 kPa total pressure. [Alkane] monitored by gas chromatography; $[\text{NO}_x]$ and $[\text{O}_3]$ by chemiluminescence. Rate constant ratio $k_{29}/k_3 = 1.42$. Using our value of k_3 (this paper) we obtain $k_{29} = 2.3 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 297 K. $\text{OH} + \text{n-C}_4\text{H}_{10} \longrightarrow \text{C}_4\text{H}_9 + \text{H}_2\text{O} \quad (3)$

REVIEW ARTICLE

-
- ATKINSON, DARNALL, LLOYD, WINER and PITTS 1979⁹
 Review of gas phase reactions of OH with organic compounds.
 Quotes Ref. 1.

OH + N-NONANE

EXPERIMENTAL DATA

-
- 299 ATKINSON, ASCHMANN, CARTER, WINER and PITTS 1982¹⁴
 Photolysis of $\text{CH}_3\text{ONO}(9-17 \text{ ppm})/\text{NO}(5 \text{ ppm})/\text{n-nonane}(0.5-1.0 \text{ ppm})/\text{n-hexane}(0.5-1.0 \text{ ppm})/\text{air}$ mixtures at 299 K. Reactants monitored by gas chromatography.
 $\text{OH} + \text{n-C}_6\text{H}_{14} \longrightarrow \text{C}_6\text{H}_{13} + \text{H}_2\text{O} \quad (6)$
 $\text{OH} + \text{n-C}_9\text{H}_{20} \longrightarrow \text{C}_9\text{H}_{19} + \text{H}_2\text{O} \quad (30)$
 The rate constant ratio $k_{30}/k_6 = 1.87$ was obtained. Using $k_3/k_6 = 0.453$ determined in other work,¹⁵ and our value of k_3 (this paper) gives, $k_{30} = 6.6 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 299 K.
 $\text{OH} + \text{n-C}_4\text{H}_{10} \longrightarrow \text{C}_4\text{H}_9 + \text{H}_2\text{O} \quad (3)$

OH + HIGHER ALKANES

EXPERIMENTAL DATA

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
<u>OH + n-DECANE</u>		
-	299	<p>ATKINSON, ASCHMANN, CARTER, WINER and PITTS 1982¹⁴</p> <p>Photolysis of CH_3ONO(9-17 ppm)/NO(5 ppm)/<i>n</i>-decane(0.5-1.0 ppm)/<i>n</i>-hexane(0.5-1.0 ppm)/air mixtures at 299 K. Reactants monitored by gas chromatography.</p> $\text{OH} + n\text{-C}_6\text{H}_{14} \longrightarrow \text{C}_6\text{H}_{13} + \text{H}_2\text{O} \quad (6)$ $\text{OH} + n\text{-C}_{10}\text{H}_{22} \longrightarrow \text{C}_{10}\text{H}_{21} + \text{H}_2\text{O} \quad (31)$ <p>$k_{31}/k_6 = 2.00$ at 299 K. Using the rate constant ratio $k_3/k_6 = 0.453$ determined in other work,¹⁵ and our value of k_3 (this paper) we obtain $k_{31} = 7.1 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$.</p> $\text{OH} + n\text{-C}_4\text{H}_{10} \longrightarrow \text{C}_4\text{H}_9 + \text{H}_2\text{O} \quad (3)$ <p>Agreement between replicate irradiations not as good for <i>n</i>-decane as for other <i>n</i>-alkanes due to wall adsorption-desorption problems.</p>

Discussion

Kinetic rate data for the reactions between OH radicals and methane, ethane, propane, and butane are abundant in the literature. There are, however, relatively few data on analogous reactions with higher alkanes, particularly at temperatures above 300 K. Neopentane is an exception to this and has already been covered in an earlier section. Limited rate data are available on the reactions between OH radicals and all the *n*-alkanes from *n*-pentane to *n*-decane at room temperature.^{4,6-8,12,14-16} At higher temperatures Baldwin and Walker determined¹⁰ a rate constant for the reaction between OH and *n*-pentane at 753 K, and the analogous reaction with *n*-octane was investigated by Greiner¹ over the temperature range 300-500 K. Experimental data on many of the branched alkanes are equally sparse,^{1,3,5,6,8,12,13,15,20} with much of the work being carried out by Atkinson and co-workers. 2,2,3,3-tetramethylbutane is better represented than the rest, with two sets of absolute data in the temperature range 300-740 K.^{1,21}

There are generally very few absolute rate data available for the higher alkanes, most of which were obtained in Greiner's flash photolysis experiments,¹ with Tully *et al.* providing the only other absolute rate measurements.²¹ The remaining data are relative measurements, many of which are presented by Atkinson and co-workers, using *n*-butane

as reference compound.^{5,6,8,14,15,20} Their results for reactions between OH radicals and alkanes are usually consistent with their previous work and are generally in good agreement with both absolute and relative data from other sources. On this basis we believe that their experimental rate data are reliable and we are reasonably confident that rate constant values derived from their work are accurate with error limits of $\pm 50\%$ in most cases.

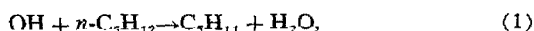
For each of the alkanes, we recommend a rate constant for their reaction with OH radicals at 298 K. For some reactions we may make our recommendation on perhaps only one or two data points; this is taken into consideration and reflected in our suggested error limits. The only alkane for which a temperature dependence is recommended is 2,2,3,3-tetramethylbutane. We feel that there are generally insufficient data to justify such recommendations for the other alkanes covered in this section.

OH + *n*-Pentane

With the exception of the rate constant determined by Baldwin and Walker¹⁰ at 753 K, all the kinetic data for the reaction between OH radicals and *n*-pentane were obtained close to 300 K. Furthermore, all experimental results are relative rate measurements.

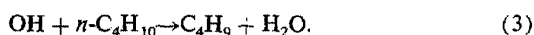
Wu *et al.*⁷ compared the decay rate of *n*-pentane with

that of *cis*-2-butene giving the ratio $k_1/k_2 = 0.12$ at 303 K:



k_1 is put on an absolute basis using k_2 derived from an Arrhenius expression,² giving $k_1 = 3.8 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Clearly this value is strongly dependent on the reference rate constant k_2 for which there is considerable discrepancy between literature values. Similar treatment of results from analogous work on isobutane, *n*-hexane, and cyclohexane⁷ has, however, produced results in reasonable agreement with absolute data.

Atkinson and co-workers³ made two relative measurements of k_1 at about 300 K,^{8,14} using *n*-butane as reference alkane in each case. Using our value of k_3 (this paper) we obtain $k_1 = 2.2 \times 10^{12}$ and $k_1 = 2.6 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively:

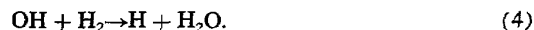


Cox *et al.*¹³ compared the decay rate of *n*-pentane with that of ethane in the presence of OH radicals. Using a value of k_5 from Ref. 19 gives $k_1 = 3.0 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 300 K:



Barnes *et al.*¹⁶ used both "photolytic" and "dark" sources of OH radicals. The decay rate of *n*-pentane was compared with that of propene and then normalized to ethene. Combining their ratios with k_5 from Ref. 19 gives values of k_1 that differ by nearly a factor of 2 at 300 K. With the added uncertainties associated with the pressure dependence of reaction (5), their results are not considered to be reliable.

Baldwin and Walker¹⁰ determined a value of k_1 at 753 K using their well established method of adding the alkane to slowly reacting mixtures of H_2/O_2 . After making allowances for self-heating, a value of $k_1 = 6.7 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ was derived from their experimental rate constant ratio k_1/k_4 , taking k_4 from an Arrhenius expression given in the same work:



Despite there being no comparable data at this temperature, we accept the value of Baldwin and Walker on the basis that analogous work on methane and ethane has produced rate constants consistent with absolute data.

At ambient temperatures there is considerable scatter in the data. From the rate constant ratio given by Wu *et al.*⁷ we derive a value for k_1 that is about 50%–70% greater than those given by Atkinson and co-workers,^{8,14} whereas from the photolytic work by Barnes *et al.*¹⁶ we obtain a value of k_1 about 40%–50% lower than those in Refs. 8 and 14. We recommend a value of

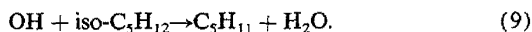
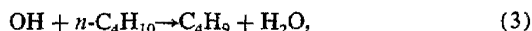
$$k_1 = 2.5 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

at 298 K with an error in $\log k$ of $\Delta \log k = \pm 0.2$. We base our recommendation on the results of Atkinson and co-workers^{8,14} since their work on other alkanes is generally consistent with absolute data.^{8,14,15,20}

OH + 2-Methylbutane

There are three experimental determinations of the rate constant for the reaction between OH radicals and 2-methylbutane.^{6,8,20} All are relative rate measurements at room temperature and in each case the decay rate of 2-methylbutane is compared with that of *n*-butane.

Lloyd *et al.*⁶ derived the rate constant ratio $k_9/k_3 = 1.1$, from which we obtain $k_9 = 1.8 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 305 K using our value of k_3 (this paper):



In similar work,^{8,20} Atkinson and co-workers obtained values of k_9/k_3 from which we derive the rate constants, $k_9 = 2.1 \times 10^{12}$ and $k_9 = 2.5 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively, using our value of k_3 (this paper).

Although there are no absolute rate data available for reaction (9), the three relative measurements are in good agreement. We recommend a value of

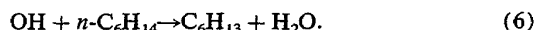
$$k_9 = 2.4 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

at 298 K with error limits of $\Delta \log k = \pm 0.2$.

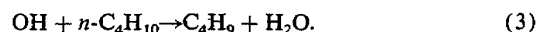
OH + *n*-Hexane

There are few data on the reaction between *n*-hexane and OH radicals, all of which are relative measurements at ambient temperatures.

