Evaluated Kinetic Data for Combustion Modelling

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Evaluated Kinetic Data for Combustion Modeling: Supplement II
Journal of Physical and Chemical Reference Data **34**, 757 (2005); https://doi.org/10.1063/1.1748524

Evaluated Kinetic Data for Combustion Modeling. Supplement I
Journal of Physical and Chemical Reference Data **23**, 847 (1994); https://doi.org/10.1063/1.555953

Evaluated Kinetic Data for Combustion Modelling

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This compilation contains critically evaluated kinetic data on elementary homogeneous gas phase chemical reactions for use in modelling combustion processes. Data sheets are presented for some 196 reactions. Each data sheet sets out relevant thermodynamic data, rate coefficient measurements, an assessment of the reliability of the data, references, and recommended rate parameters. Tables summarizing the preferred rate data are also given. The reactions considered are limited largely to those involved in the combustion of methane and ethane in air but a few reactions relevant to the chemistry of exhaust gases and to the combustion of aromatic compounds are also included.

Key words: chemical kinetics; combustion; gas phase; kinetic data; rate coefficient.

Contents

1. Introduction

This compilation of critically evaluated kinetic data is intended for use in computer modelling of combustion processes. It has been prepared as part of the project "Kinetics and Mechanisms of Chemical Processes in Combustion" which is one of the projects within the third European Community Energy Research and Development Programme. The formal cut off point for the literature searching was January, 1989 but the group continued to monitor the literature during the preparation of the manuscript and every attempt was made to incorporate more recent studies having a significant effect on the recommendations.

2. Guide to the Data Sheets

## 2.1. Scope and Reaction Ordering

The field of combustion is too large for a comprehensive treatment of all combustion reactions; some selectivity has been necessary. The present collection is limited to reactions of importance in the combustion of methane and ethane in air but it also contains a few reactions relevant to the chemistry of exhaust gases mainly involving NO_x chemistry, and to the combustion of aromatic compounds.

The reactions are grouped and ordered using a system widely adopted in publications of the National Institute of Standards and Technology. The grouping is made on the basis of the attacking atom or radical in the order set out in the following list.

O Atom Reactions
O_2 Reactions
H Atom Reactions
H_2 Reactions
OH Radical Reactions
H_2O Reactions
HO_2 Radical Reactions
H_2O_2 Reactions
N Atom Reactions
NH Radical Reactions
NH_2 Radical Reactions
C_2 Radical Reactions
CH Radical Reactions

$^3CH_2$ Radical Reactions
$^1CH_2$ Radical Reactions
CH_3 Radical Reactions
CH_4 Reactions
CHO Radical Reactions
HCHO Reactions
CH_2OH Radical Reactions
CH_3O Radical Reactions
CH_3OOH Reactions
CN Radical Reactions
NCO Radical Reactions
C_2H Radical Reactions
C_2H_3 Radical Reactions
C_2H_4 Reactions
C_2H_5 Radical Reactions
C_2H_6 Reactions
CHCO Radical Reactions
CH_2CHO Radical Reactions
CH_3CO Radical Reactions
CH_3CHO Reactions
C_2H_5O Radical Reactions
C_2H_5OOH Reactions
C_6H_5 Radical Reactions
C_6H_6 Reactions
C_6H_5O Radical Reactions
$C_6H_5CH_2$ Radical Reactions
$C_6H_5CH_3$ Reactions
p-$C_6H_4(CH_3)_2$ Reactions
$C_6H_5C_2H_5$ Radical Reactions

Thus the reaction

$$CN + CH_4 \rightarrow HCN + CH_3$$
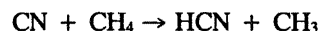
will be found under CN radical reactions. For reactions not classified by this rule e.g. radical-radical reactions, the rule that species higher on the list take precedence over those lower applies. Thus the reaction

$$OH + CH_3 + M \rightarrow CH_3OH + M$$
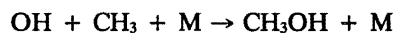
will be found under OH radical reactions. The same rule applies to reactions between species of a non-radical nature. For the purposes of the classification O_2 and NO are treated as radicals only in their reactions with non-radical species.

For each reaction a data sheet is presented setting out relevant thermodynamic data, rate coefficient measurements, an asessment of the reliability of the data, references, and, as well, preferred values of the rate coefficients are suggested. In deciding on a format for the presentation we have been influenced by the data sheets prepared by the CODATA Task Group for Modelling Atmospheric Chemistry[1]. Our format follows theirs closely but we have made more extensive use of graphs because of the need to convey some idea of the quality of the data over a wide temperature range.

The evaluations were carried out at a series of meetings, the last one being in January, 1989. The literature searching was terminated in December, 1988 but material available to us in pre-print form at that time was also included.

2.2. Conventions Concerning Rate Coefficients

It is assumed that all reactions in the compilation are elementary reactions.

The relationship between rate and rate coefficient for a reaction described by a stoichiometric equation such as

$$A + A \rightarrow B + C$$
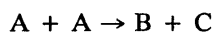
is given by

$$\text{Rate} = -(\tfrac{1}{2})d[A]/dt = d[B]/dt = d[C]/dt = k[A]^2 .$$

2.3. Guide to the Tables

Each data sheet begins with a heading giving all the reaction paths considered feasible whether there is evidence for their occurrence or not.

These are followed by the thermodynamic quantities $\Delta H°$ and $\Delta S°$ at 298 K and an expression for the equilibrium constant, K, in units of atmospheres, for each of the reaction channels for which there are data available. All data refer to a standard state of 1 atmosphere. The source of the thermodynamic data is discussed later in this Preface.

The kinetic data for the reactions are summarized under the two headings (i) Rate Coefficient Measurements (ii) Reviews and Evaluations. To keep the size of the compilation within reasonable bounds, in most cases only the rate coefficient measurements back to the most recent comprehensive review are recorded. Where there is no suitable review, or where there are only few measurements, all of the measured values are tabulated. Also to limit the size of the review, if in a particular study, measurements of the rate coefficient have been made over a range of temperatures, the results are tabulated as a temperature dependent expression (usually Arrhenius in form) rather than as the individually reported data points. For bimolecular reactions the temperature dependence of the rate coefficient is expressed either as $k = A \exp(-B/T)$ or $AT^n \exp(-C/T)$ whichever is the more

appropriate, where A, n, B and C are constants. In some cases the form with $C = 0$, leading to $k = AT^n$, gives the best representation. The expressions used for pressure dependent combination and dissociation reactions are discussed in detail later.

The tables of data are supplemented by a series of Comments summarizing the experimental details. For measurements giving rate coefficient ratios the absolute value derived from them and given in the table may be different from that quoted in the original paper because the evaluator has chosen to use a value of the reference rate coefficient different from that used by the original author. Such differences are indicated and justified by appropriate entries in the *Comments* section.

Under *Preferred Values* the rate coefficient values recommended for use by modellers are presented as a temperature dependent expression over a stated temperature range. Wherever possible an attempt has been made to make recommendations for high temperatures even if this requires a considerable extrapolation from the low temperature data and consequent assignment of large error limits. However, in many cases, particularly for reactions likely to have a large activation energy, or where alternative reaction channels may become important, it has not been considered safe to extrapolate much beyond the range of existing measurements.

Wherever possible the preferred values are based almost exclusively on experimental data but in a few cases estimates have been made based on analogous reactions. No attempt has been made to include calculated values of rate parameters but theoretical and empirical estimates have not been ignored. They have often provided valuable background and guidance on whether experimental values are 'reasonable'.

The preferred rate constant expression is followed by a statement of the error limits in log k at the extremes of the recommended temperature range. Some comments on the assignment of errors are given later in this Introduction.

The section "*Comments on Preferred Values*" contains a brief account of how expressions for the preferred values were arrived at and comments on the quality of the available data.

The data sheets conclude with a list of the relevant references and in many cases graphs to illustrate the quality of the data. Where there are few data points for a particular reaction all are recorded but for well studied reactions, where much data are available, for the sake of clarity, expressions, rather than the original points, are displayed in some cases.

2.4. Treatment of Combination and Dissociation Reactions

The rates of combination and the reverse dissociation reactions

$$A + B + M \rightleftharpoons AB + M,$$
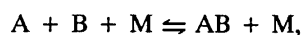
depend on the temperature, T, the nature, and the concentration of the third body [M]. The rate coefficients of these reactions have to be expressed in a form which is more complicated than those for simple bimolecular reactions. The combination reactions are described by a pseudo-second-order rate law.

$$\frac{d[AB]}{dT} = k[A][B]$$

in which the second-order rate constant depends on [M]. The low pressure third-order limit is characterized by k_0,

$$k_0[M] = \lim_{[M] \to 0} k([M])$$

The high-pressure second-order limit is characterized by k_∞,

$$k_\infty = \lim_{[M] \to \infty} k([M])$$

which is independent of [M]. For a combination reaction in the low-pressure range, the summary table gives a second-order rate constant expressed as the product of a third-order rate constant and the third body concentration. The transition between the third-order and the second-order range is represented by a reduced fall off expression of k/k_∞ as a function of

$$k_0[M]/k_\infty = [M]/[M]_c,$$

where the "centre of the falloff curve" $[M]_c$ indicates the third body concentration for which the extrapolated k_0 would be equal to k_∞. The dependence of k on [M] in general is complicated and has to be analyzed by unimolecular rate theory. For moderately complex molecules at not too high temperatures, however, a simple approximate relationship holds:

$$k = \frac{k_0 k_\infty [M]}{k_0[M] + k_\infty} F = k_0[M] \left(\frac{1}{1+[M]/[M]_c}\right)F$$

$$= k_\infty \left(\frac{[M]/[M]_c}{1+[M]/[M]_c}\right)F$$

where the first factors at the rhs represent the Lindemann-Hinshelwood expression, and the additional broadening factor F, at not too high temperature, is approximately given by

$$\log F \cong \frac{\log F_c}{1+\left[\dfrac{\log([M]/[M]_c)}{N}\right]^2}$$

where $n = 0.75 - 1.27 \log F_c$. In this way the three quantities, k_0, k_∞, and F_c with

$$[M]_c = \frac{k_\infty}{k_0},$$

characterize the falloff curve for the present application.

Alternatively, the three quantities k_∞, $[M]_c$, and F_c (or k_0, $[M]_c$, and F_c) can be used. The temperature dependence of F_c, which is sometimes significant, can be estimated by the procedure of Troe[2-4]. The results can usually be represented[4] approximately by an equation

$$F_c = (1-a)\exp(-T/T^{***}) + a\exp(-T/T^*) + \exp(-T^{**}/T).$$

The two first terms are of importance for atmospheric conditions, but the last term in most cases becomes relevant only at high temperatures.

Theoretical predictions[2-4] of F_c have been derived from rigid RRKM-type models including weak collision effects. Systematic calculations of this type have been presented by Patrick and Golden[5] for reactions of atmospheric interest. It is debatable whether these calculations can be applied to radical recombination reactions without barriers, where rotational effects are important. Changes in F_c would require changes in the limiting k_0 and k_∞ values. For the purpose of this evaluation, this will be irrelevant in most cases, if the preferred k_0 and k_∞ are used consistently together with the preferred F_c values.

If detailed calculations are made it is sometimes found that alternative expressions for F_c may be more appropriate.

The dependence of k_0 and k_∞ on the temperature is represented in the T exponent n,

$$k \propto T^{-n}$$

(except for the cases with an established energy barrier in the potential). We have used this form of temperature dependence because it often gives a better fit to the data over a wider range of temperature than does the Arrhenius expression. The dependence of k_0 on the nature of the third body M generally is represented by the relative efficiencies of M_1 and M_2.

$$k_0(M_1)/[M_1] : k_0(M_2)/[M_2] .$$

2.5. Assignment of Errors

The reliability of a preferred expression for k is expressed in terms of an estimated $\Delta\log k$ at the extremes of the temperature range covered by the recommended expression. Thus a quoted $\Delta\log k = X$ is equivalent to the statement that k is uncertain by a factor F where $X = \log F$.

No attempt has been made to assign explicit error limits to the temperature coefficient of k. The assignment of error limits in $\Delta\log k$ at the extremes of the temperature range indicates how the quality of the data varies with temperature without attempting to define the form which this variation takes. In the opinion of the evaluators the available data rarely merits a more elaborate assignment of errors over a wide temperature range.

The assignment of error limits in k is a subjective assessment by the evaluators. Modern techniques are capable in favourable circumstances of measuring rate coefficients with a precision represented by a standard deviation as small as 10%. However, data obtained in different laboratories on the same reaction and often by the same technique are rarely concordant to the extent that might be expected from the precision of the measurements; mean values may differ by many standard deviations. This is indicative of systematic errors which are difficult to detect and which cannot be simply incorporated into quoted error limits.

2.6. Thermodynamic Data

There are substantial uncertainties associated with the thermodynamic data of a number of species appearing in the compilation. For the sake of internal consistency the thermodynamic data have been taken from a single compilation, that prepared for the Sandia Chemkin Program.[6] That compilation is sufficiently comprehensive to cover most of the species appearing in the kinetics tables. In a few cases the present evaluation of the kinetic data have led to an assignment of enthalpies of formation at variance with those in the thermodynamic data base.This has been commented on in the text but has not been incorporated into the thermodynamic data quoted. The Sandia compilation does not include data for aromatic compounds. The data for these have been derived from a variety of sources.

In the present tables the standard enthalpy change at 298 K and the equilibrium constant as a function of temperature are given for each reaction channel. the equilibrium constant is expressed in the form $K = AT^n\exp(B/T)$, where A, B and n are constants. The quality of the thermodynamic data rarely justify the use of expressions for $K(T)$ involving more than three constants even though the Sandia data compilation expresses the thermodynamic quantities in terms of polynomials involving seven coefficients. To obtain the expression for $K(T)$ values of K were calculated from the Sandia data base at several temperatures over the range 300–6000 K and fitted to the three constant expressions by a least squares procedure.

Because of the great sensitivity of K to the thermodynamic quantities, particularly $\Delta H°$, any rate coefficient calculated from the equilibrium constant and the rate coefficient for the reaction in one direction may be subject to substantial uncertainty.

Wherever kinetic data are available for the rate coefficient for the reaction in both forward and reverse directions, an attempt has been made to reconcile it with the thermodynamic data quoted. For a number of important species there are no thermodynamic data available pointing to the need for experimental measurements aimed at providing such data, particularly for key radicals.

2.7. Acknowledgements

We gratefully acknowledge the assistance of Drs. S. Butler, J. Davies, H. H. Grotheer, G. Hayman, D. Horne, K. Hughes, M. Jenkin, T. Murrel, J. Pimpel, K. Proudler, S. Saunders, P. Seakins, N. Stothard and S. Watts in the preparation of these data sheets.

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3. Index of Reactions and Summary Table
3.1. Guide to the Summary Tables

There are three tables. In Table 1 all of the reactions whose rate data were evaluated in the present programme are listed. For each reaction the preferred value of the rate coefficient, the temperature range over which it applies, and the associated error limits are given.

For many reactions more than one set of products is possible. All of the channels considered feasible are given and wherever possible rate parameters are recommended for each channel, or branching ratios are given. For such multichannel reactions, however, where the dominant channel has been identified that channel only is specified although others are conceivable.

All of the reactions evaluated are listed in Table 1 but only the rate data for bimolecular processes are given. The data for decomposition and recombination reactions are listed separately in Tables 2 and 3.

Tables 2 and 3 contain the preferred rate parameters for decomposition and combination reactions respectively. The rate data are expressed in terms of the symbolism developed by Troe and described in Sec. 2.4.

3.2. Summary of Preferred Rate Data

TABLE 1. Bimolecular reactions

Reaction	k/cm^3 molecule^{-1}s^{-1}	Temp/K	Error limits ($\Delta \log k$)	Page
O Atom Reactions				430
O + H$_2$ → OH + H	$8.5 \times 10^{-20}T^{2.67} \exp(-3160/T)$	300–2500	± 0.5 at 300 K falling to ± 0.2 for $T > 500$ K	430
O + OH → O$_2$ + H	$2.0 \times 10^{-11} \exp(112/T)$ $2.4 \times 10^{-11} \exp(-353/T)$	220–500 1000–2000	± 0.2 ± 0.1	432
O + HO$_2$ → OH + O$_2$	5.3×10^{-11}	300–1000	± 0.3 at 300 K rising to ± 0.5 at 1000 K.	434
O + H$_2$O$_2$ → OH + HO$_2$	$1.1 \times 10^{-12} \exp(-2000/T)$	300–500	± 0.3	437
O + NH$_3$ → OH + NH$_2$	$1.6 \times 10^{-11} \exp(-3670/T)$	500–2500	± 0.5	439
O + CH → CO + H → CHO$^+$ + e	6.6×10^{-11} $4.2 \times 10^{-13} \exp(-850/T)$	300–2000 300–2500	± 0.5 ± 0.5	441
O + ^{3}CH$_2$ → CO + 2H → CO + H$_2$	2×10^{-10} $k_1/k = 0.6 \pm 0.3$ over whole range	300–2500	± 0.2 at 300 K rising to ± 0.7 at 2500 K.	443
O + CH$_3$ → HCHO + H	1.4×10^{-10}	300–2500	± 0.2	444
O + CH$_4$ → OH + CH$_3$	$1.5 \times 10^{-15} T^{1.56} \exp(-4270/T)$	300–2500	± 0.3 at 300 K falling to ± 0.15 at 2500 K.	445
O + CHO → OH + CO → CO$_2$ + H	5.0×10^{-11} 5.0×10^{-11}	300–2500 300–2500	± 0.3 ± 0.3	448
O + HCHO → OH + CHO	$6.9 \times 10^{-13} T^{0.57} \exp(-1390/T)$	250–2200	± 0.1 at 250 K rising to ± 0.3 at 2200 K.	449
O + CH$_3$O → O$_2$ + CH$_3$ → OH + HCHO	2.5×10^{-11} $k_2/k = (0.12 \pm 0.1)$ at 300 K	300–1000	± 0.3 at 300 K rising to ± 0.7 at 1000 K.	451
O + CN → CO + N(^{4}S) → CO + N(^{2}D)	1.7×10^{-11}	300–5000	± 0.2 at 300 K rising to ± 0.6 × 5000 K.	452
O + NCO → NO + CO → O$_2$ + CN	7.0×10^{-11}	1450–2600	± 0.8	454
O + HCN → NCO + H → CO + NH → OH + CN	$2.3 \times 10^{-18} T^{2.1} \exp(-3075/T)$	450–2500	± 0.2 at 450 K rising to ±0.3 at 2500 K.	455
O + CH$_3$OOH → OH + CH$_2$COOH → OH + CH$_3$O$_2$	$6.9 \times 10^{-13} T^{0.57} \exp(-1390/T)$ [estimate]	250–2200	± 0.1 at 250 K rising to ± 0.3 at 2200 K.	458
O + C$_2$H → CO + CH	1.7×10^{-11}	300–2500	± 1.0	458
O + C$_2$H$_2$ → CO + ^{3}CH$_2$ → CHCO + H	$3.6 \times 10^{-20} T^{2.8} \exp(-250/T)$ $k_1/k = 0.5 \pm 0.3$ over whole range.	300–2500	± 0.2	459
O + C$_2$H$_3$ → OH + C$_2$H$_2$ → CO + CH$_3$ → HCO + CH$_2$	5×10^{-11}	300–2000	± 0.5	463
O + C$_2$H$_4$ → CH$_2$CHO + H → HCO + CH$_3$ → HCHO + CH$_2$ → CH$_2$CO + H$_2$	$5.75 \times 10^{-18} T^{2.08}$ $k_1/k = 0.35 \pm 0.05$ at p> 3 Torr $k_2/k = 0.6 \pm 0.10$	300–2000 over whole temperature range	± 0.1 for $T < 1000$ K rising to ± 0.3 at 2000 K.	464
O + C$_2$H$_5$ → CH$_3$CHO + H → HCHO + CH$_3$	1.1×10^{-10} $k_2/k = 0.17 \pm 0.2$ at 300 K	300–2500	± 0.3 from 300 to 1000 K ± 0.5 from 1000 to 2500 K	467