The earliest study of this system was made by Campbell *et al.*⁴ using *n*-butane as the reference alkane. Using our value of k_3 derived from our recommended rate expression (this paper) gives $k_6 = 3.9 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 292 K:



Lloyd *et al.* determined k_6 relative to *n*-butane to give⁶ $k_6/k_3 = 2.09$ at 305 K:



Atkinson *et al.*, using a similar method,¹⁵ obtained the ratio $k_6/k_3 = 2.21$ at 299 K. We obtain a value of $k_6 = 3.5 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 298 K from both experimental ratios using values of k_3 derived from our recommended rate expression (this paper).

The only other value of k_6 is obtained from the rate constant ratio determined by Wu *et al.* where the rate of decay of *n*-hexane is compared with *cis*-2-butene.⁷ A value of $k_6 = 3.5 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 303 K is obtained using k_2 derived from the Arrhenius expression in Ref. 2:



Despite there being few kinetic data for reaction (6), all the rate constants are in good agreement with each other. Although we can make no comparisons with absolute data, we are reasonably confident that the value obtained by Atkinson *et al.*¹⁵ is accurate to within error limits of $\pm 50\%$. This statement is backed up by the fact that rate constants given for neopentane and cyclohexane in the same work compare favorably with absolute data. We therefore recom-

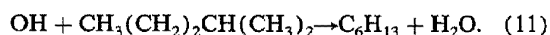
mend

$$k_6 = 3.5 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

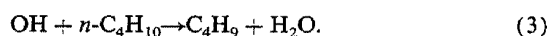
at 298 K with error limits of $\Delta \log k = \pm 0.15$.

OH + 2-Methylpentane

There are three relative rate measurements of reaction (11) at room temperature,^{6,12,20}

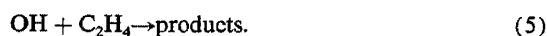


Lloyd *et al.*⁶ used *n*-butane as reference alkane in their system,



Using their rate constant ratio and our recommended value of k_3 (this paper) we derive, $k_{11} = 2.9 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 305 K. In similar work Atkinson *et al.*²⁰ compared the rate of decay of 2-methylpentane with that of *n*-butane in the presence of OH radicals. We derive a value of $k_{11} = 3.5 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 297 K using their rate constant ratio and our value of k_3 (this paper).

Cox *et al.*¹² obtained the rate constant ratio k_{11}/k_5 at 300 K from which we derive a value of k_{11} (taking k_5 from Ref. 19) which is in good agreement with the earlier work of Lloyd *et al.*,⁶



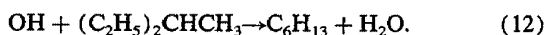
In the absence of absolute data we base our recommendation of

$$k_{11} = 3.4 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

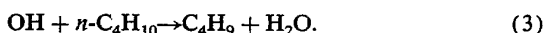
at 298 K on the three relative rate measurements^{6,12,20} with error limits of $\Delta \log k = \pm 0.2$.

OH + 3-Methylpentane

Two sets of experimental rate data are available on reaction (12),^{6,20}



In both cases the decay rate of 3-methylpentane is compared with that of *n*-butane at room temperature. Their rate constant ratios are put on an absolute basis using our value of k_3 (this paper),



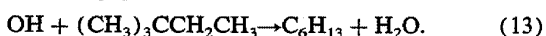
We recommend a value of

$$k_{12} = 3.7 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1},$$

with error limits of $\Delta \log k = \pm 0.2$ at 298 K, based on the two available relative measurements.^{6,20}

OH + 2,2-Dimethylbutane

The only experimental rate data available on the reaction between OH radicals and 2,2-dimethylbutane come from a recent paper by Atkinson *et al.*,²⁰



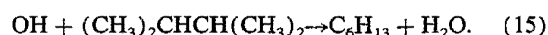
Using *n*-butane as reference compound, the authors obtain a rate constant ratio from which we derive a value of

$$k_{13} = 1.6 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

at 297 K, using our value of k_3 (this paper). We recommend this value with error limits of $\Delta \log k = \pm 0.2$ at 298 K.

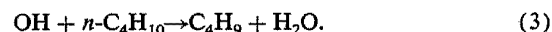
OH + 2,3-Dimethylbutane

The kinetics of reaction (15) was investigated by Greiner between 300 and 500 K using a flash photolysis system,¹



The experimental rate data appear to have a slight downward trend with increasing temperature but this is considered to be a measure of the experimental precision rather than indicative of a genuine negative temperature coefficient. The author derived the expression $k_{15} = 2.88 \times 10^{12} \exp(130/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ over the temperature range 300–500 K.

All other data are relative rate measurements at about 300 K and mainly obtained by Atkinson and co-workers. Atkinson *et al.*³ compared the decay of 2,3-dimethylbutane in the presence of OH radicals with that of ethane at 303 K and a value of $k_{15} = 2.4 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ is obtained. Darnall *et al.*⁵ obtained a value of $k_{15} = 3.1 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 305 K, using isobutene as the reference compound in their photolysis system. This result compares favorably with a value of k_{15} obtained by Darnall *et al.* in later work,⁸ in which *n*-butane was used as the reference alkane,



Using the same reference alkane, Atkinson *et al.*¹⁵ obtained a rate constant ratio from which we derive a value of $k_{15} = 3.9 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 299 K using our value of k_3 (this paper).

Cox *et al.*¹² compared the decay rate of 2,3-dimethylbutane with that of ethene to give a value of $k_{15} = 2.3 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 300 K. The reaction between ethene and OH radicals is pressure dependent and there is considerable discrepancy between literature values for the rate constant (factor of 2),



Taking k_5 from Refs. 17 and 19, we have, however, obtained a value of k_{15} which is in reasonable agreement with other data at ambient temperatures.

Although the literature values of k_{15} at room temperature show a considerable degree of scatter, the most reliable data suggest a value of

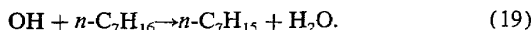
$$k_{15} = 3.5 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

at 298 K with error limits of $\Delta \log k = \pm 0.2$. We feel that there are insufficient data to make a recommendation for the temperature dependence of the rate constant for reaction (15).

Cohen combined data from Refs. 1 and 8 with transition state calculations to give the rate expression¹⁸ $k_{15} = 2.5 \times 10^{13} T^{3.0} \exp(1200/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ between 300 and 2000 K.

OH + *n*-Heptane

Atkinson *et al.*¹⁴ derived a rate constant for reaction (19) at 299 K using *n*-butane as reference alkane:



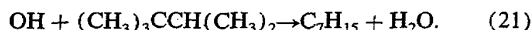
The relative rate constant is placed on an absolute basis using our recommended value for *n*-butane (this paper). No other rate data for reaction (19) are reported in the literature and so no direct comparisons can be made. In the same work, however, a rate constant is given for the analogous reaction between propane and OH radicals which is in excellent agreement with absolute data for that reaction. We are therefore satisfied that the value of

$$k_{19} = 4.5 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1},$$

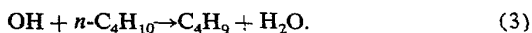
given by Atkinson *et al.*,¹⁴ is accurate within error limits of $\Delta \log k = \pm 0.2$ at 298 K.

OH + 2,2,3-Trimethylbutane

Greiner¹ obtained absolute rate parameters for the reaction between 2,2,3-trimethylbutane and OH radicals between 300 and 500 K. Although the rate data obtained tend to decrease slightly with increasing temperature up to about 370 K, it is considered to be a measure of the experimental precision rather than indicative of a genuine negative temperature coefficient. The author derived the rate expression $k_{21} = 4.79 \times 10^{12} \exp(-115/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ over this temperature range:



Darnall *et al.* determined a value for k_{21} by comparison of the decay rate of 2,2,3-trimethylbutane with that of isobutene in the presence of OH radicals at 305 K.⁵ The authors give $k_{21} = 2.3 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ which is about 20% lower than Greiner's value but is within the bounds of experimental error. Atkinson *et al.*²⁰ also made a relative measurement of k_{21} at 297 K using *n*-butane as reference alkane:



Using our value of k_3 (this paper) we derive a value of k_{15} which is in good agreement with the earlier works of Greiner¹ and Darnall *et al.*⁵

Baldwin *et al.*¹³ made the only determination of k_{21} at higher temperatures. Their static system involved the addition of 2,2,3-trimethylbutane to slowly reacting mixtures of H_2/O_2 at 753 K. After correction for the effects of self-heating and the unimolecular decay of the alkane, the rate constant $k_{21} = 4.5 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ is given. Although no comparison can be made with other data at this temperature, rate data for other alkanes in the presence of OH radicals given by Baldwin *et al.* using an identical method, are generally consistent with absolute results.

In the absence of further data at both ambient and high-temperature, we recommend

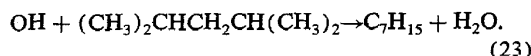
$$k_{21} = 2.6 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

at 298 K with error limits of $\Delta \log k = \pm 0.15$. We feel that there are insufficient data to justify making a recommendation for the temperature dependence of the rate constant for reaction (21).

Cohen made an evaluation based on data from Refs. 1 and 8 and transition state calculations. The recommended expression of $k_{21} = 1.5 \times 10^4 T^{2.8} \exp(925/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ between 300 and 2000 K is in good agreement with experimental values.

OH + 2,4-Dimethylpentane

The only experimental rate data available on the reaction between OH radicals and 2,4-dimethylpentane come from a recent paper by Atkinson *et al.*,²⁰



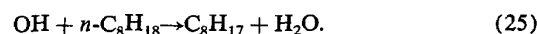
Using *n*-butane as reference compound, the authors obtain a rate constant ratio from which we derive a value of

$$k_{23} = 3.3 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

at 297 K, using our value of k_3 (this paper). We recommend this value with error limits of $\Delta \log k = \pm 0.2$.