TABLE 1. Bimolecular reactions — Continued

Reaction	k/cm^3 molecule^{-1}s^{-1}	Temp/K	Error limits ($\Delta \log k$)	Page
O + C$_2$H$_6$ → OH + C$_2$H$_5$	$1.66 \times 10^{-15} T^{1.5} \exp(-2920/T)$	300–1200	± 0.3 at 300 K falling to ± 0.15 at 1200 K.	468
O + CHCO → 2CO + H	1.6×10^{-10}	300–2500	± 0.3	470
O + CH$_2$CO → CH$_2$O + CO → HCO + H + CO → HCO + HCO	$3.8 \times 10^{-12} \exp(-680/T)$	230–500	± 0.3	471
O + CH$_3$CHO → OH + CH$_3$CO → OH + CH$_2$CHO	$9.7 \times 10^{-12} \exp(-910/T)$	300–1500	± 0.05 at 300 K rising to ± 0.5 at 1500 K.	473
O + C$_2$H$_5$OOH → OH + C$_2$H$_4$OOH → OH + C$_2$H$_5$OO	$6.9 \times 10^{-13} T^{0.57} \exp(-1390/T)$ [estimate]	250–2200	± 0.1 at 150 K rising to ± 0.3 at 2200 K.	475
O + C$_6$H$_6$ → OH + C$_6$H$_5$ → C$_6$H$_5$OH	$1.2 \times 10^{-22} T^{3.7} \exp(-570/T)$	300–1000	± 0.5	475
O + C$_6$H$_5$CH$_2$ → HCO + C$_6$H$_6$ → C$_6$H$_5$CH + H → CH$_2$O + C$_6$H$_5$	5.5×10^{-10} No recommendation	300	±0.3	478
O + C$_6$H$_5$CH$_3$ → products	$5.3 \times 10^{-15} T^{1.21} \exp(-1260/T)$	300–2800	± 0.1 at 300 K rising to ± 0.4 at 2800 K	478
O + p-C$_6$H$_4$(CH$_3$)$_2$ → products	$2.6 \times 10^{-11} \exp(-1409/T)$	300–600	± 0.3	481
O + C$_6$H$_5$C$_2$H$_5$ → products	1.0×10^{-13}	298	± 0.3	483
O$_2$ Reactions				483
O$_2$ + CH$_4$ → HO$_2$ + CH$_3$	$6.6 \times 10^{-11} \exp(-28630/T)$	500–2000	± 0.5 at 500 K rising to ± 1.0 at 2000 K.	483
O$_2$ + C$_2$H$_6$ → HO$_2$ + C$_2$H$_5$	$1.0 \times 10^{-10} \exp(-26100/T)$	500–2000	± 0.5 at 500 K rising to ± 1.0 at 2000 K	484
O$_2$ + HCHO → HO$_2$ + HCO	$1.0 \times 10^{-10} \exp(-20460/T)$	700–1000	± 0.5	484
O$_2$ + CH$_3$CHO → HO$_2$ + CH$_3$CO	$5.0 \times 10^{-11} \exp(-19700/T)$	600–1100	± 0.5 at 600 K rising to ± 1.0 at 1100 K.	485
H Atom Reactions				486
H + O$_2$ → OH + O	$3.3 \times 10^{-10} \exp(-8460/T)$	300–2500	± 0.1 at 300 K rising to ± 0.2 at 2500 K.	486
H + O$_2$ + Ar → HO$_2$ + Ar	See Table 3			488
H + O$_2$ + H$_2$ → HO$_2$ + H$_2$	See Table 3			488
H + O$_2$ + N$_2$ → HO$_2$ + N$_2$	See Table 3			488
H + O$_2$ + H$_2$O → HO$_2$ + H$_2$O	See Table 3			488
H + H + Ar → H$_2$ + Ar	See Table 3			492
H + H + H$_2$ → H$_2$ + H$_2$	See Table 3			495
H + OH + H$_2$O → H$_2$O + H$_2$O	See Table 3			497
H + OH + Ar → H$_2$O + Ar	See Table 3			496
H + HO + N$_2$ → H$_2$O + N$_2$	See Table 3			498

TABLE 1. Bimolecular reactions — Continued

Reaction	k/cm^3 molecule^{-1}s^{-1}	Temp/K	Error limits ($\Delta \log k$)	Page
H + HO$_2$ → H$_2$ + O$_2$	7.1×10^{-11} exp($-710/T$)	300–1000	± 0.3	499
→ 2 OH	2.8×10^{-10} exp($-440/T$)	300–1000	± 0.3	
→ H$_2$O + O	5.0×10^{-11} exp($-866/T$)	300–1000	± 0.3	
H + H$_2$O → OH + H$_2$	7.5×10^{-16} $T^{1.6}$ exp($-9270/T$)	300–2500	±0.2	504
H + H$_2$O$_2$ → H$_2$ + HO$_2$	2.8×10^{-12} exp($-1890/T$)	300–1000	± 0.3	506
→ OH + H$_2$O	1.7×10^{-11} exp($-1800/T$)	300–1000	± 0.3	
H + NH → H$_2$ + N	1.7×10^{-11}	1500–2500	± 1.0	509
H + NH$_2$ → H$_2$ + NH	1.0×10^{-11}	2000–3000	± 1.0	509
H + ^{3}CH$_2$ → H$_2$ + CH	1.0×10^{-11} exp($900/T$)	300–3000	± 0.7	510
H + CH$_3$ → H$_2$ + ^{1}CH$_2$	1.0×10^{-10} exp($-7600/T$)	300–2500	± 1.0	511
→ CH$_4$	See Table 3			
H + CH$_4$ → H$_2$ + CH$_3$	2.2×10^{-20} $T^{3.0}$ exp($-4045/T$)	300–2500	± 0.2	516
H + CHO → H$_2$ + CO	1.5×10^{-10}	300–2500	± 0.3	519
H + HCHO → H$_2$ + HCO	3.8×10^{-14} $T^{1.05}$ exp($-1650/T$)	300–2200	± 0.1 at 300 K rising to ± 0.5 at 2200 K	521
H + CH$_3$O → H$_2$ + HCHO	3.0×10^{-11}	300–1000	± 0.5	523
H + HNCO → NH$_2$ + CO	No recommendation			523
→ H$_2$ + NCO	3.4×10^{-10} $T^{-0.27}$ exp($-10190/T$)	500–1000	± 1.0	
H + NCO → NH + CO	8.7×10^{-11}	1400–1500	± 0.5	524
→ HCN + O				
H + C$_2$H$_2$ → H$_2$ + C$_2$H	1.0×10^{-10} exp($-14000/T$)	1000–3000	± 1.0	525
→ C$_2$H$_3$	See Table 3			
H + C$_2$H$_3$ → H$_2$ + C$_2$H$_2$	2.0×10^{-11}	300–2500	± 0.5	528
→ C$_2$H$_4$	See Table 3			
H + C$_2$H$_4$ → C$_2$H$_3$ + H$_2$	9.0×10^{-10} exp($-7500/T$)	700–2000	± 0.5	529
→ C$_2$H$_5$	See Table 3			
H + C$_2$H$_5$ → 2CH$_3$	6.0×10^{-11}	300–2000	± 0.3	531
→ C$_2$H$_6$	See Table 3			
H + C$_2$H$_6$ → H$_2$ + C$_2$H$_5$	2.4×10^{-15} $T^{1.5}$ exp($-3730/T$)	300–2000	± 0.15 at 300 K rising to ± 0.3 at 2000 K	533
H + CHCO → CH$_2$ + CO				
→ H$_2$ + C$_2$O	2.5×10^{-10}	300–2500	± 0.4	536
→ HCCOH				
H + CH$_2$CO → CH$_3$ + CO	3.0×10^{-11} exp($-1700/T$)	200–2000	± 0.5 at 200 K rising to ± 1.0 at 2000 K.	537
→ CH$_2$CHO	k_2/k very small			
H + CH$_3$CHO → H$_2$ + CH$_3$CO	6.8×10^{-15} $T^{1.16}$ exp($-1210/T$)	300–2000	± 0.1 at 300 rising to ± 0.4 at 2000 K.	539
→ H$_2$ + CH$_2$CHO				
H + C$_6$H$_5$ + M → C$_6$H$_6$ + M	See Table 3			541
H + C$_6$H$_6$ → H$_2$ + C$_6$H$_5$	No recommendation			541
→ C$_6$H$_7$	See Table 3			
H + C$_6$H$_5$O + M → C$_6$H$_5$OH + M	See Table 3			544

TABLE 1. Bimolecular reactions — Continued

Reaction	k/cm^3 molecule^{-1}s^{-1}	Temp/K	Error limits ($\Delta \log k$)	Page
H + C$_6$H$_5$OH → C$_6$H$_5$O + H$_2$	1.9×10^{-10} exp($-6240/T$)	1000–1150	± 0.3	544
→ C$_6$H$_6$ + OH	3.7×10^{-11} exp($-3990/T$)	1000–1150	± 0.3	
H + C$_6$H$_5$CH$_2$ + M → C$_6$H$_5$CH$_3$ + M	See Table 3			545
H + C$_6$H$_5$CH$_3$ → H$_2$ + C$_6$H$_5$CH$_2$	6.6×10^{-22} $T^{3.44}$ exp($-1570/T$)	600–2800	± 0.3 at 600 K rising to	546
→ H$_2$ + C$_6$H$_4$CH$_3$	No recommendation		± 0.5 at 2800 K.	
→ C$_6$H$_6$ + CH$_3$	No recommendation			
→ C$_6$H$_6$CH$_3$	See Table 3			
H + p-C$_6$H$_4$(CH$_3$)$_2$ → products	5.8×10^{-13}	298	± 0.1	549
H + C$_6$H$_5$C$_2$H$_5$ → H$_2$ + C$_6$H$_5$C$_2$H$_4$	2.4×10^{-12}	773	± 0.1	549
→ C$_6$H$_6$C$_2$H$_5$	See Table 3			

H$_2$ Reactions   550

Reaction	k/cm^3 molecule^{-1}s^{-1}	Temp/K	Error limits ($\Delta \log k$)	Page
H$_2$ + Ar → 2H + Ar	See Table 2			550
H$_2$ + H$_2$ → 2H + H$_2$	See Table 2			550

OH Radical Reactions   552

Reaction	k/cm^3 molecule^{-1}s^{-1}	Temp/K	Error limits ($\Delta \log k$)	Page
OH + H$_2$ → H$_2$O + H	1.7×10^{-16} $T^{1.6}$ exp($-1660/T$)	300–2500	± 0.1 at 300 K rising to ± 0.3 at 2500 K	552
OH + OH → H$_2$O + O	2.5×10^{-15} $T^{1.14}$ exp($-50/T$)	250–2500	± 0.2	555
OH + OH + M → H$_2$O$_2$ + M	See Table 3			556
OH + HO$_2$ → H$_2$O + O$_2$	4.8×10^{-11} exp($250/T$)	300–2000	± 0.2 at 300 K rising to ± 0.5 at 2000 K.	558
OH + H$_2$O$_2$ → H$_2$O + HO$_2$	1.3×10^{-11} exp($-670/T$)	300–1000	± 0.2	562
OH + NH → NO + H$_2$	8.0×10^{-11}	300–1000	± 0.5	565
→ H$_2$O + N				
OH + NH$_2$ → O + NH$_3$	3.3×10^{-14} $T^{0.405}$ exp($-250/T$)	500–2500	± 0.5	565
→ H$_2$O + NH	No recommendation			
OH + CO → H + CO$_2$	1.05×10^{-17} $T^{1.3}$ exp($250/T$)	300–2000	± 0.2 at 300 K rising to ± 0.5 at 2000 K.	566
OH + CH$_3$ → H + CH$_2$OH				
→ H + CH$_3$O	6.0×10^{-11}	300–2000	± 0.7	570
→ H$_2$O + ^{1}CH$_2$				
→ CH$_3$OH	See Table 3			
OH + CH$_4$ → H$_2$O + CH$_3$	2.6×10^{-17} $T^{1.83}$ exp($-1400/T$)	250–2500	± 0.07 at 250 K rising to ± 0.15 at 1200 K.	571
OH + CHO → H$_2$O + CO	1.7×10^{-10}	300–2500	± 0.3	574
OH + HCHO → H$_2$O + CHO	5.7×10^{-15} $T^{1.18}$ exp($225/T$)	300–3000	± 0.1 at 300 K rising to ± 0.7 at 3000 K.	575
OH + CN → O + HCN	1.0×10^{-10}	1500–3000	± 0.5	578
→ NCO + H				
OH + HCN → H$_2$O + CN	1.5×10^{-11} exp($-5400/T$)	1500–2500	± 0.5	579
→ HOCN + H	No recommendation			
→ HNCO + H				

TABLE 1. Bimolecular reactions — Continued

Reaction	k/cm^3 molecule^{-1}s^{-1}	Temp/K	Error limits (Δ log k)	Page
OH + CH$_3$OOH → H$_2$O + CH$_3$OO	1.2×10^{-12} exp(130/T)	300–1000	± 0.2 at 300 K rising to ± 0.4 at 1000 K	582
→ H$_2$O + CH$_2$OOH	1.8×10^{-12} exp(220/T)	300–1000	± 0.1 at 300 K rising to ±0.3 at 1000 K	
OH + C$_2$H$_2$ → H$_2$O + C$_2$H ⎤ → H + CH$_2$CO ⎦	1.0×10^{-10} exp($-6500/T$)	1000–2000	± 1.0	583
→ C$_2$H$_2$OH	See Table 3			
OH + C$_2$H$_4$ → H$_2$O + C$_2$H$_3$	3.4×10^{-11} exp($-2990/T$)	650–1500	± 0.5	586
OH + C$_2$H$_6$ → H$_2$O + C$_2$H$_5$	1.2×10^{-17} $T^{2.0}$ exp($-435/T$)	250–2000	± 0.07 at 250 K rising to ± 0.15 at 2000 K	589
OH + CH$_2$CO → CH$_2$OH + CO ⎤ → H$_2$CO + HCO ⎦	1.7×10^{-11}	300–2000	± 1.0	592
OH + CH$_3$CHO → H$_2$O + CH$_3$CO ⎤ → H$_2$O + CH$_2$CHO ⎦	3.9×10^{-14} $T^{0.73}$ exp(560/T)	250–1200	± 0.1 at 250 K rising to ± 0.3 at 1200 K	593
OH + C$_2$H$_5$OOH → H$_2$O + C$_2$H$_5$OO ⎤ → H$_2$O + C$_2$H$_4$OOH ⎦	3.0×10^{-12} exp(190/T) [estimate]	250–1000	± 0.3 at 250 K rising to ± 0.7 at 1000 K	595
OH + C$_6$H$_6$ → H$_2$O + C$_6$H$_5$	2.7×10^{-16} $T^{1.42}$ exp($-730/T$)	400–1500	± 0.3	595
→ H + C$_6$H$_5$OH	2.2×10^{-11} exp($-5330/T$)	1000–1150	± 0.3	
→ C$_6$H$_6$OH	See Table 3			
OH + C$_6$H$_5$OH → C$_6$H$_5$(OH)$_2$	See Table 3			598
→ H$_2$O + C$_6$H$_5$O ⎤				
→ H$_2$O + C$_6$H$_4$OH ⎦	1.0×10^{-11}	1000–1150	± 0.5	
OH + C$_6$H$_5$CH$_3$ → H$_2$O + C$_6$H$_2$CH$_2$	8.6×10^{-15} exp($-1440/T$)	400–1200	± 0.5 at 400 K reducing to ±0.3 at 1200 K	598
→ C$_6$H$_5$CH$_3$OH	See Table 3			
OH + p-C$_6$H$_4$(CH$_3$)$_2$ → C$_6$H$_4$CH$_2$CH$_3$ + H$_2$O	6.4×10^{-11} exp($-1440/T$)	500–960	±0.1	601
→ p-C$_6$H$_4$(CH$_3$)$_2$OH	See Table 3			
OH + C$_6$H$_5$C$_2$H$_5$ → HOC$_6$H$_5$C$_2$H$_5$	See Table 3			
→ H$_2$O + C$_6$H$_5$C$_2$H$_4$ ⎤ → H$_2$O + C$_6$H$_4$C$_2$H$_5$ ⎦	8.7×10^{-12}	773	± 0.1	603
H$_2$O Reactions				603
H$_2$O + M → H + OH + M	See Table 2			603
HO$_2$ Radical Reactions				604
HO$_2$ + HO$_2$ → H$_2$O$_2$ + O$_2$	3.1×10^{-12} exp($-775/T$)	550–1250	± 0.15 at 550 K rising to ± 0.3 at 1250 K	604
HO$_2$ + NH$_2$ → NH$_3$ + O$_2$ ⎤ → HNO + H$_2$O ⎦	2.6×10^{-11}	300–400	± 0.4	607
HO$_2$ + CH$_3$ → OH + CH$_3$O	3×10^{-11}	300–2500	± 0.7	608
→O$_2$ + CH$_4$	No recommendation			
HO$_2$ + CH$_4$ → H$_2$O$_2$ + CH$_3$	1.5×10^{-11} exp($-12400/T$)	600–1000	± 0.2 at 600 K rising to ± 0.3 at 1000 K	608
HO$_2$ + HCHO → H$_2$O$_2$ + CHO	5.0×10^{-12} exp($-6580/T$)	600–1000	± 0.5	609

TABLE 1. Bimolecular reactions — Continued

Reaction	k/cm^3 molecule^{-1}s^{-1}	Temp/K	Error limits ($\Delta \log k$)	Page
$HO_2 + C_2H_4 \rightarrow OH + C_2H_4O$	$3.7 \times 10^{-12} \exp(-8650/T)$	600–900	± 0.15 at 600 K rising to ± 0.25 at 900 K.	612
$HO_2 + C_2H_6 \rightarrow H_2O_2 + C_2H_5$	$2.2 \times 10^{-11} \exp(-10300/T)$	500–1000	± 0.2 at 500 K rising to ± 0.3 at 1000 K.	614
$HO_2 + CH_3CHO \rightarrow H_2O_2 + CH_3CO$	$5.0 \times 10^{-12} \exp(-6000/T)$	900–1200	± 0.7	614
H_2O_2 Reactions				615
$H_2O_2 + M \rightarrow 2OH + M$	See Table 2			615
N Atom Reactions				616
$N + CN \rightarrow N_2 + C$	3×10^{-10}	300–2500	± 1.0	616
$N + NCO \rightarrow NO + CN$	No recommendation			617
$\rightarrow N_2 + CO$	3.3×10^{-11}	1700	± 0.5	
NH Radical Reactions				617
$NH + O_2 \rightarrow NO + OH$ $\rightarrow NO_2 + H$ $\rightarrow HNO + O$	$1.26 \times 10^{-13} \exp(-770/T)$	270–550	± 0.2 at 270 K rising to ± 0.5 at 550 K.	617
$NH + NO \rightarrow N_2O + H$ $\rightarrow HN_2 + O$ $\rightarrow N_2 + OH$	5.0×10^{-11}	270–380	± 0.2	618
NH_2 Radical Reactions				621
$NH_2 + O_2 \rightarrow$ products	$<3 \times 10^{-18}$	298		621
$NH_2 + NO \rightarrow N_2 + H_2O$ $\rightarrow N_2 + H + OH$ $\rightarrow N_2H + OH$ $\rightarrow N_2O + H_2$	$1.8 \times 10^{-12} \exp(650/T)$ $(k_2 + k_3)/k \approx 0.12$ at 298 K.	220–2000	± 0.5	622
$^1C_2$ and $^3C_2$ Radical Reactions	See data sheets.			625
CH Radical Reactions				627
$CH + O_2 \rightarrow CHO + O$ $\rightarrow CO + OH$	5.5×10^{-11}	300–2000	± 0.3 at 300 K rising to ± 0.5 at 2000 K.	627
$CH + H_2 \rightarrow CH_2 + H$ $\rightarrow CH_3$	$2.4 \times 10^{-10} \exp(-1760/T)$	300–1000	± 0.3	630
$CH + H_2O \rightarrow$ products	$9.5 \times 10^{-12} \exp(380/T)$	300–1000	± 1.0	632
$CH + CO \rightarrow$ products	$4.6 \times 10^{-13} \exp(860/T)$	300–1000	± 1.0	632
$CH + CO_2 \rightarrow$ products	$5.7 \times 10^{-12} \exp(-345/T)$	300–1000	± 1.0	633
$CH + CH_4 \rightarrow$ products	$5.0 \times 10^{-11} \exp(200/T)$	200–700	± 1.0	634
$CH + C_2H_2 \rightarrow$ products	$3.5 \times 10^{-10} \exp(61/T)$	200–700	± 1.0	634
$CH + C_2H_4 \rightarrow$ products	$2.2 \times 10^{-10} \exp(173/T)$	200–700	± 1.0	635
$CH + C_2H_6 \rightarrow$ products	$1.8 \times 10^{-10} \exp(132/T)$	200–700	± 1.0	636

TABLE 1. Bimolecular reactions — Continued

Reaction	k/cm³ molecule^{-1}s^{-1}	Temp/K	Error limits (Δ log k)	Page
CH + C$_3$H$_8$ → products	1.9×10^{-10} exp(240/T)	300–700	± 1.0	636
CH + n-C$_4$H$_{10}$ → products	4.4×10^{-10} exp(28/T)	250–700	± 1.0	637
CH + i-C$_4$H$_{10}$ → products	2.0×10^{-10} exp(240/T)	300–700	± 1.0	637
CH + neo-C$_5$H$_{12}$ → products	1.6×10^{-10} exp(340/T)	300–700	± 1.0	638
CH + CH$_3$C$_2$H → products	No recommendation			638
CH + CH$_2$O → products	1.6×10^{-10} exp(260/T)	300–700	± 1.0	639
^{3}CH$_2$ Radical Reactions				639
^{3}CH$_2$ + O$_2$ → CO + H + OH → CO$_2$ + H + H → CO + H$_2$O → CO$_2$ + H$_2$ → HCHO + O	4.1×10^{-11} exp($-750/T$)	300–1000	± 0.3 at 300 K rising to ± 0.5 at 1000 K.	639
^{3}CH$_2$ + ^{3}CH$_2$ → C$_2$H$_2$ + H$_2$ → C$_2$H$_2$ + 2H	2.0×10^{-10} exp($-400/T$) k_2/k = 0.9 ± 0.1 over range 300–3000 K.	300–3000	± 0.5	640
^{3}CH$_2$ + CH$_3$ → C$_2$H$_4$ + H	7.0×10^{-11}	300–3000	± 0.3 at 300 K rising to ± 0.5 at 3000 K.	641
^{3}CH$_2$ + C$_2$H$_2$ → C$_3$H$_4$	See Table 3			642
^{3}CH$_2$ + C$_2$H$_4$ → C$_3$H$_6$ → c-C$_3$H$_6$ → CH$_2$CHCH$_2$ + H	See Table 3			643
^{1}CH$_2$ Radical Reactions				644
^{1}CH$_2$ + Ar → ^{3}CH$_2$ + Ar	6.0×10^{-12}	300–2000	± 0.3	644
^{1}CH$_2$ + N$_2$ → ^{3}CH$_2$ + N$_2$	1.0×10^{-11}	300–2000	± 0.3	644
^{1}CH$_2$ + CH$_4$ → ^{3}CH$_2$ + CH$_4$	1.2×10^{-11}	300–2000	± 0.4	644
^{1}CH$_2$ + C$_2$H$_2$ → ^{3}CH$_2$ + C$_2$H$_2$	8.0×10^{-11}	300–2000	± 0.4	644
^{1}CH$_2$ + C$_2$H$_4$ → ^{3}CH$_2$ + C$_2$H$_4$	2.3×10^{-11}	300–2000	± 0.4	644
^{1}CH$_2$ + C$_2$H$_6$ → ^{3}CH$_2$ + C$_2$H$_6$	3.6×10^{-11}	300–2000	± 0.4	644
^{1}CH$_2$ + O$_2$ → CO + H + OH → CO$_2$ + H$_2$ → CO + H$_2$O → ^{3}CH$_2$ + O$_2$	5.2×10^{-11}	300–1000	± 0.3 at 300 K rising to ± 0.5 at 1000 K	645
^{1}CH$_2$ + H$_2$ → CH$_3$ + H	1.2×10^{-10}	300–1000	± 0.1 at 300 K rising to ± 0.3 at 1000 K	646
^{1}CH$_2$ + C$_2$H$_2$ → CH$_2$CCH$_2$ → CH$_3$CCH → CH$_2$CCH + H → ^{3}CH$_2$ + C$_2$H$_2$	See Table 3 See earlier entry			646
^{1}CH$_2$ + C$_2$H$_4$ → C$_3$H$_6$ → ^{3}CH$_2$ + C$_2$H$_4$	See Table 3 See earlier entry			647
CH$_3$ Radical Reactions				648
CH$_3$ + M → CH$_2$ + H + M	See Table 2			648

TABLE 1. Bimolecular reactions — Continued

Reaction	k/cm^3 molecule^{-1}s^{-1}	Temp/K	Error limits (Δ log k)	Page
CH$_3$ + O$_2$ → CH$_3$O + O	2.2×10^{-10} exp($-15800/T$)	300–2500	± 0.5	649
→ HCHO + OH	5.5×10^{-13} exp($-4500/T$)	1000–2500	± 0.5	
→ CH$_3$O$_2$	See Table 3			
CH$_3$ + H$_2$ → CH$_4$ + H	1.14×10^{-20} $T^{2.74}$ exp($-4740/T$)	300–2500	± 0.15 in the range 300–700 K. ± 0.3 in the range 700–2500 K.	653
CH$_3$ + CH$_3$ → C$_2$H$_5$ + H	5×10^{-11} exp($-6800/T$)	1300–2500	± 0.6	655
→ C$_2$H$_4$ + H$_2$	No recommendation (see data sheets)			
→ C$_2$H$_6$	See Table 3			
CH$_3$ + HCHO → CH$_4$ + HCO	6.8×10^{-12} exp($-4450/T$)	300 1000	± 0.3	659
CH$_3$ + C$_2$H$_2$ + M → C$_3$H$_5$ + M	See Table 3			661
→ CH$_4$ + C$_2$H	No recommendation			
CH$_3$ + C$_2$H$_4$ → CH$_4$ + C$_2$H$_3$	6.9×10^{-12} exp($-5600/T$)	400–3000	± 0.5	663
→ n-C$_3$H$_7$	See Table 3			
CH$_3$ + C$_2$H$_5$ → CH$_4$ + C$_2$H$_4$	1.9×10^{-12}	300–800	± 0.4	665
→ C$_3$H$_8$	See Table 3			
CH$_3$ + C$_2$H$_6$ → CH$_4$ + C$_2$H$_5$	2.5×10^{-31} $T^{6.0}$ exp($-3043/T$)	300–1500	± 0.1 at 300 K rising to ± 0.2 at 1500 K.	668
CH$_3$ + CH$_3$CHO → CH$_4$ + CH$_3$CO	3.3×10^{-30} $T^{5.64}$ exp($-1240/T$)	300–1250	± 0.3	671
→ CH$_4$ + CH$_2$CHO	No recommendation (see data sheets)			

CH$_4$ Reactions   673

Reaction	k/cm^3 molecule^{-1}s^{-1}	Temp/K	Error limits (Δ log k)	Page
CH$_4$ + M → CH$_3$ + H + M	See Table 2			673

CHO Radical Reactions   677

Reaction	k/cm^3 molecule^{-1}s^{-1}	Temp/K	Error limits (Δ log k)	Page
CHO + O$_2$ → CO + HO$_2$				677
→ OH + CO$_2$	5.0×10^{-12}	300–2500	± 0.3	
→ HCO$_3$				
CHO + CHO → HCHO + CO	5.0×10^{-11}	300	± 0.3	680

HCHO Reactions   681

Reaction	k/cm^3 molecule^{-1}s^{-1}	Temp/K	Error limits (Δ log k)	Page
HCHO + M → H + CHO + M	See Table 2			681
→ H$_2$ + CO + M				

CH$_2$OH Reactions   684

Reaction	k/cm^3 molecule^{-1}s^{-1}	Temp/K	Error limits (Δ log k)	Page
CH$_2$OH + O$_2$ → CH$_2$O + HO$_2$	2.6×10^{-9} $T^{-1.0}$ + 1.2×10^{-10} exp($-1800/T$)	300–1200	± 0.1 at 300 K rising to ± 0.3 at 1200 K.	684

CH$_3$O Radical Reactions   687

Reaction	k/cm^3 molecule^{-1}s^{-1}	Temp/K	Error limits (Δ log k)	Page
CH$_3$O + M → HCHO + H + M	See Table 2			687
CH$_3$O + O$_2$ → HCHO + HO$_2$	6.7×10^{-14} exp($-1070/T$)	300–1000	± 0.2 at 500 K rising to ± 0.3 at 300 K and 1000 K.	688

CH$_3$OOH Reactions   690

Reaction	k/cm^3 molecule^{-1}s^{-1}	Temp/K	Error limits (Δ log k)	Page
CH$_3$OOH + M → CH$_3$O + OH + M	See Table 2			690

TABLE 1. Bimolecular reactions — Continued

Reaction	k/cm^3 molecule$^{-1}s^{-1}$	Temp/K	Error limits ($\Delta \log k$)	Page
CN Radical Reactions				691
$CN + O_2 \rightarrow NCO + O$	$1.1 \times 10^{-11} \exp(205/T)$	300–2500	$\pm$ 0.25 at 300 K rising to $\pm$ 0.5 at 2500 K.	691
$CN + H_2O \rightarrow HCN + OH$ ⎤ $\rightarrow HOCN + H$ ⎦	$1.3 \times 10^{-11} \exp(-3750/T)$	500–3000	$\pm$ 0.3 at 500 K rising to $\pm$ 0.5 at 3000 K.	694
$CN + CH_4 \rightarrow HCN + CH_3$	$1.5 \times 10^{-11} \exp(-940/T)$	260–400	$\pm$ 0.3	695
NCO Radical Reactions				697
$NCO + M \rightarrow N + CO + M$	See Table 2			697
$NCO + NO \rightarrow N_2O + CO$ ⎤ $\rightarrow N_2 + CO_2$ ⎥ $\rightarrow N_2 + CO + O$ ⎦	$1.7 \times 10^{-11} \exp(200/T)$	300–600	$\pm$ 0.5	698
C_2H Radical Reactions				699
$C_2H + O_2 \rightarrow CO_2 + CH$ ⎤ $\rightarrow 2CO + H$ ⎥ $\rightarrow C_2HO + O$ ⎥ $\rightarrow CO + HCO$ ⎦	3.0×10^{-11}	300	$\pm$ 0.5	699
$C_2H + H_2 \rightarrow C_2H_2 + H$	$2.5 \times 10^{-11} \exp(-1560/T)$	300–2500	$\pm$ 0.3 at 300 K rising to $\pm$ 0.7 at 2500 K	700
$C_2H + C_2H_2 \rightarrow C_4H_2 + H$	5.0×10^{-11}	300–2700	$\pm$ 0.3	702
$C_2H + CH_4 \rightarrow$ products	2.0×10^{-12}	298	$\pm$ 1	702
$C_2H + C_2H_6 \rightarrow$ products	No recommendation			
C_2H_3 Radical Reactions				704
$C_2H_3 + M \rightarrow C_2H_2 + H + M$	See Table 2			704
$C_2H_3 + O_2 \rightarrow HCHO + CHO$	9.0×10^{-12}	300–2000	$\pm$ 0.3 at 300 K rising to $\pm$ 0.5 at 2000 K	705
C_2H_5 Radical Reactions				706
$C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$	$1.7 \times 10^{-14} \exp(1100/T)$	600–1200	$\pm$ 0.3	706
$C_2H_5 + C_2H_5 \rightarrow C_2H_6 + C_2H_4$ $\rightarrow n\text{-}C_4H_{10}$	2.4×10^{-12} See Table 3	300–1200	$\pm$ 0.4	707
C_2H_6 Reactions				710
$C_2H_6 + M \rightarrow CH_3 + CH_3 + M$	See Table 2			710
CHCO Reactions				713
$CHCO + O_2 \rightarrow CO_2 + HCO$ ⎤ $\rightarrow 2CO + OH$ ⎥ $\rightarrow C_2O + HO_2$ ⎥ $\rightarrow CHO_2CO$ ⎦	$2.7 \times 10^{-12} \exp(430/T)$ M = He, 2 Torr	300–550	$\pm$ 0.7	713
CH_2CHO Radical Reactions				714
$CH_2CHO + O_2 \rightarrow HO_2 + CH_2CHO$ ⎤ $\rightarrow HCHO + CO + OH$ ⎥ $\rightarrow O_2CH_2CHO$ ⎦	$k_\infty = 2.6 \times 10^{-13}$ $k_2 = 3.0 \times 10^{-14}$	250–1000 300	$\pm$ 0.2 $\pm$ 0.3	714

TABLE 1. Bimolecular reactions — Continued

Reaction	k/cm^3 molecule^{-1}s^{-1}	Temp/K	Error limits (Δ log k)	Page
CH$_3$CO Radical Reactions				716
CH$_3$CO + O$_2$ + M → CH$_3$CO$_3$ + M	See Table 3			716
CH$_3$CHO Reactions				716
CH$_3$CHO + M → CH$_3$ + HCO + M	See Table 2			716
C$_2$H$_5$O Reactions				717
C$_2$H$_5$O + M → HCHO + CH$_3$ + M ⎤ → CH$_3$CHO + H + M ⎦	See Table 2			717
C$_2$H$_5$O + O$_2$ → CH$_3$CHO + HO$_2$	1.0×10^{-13} exp($-830/T$)	300–1000	± 0.3 at 300 K rising to ± 0.5 at 1000 K	717
C$_2$H$_5$OOH Reactions				718
C$_2$H$_5$OOH + M → C$_2$H$_5$O + OH + M	See Table 2			718
C$_6$H$_5$ Radical Reactions				718
C$_6$H$_5$ + M → C$_2$H$_2$ + C$_4$H$_3$ + M ⎤ → C$_2$H$_3$ + C$_4$H$_2$ + M ⎥ → linear-C$_6$H$_5$ + M ⎦	See Table 2			718
C$_6$H$_6$ Reactions				721
C$_6$H$_6$ + M → C$_6$H$_5$ + H + M ⎤ → C$_4$H$_4$ + C$_2$H$_2$ + M ⎦	See Table 2			721
C$_6$H$_5$O Radical Reactions				724
C$_6$H$_5$O + M → C$_5$H$_5$ + CO + M	See Table 2			724
C$_6$H$_5$CH$_2$ Radical Reactions				725
C$_6$H$_5$CH$_2$ + M → C$_3$H$_3$ + 2C$_2$H$_2$ + M ⎤ → C$_4$H$_4$ + C$_3$H$_3$ + M ⎥ → C$_5$H$_5$ + C$_2$H$_2$ + M ⎥ → C$_7$H$_7$(BCH) + M ⎦	See Table 2			725
C$_6$H$_5$CH$_3$ Reactions				728
C$_6$H$_5$CH$_3$ + M → C$_6$H$_5$CH$_2$ + H + M ⎤ → C$_6$H$_5$ ⎹ CH$_3$ ⎹ M ⎦	See Table 2			728
p-C$_6$H$_4$(CH$_3$)$_2$ Reactions				731
p-C$_6$H$_4$(CH$_3$)$_2$ + M → C$_6$H$_4$CH$_2$CH$_3$ + H + M	See Table 2			731
C$_6$H$_5$C$_2$H$_5$ Reactions				733
C$_6$H$_5$C$_2$H$_5$ + M → C$_6$H$_5$CH$_2$ + CH + M ⎤ → C$_6$H$_6$ + C$_2$H$_4$ + M ⎥ → C$_6$H$_5$CHCH$_2$ + H$_2$ + M ⎥ → C$_6$H$_5$ + C$_2$H$_5$ + M ⎥ → C$_6$H$_5$CHCH$_3$ + H + M ⎦	See Table 2			733

TABLE 2. Decomposition reactions

Reaction	k_∞/s^{-1} k_0/cm^3 molecule^{-1} s^{-1} F_c $k/s^{-1} = \dfrac{k_0\,k_\infty\,[M]}{k_0[M] + k_\infty}\,F$	Temp/K	Error limits (Δ log k)	Page
$H_2 + Ar \rightarrow 2H + Ar$	$k_0 = 3.7 \times 10^{-10}\exp(-48350/T)$	2500–8000	± 0.3	550
$H_2 + H_2 \rightarrow 2H + H_2$	$k_0 = 1.5 \times 10^{-9}\exp(-48350/T)$	2500–8000	± 0.5	550
$H_2O + N_2 \rightarrow H + OH + N_2$	$k_0 = 5.8 \times 10^{-9}\exp(-52920/T)$	2000–6000	± 0.5	603
$H_2O_2 + M \rightarrow 2\,OH + M$	$k_0(Ar) = 3 \times 10^{-8}\exp(-21600/T)$ $k_0(N_2) = 2 \times 10^{-7}\exp(-22900/T)$ $k_\infty = 3 \times 10^{14}\exp(-24400/T)$ $F_c(Ar) = 0.5$	1000–1500 700–1500 1000–1500 700–1500	± 0.2 ± 0.2 ± 0.5 $\Delta F_c = \pm 0.1$	615
$CH_3 + M \rightarrow CH_2 + H + M$	$k_0 = 1.7 \times 10^{-8}\exp(-45600/T)$	1500–3000	± 0.5	648
$CH_4 + M \rightarrow CH_3 + H + M$	$k_0(Ar) = 1.2 \times 10^{-6}\exp(-47000/T)$ $k_0(CH_4) = 1.4 \times 10^{-5}\exp(-48100/T)$ $k_\infty = 2.4 \times 10^{16}\exp(-52800/T)$ $F_c\,(Ar) = \exp(-0.45 - T/3231)$ $F_c\,(CH_4) = \exp(-0.37 - T/2210)$	1000–3000 1000–2000 1000–3000 1000–3000 1000–2000	± 0.3 ± 0.3 ± 0.5 $\Delta F_c = \pm 0.1$ $\Delta F_c = \pm 0.1$	673
$HCHO + M \rightarrow H + CHO + M$] $\rightarrow H_2 + CO + M$]	$k_0(1) = 2.1 \times 10^{-8}\exp(-39200/T)$ $k_1/k_2 = 0.5$ at 2200 K	1500–2500	± 0.3	681
$CH_3O + M \rightarrow HCHO + H + M$	$k_0 = 3.16 \times 10^2\,T^{-27}\exp(-15400/T)$ [estimate]	300–1000	± 1.0	687
$CH_3OOH + M \rightarrow CH_3O + OH + M$	$k_\infty = 4 \times 10^{15}\exp(-21600/T)$	400–1000	± 0.5 at 600 K rising to ± 1.0 at 400 and 1000 K	690
$NCO + Ar \rightarrow N + CO + Ar$	$k_0 = 1.7 \times 10^{-9}\exp(-23500/T)$	1450–2600	± 0.4	697
$C_2H_3 + M \rightarrow C_2H_2 + H + M$	$k_0 = 6.9 \times 10^{17}\,T^{-75}\exp(-22900/T)$ $k_\infty = 2 \times 10^{14}\exp(-20000/T)$ $F_c = 0.35$	500–2500 500–2500 500–2500	± 0.5 ± 0.5 $\Delta F_c = \pm 0.1$	704
$C_2H_6 + M \rightarrow 2CH_3 + M$	$k_0(Ar) = 1.1 \times 10^{25}\,T^{-8.24}\exp(-47090/T)$ $k_0(C_2H_6) = 4.5 \times 10^{-2}\exp(-41930/T)$ $k_\infty = 1.8 \times 10^{21}\,T^{-1.24}\exp(-45700/T)$ $F_c(Ar) = 0.38\exp(-T/73)+0.62\exp(-T/1180)$ $F_c(C_2H_6) = 0.54\exp(-T/1250)$	300–2000 800–1000 300–2000 300–2000 800–1000	± 0.5 ± 0.5 ± 0.3 $\Delta F_c = \pm 0.1$ $\Delta F_c = \pm 0.1$	710
$CH_3CHO + M \rightarrow CH_3 + CHO + M$	$k(1\text{ atm.}) = 7 \times 10^{15}\exp(-41100/T)$ (pressure dependent region)	750–1200	± 0.4	716
$C_2H_5O + M \rightarrow HCHO + CH_3 + M$	$k_\infty = 8 \times 10^{13}\exp(-10830/T)$ [estimate]	300–600	± 1.0	717
$C_2H_5OOH + M \rightarrow C_2H_5O + OH + M$	$k_\infty\ 4 \times 10^{15}\exp(-21600/T)$	400–1000	± 1.0	718
$C_6H_5 + M \rightarrow C_2H_2 + C_4H_3 + M$] $\rightarrow C_2H_3 + C_4H_2 + M$]	No recommendation			718
$\rightarrow$ linear-CH_5 + M	$4.0 \times 10^{13}\exp(-36700/T)$	1450–1900	± 0.4	
$C_6H_6 + M \rightarrow C_6H_5 + H + M$] $\rightarrow C_4H_4 + H_2 + M$]	$9.0 \times 10^{15}\exp(-54060/T)$	1200–2500	± 0.4 at 1200 K reducing to ± 0.3 at 2500 K	721
$C_6H_5O + M \rightarrow C_5H_5 + CO + M$	$2.5 \times 10^{11}\exp(-22100/T)$	1000–1580	± 0.2	724

TABLE 2. Decomposition reactions — Continued

Reaction	k_∞/s^{-1} k_0/cm^3 molecule^{-1} s^{-1} F_c $k/s^{-1} = \dfrac{k_0\, k_\infty\, [M]}{k_0[M] + k_\infty} F$	Temp/K	Error limits (Δ log k)	Page
$C_6H_5CH_2 + M \rightarrow C_3H_3 + 2C_2H_2 + M$ $\rightarrow C_4H_4 + C_3H_3 + M$ $\rightarrow C_5H_5 + C_2H_2 + M$ $\rightarrow C_7H_7$ (BCH) + M	$5.1 \times 10^{13} \exp(-36370/T)$	1350–1900	$\pm$ 0.3 at 1350 K rising to $\pm$ 0.5 1900 K	725
$C_6H_5CH_3 + M \rightarrow C_6H_5CH_2 + H + M$ $\rightarrow C_6H_5 + CH_3 + M$	$3.1 \times 10^{15} \exp(-44890/T)$ No recommendation	920–2200	$\pm$ 0.3 at 900 K rising to $\pm$ 0.5 at 2200 K	728
p-$C_6H_4(CH_3)_2 + M \rightarrow p$-$C_6H_4CH_2CH_3 + H + M$	$4.0 \times 10^{15} \exp(-42600/T)$	1400–1800	$\pm$ 0.5	731
$C_6H_5C_2H_5 + M \rightarrow C_6H_5CH_2 + CH + M$ $\rightarrow C_6H_6 + C_2H_4 + M$ $\rightarrow C_6H_5CHCH_2 + H_2 + M$ $\rightarrow C_6H_5 + C_2H_5 + M$ $\rightarrow C_6H_5CHCH_3 + H + M$	$6.1 \times 10^{15} \exp(-37800/T)$ No recommendations	770–1800	$\pm$ 0.1 at 770 K rising to $\pm$ 0.4 at	733