OH + *n*-Octane

The only two sets of data on the reaction between *n*-octane and OH radicals are provided by Greiner¹ and Atkinson *et al.*¹⁴ In Greiner's flash photolysis system, rate data were obtained for reaction (25) between 300 and 500 K:



From his results, Greiner derived the rate expression, $k_{25} = 1.78 \times 10^{13} \exp(-365/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ over this temperature range.

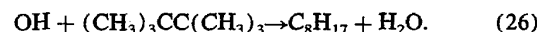
Atkinson *et al.*¹⁴ obtained a rate constant ratio relative to *n*-butane to give $k_{25} = 5.6 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 299 K. Their value of k_{25} is in good agreement with that of Greiner's absolute data at ambient temperatures.¹ We recommend a value of

$$k_{25} = 5.5 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

at 298 K with error limits of $\Delta \log k = \pm 0.2$. We feel that there are insufficient data to make any recommendations for k_{25} above ambient temperatures.

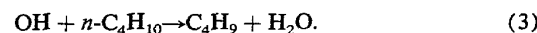
OH + 2,2,3,3-Tetramethylbutane

Greiner¹ obtained absolute rate data for reaction (26) between 300 and 500 K,



The author derived the rate expression $k_{26} = 9.77 \times 10^{12} \exp(-800/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ over the temperature range 300–500 K, using the experimental results.

Atkinson *et al.*²⁰ obtained a rate constant ratio at 297 K using *n*-butane as the reference compound:



Taking our recommended value of k_3 from this paper, we derive a value of k_{26} that is in excellent agreement with Greiner's value at room temperature.

At higher temperature, Baldwin *et al.*¹¹ obtained a value of k_{26} at 753 K using their method of adding the alkane to slowly reacting mixtures of H_2/O_2 . Allowances were made

for the effects of self-heating and for the unimolecular decay of the alkane giving $k_{26} = 3.0 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

Recent flash photolysis work by Tully *et al.*²¹ gives rate constants for reaction (26) over the temperature range 290–738 K. Their data are in excellent agreement with those obtained by Greiner¹ and Atkinson *et al.*²⁰ but agreement with the high-temperature value of Baldwin *et al.*,¹¹ which is about 50% lower, is not so good. Tully *et al.* give a rate expression derived from the best fit to their data, $k_{26} = 2.86 \times 10^6 T^{2.20} \exp(-70/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ which, unlike Greiner's expression, takes into account curvature of the Arrhenius plots. Furthermore, there is good agreement with Cohen's expression¹⁸ which is based on data from Ref. 1 and transition state calculations.

At 298 K we recommend a value of

$$k_{26} = 6.6 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1},$$

with error limits of $\Delta \log k = \pm 0.15$. In the absence of further data in the intermediate temperature range (500–750 K), we recommend Cohen's expression,

$$k_{26} = 1.0 \times 10^7 T^{2.0} \exp(-90/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1},$$

between 300 and 700 K, with error limits of $\Delta \log k = \pm 0.15$ at 300 K rising to $\Delta \log k = \pm 0.3$ at 700 K.

OH + 2,2,4-Trimethylpentane

The only absolute kinetic rate data on the reaction between 2,2,4-trimethylpentane and OH radicals come from the flash photolysis work of Greiner.¹ Rate constants are given from 300 to 500 K and an Arrhenius expression is fitted to the data, giving $k_{29} = 9.33 \times 10^{12} \exp(-425/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ over this temperature range:



The only comparison that can be made with other work is with the relative measurement of Atkinson *et al.*²⁰ Using *n*-butane as reference compound, Atkinson *et al.* obtain a rate constant ratio from which we derive a value of k_{29} at 297 K (taking a value of k_3 from this paper) which is in excellent agreement with Greiner's room-temperature result.¹ We recommend a value of

$$k_{29} = 2.3 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

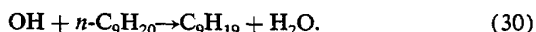
at 298 K with error limits of $\Delta \log k = \pm 0.2$, based on data from Refs. 1 and 20. Clearly more high-temperature data are required before we can make any recommendations for k_{29} above ambient temperatures.

OH + *n*-Nonane

The only available data on the reaction between *n*-nonane and OH radicals is a relative measurement made by Atkinson *et al.*¹⁴ Using *n*-butane as reference alkane, authors give a value of

$$k_{30} = 6.6 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

at 299 K:

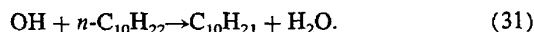


No other rate data for reaction (30) are reported in the liter-

ature and so no direct comparisons can be made. In the same work, however, a rate constant is given for the analogous reaction between propane and OH radicals which is in excellent agreement with absolute data for that reaction. We are therefore satisfied that the value of k_{30} given by Atkinson *et al.* is accurate within error limits of $\Delta \log k = \pm 0.2$ at 298 K.

OH + *n*-Decane

Atkinson *et al.*¹⁴ have determined the only rate constant for the reaction between *n*-decane and OH radicals:



Their method was identical to that for the analogous reaction with *n*-nonane, and a value of

$$k_{31} = 7.1 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

is obtained at 299 K. The authors found, however, that the agreement between replicate irradiations was poor, probably due to wall adsorption-desorption problems. We therefore recommend their value of k_{31} within error limits of $\Delta \log k = \pm 0.3$ at 298 K.

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10. OH + CYCLOALKANES

THERMODYNAMIC DATA

Thermodynamic data are unavailable for cycloalkyl radicals.

RECOMMENDED RATE CONSTANT

OH + Cyclobutane: $k = 7.0 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 298 K.

Suggested Error Limits for Evaluated Rate Constant: $\Delta \log k = \pm 0.3$.

OH + Cyclopentane: $k = 3.0 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 298 K.

Suggested Error Limits for Evaluated Rate Constant: $\Delta \log k = \pm 0.2$.

OH + Cyclohexane: $k = 4.5 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 298 K.

Suggested Error Limits for Evaluated Rate Constant: $\Delta \log k = \pm 0.15$.

OH + Methylcyclohexane: $k = 6.6 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 298 K.

Suggested Error Limits for Evaluated Rate Constant: $\Delta \log k = \pm 0.2$.

EXPERIMENTAL DATA

Rate Constant $k/\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	Temperature T/K	Reference and Comments
<u>OH + CYCLOBUTANE</u>		
-	298	<p>GORSE and VOLMAN 1974² VOLMAN 1975⁴</p> <p>Static photolysis. $\text{H}_2\text{O}_2(5.9\%)/\text{O}_2(34\%)/\text{CO}$ mixtures at total pressure of 2.12 kPa, photolysed at 254 nm in the presence of $\text{c-C}_4\text{H}_8$. $[\text{CO}_2]$ monitored by gas chromatography.</p> $\text{OH} + \text{c-C}_4\text{H}_8 \longrightarrow \text{c-C}_4\text{H}_7 + \text{H}_2\text{O} \quad (1)$ $\text{OH} + \text{CO} \longrightarrow \text{CO}_2 + \text{H} \quad (2)$ <p>After correction for 6.5% n-butane impurity in $\text{c-C}_4\text{H}_8$, $k_1/k_2 = 7.92$. Using our value of k_2 (Vol.3 p.203) gives $k_1 = 7.0 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 298 K. Used by Ref. 9.</p>
$8.1 \times 10^6 T^{2.0} \exp(-30/T)$	300-2000	<p>COHEN 1982⁹</p> <p>Theoretical expression derived using transition state theory and experimental data of Ref. 2.</p>

OH + CYCLOALKANES

REVIEW ARTICLES

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
-	-	ATKINSON, DARNALL, LLOYD, WINER and PITTS 1979 ⁷ Review of gas phase reactions of OH with organic compounds. Quotes Ref. 2.
$8.4 \times 10^6 T^{2.0} \exp(-30/T)$	298-2000	COHEN and WESTBERG 1983 ¹³ Evaluation. Based on data from Ref. 2.

OH + CYCLOPENTANE

EXPERIMENTAL DATA

-	298	VOLMAN 1975 ⁴ No experimental details given but probably similar to those in Ref. 2. $\text{OH} + \text{c-C}_5\text{H}_{10} \longrightarrow \text{c-C}_5\text{H}_9 + \text{H}_2\text{O} \quad (3)$ $k_3 = 3.7 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1} \text{ at } 298 \text{ K.}$ Used by Ref. 9.
-	300	DARNALL, ATKINSON and PITTS 1978 ^b Photolysis of $\text{NO}_x/\text{cyclopentane}(0.155\text{--}0.174 \text{ ppm})/\text{n-butane}(0.073\text{--}0.075 \text{ ppm})/\text{air}$ mixtures at 100 kPa total pressure and 300 K. Alkane concentrations monitored by gas chromatography. $\text{c-C}_5\text{H}_{10}$ decay compared with that of $\text{n-C}_4\text{H}_{10}$ giving the rate constant ratio, $k_3/k_4 = 1.73$. $\text{OH} + \text{c-C}_5\text{H}_{10} \longrightarrow \text{c-C}_5\text{H}_9 + \text{H}_2\text{O} \quad (3)$ $\text{OH} + \text{n-C}_4\text{H}_{10} \longrightarrow \text{C}_4\text{H}_9 + \text{H}_2\text{O} \quad (4)$ Using our value of k_4 (this paper) gives $k_3 = 2.8 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ at 300 K. Used by Ref. 9.
-	299	ATKINSON, ASCHMANN, WINER and PITTS 1982 ⁸ Static system. $\text{CH}_3\text{ONO}(4\text{--}15 \text{ ppm})/\text{NO}(5 \text{ ppm})/\text{cyclopentane}(0.5\text{--}1.0 \text{ ppm})/\text{cyclohexane}(0.5\text{--}1.0 \text{ ppm})/\text{air}$ mixtures photolysed >290 nm and 299 K. Organic reactants monitored by gas chromatography. $\text{OH} + \text{c-C}_5\text{H}_{10} \longrightarrow \text{c-C}_5\text{H}_9 + \text{H}_2\text{O} \quad (3)$ $\text{OH} + \text{n-C}_4\text{H}_{10} \longrightarrow \text{C}_4\text{H}_9 + \text{H}_2\text{O} \quad (4)$ $\text{OH} + \text{c-C}_6\text{H}_{12} \longrightarrow \text{c-C}_6\text{H}_{11} + \text{H}_2\text{O} \quad (5)$ $k_3/k_5 = 0.704 \text{ at } 299 \text{ K.}$ Using the ratio k_4/k_5 (obtained in the same work) and our value of k_4 (this paper) $k_3 = 3.3 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$.

OH + CYCLOALKANES

EXPERIMENTAL DATA - CONTINUED

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
$4.8 \times 10^6 T^{2.1} \exp(430/T)$	300-2000	COHEN 1982 ⁹ Theoretical expression derived using transition state theory and experimental data of Refs. 4 and 6.

REVIEW ARTICLES

-	-	ATKINSON, DARNALL, LLOYD, WINER and PITTS 1979 ⁷ Review of gas phase reactions of OH with organic compounds. Quotes Refs. 4 and 6.
$4.8 \times 10^6 T^{2.1} \exp(430/T)$	300-2000	COHEN and WESTBERG 1983 ¹³ Evaluation. Based on data from Refs. 4 and 6.

OH + CYCLOHEXANE

EXPERIMENTAL DATA

4.79×10^{12}	295	GREINER 1970 ¹
5.06×10^{12}	338	Flash photolysis of $\text{H}_2\text{O}(1\%)/\text{Ar}$ mixtures in the presence of
4.64×10^{12}	338	cyclohexane(7.4-19 Pa). [OH] monitored by absorption
7.10×10^{12}	370	spectroscopy at 306.4 nm.
5.98×10^{12}	373	$\text{OH} + \text{c-C}_6\text{H}_{12} \longrightarrow \text{c-C}_6\text{H}_{11} + \text{H}_2\text{O}$ (5)
6.29×10^{12}	425	A correction of 10-15% was made for the effect of the
6.07×10^{12}	425	secondary reaction
7.47×10^{12}	497	$\text{OH} + \text{c-C}_6\text{H}_{11} \longrightarrow \text{products.}$ (6) Author derived the expression $k_5 = 1.41 \times 10^{13} \exp(-320/T)$ $\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$ over the temperature range 300-500 K. Used by Ref. 9.
-	298	GORSE and VOLMAN 1974 ² VOLMAN 1975 ⁴ Static photolysis. $\text{H}_2\text{O}_2(5.9\%)/\text{O}_2(34\%)/\text{CO}$ mixtures at 2.12 kPa total pressure irradiated at 254 nm in the presence of cyclohexane. $[\text{CO}_2]$ monitored by gas chromatography. $\text{OH} + \text{CO} \longrightarrow \text{CO}_2 + \text{H}$ (2) $\text{OH} + \text{c-C}_6\text{H}_{12} \longrightarrow \text{c-C}_6\text{H}_{11} + \text{H}_2\text{O}$ (5) $k_5/k_2 = 44.8$. Using our value of k_2 (Vol.3 p.203) gives $k_5 = 4.0 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ at 298 K.

OH + CYCLOALKANES

EXPERIMENTAL DATA - CONTINUED

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
-	303	<p>WU, JAPAR and NIKI 1976⁵</p> <p>Photolysis of NO_2 at ppm level in $\text{NO}(\text{ppm})/\text{cyclohexane}(\text{ppm})/\text{air}$ or $\text{He}/\text{O}_2(21\%)$ mixtures. NO, NO_2 and O_3 concentrations monitored with NO/O_3 chemiluminescence detectors. [cyclohexane] measured by gas chromatography.</p> <p>Cyclohexane removed by reaction with OH, O and O_3 but last two contribute <6% to total decay. Decay rate of cyclohexane compared with that of cis-2-butene, leading to $k_5/k_7 = 0.12$.</p> $\text{OH} + \text{c-C}_6\text{H}_{12} \longrightarrow \text{c-C}_6\text{H}_{11} + \text{H}_2\text{O} \quad (5)$ $\text{OH} + \text{cis-CH}_3\text{CH=CHCH}_3 \longrightarrow \text{products} \quad (7)$ <p>Using k_7 derived from the Arrhenius expression given in Ref. 3, $k_5 = 3.9 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ at 303 K.</p>
-	299	<p>ATKINSON, ASCHMANN, WINER and PITTS 1982⁸</p> <p>Static system. $\text{CH}_3\text{ONO}(4\text{--}15 \text{ ppm})/\text{NO}(5 \text{ ppm})/\text{cyclohexane}(0.5\text{--}1.0 \text{ ppm})/\text{n-C}_4\text{H}_{10}(0.5\text{--}1.0 \text{ ppm})/\text{air}$ mixtures photolysed $\geq 290 \text{ nm}$ and 299 K. Organic reactants monitored by gas chromatography.</p> $\text{OH} + \text{n-C}_4\text{H}_{10} \longrightarrow \text{C}_4\text{H}_9 + \text{H}_2\text{O} \quad (4)$ $\text{OH} + \text{c-C}_6\text{H}_{12} \longrightarrow \text{c-C}_6\text{H}_{11} + \text{H}_2\text{O} \quad (5)$ <p>$k_5/k_4 = 2.92$. Using our value of k_4 (this paper) we obtain $k_5 = 4.7 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ at 299 K.</p>
$1.4 \times 10^8 T^{1.6} \exp(400/T)$	300-2000	<p>COHEN 1982⁹</p> <p>Theoretical expression derived using transition state theory and experimental data of Ref. 1.</p>
-	299	<p>ATKINSON, ASCHMANN and PITTS 1983¹⁰</p> <p>Photolysis of $\text{CH}_3\text{ONO}(3\text{--}6 \text{ ppm})/\text{NO}(5 \text{ ppm})/\text{cyclohexane}(1\text{--}2 \text{ ppm})/\text{propene}(1\text{--}2 \text{ ppm})/\text{air}$ mixtures at $\geq 290 \text{ nm}$ and 299 K. [cyclohexane] and [propene] monitored by gas chromatography.</p> $\text{OH} + \text{c-C}_6\text{H}_{12} \longrightarrow \text{c-C}_6\text{H}_{11} + \text{H}_2\text{O} \quad (5)$ $\text{OH} + \text{C}_3\text{H}_6 \longrightarrow \text{products} \quad (8)$ <p>Authors obtain $k_5/k_8 = 0.270$ and using a mean value of $k_8 = 1.52 \times 10^{13} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$, $k_5 = 4.1 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ at 299 K.</p>

REVIEW ARTICLES

-	-	<p>ATKINSON, DARNALL, LLOYD, WINER and PITTS 1979⁷</p> <p>Review of gas phase reactions of OH with organic compounds. Quotes Refs. 1, 2 and 5.</p>
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OH + CYCLOALKANES

REVIEW ARTICLES - CONTINUED

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments
$1.4 \times 10^8 T^{1.6} \exp(400/T)$	300-2000	COHEN and WESTBERG 1983 ¹³ Evaluation. Based on data from Refs. 1 and 2.

OH + METHYLCYCLOHEXANE

EXPERIMENTAL DATA

- 297 ATKINSON, CARTER, ASCHMANN, WINER and FITTS 1984¹²
 Photolysis of CH_3ONO (8-27 ppm)/ NO (5 ppm)/methylcyclohexane (0.5-1.0 ppm)/n-butane (0.5-1.0 ppm)/air mixtures at wavelengths ≥ 290 nm. The reactions were carried out at 297 K and about 97 kPa total pressure. [Alkane] monitored by gas chromatography; $[\text{NO}_x]$ and $[\text{O}_3]$ by chemiluminescence.

$$\text{OH} + \text{C}_6\text{H}_{11}\text{CH}_3 \longrightarrow \text{C}_7\text{H}_{13} + \text{H}_2\text{O} \quad (9)$$
 Rate constant ratio $k_9/k_4 = 4.12$. Using our value of k_4 (this paper) we obtain $k_9 = 6.6 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ at 297 K.

OH + BI- AND TRI-CYCLOALKANES

EXPERIMENTAL DATA

- 299 ATKINSON, ASCHMANN and CARTER 1982¹¹
 Static system. CH_3ONO (5-15 ppm)/ NO (5 ppm)/cyclohexane (1.0 ppm)/reactant alkane (1.0 ppm)/air mixtures photolysed ≥ 290 nm and 299 K. The reactions of cyclohexane (reference alkane) and reactant alkanes (RH) with reactive species other than OH were negligible (<1%) under the experimental conditions used. Organic reactants monitored by gas chromatography.

$$\text{OH} + \text{RH} \longrightarrow \text{R} + \text{H}_2\text{O} \quad (10)$$
 k_{10} determined from the experimental rate constant ratio k_{10}/k_3 , using $k_3 = 4.56 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ from Ref. 8.