TABLE 3. Combination reactions

Reaction	k_∞/cm^3 molecule^{-1}s^{-1} k_0/cm^6 molecule^{-2} s^{-1} F_c k/cm^3 molecule^{-1}s^{-1} $= \dfrac{k_0\,k_\infty\,[M]}{k_0[M]\,+\,k_\infty}\,F$	Temp/K	Error limits (Δ log k)	Page
H + O$_2$ + Ar → HO$_2$ + Ar	$k_0 = 1.7 \times 10^{-30}\,T^{-0.8}$	300–2000	± 0.5	488
H + O$_2$ + H$_2$ → HO$_2$ + H$_2$	$k_0 = 5.8 \times 10^{-30}\,T^{-0.8}$	300–2000	± 0.5	488
H + O$_2$ + N$_2$ → HO$_2$ + N$_2$	$k_0 = 3.9 \times 10^{-30}\,T^{-0.8}$	300–2000	± 0.5	488
H + O$_2$ + H$_2$O → HO$_2$ + H$_2$O	$k_0 = 4.3 \times 10^{-30}\,T^{-0.8}$	300–2000	± 0.5	488
H + H + Ar → H$_2$ + Ar	$k_0 = 1.8 \times 10^{-30}\,T^{-1.0}$	300–2500	± 0.5	492
H + H + H$_2$ → H$_2$ + H$_2$	$k_0 = 2.7 \times 10^{-31}\,T^{-0.6}$	100–5000	± 0.5	495
H + OH + H$_2$O → H$_2$O + H$_2$O	$k_0 = 3.9 \times 10^{-25}\,T^{-2.0}$	300–3000	± 0.3	497
H + OH + Ar → H$_2$O + Ar	$k_0 = 2.3 \times 10^{-26}\,T^{-2.0}$	300–3000	± 0.3	496
H + OH + N$_2$ → H$_2$O + N$_2$	$k_0 = 6.1 \times 10^{-26}\,T^{-2.0}$	300–3000	± 0.3	498
H + CH$_3$ + M → CH$_4$ + M	k_0(He) $= 6.2 \times 10^{-29}\,(T/3000)^{-1.8}$ k_0(Ar) $= 6 \times 10^{-29}\,(T/300)^{-1.8}$ k_0(C$_2$H$_6$) $= 3 \times 10^{-28}\,(T/300)^{-1.8}$ $k_\infty = 3.5 \times 10^{-10}$ F_c(He,Ar) $= \exp(-0.45 - T/3231)$ F_c(C$_2$H$_6$) $= \exp(-0.34 - T/3053)$	300–1000 300–1000 300–1000 300–1000 300–1000 300–1000	± 0.3 ± 0.5 ± 0.5 ± 0.3 ΔF_c = ± 0.1 ΔF_c = ± 0.1	512
H + C$_2$H$_2$ + He → C$_2$H$_3$ + He	$k_\infty = 1.4 \times 10^{-11} \exp(-1300/T)$ $k_0 = 3.3 \times 10^{-30} \exp(-740/T)$ $F_c = 0.44$	200–400 200–400 200–400	± 0.3 ± 0.5 ΔF_c = ± 0.1	527
H + C$_2$H$_3$ + M → C$_2$H$_4$ + M	No recommendation			528
H + C$_2$H$_4$ + M → C$_2$H$_5$ + M	No recommendation			529
H + C$_2$H$_5$ + M → C$_2$H$_6$ + M	No recommendation			531
H + C$_6$H$_5$ + M → C$_6$H$_6$ + M	$k_\infty = 1.3 \times 10^{-10}$	1400–1700	± 0.5	541
H + C$_6$H$_6$ + M → C$_6$H$_7$ + M	$k_\infty = 6.7 \times 10^{-11} \exp(-2170/T)$	300–1000	± 0.2	541
H + C$_6$H$_5$O + M → C$_6$H$_5$OH + M	$k_\infty = 4.2 \times 10^{-10}$	1000	± 0.3	544
H + C$_6$H$_5$CH$_2$ + M → C$_6$H$_5$CH$_3$ + M	$k_\infty = 5.5 \times 10^{-10}$	300–2000	± 0.2 at 300 K rising to ± 0.7 at 2000 K.	545
H + C$_6$H$_5$CH$_3$ + M → C$_6$H$_6$CH$_3$ + M	$k_\infty = 1.2 \times 10^{-13}$	298	± 0.2	546
H + C$_6$H$_5$C$_2$H$_5$ + M → C$_6$H$_6$C$_2$H$_5$ + M	$k_\infty = 3.3 \times 10^{-13}$	298	± 0.1	549
OH + OH + M → H$_2$O$_2$ + M	k_0(N$_2$) $= 8 \times 10^{-31}\,(T/300)^{-0.76}$ k_0(H$_2$O) $= 4 \times 10^{-30}$ $k_\infty = 1.5 \times 10^{-11}\,(T/300)^{-0.37}$ F_c(N$_2$) $= 0.5$	250–1400 300–400 200–1500 200–1500	± 0.4 ± 0.5 ΔF_c = ± 0.2	556
OH + CH$_3$ + M → CH$_3$OH + M	No data available for this channel (See Table 1)			570
OH + C$_2$H$_2$ + M → C$_2$H$_2$OH + M	See data sheet			583

TABLE 3. Combination reactions — Continued

Reaction	k_∞/cm^3 molecule^{-1}s^{-1} k_0/cm^6 molecule^{-2} s^{-1} F_c k/cm^3 molecule^{-1}s^{-1} = $\dfrac{k_0 \, k_\infty \, [M]}{k_0[M] + k_\infty}$ F	Temp/K	Error limits (Δ log k)	Page
OH + C$_6$H$_6$ + M → C$_6$H$_6$OH + M	k_∞ = 3.8 × 10^{-12} exp($-340/T$)	240–340	± 0.2	595
OH + C$_6$H$_5$OH + M → C$_6$H$_5$(OH)$_2$ + M	k_∞ = 2.8 × 10^{-11}	298	± 0.1	598
OH + C$_6$H$_5$CH$_3$ + M → HOC$_6$H$_5$CH$_3$ + M	k_∞ = 3.8 × 10^{-12} exp(180/T)	200–300	± 0.4	598
OH + C$_6$H$_4$(CH$_3$)$_2$ + M → C$_6$H$_4$(CH$_3$)$_2$OH + M	k_∞ = 1.4 × 10^{-11}	300–320	± 0.1	601
OH + C$_6$H$_5$C$_2$H$_5$ + M → HOC$_6$H$_5$C$_2$H$_5$ + M	7.5 × 10^{-12} at p ≤ 1 atm.	298	± 0.1	603
^{3}CH$_2$ + C$_2$H$_2$ + M → C$_3$H$_4$ + M	2.0 × 10^{-11} exp($-3330/T$) at p = ≤ 10 Torr.	300–1000	± 0.3	642
^{3}CH$_2$ + C$_2$H$_4$ + M → C$_3$H$_6$ + M → c-C$_3$H$_6$ + M → C$_3$H$_5$ + H + M	5.3 × 10^{-12} exp($-2660/T$)	300–1000	± 0.2 at 300 K rising to ± 0.3 at 1000 K	643
^{1}CH$_2$ + C$_2$H$_2$ + M → CH$_2$CCH$_2$ + M → CH$_3$CCH + M → CH$_2$CCH + H + M	3.7 × 10^{-10} independent of p	300–1000	± 0.3 at 300 K rising to ± 0.7 at 1000 K.	646
^{1}CH$_2$ + C$_2$H$_4$ + M → C$_3$H$_6$	1.1 × 10^{-10} independent of p	300–1000	± 0.2 at 300 K rising to ± 0.5 at 1000 K.	647
CH$_3$ + O$_2$ + M → CH$_3$O$_2$ + M	k_0(Ar) = 1.5 × 10^{-22} $T^{-3.3}$ k_0(N$_2$) = 1.6 × 10^{-22} $T^{-3.3}$ k_∞ = 1.3 × 10^{-15} $T^{-1.2}$ F_c = 0.466 − 1.30 × 10^{-4} T	300–800 300–800 300–800 300–800	± 0.3 ± 0.3 ± 0.3	650
CH$_3$ + CH$_3$ + Ar → C$_2$H$_6$ + Ar	k_∞ = 6 × 10^{-11} k_0 = 3.5 × 10^{-7} $T^{-7.0}$ exp($-1390/T$) F_c = 0.38 exp($-T/73$) + 0.62exp($-T/1180$)	300–2000 300–2000 300–2000	± 0.05 at 300 K rising to ± 0.3 at 2000 K ± 0.3 ΔF_c = ± 0.1	656
CH$_3$ + C$_2$H$_2$ + M → C$_3$H$_5$ + M	k_∞ = 1 × 10^{-12} exp($-3900/T$)	300–600	± 0.5	661
CH$_3$ + C$_2$H$_4$ + M → n-C$_3$H$_7$ + M	3.5 × 10^{-13} exp($-3700/T$)	300–600	± 0.3	663
CH$_3$ + C$_2$H$_5$ + M → C$_3$H$_8$ + M	k_∞ = 4.7 × 10^{-11}	300–800	± 0.3	665
C$_2$H$_5$ + C$_2$H$_5$ + M → n-C$_4$H$_{10}$ + M	k_∞ = 1.9 × 10^{-11}	300–1200	± 0.3	707
CH$_3$CO + O$_2$ + M → CH$_3$CO$_3$ + M	2 × 10^{-12} for p = 1–4 Torr.	300	± 0.3	716

4. Data Sheets

$O + H_2 \rightarrow OH + H$

Thermodynamic Data

$\Delta H^{\circ}_{298} = 7.76 \text{ kJ mol}^{-1}$

$\Delta S^{\circ}_{298} = 6.67 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p = 1.8 \ T^{0.027} \exp(-917/T)$

Rate Coefficient Data

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	T [K]	Reference	Comments
Rate Coefficient Measurements			
$3.7 \cdot 10^{-10} \exp(-6916/T)$	1400–1900	Schott, Getzinger, and Seitz (1974)[1]	(a)
$5.2 \cdot 10^{-11} \exp(-4950/T)$	363–490	Campbell and Handy (1975)[2]	(b)
$8.3 \cdot 10^{-12} \exp(-4330/T)$	347–832	Dubinsky and McKenney (1975)[3]	(c)
$9.1 \cdot 10^{-18}$	298	Light and Matsumoto (1980)[4]	(d)
$3.8 \cdot 10^{-10} \exp(-6916/T)$	2097–2481	Pamidimukkala and Skinner (1982)[5]	(e)
$3.1 \cdot 10^{-10} \exp(-6976/T)$	1700–2500	Frank and Just (1985)[6]	(f)
$8.5 \cdot 10^{-20} \ T^{2.67} \exp(-3163/T)$	504–2495	Sutherland *et al*. (1986)[7]	(g)
Reviews and Evaluations			
$3.0 \cdot 10^{-14} \ T^{1.0} \exp(-4474/T)$	400–2000	Baulch *et al*. (1972)[8]	
$1.8 \cdot 10^{-20} \ T^{2.8} \exp(-2983/T)$	400–1600	Cohen and Westberg (1983)[9]	
$2.5 \cdot 10^{-17} \ T^{2.0} \exp(-3800/T)$	300–2500	Warnatz (1984)[10]	

Comments

(a) Shock wave initiated combustion of $H_2/O_2/CO/CO_2/$ Ar mixtures; [OH] monitored by chemiluminescence of CO + O reaction. Numerical integration of 12 reaction mechanism with fitting of $k(O + H_2)/k(H + O_2)$ to experimental results. Based on $k(H + O_2) = 2.0 \cdot 10^{-7} \ T^{-0.91} \exp(-8369/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [11].

(b) Diffusion-stirred discharge-flow reactor; [O] by air afterglow chemiluminescence. Total pressure ≈ 0.4 kN m^{-2}.

(c) Discharge-flow system; [O] by resonance fluorescence at 130.6 nm and air afterglow chemiluminescence. Given parameters based on resonance fluorescence measurements.

(d) State-selective reaction rate for H_2 ($v = 0$). Discharge-flow reactor; [OH ($v = 0$)] and [OH ($v = 1$)] from laser induced fluorescence. H_2 ($v = 1$) suppressed by addition of CO_2 and controlled by VUV absorption. Total pressure 3 Torr.

(e) Shock heating of $H_2/N_2O/Ar$ mixtures; [O] by atomic resonance absorption spectroscopy. Numerical modelling of 11 reaction mechanism.

(f) Shock heating of $H_2/N_2O/Ar$ mixtures; [H] and [O] by atomic resonance absorption spectroscopy. Total densities $6 \cdot 10^{-6} - 1.3 \cdot 10^{-5}$ mol cm^{-3}.

(g) Flash-photolysis – shock tube technique combined with atomic resonance absorption and resonance fluorescence spectroscopy.

Preferred Values

$k = 8.5 \cdot 10^{-20} \ T^{2.67} \exp(-3163/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over range 300–2500 K

Reliability

$\Delta \log k = \pm 0.5$ at 300 K reducing to ± 0.2 for $T > 500$ K

Comments on Preferred Values

The rate coefficient given by Sutherland *et al*.[7] is taken as the recommendation due to the extremely large temperature range and the sophisticated methods used.

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O + H₂ → OH + H

$$O + H_2 \rightarrow OH + H$$

T/K

EXPERIMENTAL DATA

■ Dubinsky and McKenny 1975
△ Dubinsky and McKenny 1975
▲ Campbell and Handy 1975
○ Light and Matsumoto 1980
● Pamidimukkala and Skinner 1982
⬓ Frank and Just 1985
◮ Sutherland et al 1986
◒ Sutherland et al 1986
+ Clyne and Thrush 1963
× Wong and Potter 1965
◇ Balakhnin et al 1966
—— Ripley and Gardiner 1966
— — — Gutman and Schott 1967
···· Gutman et al 1967
▽ Hoyermann et al 1967
▼ Westenberg and DeHaas 1967
◆ Westenberg and DeHaas 1967
⊢——⊣ Balakhnin et al 1968
◈ Campbell and Thrush 1968
—·—·—·— Kurzius 1968
⊢——⊣ Browne et al 1969
— — Schott 1969
—··—··— Wakefield 1969
◇ Westenberg and DeHaas 1969
◰ Balakhnin et al 1970
— — Dean and Kistiakowsky 1970
— ·· — ·· — Jachimowski and Houghton 1970
◙ Brabbs et al 1971

——— This Recommendation 1989

Log(k/cm³molecule⁻¹s⁻¹)

$\mathrm{Log}(k/\mathrm{cm}^3\,\mathrm{molecule}^{-1}\,\mathrm{s}^{-1})$

$10^3 T^{-1}/K^{-1}$

O + OH → H + O₂

Thermodynamic Data

$\Delta H^{\circ}_{298} = -70.2$ kJ mol^{-1}

$\Delta S^{\circ}_{298} = -24.9$ J K^{-1}mol^{-1}

$K_p = 3.3 \cdot 10^{-3}\ T^{0.374} \exp(+8620/T)$

Rate Coefficient Data

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$4.4 \cdot 10^{-11}$	425	Campbell and Handy (1977)[1]	(a)
$2.0 \cdot 10^{-11} \exp(+112/T)$	221–499	Lewis and Watson (1980)[2]	(b)
$3.8 \cdot 10^{-11}$	298	Howard and Smith (1980)[3]	(c)
$6.7 \cdot 10^{-10}\ T^{-0.5}$	250–515	Howard and Smith (1981)[4]	(c)
$3.1 \cdot 10^{-11}$	300	Brune, Schwab, and Anderson (1983)[5]	(d)
$3.3 \cdot 10^{-11}$	296	Temps (1983)[6]	(e)
Reviews and Evaluations			
$3.8 \cdot 10^{-11}$	300	Baulch et al. (1972,1980)[7,8]	
$3.0 \cdot 10^{-11}$	300–2500	Warnatz (1984)[9]	
$7.5 \cdot 10^{-10}\ T^{-0.5} \exp(-30/T)$	200–2500	Tsang and Hampson (1986)[10]	

Comments

(a) Discharge-flow system; reaction of O(^{3}P) atoms in H₂/ CO/N₂ mixtures monitored by observing the chemiluminescence of CO + O recombination. Relative measurement k(O + OH)/k(CO + OH) = 260. Given k based on k(CO + OH) = $1.7 \cdot 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

(b) Low-pressure discharge-flow system. [OH] and [O] by resonance fluorescence. Results also described by k = $2.4 \cdot 10^{-10}\ T^{-0.362}$ cm^3 molecule^{-1} s^{-1}.

(c) Flow system; O formed by microwave discharge, OH by flash photolysis of H₂O. [OH] monitored by resonance fluorescence. Total pressure 3.75 Torr.

(d) Fast-flow reactor; [OH] by laser magnetic resonance, [O], [H], and [OH] by resonance fluorescence, [O] by resonance absorption. Total pressures 1.0–3.0 Torr.

(e) Isothermal flow system; FIR-LMR spectroscopy.

Preferred Values

$k = 2.0 \cdot 10^{-11} \exp(+112/T)$ cm^3 molecule^{-1} s^{-1} over range 220–500 K

$k = 2.4 \cdot 10^{-11} \exp(-353/T)$ cm^3 molecule^{-1} s^{-1} over range 1000–2000 K

Reliability

$\Delta \log k = \pm 0.2$ over range 220–500 K

$\Delta \log k = \pm 0.1$ over range 1000–2000 K

Comments on Preferred Values

According to the potential energy surface two sets of rate parameters are recommended. In the low temperature region the results of Lewis and Watson[2] have been chosen whereas for higher temperatures the parameters have been calculated from the rate of the reverse reaction H + O₂ → O + OH and the equilibrium constant.

For clarity, rate data measured before 1972 are included in the Arrhenius plot (see Baulch et al.[7] for Ref.).