OH + CYCLOALKANES

EXPERIMENTAL DATA - CONTINUED

Rate Constant $k/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$	Temperature T/K	Reference and Comments	
		RH	k_{10}/k_5 $k_{10}/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$
		Bicyclo[2.2.1]heptane	0.731 3.3×10^{12}
		Bicyclo[2.2.2]octane	1.96 8.9×10^{12}
		Bicyclo[3.3.0]octane	1.47 6.7×10^{12}
		cis-Bicyclo[4.3.0]nonane	2.29 1.0×10^{13}
		trans-Bicyclo[4.3.0]nonane	2.35 1.1×10^{13}
		cis-Bicyclo[4.4.0]decane	2.65 1.2×10^{13}
		trans-Bicyclo[4.4.0]decane	2.72 1.2×10^{13}
		Tricyclo[5.2.1.0 ^{2,6}]decane	1.51 6.9×10^{12}
		Tricyclo[3.3.1.1 ^{3,7}]decane	3.07 1.4×10^{13}

Discussion

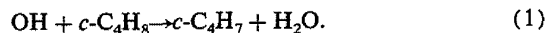
There are few available data on the reactions between OH radicals and cycloalkanes. No kinetic rate data are reported on the reaction between OH radicals and cyclopropane, and only limited data for the corresponding reactions with cyclobutane,² cyclopentane,^{4,6,8} cyclohexane,^{1,2,5,8,10} and methylcyclohexane¹² are found in the literature. In addition, Atkinson *et al.*¹¹ determined rate constants for the reactions between OH and some bi- and tricycloalkanes at 299 K. With the exception of Greiner's flash photolysis work on cyclohexane,¹ all the rate constants are obtained from relative measurements, predominantly by Atkinson and co-workers. In some cases we have recommended a rate constant at 298 K based on only one or two data points. Clearly this is not entirely satisfactory and more experimental data are required before we can be confident in our quoted value. This uncertainty is, however, reflected in the error limits that we have given. We feel that there are insufficient data at temperatures greater than 300 K to justify the recommendation of a temperature dependence in the rate constant of any alkane covered in this section.

Cohen recently evaluated kinetic data for the reactions between OH radicals and cyclobutane, cyclopentane, and cyclohexane.⁹ The recommended rate expressions given are based on both experimental data and transition state calculations. Rate constants derived from Cohen's expressions at

298 K agree within $\pm 10\%$ of our recommended values for each of these cycloalkanes.

OH + Cyclobutane

Gorse and Volman^{2,4} investigated the reaction between OH and cyclobutane using a photochemical method. The decay rate of cyclobutane was compared with that of CO. A value of $k_1 = 7.0 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ was derived at 298 K:



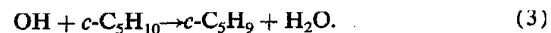
Since no other values of k_1 are given in the literature, it is difficult to evaluate their data. Gorse and Volman have, however, derived rate constants from analogous work on the alkanes propane and *n*-butane,² which although tending to be high, do compare reasonably well with absolute data at 298 K. We therefore make a tentative recommendation of

$$k_1 = 7.0 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

at 298 K, with error limits of $\Delta \log k = \pm 0.3$.

OH + Cyclopentane

There are few data on the reaction between OH radicals and cyclopentane:



Volman⁴ gives a value of $k_3 = 3.7 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 298 K, but gives no experimental details. Atkinson and co-workers give two values of k_3 at around 300 K using *n*-butane as reference alkane.^{6,8} Despite both values being in good agreement with each other, there is a lack of comparable data from other sources. Using the same experimental methods, however, rate constants have been obtained for OH radicals with propane,^{6,8} isobutane,⁶ and neopentane^{6,8} by the same authors, all of which agree very closely with absolute data at the same temperature. On this basis we therefore accept the values of k_3 given by Atkinson *et al.* and recommend

$$k_3 = 3.0 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

with error limits of $\Delta \log k = \pm 0.2$ at 298 K.

OH + Cyclohexane

The reaction between OH and cyclohexane has been investigated to a greater extent than other cycloalkanes. Greiner studied the kinetics of reaction (5) between 295 and 497 K using a flash photolysis system,¹



The expression $k_5 = 1.41 \times 10^{13} \exp(-320/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ was derived over the temperature range 300–500 K, which leads to a value of $k_5 = 4.8 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 298 K. Greiner has obtained rate expressions for a variety of other alkanes using the same experimental method,¹ and where comparison with other data is possible, his results are generally in very good agreement.

Gorse and Volman^{2,4} determined a value of $k_5 = 4.0 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 298 K using CO as the reference reactant in their photochemical system. Wu *et al.*⁵ compared the decay rate of cyclohexane with that of *cis*-2-butene. Taking the rate constant for OH + *cis*-2-butene from Ref. 3, we obtain $k_5 = 3.9 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 303 K. Although this value for k_5 appears low compared to Greiner's result,¹ it must be remembered that it is strongly dependent on the reference rate constant for which there is considerable discrepancy between literature values.⁹ Two values of k_5 were determined by Atkinson and co-workers,^{8,10} both in good agreement with Greiner's absolute data, using *n*-butane and propene as reference reactants.

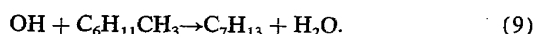
Both Greiner's and Atkinson's results are generally consistent with absolute data for the reactions between other alkanes and OH radicals, and on this basis we accept their rate data for cyclohexane and recommend a value of

$$k_5 = 4.5 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

at 298 K with error limits of $\Delta \log k = \pm 0.15$.

OH + Methylcyclohexane

In a recent paper, Atkinson *et al.*¹² reported the rate constant for the reaction between OH radicals and methylcyclohexane for the first time:



Using *n*-butane as reference compound, the authors obtain a rate constant ratio from which we derive a value of

$$k_9 = 6.6 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

at 298 K. In the absence of confirmatory data we tentatively recommend their value with error limits of $\Delta \log k = \pm 0.2$.

OH + Bi- and Tricycloalkanes

Atkinson *et al.*¹¹ determined rate constants for the reactions between OH radicals and some bi- and tricycloalkanes using cyclohexane as the reference alkane. Their results are tabulated in the text. No recommendations are given in this work.

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11. General Formulas for the Rate Constants for the Reactions of OH Radicals with Alkanes

Values for the rate constants for hydroxyl radical reactions with hydrocarbons are required for modeling combustion processes and atmospheric chemistry. As the material in this article demonstrates, only a relatively small number of such rate constants have been measured and, of those, only a very few have been studied over a wide temperature range. To provide the required data for modeling, attempts have been made to devise methods for predicting unknown rate data for OH radical reactions by extrapolation from existing data.

Various methods have been tried. Here we discuss three types of approach: (1) empirical additivity schemes, (2) transition-state methods, and (3) correlation with molecular properties and analogous reactions; and we compare their predictions with our evaluations.

11.1. Empirical Additivity Schemes

Greiner¹ measured the rate constants for the reaction of OH with several alkanes over the temperature range 295–500 K and, on the basis of these results, proposed that the overall rate constant, k_{RH} , for OH abstracting a hydrogen

atom from an alkane may be expressed as

$$k_{RH} = n_p k_p + n_s k_s + n_t k_t, \quad (1)$$

where n_p , n_s , and n_t are, respectively, the numbers of primary, secondary, and tertiary hydrogens in the alkane, and k_p , k_s , and k_t are the corresponding rate constants for abstraction of a primary, secondary, and tertiary hydrogen. The k_p , k_s , and k_t are considered to be independent of each other over the whole temperature range and from one alkane to another.

Others before have adopted the same approach for the reactions of atoms and radicals with alkanes.²⁻⁴ Greiner derived values of k_p , k_s , and k_t and as more data have become available these values have been updated, notably by Atkinson and his co-workers⁵⁻⁷ and by Baldwin and Walker.⁸ The first of these groups in their earlier papers^{5,6} derived for k_{RH} at 300 K the expression

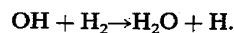
$$k_{RH}/\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1} = 3.91 \times 10^{10} n_p + 3.49 \times 10^{11} n_s + 1.26 \times 10^{12} n_t, \quad (2)$$

using data from Refs. 1, and 9-23. To obtain the temperature dependence of k_p , k_s , and k_t , the data of Greiner¹ for propane, *n*-butane, isobutane, neopentane, 2,3-dimethylbutane, 2,2,3,3-tetramethylbutane, 2,2,4-trimethylpentane, and *n*-octane were used, and of Perry *et al.*¹⁵ for *n*-butane. They obtained

$$k_{RH}/\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1} = 6.08 \times 10^{11} \exp(-823/T) n_p + 1.45 \times 10^{12} \exp(-428/T) n_s + 1.26 \times 10^{12} n_t \quad (3)$$

for the temperature range 300-500 K.

Baldwin and Walker⁸ adopted a rather different approach. They reasoned that the work from any one laboratory using a particular technique may well contain systematic errors and therefore in making comparisons with others' work it may be more valid to compare rate constant ratios, in which systematic errors may have cancelled to some extent, rather than compare absolute rate constant values. They therefore combined together values of k_{RH}/k_{H_2} from different laboratories, where k_{H_2} refers to the reaction



The values of k_{RH}/k_{H_2} used were those of Greiner¹ covering the temperature range 300-500 K and their own values⁸ determined at 753 K. These gave

$$k_{RH}/k_{H_2} = 0.214 \exp(1070/T) n_p + 0.173 \exp(1820/T) n_s + 0.273 \exp(2060/T) n_t.$$

Evaluation by Baldwin and Walker of the experimental data for k_{H_2} gave $k_{H_2}/\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1} = 1.28 \times 10^8 T^{1.5} \times \exp(-1480/T)$, which when combined with the above expression for k_{RH}/k_{H_2} gives

$$k_{RH}/\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1} = 2.74 \times 10^7 T^{1.5} \exp(-410/T) n_p + 2.21 \times 10^7 T^{1.5} \exp(340/T) n_s + 3.49 \times 10^7 T^{1.5} \exp(580/T) n_t. \quad (4)$$

Equations (3) and (4) are identical at 300 K within the

error limits of the experimental values, but differ considerably at higher temperatures.

In their most recent study, Atkinson *et al.*⁷ have modified Eqs. (2) and (3) to deal with the effects of neighboring groups on k_s and k_t . On the basis of largely their own data on 19 acyclic hydrocarbons and some cyclic compounds, they propose the following formula for k_{RH} at 298 K:

$$k_{RH} = n_p k_p + \sum_{n_\beta=0}^{\max n_\beta} n_s(n_\beta) k_s^0 F_s^{n_\beta} + \sum_{n'_\beta=0}^{\max n'_\beta} n_t(n'_\beta) k_t^0 F_t^{n'_\beta}. \quad (5)$$

k_p , k_s^0 , and k_t^0 are rate constants for the CH_3 , $\text{CH}_2(\text{CH}_3)_2$, and $\text{CH}(\text{CH}_3)_3$ groups, respectively. n_β and n'_β are the number of carbons in the β position relative to the group center. n_p is the number of CH_3 - groups in the molecule; $n_s(n_\beta)$ is the number of $-\text{CH}_2-$ groups with n_β next nearest neighbors; and $n_t(n'_\beta)$ is the number of $-\text{CH}-$ groups with n'_β next nearest neighbors. F_s and F_t are constant factors modifying k_s^0 and k_t^0 , respectively, due to the replacement of CH_3 groups by other groups.