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O + OH → H + O₂

$O + HO_2 \rightarrow OH + O_2$
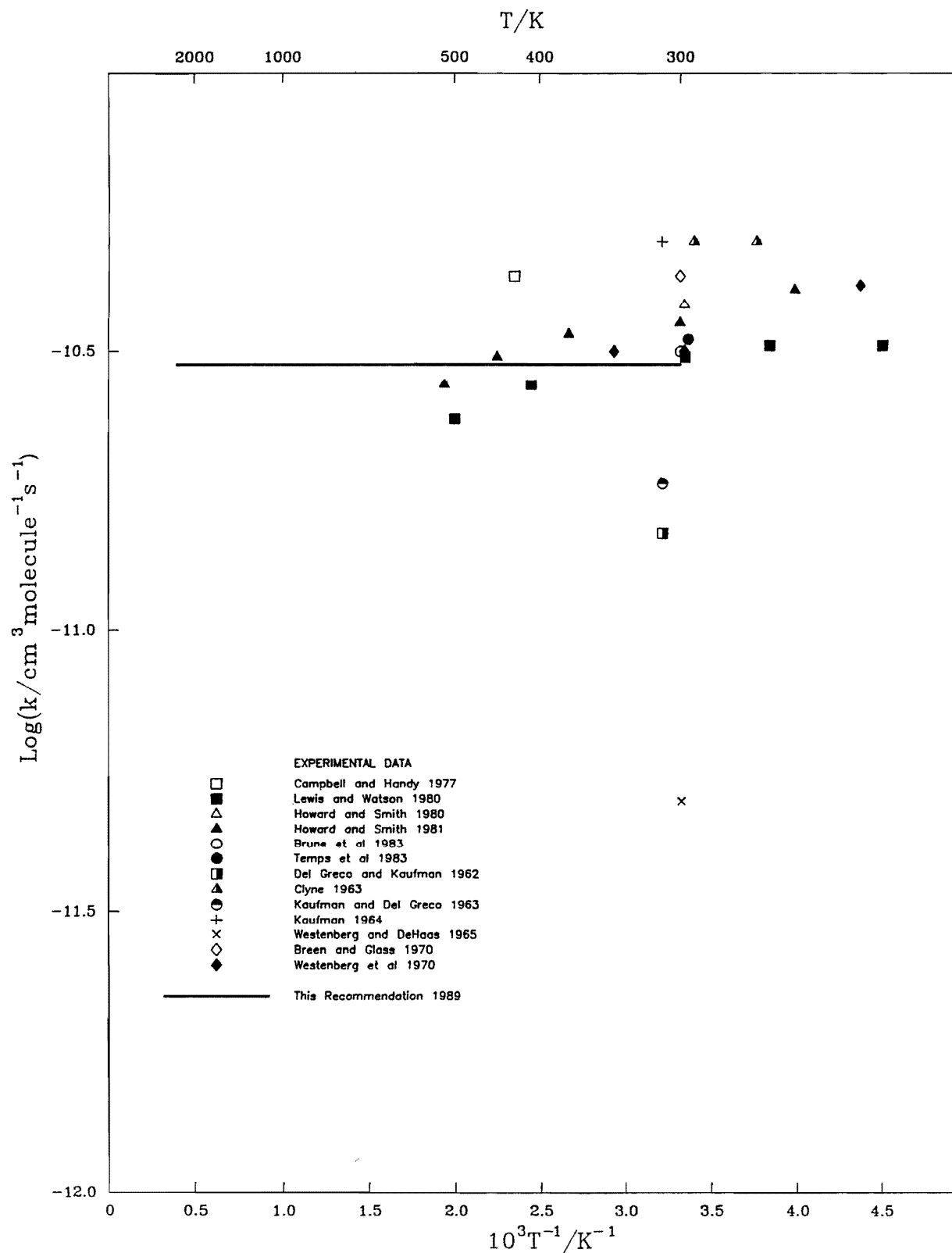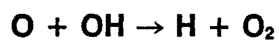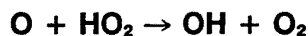
Thermodynamic Data

$\Delta H^{\circ}_{298} = -221 \text{ kJ mol}^{-1}$

$\Delta S^{\circ}_{298} = -1.29 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p = 8.29 \ T^{-0.304} \exp(+26400/T)$

Rate Coefficient Data

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	$T[\text{K}]$	Reference	Comments
Rate Coefficient Measurements			
$5.5 \cdot 10^{-11}$	1050	Day, Thompson, and Dixon-Lewis (1973)[1]	(a)
$1.7 \cdot 10^{-11}$	1000	Dixon-Lewis and Rhodes (1975)[2]	(b)
$3.5 \cdot 10^{-11}$	293	Burrows, Harris and Thrush (1977)[3]	(c)
$3.3 \cdot 10^{-11}$	298	Hack *et al*. (1979)[4]	(d)
$3.1 \cdot 10^{-11}$	296	Burrows *et al*. (1979)[5]	(e)
$7 \cdot 10^{-11}$	298	Lii, Sauer, and Gordon (1980)[6]	(f)
$5.4 \cdot 10^{-11}$	296	Sridharan, Qiu, and Kaufman (1982)[7]	(g)
$3.1 \cdot 10^{-11} \exp(+200/T)$	230–370	Keyser (1982)[8]	(h)
$6.2 \cdot 10^{-11}$	298	Ravishankara, Wine, and Nicovich (1983)[9]	(i)
$5.2 \cdot 10^{-11}$	300	Brune, Schwab, and Anderson (1983)[10]	(j)
$2.9 \cdot 10^{-11} \exp(+228/T)$	266–391	Nicovich and Wine (1987)[11]	(k)
Reviews and Evaluations			
$1.0 \cdot 10^{-10} \exp(-349/T)$	300–800	Baulch *et al*. (1976)[12]	
$3.2 \cdot 10^{-11}$	298	Baulch *et al*. (1980)[13]	
$3.3 \cdot 10^{-11}$	298	Kaufman and Sherwell (1983)[14]	
$3.3 \cdot 10^{-11}$	300–1000	Warnatz (1984)[15]	
$2.8 \cdot 10^{-11} \exp(+200/T)$	300–1000	Tsang and Hampson (1986)[16]	

Comments

(a) Computer simulation of burning velocities of rich H_2/O_2/N_2 flames. No great accuracy.

(b) Flat flame study; evaluation of existing experimental data.

(c) Fast flow system; [OH] and [H_2O_2] by laser magnetic resonance.

(d) Isothermal discharge-flow tube; total pressures 1–10 mbar He. [O] by ESR, [HO_2] by LMR.

(e) Fast flow system; total pressure $\approx$ 1 Torr. [OH] and [HO_2] by laser magnetic resonance. Value of k based on either $k(O + OH)$ or $k(OH + H_2O_2)$ from Ref. 17.

(f) Pulse radiolysis of $H_2/O_2/Ar$ mixtures at total pressure of 1200 Torr. [HO_2] and [O_3] by absorption measurements. Numerical integration of a system of 10 reactions and adjusting of k to fit the experimental results.

(g) Discharge-flow tube. [HO_2] monitored by rapid conversion to OH with large excess of NO, [OH] by laser induced fluorescence, [H] and [O] by VUV resonance fluorescence.

(h) Discharge-flow system. [HO_2] monitored by rapid conversion to OH with large excess of NO. [OH], [H], and [O] by resonance fluorescence.

(i) Laser photolysis of a mixture of H_2O_2 and O_3 in N_2 or Ar under slow flow conditions. [O] by time-resolved resonance fluorescence, [H_2O_2] by absorption measurements. k found to be independent of pressure in the range 10–500 Torr.

(j) Discharge-flow system. [HO_2] by LMR and conversion to OH by NO. [OH] by LMR and resonance fluorescence, [O] by resonance fluorescence and resonance absorption. No pressure dependence of k observed.

(k) Pulsed laser photolysis of $H_2O_2/O_3/N_2$ mixtures (80 Torr) under slow flow conditions. Time-resolved resonance fluorescence of O(^{3}P).

Preferred Values

$k = 5.4 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over range 300–1000 K

Reliability

$\Delta \log k = \pm 0.3$ at 300 K rising to ± 0.5 at 1000 K

Comments on Preferred Values

The recommendation is based on the value of Sridharan *et al*.[7] which is in agreement with the majority of the other measurements within the error limits.

References

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O + HO₂ → OH + O₂

$$O + HO_2 \rightarrow OH + O_2$$

EXPERIMENTAL DATA

☐ Day et al 1972
■ Day et al 1973
△ Peeters and Mahnen 1973
▲ Dixon—Lewis and Rhodes 1975
○ Burrows et al 1977
● Hack et al 1979
⬕ Burrows et al 1979
▲ Lii et al 1980
⊖ Sridharan et al 1982
+ Keyser 1982
× Ravishankara et al 1983
◇ Brune et al 1983
◆ Keyser 1983
⬓ Nicovich and Wine 1987

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$$O + H_2O_2 \rightarrow HO_2 + OH \quad (1)$$
$$\rightarrow H_2O + O_2 \quad (2)$$
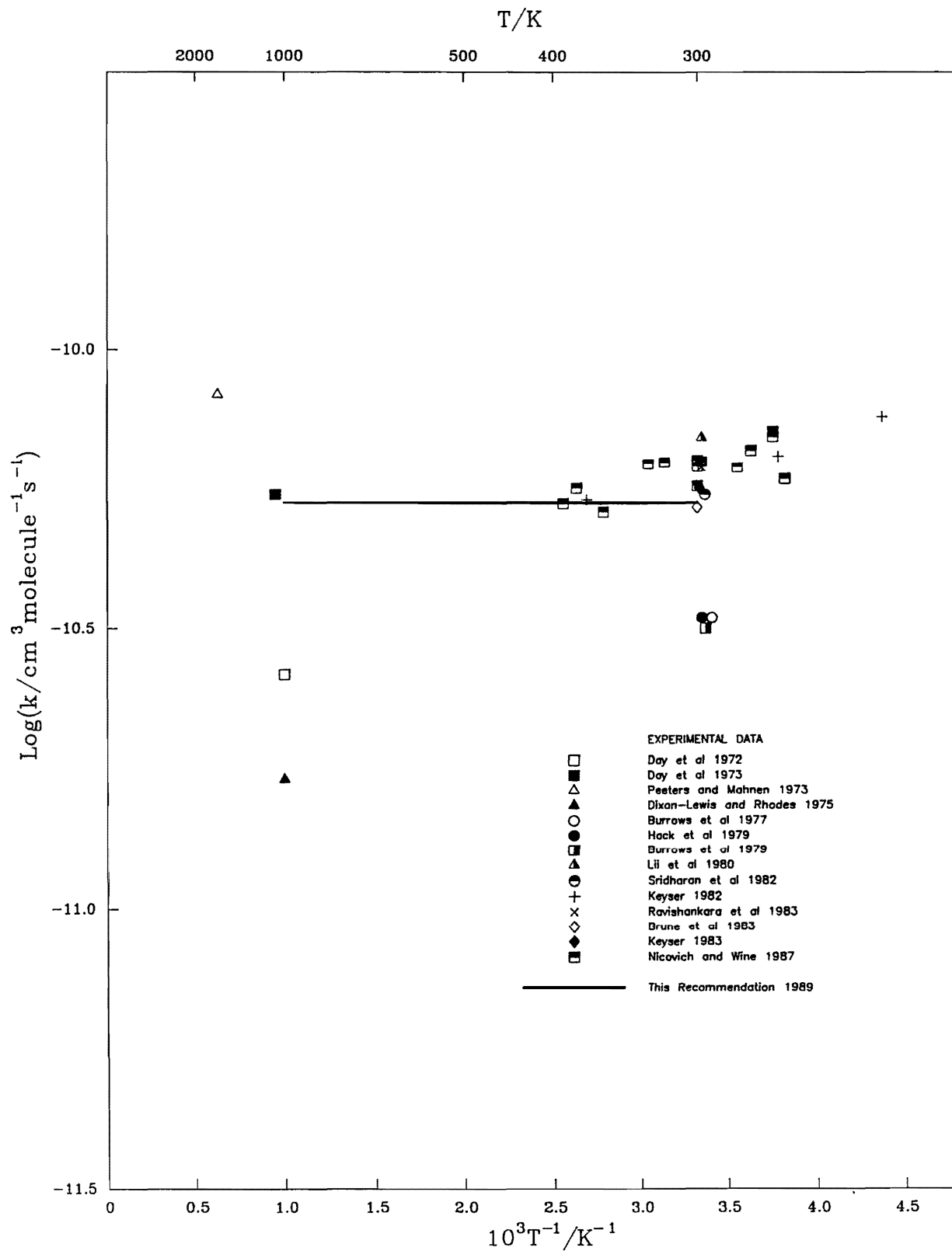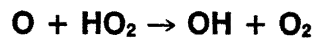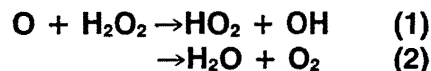
Thermodynamic Data

$\Delta H^\circ_{298} (1) = -63.6 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (1) = 18.8 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(1) = 1.02 \cdot 10^3 \ T^{-0.666} \exp(+7390/T)$

$\Delta H^\circ_{298} (2) = -354.9 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (2) = 0.07 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(2) = 5.27 \cdot 10^2 \ T^{-0.913} \exp(+42370/T)$

Rate Coefficient Data ($k = k_1 + k_2$)

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	$T[\text{K}]$	Reference	Comments
Rate Coefficient Measurements			
$4.7 \cdot 10^{-11} \exp(-3220/T)$	370–800	Albers et al. (1971)[1]	(a)
$2.8 \cdot 10^{-12} \exp(-2125/T)$	283–368	Davis, Wong, and Schiff (1974)[2]	(b)
$1.1 \cdot 10^{-12} \exp(-2000/T)$	298–386	Wine et al. (1983)[3]	(c)
$k_1 / k > 0.2$			
Reviews and Evaluations			
$4.6 \cdot 10^{-11} \exp(-3223/T)$	300–1000	Warnatz (1984)[4]	
$1.6 \cdot 10^{-17} \ T^2 \exp(-2000/T)$	300–2500	Tsang and Hampson (1986)[5]	

Comments

(a) Discharge-flow system; [O] monitored either by ESR combined with normal mass spectrometry or by molecular beam sampling coupled to time-of-flight mass spectrometer, [H$_2$O$_2$] by mass spectrometry. Equal probability for channels (1) and (2).

(b) Flash photolysis of O$_3$ at 600 nm; [O] by resonance fluorescence. Results confirmed by the work of Roscoe[6] on numerical simulations of O + H$_2$O$_2$ in a - fast-flow system.

(c) Pulsed laser photolysis of ozone at 532 nm. [O] monitored by time-resolved resonance fluorescence.

Preferred Values

$k = 1.1 \cdot 10^{-12} \exp(-2000/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over range 300–500 K

Reliability

$\Delta \log k = \pm 0.3$ over range 300–500 K

Comments on Preferred Values

The value of Albers et al.(1971)[1] is rejected because of the complex system studied. The value measured by Wine et al. (1983)[3], agreeing with that of Davis, Wong and Schiff (1974)[2], well within the error limits quoted, has been taken as recommended value because of the modern experimental technique.

For clarity rate data measured before 1972 are included in the Arrhenius plot (see Baulch et al.[7] for Ref.).

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O + H₂O₂ →HO₂ + OH

O + NH₃ → OH + NH₂
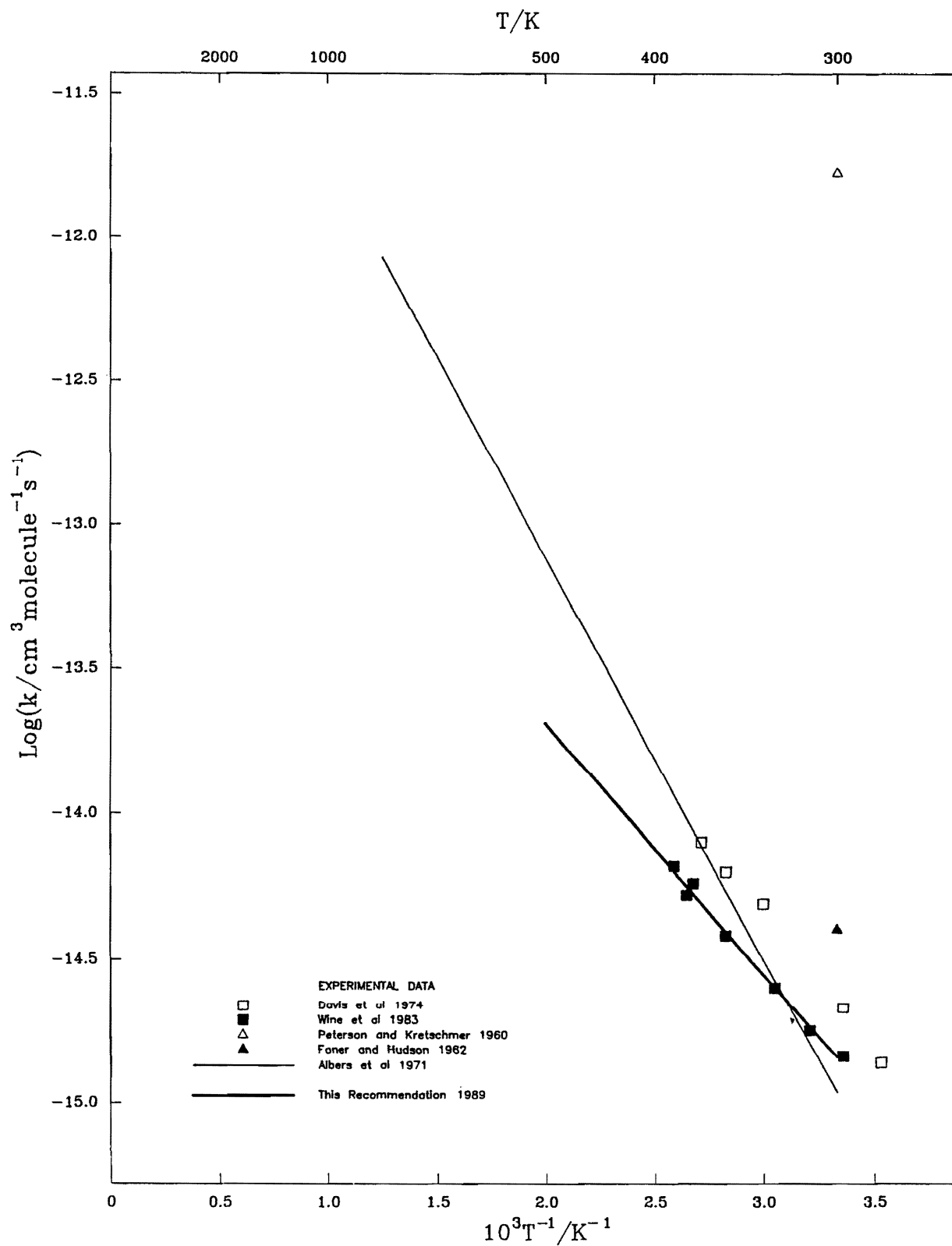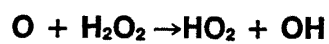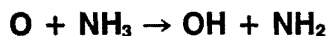
Thermodynamic Data

$\Delta H^\circ_{298} = 26.1 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} = 24.6 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p = 478 \ T^{-0.405} \exp(-3420/T)$

Rate Coefficient Data

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	$T[\text{K}]$	Reference	Comments
Reviews and Evaluations			
$2.5 \cdot 10^{-12} \exp(-3020/T)$	300–1000	Baulch *et al*. (1973)[1]	(a)
$1.8 \cdot 10^{-18} \ T^{2.1} \exp(-2620/T)$	–	Cohen (1987)[2]	(b)

Comments

(a) Review of data up to 1973.

(b) Thorough review of Refs. up to 1987, results checked and recalculated. Recommended k value based upon evaluation of previous data and also upon transition state theory calculations resulting in a higher than usual value of the T^n term.

Preferred Values

$k = 1.6 \cdot 10^{-11} \exp(-3670/T)$ cm³ molecule⁻¹ s⁻¹ over range 500– 2500 K

Reliability

$\Delta\log k = \pm 0.5$ over range 500–2500 K

Comments on Preferred Values

Studies up to 1987 have been comprehensively reviewed by Cohen[2] and only review articles are tabulated here.

The k values at high temperatures have all been obtained by fitting experimental results of flame studies[4] or shock tube studies[15,16,17] to assumed reaction mechanisms. Hence the accuracy of the resulting k value is dependent upon the sensitivity of the experimentally measured quantities to the rate of this particular reaction; in this respect the work of Salimian *et al*.[16] is the most sensitive, although all of the quoted k values agree to within a factor of 3. There is similar agreement between the studies at low temperatures, which have used discharge flow techniques[5,9,10,11], stirred flow reactors[6,8] and static photolysis techniques[12] with the exception of the more recent study of Perry[13] using laser photolysis of O_2 and [O] detection by NO_2 chemiluminescence. This study is favoured by Cohen[2] as the technique should be free from complicating secondary reactions. The expression given by Cohen[2] has a large T^n value based on transition state theory and leading to a high degree of curvature in the Arrhenius plot at high temperatures which is not evident in the experimental data.

The recommended values are based on the work of Salimian *et al*.[16] at high temperatures. At low temperatures it seems likely that most of the earlier studies are affected by secondary reactions and only that of Perry[13] is likely to be exempt from that criticism.

However, until Perry's results are confirmed, we adopt an expression with substantial error limits and lying between the results of Perry[14] and the older measurements. No T^n term has been included due to lack of direct experimental evidence for it but some curvature of the Arrhenius plot is likely.