Since n_β , n'_β , n_p , $n_s(n_\beta)$, and $n_t(n'_\beta)$ all relate to the structure of the alkane, there are, in effect, just five empirical quantities, k_p , k_s^0 , k_t^0 , F_s , and F_t required to calculate k_{RH} . Fitting this relationship to the available data,⁹⁻²³ Atkinson *et al.* obtain at 298 K,

$$k_p = 1.08 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}, \\ k_s^0 = 5.54 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}, \\ k_t^0 = 1.02 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}, \\ F_s = F_t = 1.27.$$

These values were obtained, in the main, from data on acyclic compounds but also fit the data for unstrained cyclic alkanes (cyclohexane, methylcyclohexane, *cis*-bicyclo[4,4,0]decane and *trans*-bicyclo[4,4,0]decane). The data on the strained cycloalkanes are reasonably well fitted at 298 K by

$$\ln(k^{\text{strained}}/k^{\text{unstrained}}) = 0.27 - 0.015 E/\text{kJ mol}^{-1}, \quad (6)$$

where E is the strain energy and $k^{\text{unstrained}}$ is the value of k calculated from the values of k_p , k_s^0 , k_t^0 , F_s , and F_t already given.

In Table 1 we compare the rate constant values calculated from Eq. (4), and the values calculated from Eq. (5) using the parameters of Atkinson *et al.*, with our recommended values and others experimental results at 298 K. Equations (4) and (5) conform to the experimental results to better than 10% in most cases. However, both approaches have their "failures." That of Atkinson *et al.* gives very high values for 2,4-dimethylpentane and 2,2,4-trimethylpentane; the Baldwin and Walker expression is rather better for these compounds but gives low values for the higher normal alkanes.

Atkinson *et al.*⁷ have also considered the effects of neighboring groups in deriving the temperature dependence of k_s and k_t . They assume that the effect of increasing the number of next nearest neighbors is to reduce the activation energy rather than increase the pre-exponential factor for

Table 1. Comparison of rate constants calculated from empirical additivity expressions, with our recommended values and other experimental data at 298 K.

Alkane	$10^{-12}k_{RH}/\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$			
	Equation (4)	Equation (5)	Experimental ^a	Our Evaluation
<u>n-Alkanes</u>				
Propane	0.93	0.77	0.73	0.79
n-Butane	1.64	1.61	1.55	1.6
n-Pentane	2.36	2.50	2.49	2.5
n-Hexane	3.07	3.39	3.43	3.5
n-Heptane	3.79	4.28	4.40	4.5
n-Octane	4.50	5.16	5.43	5.5
n-Nonane	5.21	6.02	6.44	6.6
n-Decane	5.93	6.93	6.87	7.1
<u>Branched Alkanes</u>				
Isobutane	1.58	1.34	1.38	1.6
Neopentane	0.44	0.43	0.46	0.54
2-Methylbutane	2.29	2.50	2.39	2.4
2-Methylpentane	3.01	3.44	3.42	3.4
3-Methylpentane	3.01	3.73	3.48	3.7
2,2-Dimethylbutane	1.15	1.55	1.60	1.6
2,3-Dimethylbutane	2.94	3.70	3.77	3.5
2,2,3-Trimethylbutane	1.79	2.61	2.54	2.6
2,4-Dimethylpentane	3.66	4.44	3.17	3.3
2,2,3,3-Tetramethylbutane	0.65	0.64	0.64	0.66
2,2,4-Trimethylpentane	2.51	3.63	2.20	2.3
<u>Unstrained Cycloalkanes</u>				
Cyclohexane	-	5.32	4.56	4.5
Methylcyclohexane	-	6.63	6.38	6.6
cis-Bicyclo[4,4,0]decane	-	13.31	12.1	-
trans-Bicyclo[4,4,0]decane	-	13.31	12.4	-

^a All experimental data based on a rate constant for the reaction of OH radicals with n-butane of $1.55 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ given in Refs. 6,29 and 30. Data are from Refs. 6,7,29 and 30.

abstraction from both secondary and tertiary groups. Thus they express k_p , k_s , and k_t in the form

$$\begin{aligned}k_p &= A_p \exp(-E_p/RT), \\k_s &= A_s^0 \exp[-(E_s^0 - n_\beta RT \ln F_s)/RT], \\k_t &= A_t^0 \exp[-(E_t^0 - n'_\beta RT \ln F_t)/RT].\end{aligned}$$

On the basis of Greiner's data¹ on propane, *n*-butane, isobutane, neopentane, 2,3-dimethylbutane, 2,2,3-trimethylbutane, 2,2,3,3-tetramethylbutane, *n*-octane, 2,2,4-trimethylpentane, and cyclohexane, and of Perry *et al.*¹⁵ for *n*-butane, all of which were obtained over the temperature range 300–500 K, Atkinson *et al.* obtain the expressions

$$k_p/\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1} = 1.72 \times 10^{12} \exp(-823/T), \quad (7)$$

$$k_s/\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1} = 2.33 \times 10^{12} \times \exp[-(528 - 70n_\beta)/T], \quad (8)$$

$$k_t/\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1} = 1.02 \times 10^{12} \exp[(70n'_\beta)/T]. \quad (9)$$

Substituting these values into Eq. (5) allows the estimation of OH radical rate constants for alkanes which do not exhibit steric hindrance and for unstrained cycloalkanes. It should be noted, however, that there appears to be an inconsistency

in the temperature dependence expression for k_s which may have arisen from the derived pre-exponential factor A_s^0 .

The only alkanes for which there are sufficient experimental data to derive an expression covering a temperature range are methane, ethane, propane, *n*-butane, isobutane, and neopentane. We compare in Figs. 1–5 our evaluations with the rate constant values predicted by Eqs. (3), (4), and (5), and also with the expressions derived by Cohen using transition state theory,²⁴ which we discuss later. Methane, because of its high C–H bond strength is considered to be exceptional and is not covered by Eqs. (3), (4), and (5).

Over a temperature range, the expression of Baldwin and Walker Eq. (4), appears to be the best of those based on empirical additivity rules. Equations (3) and (5) predict too low a curvature on the Arrhenius plots. They were based only on data up to 500 K and their extrapolation to higher temperatures is much less successful than extrapolation of Eq. (4), which even at 1000 K would probably give values of k_{RH} within 50% of the true value. It is difficult to know how it would perform at even higher temperatures, but where no experimental data are available these expressions provide a valuable first approximation to k_{RH} as do those of Cohen²⁴ which are based on the Baldwin and Walker expressions.

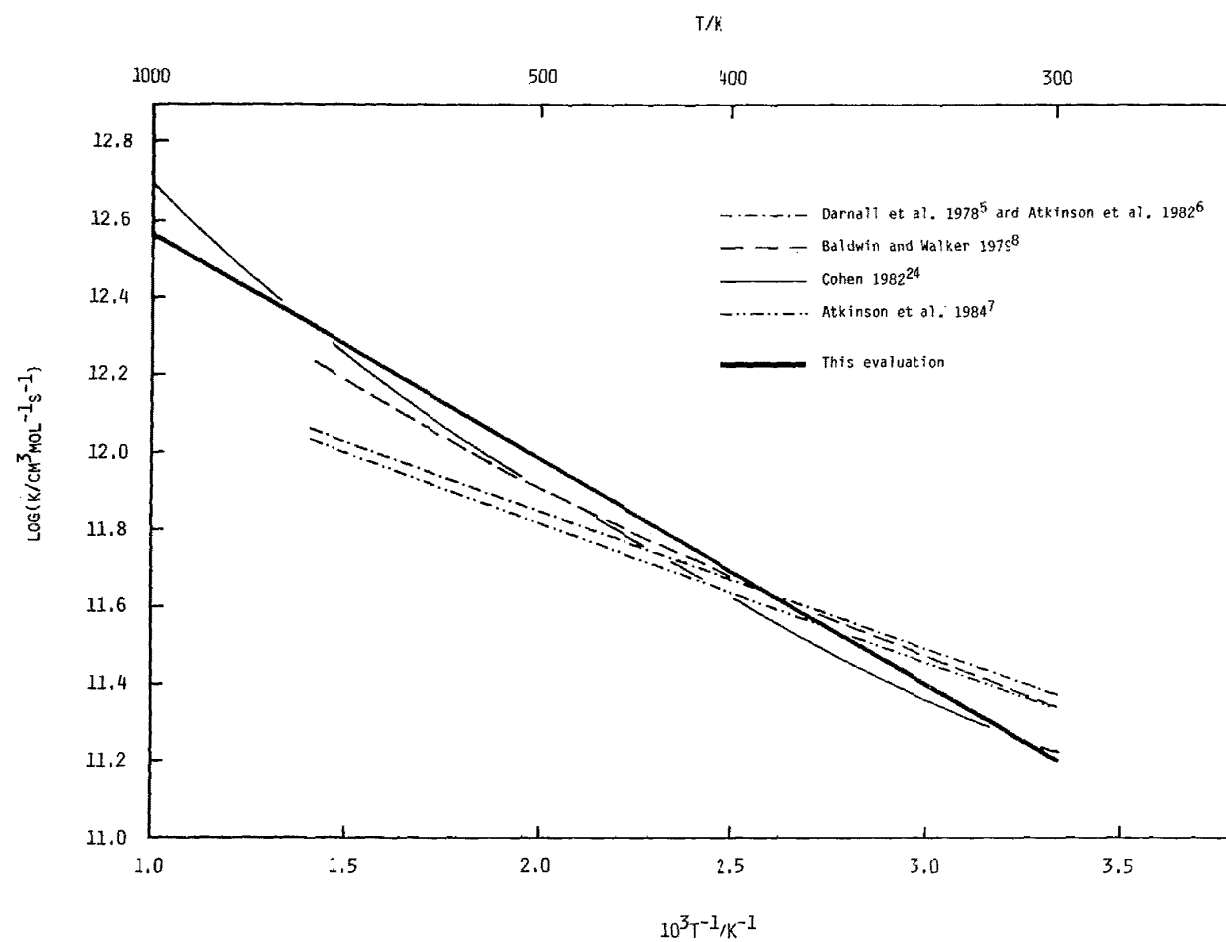
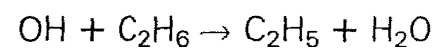


FIG. 1. OH + ethane.