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O + NH₃ → OH + NH₂

$$O + NH_3 \rightarrow OH + NH_2$$

$$O + CH \rightarrow H + CO \quad (1)$$
$$\rightarrow CHO^+ + e^- \quad (2)$$
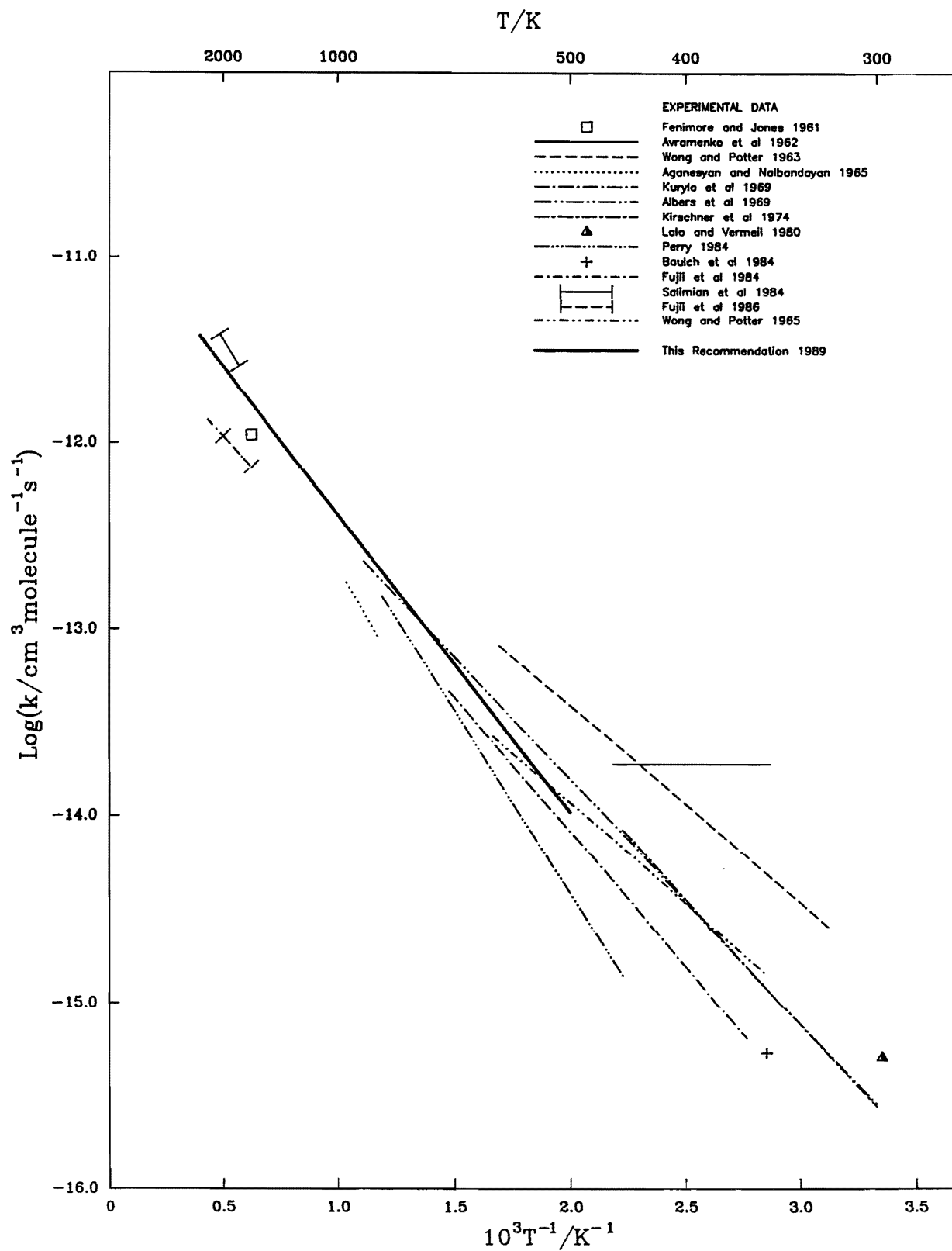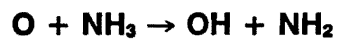
Thermodynamic Data

ΔH°_{298} (1) = -736 kJ mol^{-1}

ΔS°_{298} (1) = -31.7 J K^{-1}mol^{-1}

$K_p(1)$ = $3.34 \cdot 10^{-2}$ $T^{-0.0575}$ exp($+88500/T$)

Rate Coefficient Data

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
k_2 = $2.8 \cdot 10^{-13}$	2000–2400	Peeters and Vinckier (1975)[1]	(a)
k_2 = $9.5 \cdot 10^{-13}$ exp($-3020/T$)	1700–2100	Matsui and Nomaguchi (1978)[2]	(b)
k_2 = $2.4 \cdot 10^{-14}$	295	Vinckier (1979)[3]	(c)
E_2 / R = 805 K			
k_1 = $9.4 \cdot 10^{-11}$	298	Messing *et al.* (1980)[4]	(d)
k_1 = $3.3 \cdot 10^{-11}$	298	Homann and Schweinfurth (1981)[5]	(e)
k_2 = $1.2 \cdot 10^{-13}$	298	Becker *et al.* (1982)[6]	(f)
k_1 = $(1.7–2.5) \cdot 10^{-10}$	1500–2500	Frank, Bhaskaran, and Just (1986)[6]	(g)

Comments

(a) Flat flames of CH$_4$ and/or C$_2$H$_4$ at 16.5 and 40 Torr. Saturation current method; concentration profiles by molecular beam sampling and mass spectrometric analysis. Rate of ion generation was found to be $\sim$ [CH]·[O].

(b) Premixed CH$_4$/air flames; saturation current, [OH] by UV absorption, emission of OH*, CH*, and CO + O chemiluminescence, NO, NO$_2$, CO, and CO$_2$ by microprobe sampling, [O] from partial equilibrium assumption.

(c) Fast flow reactor; C$_2$H$_2$/O/O$_2$ system. Molecular beam sampling coupled to mass spectrometer; saturation current.

(d) IRMPD of CH$_3$OH in the presence of excess O. Total pressure 5–10 Torr Ar. [CH] by laser induced fluorescence.

(e) Discharge-flow system; reaction of C$_2$H$_2$ with O and H atoms. Total pressure 1.4–8 mbar. Mass spectrometric observation of formation of C$_3$H$_4$, C$_4$H$_2$, and CH$_2$O. Computer modelling of 25 reaction mechanism.

(f) Flow reactor; C$_2$H$_2$/O system. Saturation current method.

(g) Shock heating of highly diluted acetylene/nitrous oxide/Ar mixtures. [H], [O], and [CO] by resonance absorption spectroscopy. Total pressures 1.5–2 bar.

Preferred Values

k_1 = $6.6 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1} over range 300–2000 K

k_2 = $4.2 \cdot 10^{-13}$ exp($-850/T$) cm^3 molecule^{-1} s^{-1} over range 300–2500 K

Reliability

Δlog k_1 = $\pm$ 0.5 over range 300–2000 K

Δlog k_2 = $\pm$ 0.5 over range 300–2500 K

Comments on Preferred Values

The recommendation of k_1 is based on the given experimental data[4,5,7]. The value of k_2 is derived from the measurements at high and low temperatures available[1,2,3,6].

References

[1] J. Peeters and C. Vinckier, 15th Symp. (Int.) Combust, 969 (1975).

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O + CH → CO + H
→ CHO$^+$ + e

T/K

2000   1000   500   400   300

$Log(k/cm^3 molecule^{-1} s^{-1})$

-9.5

-10.0

-10.5

-11.0

-11.5

-12.0

-12.5

-13.0

-13.5

-14.0

(k1)

(k2)

EXPERIMENTAL DATA

Messing et al 1980
Homann and Schweinfurth 1981
Frank et al 1986
Peeters and Vinckier 1975
Vinckier 1979
Matsui and Nomaguchi 1979
Becker et al 1982
Place and Weinberg 1966

This Recommendation (k1) 1990

This Recommendation (k2) 1990

0   0.5   1.0   1.5   2.0   2.5   3.0   3.5

$10^3 T^{-1}/K^{-1}$

$$O + {}^3CH_2 \rightarrow CO + 2H \quad (1)$$
$$\rightarrow CO + H_2 \quad (2)$$
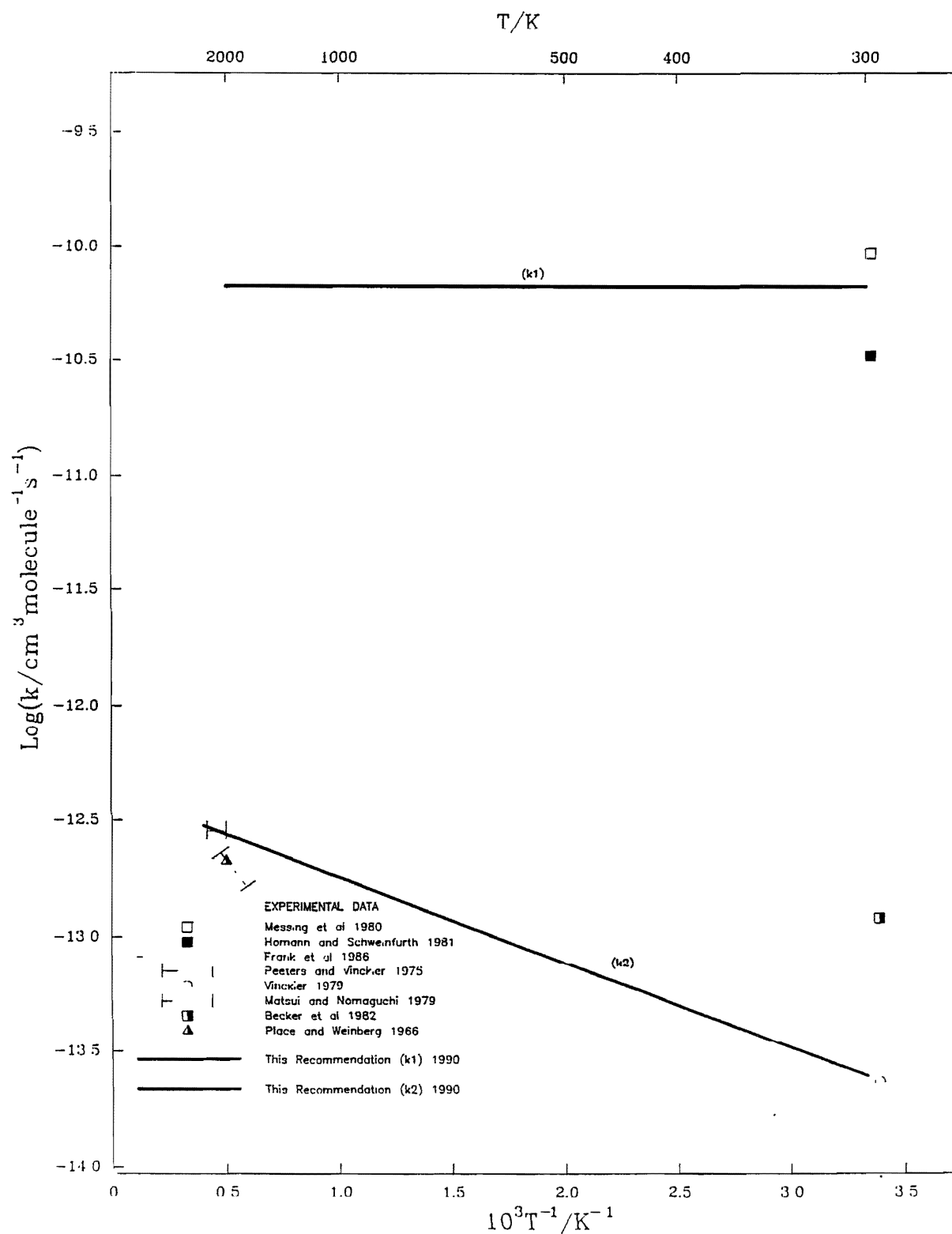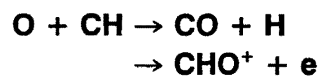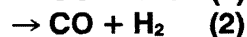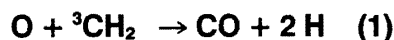
Thermodynamic Data

ΔH°_{298} (1) $= -310.8$ kJ mol^{-1}
ΔS°_{298} (1) $= 70.3$ J K^{-1}mol^{-1}
K_p(1) $= 3.81\ T^{1.11}\ \exp(+37600/T)$ atm

ΔH°_{298} (2) $= 746.7$ kJ mol^{-1}
ΔS°_{298} (2) $= -28.3$ J K^{-1}mol^{-1}
K_p(2) $= 0.122\ T^{-0.166}\ \exp(+89700/T)$

Rate Coefficient Data ($k = k_1 + k_2$)

k [cm^3 molecule^{-1} s^{-1}]	T [K]	Reference	Comments
Rate Coefficient Measurements			
$1.3 \cdot 10^{-11}$	290–600	Vinckier and Debruyn (1978,1979)[1,2]	(a)
$8 \cdot 10^{-11}$	298	Homann and Schweinfurth (1981)[3]	(b)
$1.4 \cdot 10^{-11}$	296	Böhland, Temps, and Wagner (1984)[4]	(c)
$k_1 = 2 \cdot 10^{-10}$	1500–2500	Frank, Bhaskaran, and Just (1987)[5]	(d)
$k_2 = 1 \cdot 10^{-10}$			
Reviews and Evaluations			
$8 \cdot 10^{-11}$	800–2000	Warnatz (1984)[6]	(e)
$1.9 \cdot 10^{-11}$	298	Tsang and Hampson (1986)[7]	(f)

Comments

(a) Discharge flow study of O + C_2H_2 with molecular beam sampling and mass spectrometric analysis. Rate coefficient determined from the approach of the [$^3CH_2$] signal to its steady-state value[1]. The temperature dependence, corresponding to an "activation energy" of -0.4 ± 0.8 kJ mol^{-1}, was determined from the steady state concentration of $^3CH_2$ and relies on a measured value of 13 ± 0.8 kJ mol^{-1} for the activation energy of $O(^3P)$ + C_2H_2.

(b) Discharge flow system, mass spectrometric detection. Rate coefficient extracted from 25 reaction mechanism.

(c) Discharge flow, [$O(^3P)$] and [$^3CH_2$] determined by LMR. Used [$^3CH_2$] $\approx (0.6–1.4) \cdot 10^{11}$ cm^{-3} and [$O(^3P)$]$_0$ / [$^3CH_2$]$_0$ $= 2–20$. Secondary reactions of $^3CH_2$ (e.g.with the wall, O_2, H, and $^3CH_2$) were carefully assessed.

(d) Reflected shock wave in N_2O/C_2H_2/Ar. CO, H, and O detected by resonance absorption. Numerical fits to 14 reaction mechanism.

(e) Evaluation based on Refs. 1–3.

(f) Based on an evaluation by Laufer[8] of the data from Ref. 1 reputed to determine $k(^3CH_2 + O)/k(^3CH_2 + C_2H_2)$. The low value of $k(^3CH_2 + C_2H_2)$ renders this analysis erroneous.

Preferred Values

$k = 2 \cdot 10^{-10}$ cm^3 molecule^{-1} s^{-1} over range 300–2500 K
$k_1 / k = 0.6$

Reliability

$\Delta \log k = \pm 0.3$
$\Delta(k_1/k) = \pm 0.3$

Comments on Preferred Values

The most direct measurement is that of Böhland *et al.*[4], but there is excellent agreement with the values of Frank *et al.*[5] at high temperatures. The rate constant ratio is based primarily on the data of Frank *et al.*[5], but Tsang and Hampson[7] suggested $k_1/k \approx 0.5$, based on the vibrational energy distribution in the product CO[9]. For such an exothermic reaction, the channel efficiencies would not be expected to show a temperature dependence.

References

[1]C. Vinckier and W. Debruyn, 17th Symp. (Int.) Combust., 623 (1978).
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O + CH₃ → HCHO + H
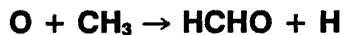
Thermodynamic Data

$\Delta H^{\circ}_{298} = -293 \text{ kJ mol}^{-1}$
$\Delta S^{\circ}_{298} = -23.0 \text{ J K}^{-1}\text{mol}^{-1}$
$K_p = 1.43 \cdot 10^{-2} \; T^{0.195} \exp(+3.54 \cdot 10^4/T)$

Rate Coefficient Data

$k[\text{ cm}^3 \text{ molecule}^{-1}\text{ s}^{-1}]$	$T[\text{ K }]$	Reference	Comments
Rate Coefficient Measurements			
$1.3 \cdot 10^{-10}$	1700–2300	Bhaskaran, Frank, and Just (1979)[1]	(a)
$1.14 \cdot 10^{-10}$	295	Plumb and Ryan (1982)[2]	(b)
$1.4 \cdot 10^{-10}$	294–900	Slagle, Sarzynski, and Gutman (1987)[3]	(c)
Reviews and Evaluations			
$1.2 \cdot 10^{-10}$	300–2500	Warnatz (1984)[4]	
$1.3 \cdot 10^{-10}$	295	Tsang and Hampson (1986)[5]	

Comments

(a) Shock-tube decomposition of C_2H_6 / O_2 mixtures with direct detection of H and O by atomic resonance absorption spectrometry. Rate coefficient derived from a computer simulation of [H] and [O] profiles.

(b) Flow-discharge with mass spectrometric detection of O and CH_3, decay of $[CH_3]$ measured under pseudo first-order conditions with [O] > > $[CH_3]$.

(c) Flow system with generation of CH_3 and $O(^3P)$ from the simultaneous in situ photolysis of CH_3COCH_3 and SO_2 and determination of $[CH_3]$ and [O] by photoionization mass spectrometry. Experiments were performed under conditions such that $[O]/[CH_3]$ > 20 and the rate coefficients were determined from the decay of CH_3. k found to be independent of pressure over the range 1–22 Torr. k confirmed by measurements of the rate of formation of HCHO, the sole observable product.

Preferred Values

$k = 1.4 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over range 300–2500 K

Reliability

$\Delta \log k = \pm 0.2$ over range 300–2500 K

Comments on Preferred Values

The experiments of Plumb and Ryan[2] and Slagle et al.[3] are in accord with the evaluations of Warnatz[4] and of Tsang and Hampson[5]. Here we have recommended the rate coefficient reported by Slagle and et al.[3], a study which also confirms that the reaction involves only one channel forming HCHO and H.

References

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O + CH₄ → OH + CH₃
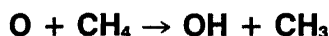
Thermodynamic Data
$\Delta H^\circ_{298} = 10.4$ kJ mol^{-1}
$\Delta S^\circ_{298} = 30.6$ J K^{-1}mol^{-1}
$K_p = 3.28 \cdot 10^2 \, T^{-0.198} \exp(-1560/T)$

Rate Coefficient Data

k [cm³ molecule^{-1} s^{-1}]	Temperature [K]	Reference	Comments
Rate Coefficient Measurements			
$1.16 \cdot 10^{-11} \exp(-3875 /T)$	450–600	Brown and Thrush (1967) [1]	(a)
$1.66 \cdot 10^{-10} \exp(-5033/T)$	375–576	Wong and Potter (1967) [2]	(b)
$3.3 \cdot 10^{-11} \exp(-4630/T)$	297–904	Westenberg and DeHaas (1969) [3]	(c)
$2.6 \cdot 10^{-10} \exp(-4000/T)$	1750–2575	Dean and Kistiakowsky (1971) [4]	(d)
$3.2 \cdot 10^{-10} \exp(-5900/T)$	1200–2000	Brabbs and Brokaw (1975) [5]	(e)
$6.8 \cdot 10^{-10} \exp(-7030/T)$	1500–2250	Roth and Just (1977) [6]	(f)
$2.01 \cdot 10^{-10} \exp(-5435/T)$	474–1156	Klemm et al. (1981) [7]	(g)
$2.63 \cdot 10^{-18} \, T^{2.36} \exp(-3730/T)$	420–1670	Felder and Fontijn (1981) [8]	(h)
$9.2 \cdot 10^{-19} \, T^{2.4} \exp(-2838/T)$	763–1755	Klemm et al. (1986) [9]	(i)
Reviews and Evaluations			
$3.5 \cdot 10^{-11} \exp(-4550/T)$	350–2000	Herron (1969) [10]	(j)
$3.5 \cdot 10^{-11} \exp(-4550/T)$	350–1000	Herron and Huie (1973) [11]	(j)
$8.5 \cdot 10^{-18} \, T^2 \exp(-3240/T)$	300–2000	Shaw (1978) [12]	(j)
$5.24 \cdot 10^{-12} \, T^{0.5} \exp(-5179 /T)$	475–2250	Klemm et al. (1981) [7]	(k)
$2.0 \cdot 10^{-17} \, T^{2.1} \exp(-3837/T)$	300–2200	Warnatz (1984) [13]	(l)
$2.69 \cdot 10^{-18} \, T^{2.3} \exp(-3570/T)$	–	Cohen (1986) [14]	(m)
$3.44 \cdot 10^{-18} \, T^{2.32} \exp(-3713/T)$	400–2000	Wagner (1986) [15]	(o)
$1.7 \cdot 10^{-15} \, T^{1.5} \exp(-4330/T)$	400–2200	Tsang and Hampson (1986) [16]	(p)
$1.15 \cdot 10^{-15} \, T^{1.56} \exp(-4270/T)$	400–2250	Klemm et al. (1986) [9]	(q)

Comments

(a) Discharge flow; ESR detection of O atoms. Some doubt about stoichiometry of reaction.

(b) Discharge, stirred reactor; time-of-flight mass spectroscopy. Assumed Δ[O]/Δ[CH₄] = 4, but Cohen[14] suggests a value of 6 to 7 at 400 K. k values probably high at least 50% (not plotted).

(c) Discharge flow; ESR detection of O atoms. Cohen[14] suggests points below 400 K are too high due to use of incorrect stoichiometry.

(d) Shock tube; fitting of d[CO₂]/dt profiles; complex system.

(e) Shock tube; monitoring CO flame band emission; complex system.

(f) Shock tube; vacuum UV detection of O atoms.

(g) Flash photolysis–resonance fluorecence (474–520 K); discharge flow–resonance fluorescence (548–1156 K). Very pure CH₄ used.

(h) Flash photolysis–resonance fluorescence. Purity of CH₄ not stated.

(i) Flash photolysis–shock tube. Very pure CH₄ used.

(j) Review of early data.

(k) Parameters based on 'collision' model of reaction.

(l) Recommended value based on Refs. 6 and 8.

(m) Temperature range not specified, but 400–2000 K likely.

(o) Fit to rate constants calculated from activated complex theory.

(p) Based on data from Refs. 6, 7, and 8.
(q) Based on data from Refs. 3, 5–9.

Preferred Values

$k = 1.15 \cdot 10^{-15} \, T^{1.56} \exp(-4270/T)$ cm³ molecule^{-1} s^{-1} over range 300–2500 K

Reliability
$\Delta \log k = \pm 0.15$ at 2500 K
$= \pm 0.05$ between 1000 and 500 K, rising to 0.1 at 400 K and at least 0.3 at 300 K.

Comments on Preferred Values

Between 400 and 2000 K there is excellent agreement between a number of reliable studies. The recommended value of k is that derived by Klemm et al.[9], who subjected the data of the more reliable studies to a rigorous analysis. Below 400 K, however, the value of k is considerably more unreliable[14], due to uncertainties in the reaction stoichiometry. All workers appear to have overestimated the value of k.

References

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O + CH₄ → OH + CH₃

$$O + CHO \rightarrow OH + CO \quad (1)$$
$$\rightarrow H + CO_2 \quad (2)$$
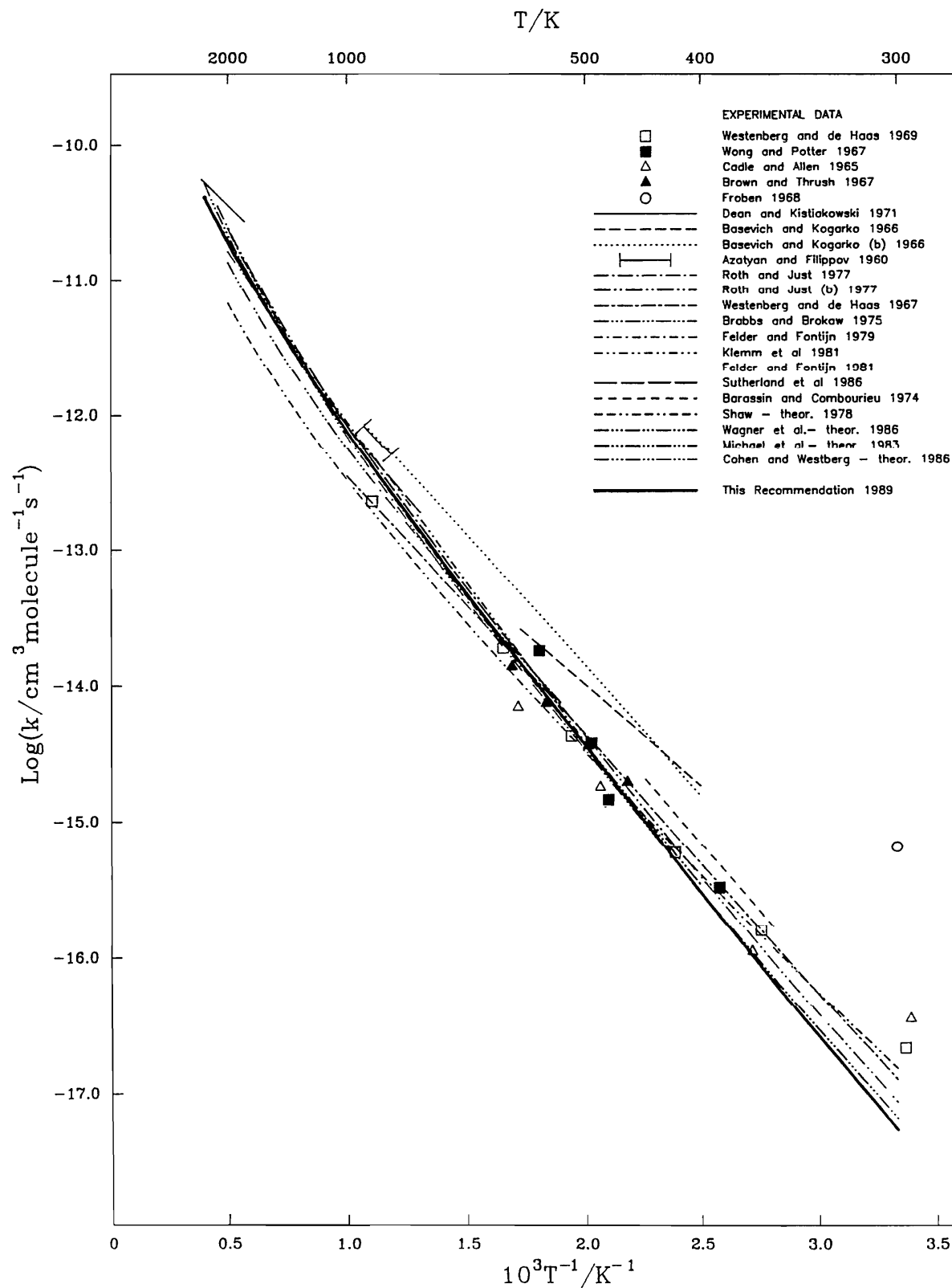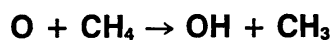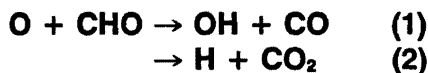
Thermodynamic Data

$\Delta H^\circ_{298} (1) = -364 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (1) = -4.32 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(1) = 20.7 \ T^{-0.482} \exp(+43600/T)$

$\Delta H^\circ_{298} (2) = -468 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (2) = -57.1 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(2) = 8.76\cdot10^{-6} \ T^{0.696} \exp(+56600/T)$

Rate Coefficient Data ($k = k_1 + k_2$)

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	$T[\text{K}]$	Reference	Comments
Rate Coefficient Measurements			
$k_1 = 5\cdot10^{-11}$	1000–1700	Browne *et al.* (1969)[1]	(a)
$k_1 / k = 0.8$	300	Niki, Daby, and Weinstock (1969)[2]	(b)
$k_2 / k_1 = 0.73$	298	Westenberg and deHaas (1972)[3]	(c)
$k_2 / k = 0.46$	300	Mack and Thrush (1973)[4]	(d)
$k = 2.1\cdot10^{-10}$	297	Washida, Martinez, and Bayes (1974)[5]	(e)
$k_1 / k = 0.4$	425	Campbell and Handy (1978)[6]	(f)
Reviews and Evaluations			
$k_1 = 5\cdot10^{-11}$	300–2000	Warnatz (1984)[7]	
$k_2 = 5\cdot10^{-11}$	300–2000		
$k_1 = 5\cdot10^{-11}$	300–2500	Tsang and Hampson (1986)[8]	
$k_2 \approx 5\cdot10^{-11}$	300–2500		

Comments

(a) Modelling study of rich and lean acetylene flames at low pressures; species profiles by gas chromatography and by absorption measurements (OH, CH, and C_2).

(b) Discharge-flow system, C_2H_4 + O reaction; time-of-flight mass spectrometry.

(c) Fast flow system; O atoms generated by microwave discharge. [O] monitored by ESR, [CO_2] by mass spectrometry.

(d) Discharge-flow system; reaction CH_2O + O studied. Products analysed by gas chromatography, [O] and [H] by ESR.

(e) Fast flow reactor; C_2H_4 + O system free of O_2; photoionisation mass spectrometry. k derived from the rate of approach of [CHO] to its steady-state value.

(f) Stirred flow reactor; $O/H_2/N_2$ or Ar system with various amounts of CO added. [O] monitored by CO + O chemiluminescence.

Preferred Values

$k_1 = 5\cdot10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over range 300–2500 K

$k_2 = 5\cdot10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over range 300–2500 K

Reliability

$\Delta \log k_1 = \pm 0.3$ over range 300–2500 K

$\Delta \log k_2 = \pm 0.3$ over range 300–2500 K

Comments on Preferred Values

The recommendations of Warnatz[7] and Tsang and Hampson[8] are adopted.

References

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O + HCHO → OH + CHO
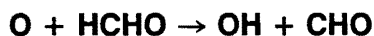
Thermodynamic Data

$\Delta H^\circ_{298} = -50.8$ kJ mol^{-1}

$\Delta S^\circ_{298} = 28.6$ J K^{-1}mol^{-1}

$K_p = 6.88 \cdot 10^2 \ T^{-0.315} \exp(+5810/T)$

Rate Coefficient Data

k [cm^3 molecule^{-1} s^{-1}]	T [K]	Reference	Comments
Rate Coefficient Measurements			
$1.5 \cdot 10^{-13}$	300	Herron and Penzhorn (1969)[1]	(a)
$1.6 \cdot 10^{-13}$	298	Niki et al. (1968)[2]	(b)
$1.0 \cdot 10^{-10}$	1400–2200	Izod et al. (1971)[3]	(c)
$1.5 \cdot 10^{-13}$	300	Mack and Thrush (1973)[4]	(d)
$8.3 \cdot 10^{-11} \exp(-2300/T)$	1875–2240	Bowman (1975)[5]	(e)
$2.8 \cdot 10^{-11} \exp(-1525/T)$	250–498	Klemm (1979)[6]	(f)
$3.8 \cdot 10^{-11} \exp(-1583/T)$	296–437	Chang and Barker (1979)[7]	(g)
$3.0 \cdot 10^{-11} \exp(-1554/T)$	298–748	Klemm et al. (1980)[8]	(h)
Reviews and Evaluations			
$5.8 \cdot 10^{-11} \exp(-1768/T)$	300–2500	Warnatz (1984)[9]	(i)
$3.0 \cdot 10^{-11} \exp(-1550/T)$	298–750	NASA (1985)[10]	(j)
$3.0 \cdot 10^{-11} \exp(-1550/T)$	250–750	Tsang and Hampson (1986)[11]	(k)

Comments

(a) Room temperature study using discharge flow of Ar/O$_2$ or N$_2$/NO. Mass spectrometric detection of reagents and products. [O] determined by titration.

(b) Room temperature discharge flow study of O + C$_2$H$_4$. Value of k concluded from mass spectrometric detection of product time profiles.

(c) CO/Ar/O$_2$ mixtures investigated in incident shock waves. Time profiles for CO and product CO$_2$ used for computer fitting of 4 variable rate constants. Not a true determination of k.

(d) Room temperature study using discharge flow of N$_2$/NO. [O] determined by titration and ESR.

(e) CH$_4$/O$_2$/Ar mixtures investigated in incident shock waves. k determined from computer fitting.

(f) Flash photolysis; resonance fluorescence detection of O atoms.

(g) Discharge flow; mass spectrometric detection of O atoms.

(h) Discharge flow; resonance fluorescence detection of O atoms.

(i) Uses high temperature data of Bowman[5] and low temperature data as cited on this sheet.

(j) Based on the results of Klemm[6], Chang and Barker[7], and Klemm et al.[8].

(k) Accepts the NASA evaluation[10].

Preferred Values

$k = 6.85 \cdot 10^{-13} \ T^{0.57} \exp(-1390/T)$ cm^3 molecule^{-1} s^{-1}

over range 250–2200 K

Reliability

$\Delta \log k = \pm 0.3$ at 2000 K reducing to ± 0.1 at 298 K

Comments on Preferred Values

The preferred values are based on the low temperature data which are all in good agreement, and on the higher temperature value of Bowman[5]. The earlier high temperature values of Izod et al.[3] exceed the preferred values by factors of 3.4 and 6.3 at 2200 and 1400 K respectively. These results are considered unreliable, however, since they were inferred from the computer modelling of reagent and product time dependences using an assumed chemical model. Three other rate coefficients were simultaneously determined, and the derived k values necessarily depend on other rate constants in the model.

References

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[9] J. Warnatz, in "Combustion Chemistry", ed. W. C. Gardiner, Springer-Verlag, New York (1984).

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[11] W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data, **15**, 1087 (1986).

[12] J. Peeters and G. Mahnen, 14th Symp. (Int.) Combust., 133 (1973).

O + HCHO → OH + CHO

$$O + CH_3O \rightarrow O_2 + CH_3 \quad (1)$$
$$\rightarrow OH + HCHO \quad (2)$$
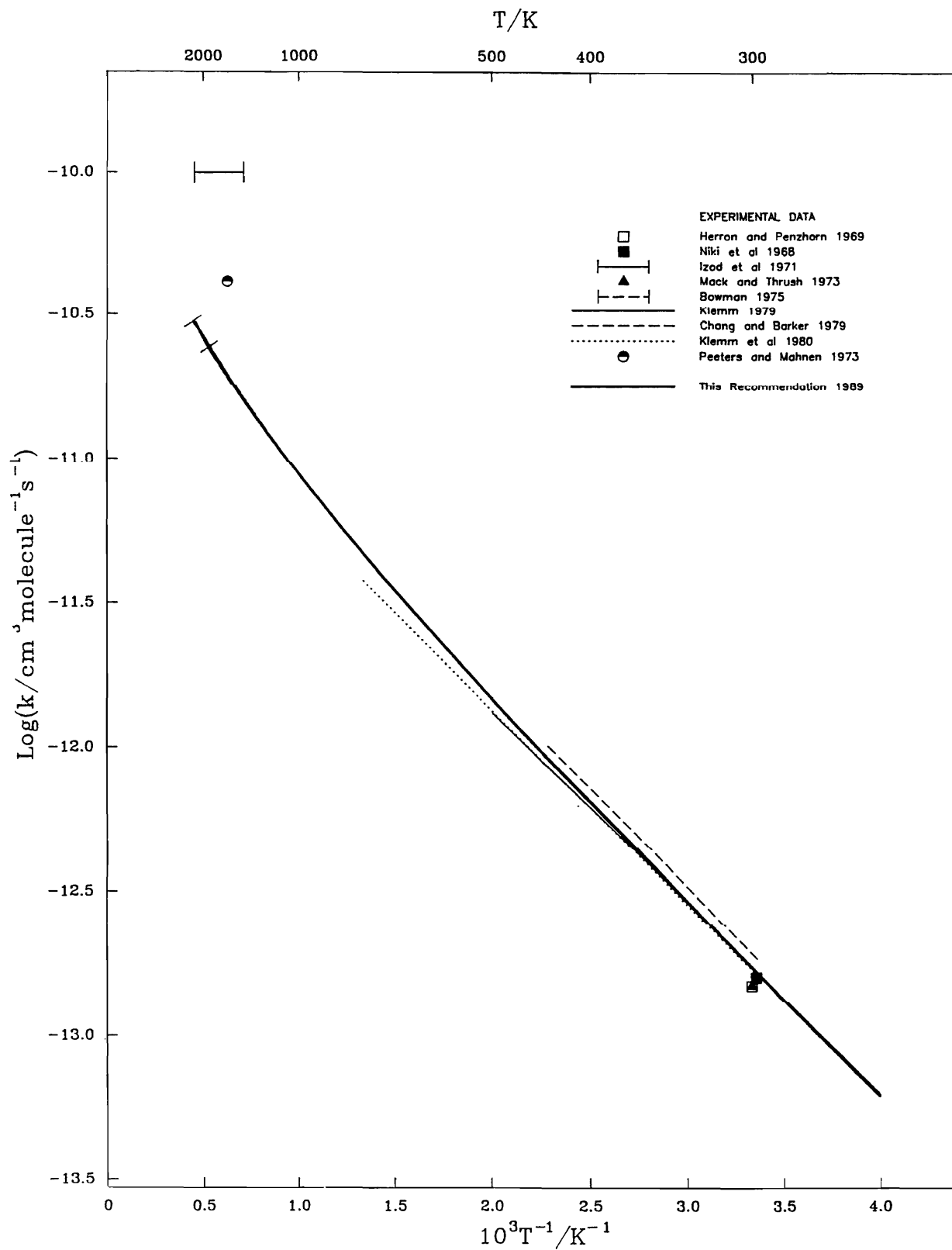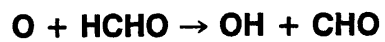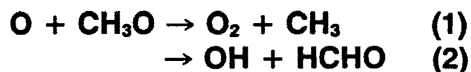
Thermodynamic Data

$\Delta H^\circ_{298} (1) = -119.6 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (1) = 9.6 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(1) = 88.8 \, T^{-4.04} \exp(+14100/T)$

$\Delta H^\circ_{298} (2) = -342 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (2) = 12.8 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(2) = 3.84 \cdot 10^2 \, T^{-0.583} \exp(+40900/T)$

Rate Coefficient Data ($k = k_1 + k_2$)

k [cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$2.5 \cdot 10^{-11}$	298	Ewig, Rhäsa and Zellner (1987)[1]	(a)
$k_2 / k = 0.12$	298		
Reviews and Evaluations			
$1.0 \cdot 10^{-11}$	300–2500	Tsang and Hampson (1986)[2]	(b)

Comments

(a) Laser photolysis of $CH_3ONO/O_3/N_2$ mixtures at 248 nm; CH_3O detected by LIF in presence of excess O.

(b) Estimate with uncertainty of a factor of 5 quoted.

Preferred Values

$k = 2.5 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1} over range 300–1000 K

$k_2 /k = 0.12$ at 298 K

Reliability

$\Delta \log k = \pm 0.7$ at 1000 K reducing to ± 0.3 at 300 K

$\Delta k_2/k = \pm 0.1$ at 298 K

Comments on Preferred Values

The recent direct measurement of this rate constant confirms that this highly exothermic reaction occurs rapidly, as predicted. The recommended value is based on the single experimental measurement at 298 K with an assumed zero temperature dependence. The branching ratio measured in recent work of Zellner and co-workers[1] at room temperature is also recommended. CH_3O is unstable at high temperatures prevalent in most combustion systems.

References

[1] F. Ewig, D. D. Rhäsa, and R. Zellner, Ber. Bunsenges. Phys. Chem. **91**, 708 (1987).

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$$\text{O} + \text{CN} \rightarrow \text{CO} + \text{N}(^4\text{S}) \quad (1)$$
$$\rightarrow \text{CO} + \text{N}(^2\text{D}) \quad (2)$$
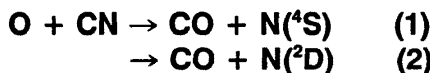
Thermodynamic Data

ΔH°_{298} (1) $= -322$ kJ mol^{-1}

ΔS°_{298} (1) $= -12.8$ J K^{-1}mol^{-1}

$K_p(1) = 0.361\ T^{-0.077}$ exp($+38700/T$)

ΔH°_{298} (2) $= -92$kJ mol^{-1}

ΔS°_{298} (2) $= 1.1$ J K^{-1} mol^{-1}

$K_p(2) = 1.92\ T^{-0.077}$ exp($+11036/T$)

Rate Coefficient Data ($k = k_1 + k_2$)

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$8.0 \cdot 10^{-12}$	1500	Shaub and Bauer (1978)[1]	(a)
$3.0 \cdot 10^{-11}$	2000	Louge and Hanson (1984)[2]	(b)
Reviews and Evaluations			
$1.7 \cdot 10^{-11}$	298	Baulch *et al*. (1981)[3]	(c)
$1.7 \cdot 10^{-11}$	298	CODATA (1984)[4]	(d)

Comments

(a) Shock tube study on C$_2$H$_2$/NO/O$_2$ mixtures. Gas chromatographic analysis of products. Computer fit of results to reaction mechanism.

(b) Shock tube study of (CN)$_2$/O$_2$/Ar mixtures. [CN] monitored by absorption at 388 nm. Computer fit of results to reaction mechanism.

(c) All data reviewed, recommendation made for low temperatures only.

(d) Low temperature data only.

Preferred Values

$k = 1.7 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1} over range 300–5000 K

Reliability

$\Delta \log k = \pm 0.2$ at 298 K rising to ± 0.6 at 5000 K

Comments on Preferred Values

All measurements up to 1978[3] and low temperature results up to 1984[4] have been reviewed. Only recent results not considered there are tabulated here.

At low temperatures there is good agreement among the data from Refs. 8–12. At higher temperatures there are two recent shock tube studies[1,2] in fair agreement and compatible with the low temperature results if the temperature coefficient of the rate constant is very small. The preferred values are based on the results of Louge and

Hanson[2] and Shaub and Bauer[1] at high temperatures, Boden and Thrush[6] between 570 and 687 K, and Refs. 8–12 at low temperatures.

Schmatjko and Wolfrum[11,12] have reported a branching ratio $k_1 / k_2 = 0.8 \pm 0.1$ at 298 K.

References

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[2] M. Y. Louge and R. K. Hanson, Int. J. Chem. Kin. **16**, 231 (1984).