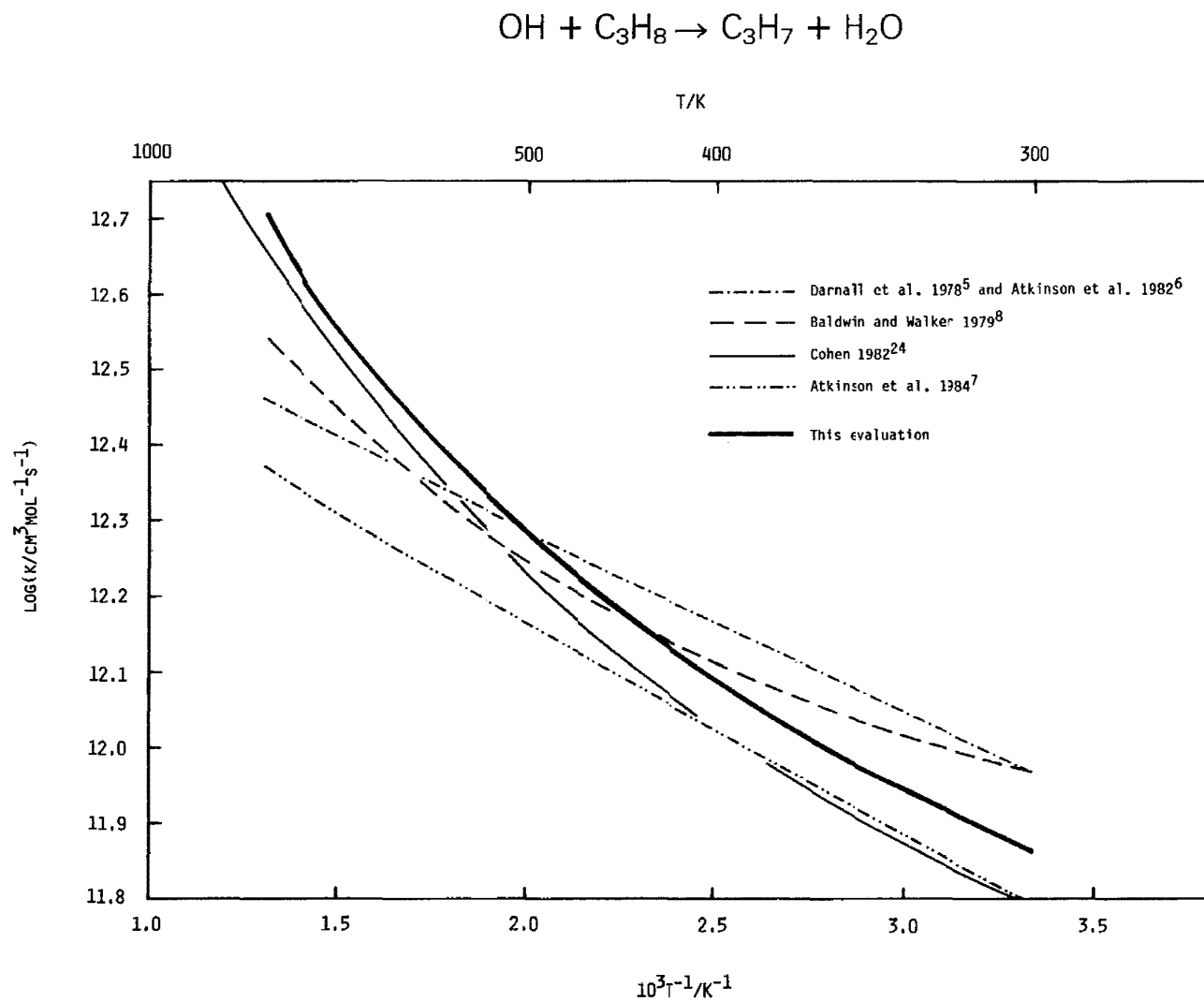


FIG. 2. OH + propane.

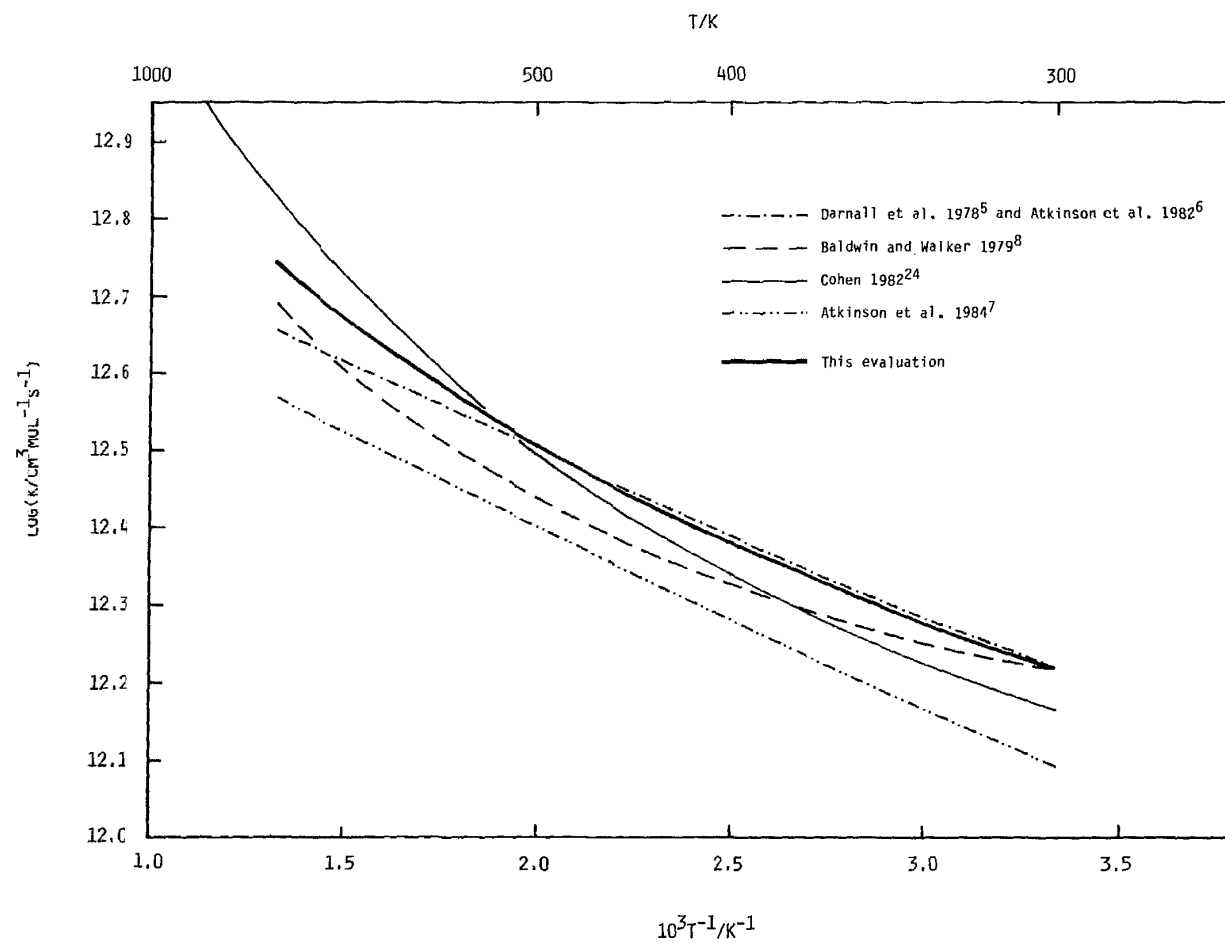
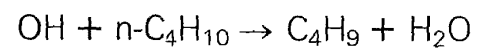


FIG. 3. OH + *n*-butane.

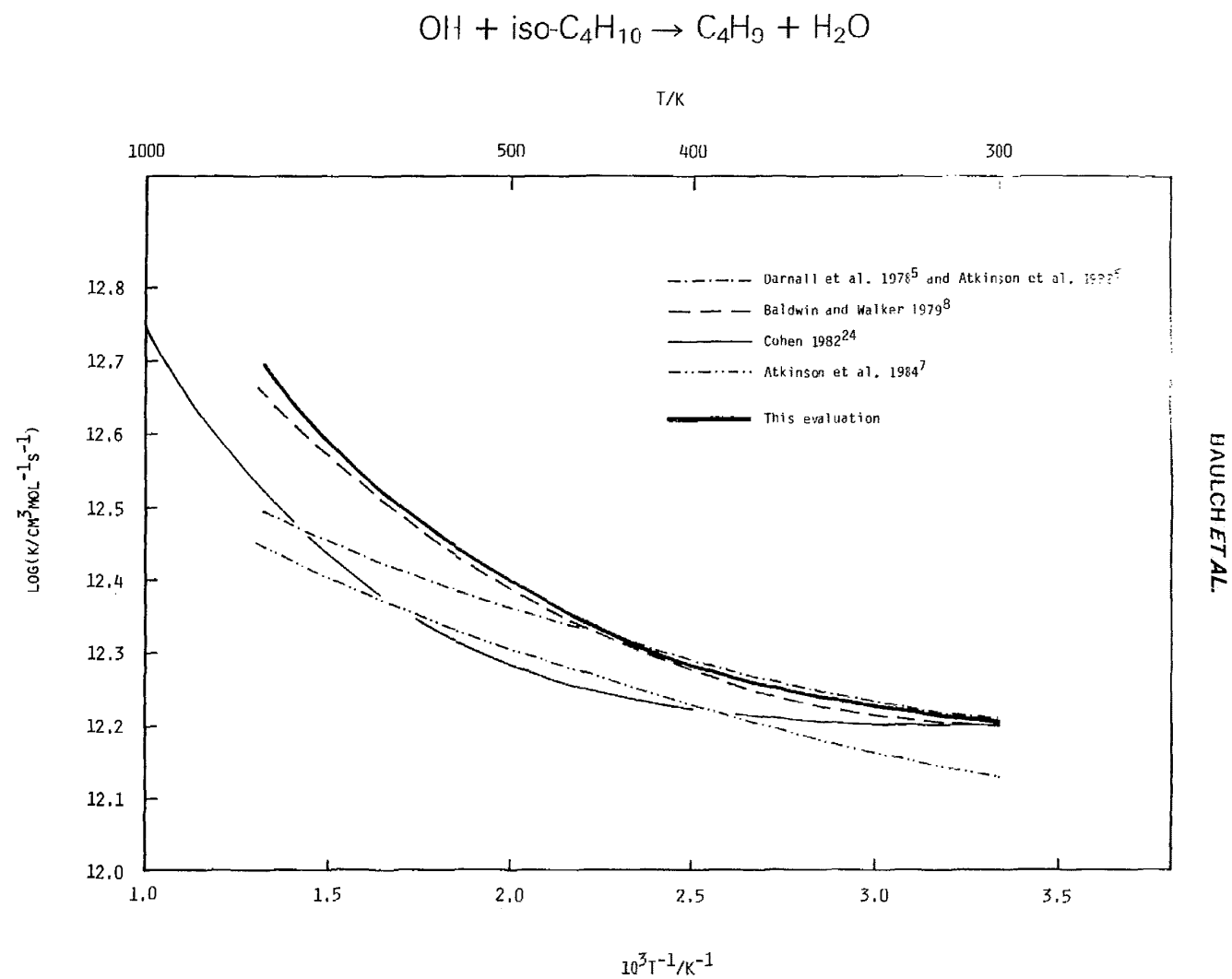


FIG. 4. OH + isobutane.

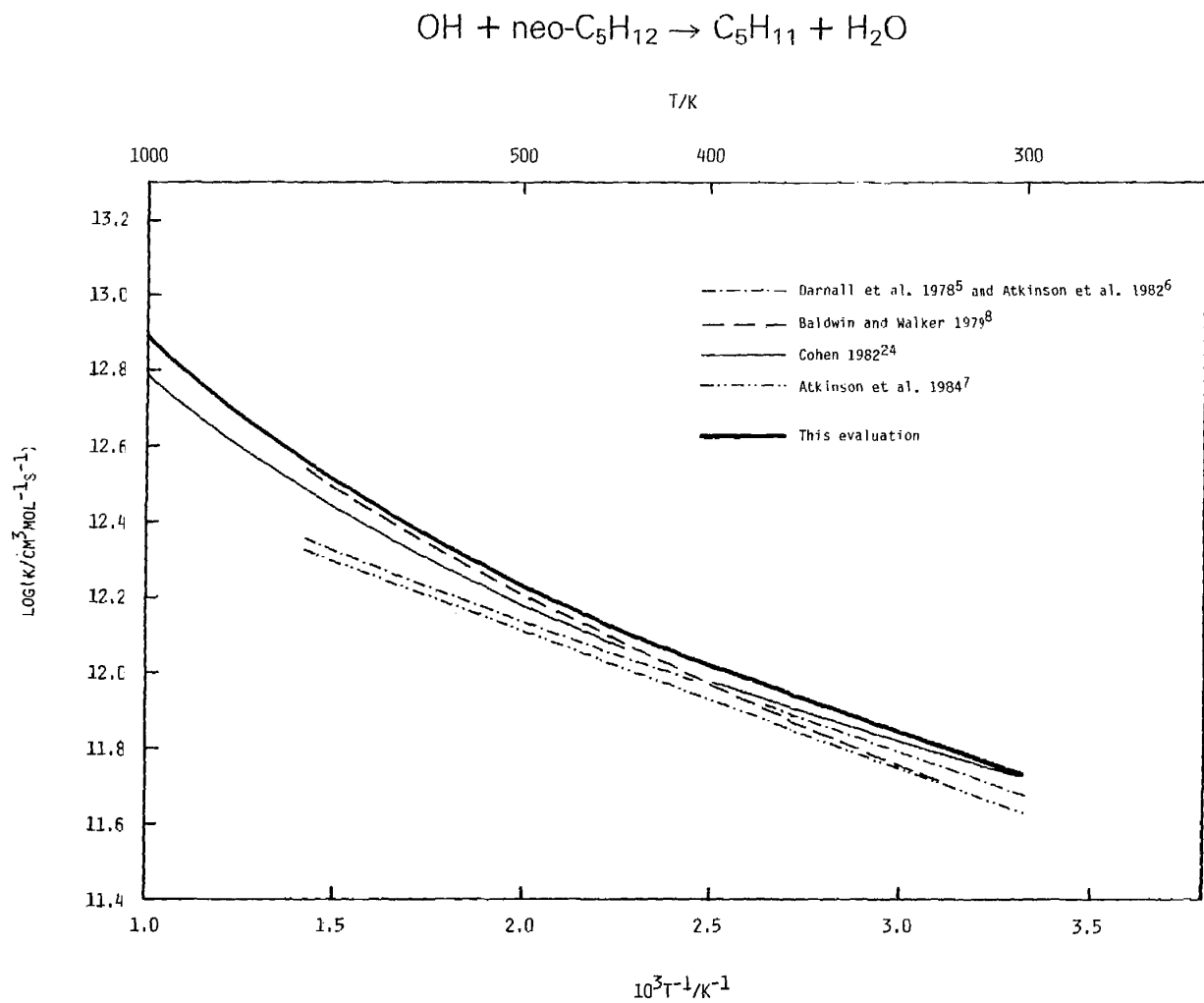


FIG. 5. OH + neopentane.

11.2. Transition State Calculations

Cohen²⁴ has applied transition state theory to the calculation of k_{RH} . He starts with the additivity assumption that k_{RH} may be expressed as

$$k_{RH} = k_p n_p + k_s n_s + k_t n_t,$$

and each of the rate constants, k_p , k_s , and k_t may be expressed in the form $AT^n \exp(B/T)$. Using a transition state model, the pre-exponential term AT^n is calculated for each of k_p , k_s , and k_t . The exponential term for each of these constants is then obtained by combining the calculated AT^n at $T = 300$ K with the experimentally measured value of k_{RH} at 300 K. The constant B is obtained by fitting the calculated rate constants to the assumed three-parameter expression. Where the alkane contains more than one type of hydrogen it is also necessary to know the ratio $k_p:k_s:k_t$ at 300 K in order to separate the measured k_{RH} into its components and hence obtain values of $\exp(B/T)$ for each of the components. Cohen has taken these ratios from the empirical expression of Baldwin and Walker, Eq. (4). In this way the theoretical calculation is "anchored" by the experimental data at one temperature, usually, but not necessarily 300 K. Values of k_{RH} are calculated at various temperatures and fitted to the overall expression $k_{RH} = AT^n \exp(B/T)$. The expressions so obtained are compared with experiment in Figs. 1–5. The agreement is often extremely good but it must be appreciated that in the model used for calculating AT^n there are a number of variable parameters allowing considerable, but not unlimited flexibility in fitting theory to experiment. The true test of the value of this technique will be in how well the theory, fitted and anchored by low-temperature experimental data, will predict values of k_{RH} at higher temperatures. Sufficient data are not yet available to make such a test.

It should be noted that in Cohen's treatment k_p , k_s , and k_t are not assumed to be the same for all molecules. It is recognized that values of k_p , k_s , and k_t are affected slightly by the molecular environment in a manner difficult to predict. Use of the experimental data to anchor the calculation should help to overcome this problem also.

11.3. Correlations with Molecular Properties and Analogous Reactions

The correlation between rate constants for OH and the corresponding rate constant for O(³P) reacting with a range of compounds has been studied by Gaffney and Levine²⁵ and by Sanhueza and Lissi.²⁶ For the alkanes, logarithmic plots of the one rate constant versus the other are roughly linear and the scatter of data points is such that it appears possible to predict the one rate constant from a knowledge of the other at 300 K to within a factor of about 2. This work has been briefly, but critically, assessed by Atkinson.²⁷

There has long been interest in the correlation between the activation energies for a series of related reactions and the dissociation energy of the bonds being broken in the reactions. Several authors have considered this for the reaction of OH radicals with alkanes.^{24,25,27,28} Atkinson²⁷ has shown that the logarithm of the abstraction rate constant per C–H

bond versus bond dissociation energy gives a good straight line allowing the assessment of k_p , k_s , and k_t at 300 K to within about $\pm 50\%$.

Heicklen²⁸ has attempted to extend this correlation to other temperatures, by assessing the variation of bond dissociation energy with temperature. Over the range 200–400 K his treatment appears to reproduce the experimental values of k_{RH} to within a factor of about 3.

A major limitation in the predictive abilities of correlations involving bond energies is the accuracy with which such energies are known. An error of ± 4 kJ mol⁻¹ in a bond dissociation energy may introduce a corresponding change in the value of k_{RH} of about a factor of 2 at 300 K. At the moment correlations of k_{RH} with molecular properties are less accurate for predicting unknown rate data than are empirical additivity schemes and seem to offer few advantages.

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