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[12] K. J. Schmatjko and J. Wolfrum, 16th Symp. (Int.) Combust., 819 (1977).

$$O + CN \rightarrow CO + N(^4S) \quad (1)$$
$$\rightarrow CO + N(^2D) \quad (2)$$

EXPERIMENTAL DATA

□	Setser and Thrush 1965
——	Boden and Thrush 1968
△	Reinhardt et al 1969
▲	Schacke and Wolfrum 1972
○	Schacke and Wolfrum 1973
— — —	Albers et al 1975
··········	Shaub 1976
▲	Schmatjko and Wolfrum 1977
⊖	Schmatjko and Wolfrum 1978
+	Shaub and Bauer 1978
×	Louge and Hanson 1984
——	This Recommendation 1989

$$O + NCO \rightarrow NO + CO \quad (1)$$
$$\rightarrow O_2 + CN \quad (2)$$
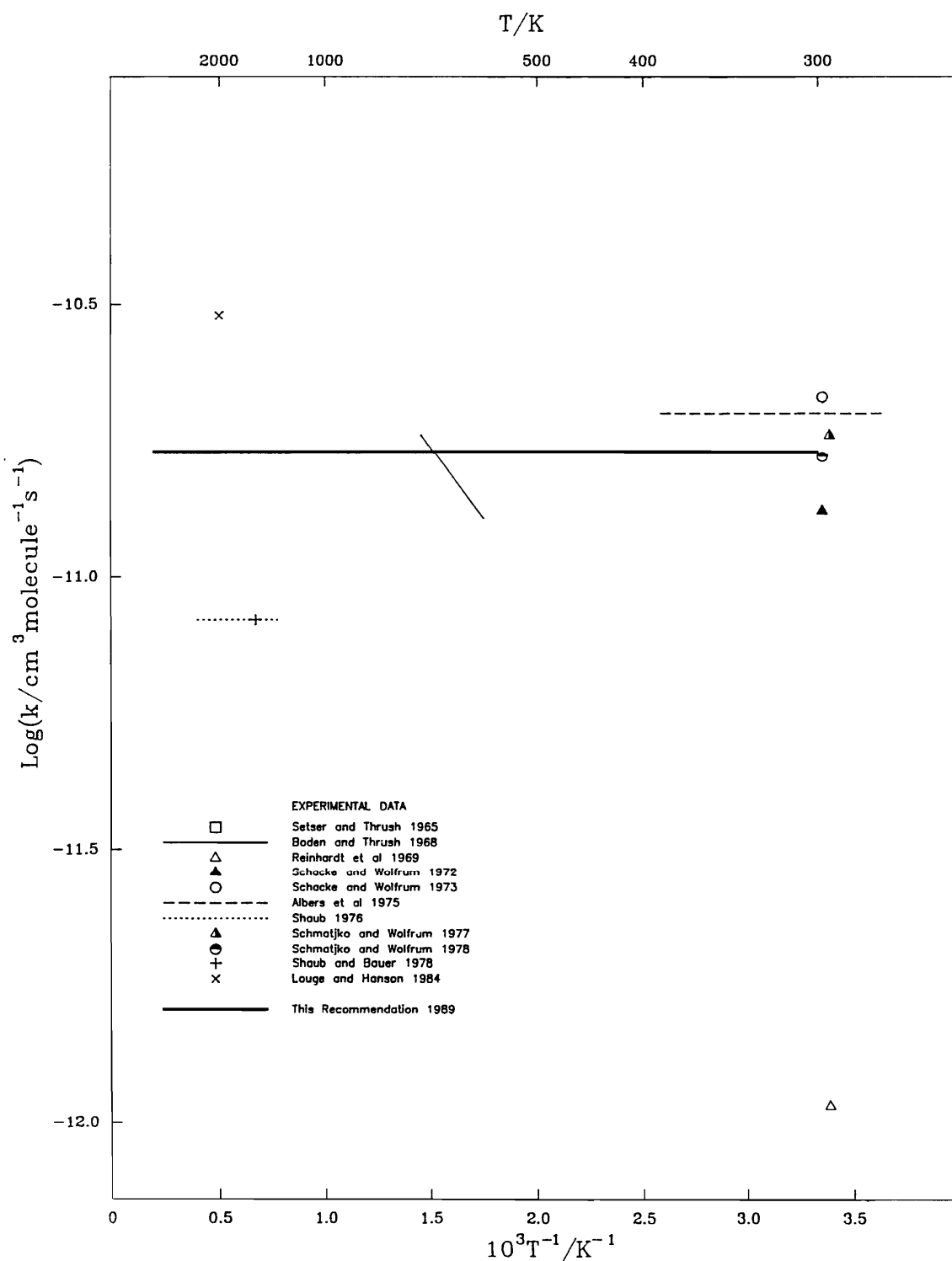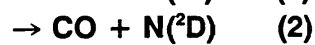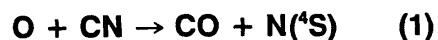
Thermodynamic Data

ΔH°_{298} (1) $= -429$ kJ mol^{-1}
ΔS°_{298} (1) $= 15.1$ J K^{-1}mol^{-1}
K_p(1) $= 9.66 \cdot 10^3 \ T^{-1.07} \exp(+51200/T)$

ΔH°_{298} (2) $= 26.6$ kJ mol^{-1}
ΔS°_{298} (2) $= 14.5$ J K^{-1}mol^{-1}
K_p(2) $= 2.91 \cdot 10^3 \ T^{-0.915} \exp(-3500/T)$

Rate Coefficient Data ($k = k_1 + k_2$)

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$3.32 \cdot 10^{-11}$	1500	Mulvihill and Phillips (1975)[1]	(a)
$1.66 \cdot 10^{-12}$	1500	Phillips (1976)[2]	(b)
$1.66 \cdot 10^{-11}$	1700	Lifshitz and Frenklach (1980)[3]	(c)
$6.61 \cdot 10^{-11}$	1450–2600	Higashihara, Saito, and Murakami (1983)[4]	(d)
$9.34 \cdot 10^{-11}$	1450	Louge and Hanson (1984)[5]	(e)
$k_1 = 5.25 \cdot 10^{-11}$	1680–2250	Higashihara *et al.* (1985)[6]	(f)

Comments

(a) Flame study of H$_2$/N$_2$/O$_2$/C$_2$N$_2$ mixtures. Analysis of products by quadrupole mass spectrometry. k derived from computer fit of data to assumed reaction mechanism.

(b) Computer modelling of system previously studied experimentally[1]. Improved data and extended mechanism used.

(c) Shock tube study of C$_2$N$_2$/O$_2$/Ar mixtures. Induction times measured. Results fitted by computer modelling of 15 reaction mechanism. Only approximate value of k obtained.

(d) Shock tube study of HCN/O$_2$/NO$_2$ mixtures. Induction times measured. Ultraviolet emission at 306 nm due to OH and infrared emission at 5.34 µm, mainly due to NO with some contribution from HCN and H$_2$O, monitored as a function of time.

(e) Shock tube study of C$_2$N$_2$/O$_2$/N$_2$O. [NCO] monitored as a function of time by absorption spectroscopy at 440.5 nm.

(f) Shock tube study of BrCN/O$_2$/Ar mixtures. [NO] monitored as a function of time by infrared emission spectroscopy.

Preferred Values

$k = 7.0 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1} over range 1450–2600 K

Reliability
$\Delta \log k = \pm 0.8$ over range 1450–2600 K

Comments on Preferred Values

All of the existing data result from computer simulation of experimental measurements. In many cases the fit is not very sensitive to the value of k. The recommendation is based on the work of Louge and Hanson[5] and Higashihara *et al.*[6], who have made the most direct studies. Both were shock tube measurements but in one [NCO] was monitored and in the other [NO]. The error limits are large, reflecting the difficulty of studying this reaction in isolation at high temperatures, but the agreement between the studies is good and they are in accord with the other values available[1,3,4].

Comparison of the results of Louge and Hanson[5], measuring k, and those of Higashihara *et al.*, measuring k_1, suggest that channel (1) is dominant at temperatures in the range 1450–2600 K, but the data are too imprecise to recommend a branching ratio.

References

[1] J. N. Mulvihill and L. F. Phillips, 15th Symp. (Int.) Combust., 1113 (1975).
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[3] A. Lifshitz and M. Frenklach, Int. J. Chem. Kin. **12**, 159 (1980).
[4] T. Higashihara, K. Saito, and I. Murakami, J. Phys. Chem. **87**, 3702 (1983).
[5] M. Y. Louge and R. K. Hanson, 19th Symp. (Int.) Combust., 665 (1984).
[6] T. Higashihara, H. Kuroda, K. Saito, and I. Murakami, Comb. Flame **61**, 167 (1985).

$$O + HCN \rightarrow NCO + H \quad (1)$$
$$\rightarrow CO + NH \quad (2)$$
$$\rightarrow OH + CN \quad (3)$$
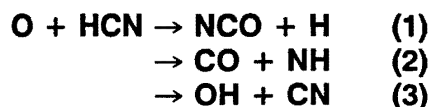
Thermodynamic Data (See Comments on Preferred Values)

$\Delta H^\circ_{298} (1) = -7.0 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (1) = -16.0 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(1) = 3.82 \cdot 10^{-3} \, T^{0.546} \exp(+995/T)$

$\Delta H^\circ_{298} (2) = -138 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (2) = 16.0 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(2) = 1.34 \cdot 10^3 \, T^{-0.747} \exp(+16300/T)$

$\Delta H^\circ_{298} (3) = 89.8 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (3) = 23.5 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(3) = 3.35 \cdot 10^3 \, T^{-0.744} \exp(-11100/T)$

Rate Coefficient Data ($k = k_1 + k_2 + k_3$)

k [cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$8.6 \cdot 10^{-12} \exp(-4090/T)$	450–650	Davies and Thrush (1968)[1]	(a)
$1.94 \cdot 10^{-10} \exp(-7460/T)$	1800–2500	Roth, Löhr, and Hermanns (1980)[2]	(b)
$k_1 = 1.21 \cdot 10^{-10} \exp(-7460/T)$			
$9.8 \cdot 10^{-12} \exp(-4000/T)$	574–840	Perry and Melius (1985)[3]	(c)
$k_1 = 8.3 \cdot 10^{-13}$	1440	Louge and Hanson (1985)[4]	(d)
$k_2 = 3.7 \cdot 10^{-11} \exp(-7740/T)$	1800–2600	Szekely, Hanson, and Bowman (1985)[5]	(e)
$k_3 < 8.3 \cdot 10^{-11} \exp(-11000/T)$	2000–2500		

Comments

(a) Discharge flow study. O atoms generated by N + NO and [O] monitored by NO + O chemiluminescence. Stoichiometry of 2.0 ± 0.4 for O removal interpreted as due to O + HCN → NCO + H, O + NCO → NO + CO, but possibility of contribution from other channels recognized.

(b) Shock tube measurements on HCN/N$_2$O/Ar mixtures. [H] and [O] monitored by absorption at 121.6 nm and 130.5 nm, respectively.

(c) Laser pulse photolysis of O$_2$, NO, or N$_2$O at 157 nm to produce O atoms. HCN in large excess. [O] monitored by NO + O chemiluminescence at 514.5 nm and [NCO] monitored by laser induced fluorescence at 416.81 nm. [NCO] measurements confirm channel (1) to be a major route over temperature range studied. Theoretical calculations suggest the following $k_1 = 3.3 \cdot 10^{-16} \, T^{1.47} \exp(-3750/T)$ cm^3 molecule^{-1} s^{-1}, $k_2 = 9.0 \cdot 10^{-16} \, T^{1.21} \exp(-3800/T)$ cm^3 molecule^{-1} s^{-1}, $k_3 = 4.5 \cdot 10^{-15} \, T^{1.58} \exp(-13300/T)$ cm^3 molecule^{-1} s^{-1}, and $k = 9.8 \cdot 10^{-12} \exp(-4000 \pm 600/T)$ cm^3 molecule^{-1} s^{-1} over the range 540–900 K.

(d) Shock tube measurements on HCN/O$_2$/N$_2$O/Ar mixtures. [NCO] monitored as a function of time by laser absorption at 440.479 nm. $k_1/k(O+C_2N_2) = 2.4^{+2.9}_{-0.9}$ obtained from computer fit. $k(O+C_2N_2) = 7.47 \cdot 10^{-12} \exp(-440/T)$ cm^3 molecule^{-1}s^{-1} used[6] to obtain k_1.

(e) Shock tube measurements on HCN/N$_2$O/Ar mixtures. [CN] and [NH] monitored as a function of time by absorption at 388 nm and 336 nm respectively. Computer fit of assumed mechanism (37 reactions).

Preferred Values

$k = 2.3 \cdot 10^{-18} \, T^{2.1} \exp(-3075/T)$ cm^3 molecule^{-1} s^{-1} over range 450–2500 K

Branching ratios: see *Comments on Preferred Values*

Reliability

$\Delta \log k = \pm 0.2$ at 450 K rising to ± 0.3 at 2500 K

Comments on Preferred Values

This reaction is particularly important in the conversion of fuel nitrogen to nitric oxide in combustion processes. It may proceed by direct abstraction (channel (3)) or by formation of an adduct which can isomerize and/or decompose (channels (1) and (2)).

The overall rate constant is reasonably well-defined over a wide temperature range, all of the experimental studies being in good agreement. The preferred values are based on all of these studies.

Experimental work and theoretical calculations[3,6] are in agreement that channel (1) predominates over the whole temperature range with channel (3) being negligible at low temperatures and becoming significant at high temperatures. There are insufficient experimental data to make recommendations for k_1, k_2, and k_3. The theoretically derived branching ratios of Perry and Melius[3] agree well with the experimental data for k_1 and k_2 and probably offer the best available guide for these quantities, but there is some discrepancy between theory and experiment for k_3[3,5].

The thermodynamic data for channel (2) should be used with caution. There are significant uncertainties associated with the data on NH.

References

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[4]M. Y. Louge and R. K. Hanson, 20th Symp. (Int.) Combust., 665 (1985).

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$$O + HCN \rightarrow NCO + H \quad (1)$$
$$\rightarrow CO + NH \quad (2)$$
$$\rightarrow OH + CN \quad (3)$$

EXPERIMENTAL DATA
Davies and Thrush 1968
Roth et al 1980
△ Perry and Melius 1985
▲ Louge and Hanson 1985
This Recommendation 1989

$$O + CH_3OOH \rightarrow OH + CH_3OO \quad (1)$$
$$\rightarrow OH + CH_2OOH \quad (2)$$
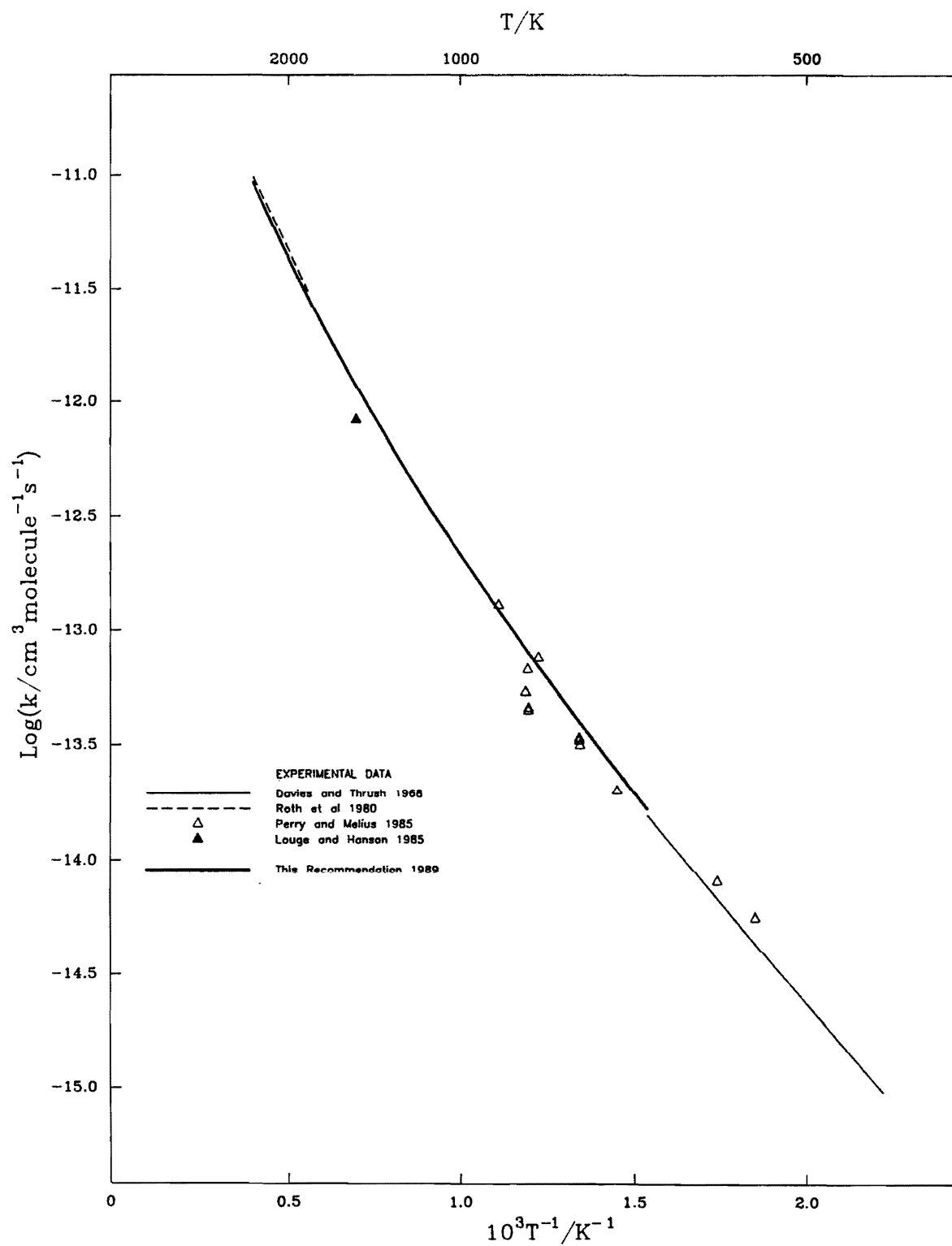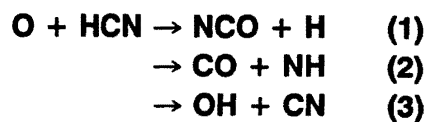
Thermodynamic Data

$\Delta H^\circ_{298} (1) = -61.0 \text{ kJ mol}^{-1}$

$\Delta H^\circ_{298} (2) = -16.0 \text{ kJ mol}^{-1}$

Comment

There are no experimental data for the reaction of $O(^3P)$ with CH_3OOH. The rate constant for the reaction of OH with CH_3OOH is equal to that for OH + HCHO, and since relative reactivities of O and OH towards H abstraction are similar, the overall expression for k ($= k_1 + k_2$) is the same as for O + HCHO i.e. $k = 6.85 \cdot 10^{-13} T^{0.57}$ $\exp(-1390/T)$ cm^3 molecule^{-1} s^{-1} over the range 300–1000 K. Comparison with the rate constant for the reaction O + $H_2O_2 \rightarrow$ OH + HO$_2$ indicates that abstraction of the peroxidic H is slower and provisionally it is suggested that channel (2) is dominant.

$$O + C_2H \rightarrow CH + CO$$
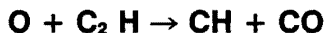
Thermodynamic Data

$\Delta H^\circ_{298} = -326 \text{ kJ mol}^{-1}$
$\Delta S^\circ_{298} = 12.1 \text{ J K}^{-1}\text{mol}^{-1}$
$K_p = 3.67 \cdot 10^2 T^{-0.645} \exp(39000 / T)$

Rate Coefficient Data

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$2.4 \cdot 10^{-11} \exp(-1585/T)$	1400–2600	Shaub and Bauer (1978)[1]	(a)
$\approx 1.7 \cdot 10^{-11}$	298	Homann and Schweinfurth (1981)[2]	(b)
$\approx 1.2 \cdot 10^{-12}$	298	Grebe and Homann (1982)[3]	(c)
Reviews and Evaluations			
$1.7 \cdot 10^{-11}$	300–2500	Warnatz (1984)[4]	
$3.0 \cdot 10^{-11}$	300–2500	Tsang and Hampson (1986)[5]	

Comments

(a) Shock heating of $C_2H_2/O_2/Ar$ mixtures; final product concentrations from gas chromatography. Numerical modelling of 17 reaction mechanism, k adjusted to give best fit to experimental results.

(b) Discharge-flow system; C_2H_2/O system with and without added H. [C_3H_4], [C_4H_2], and [CH_2O] by mass spectrometry. Numerical modelling of 27 reaction mechanism; reaction plays only a minor role.

(c) Discharge-flow reactor; $C_2H_2/H/O$ system. Measurement of CH (A$^2\Delta$–X$^2\Pi$) and $C_2(d^3\Pi_g$–A$^3\Pi_u)$ chemiluminescence at 431.4 nm and 516.5 nm and the quasi-continuous C_2H^* radiation. Numerical modelling of 37 reaction mechanism. Rate coefficient given for formation of CH(A$^2\Delta$).

Preferred Values

$k = 1.7 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1} over range 300–2500 K

Reliability

$\Delta \log k = \pm 1.0$ over range 300–2500 K

Comments on Preferred Values

The high value of Homann and Schweinfurth[2] is adopted as the recommendation because of its agreement with the high temperature value of Shaub and Bauer[1] and the fact that only the path to excited CH has been considered in the work of Grebe and Homann[3].

References

[1]W. M. Shaub and S. H. Bauer, Comb. Flame **32**, 35 (1978).

[2]K. H. Homann and H. Schweinfurth, Ber. Bunsenges. Phys. Chem. **85**, 569 (1981).

[3]J. Grebe and K. H. Homann, Ber. Bunsenges. Phys. Chem. **86**, 587 (1982).

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[5]W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data **15**, 1087 (1986).

$$O + C_2H_2 \rightarrow {}^3CH_2 + CO \quad (1)$$
$$\rightarrow H + C_2HO \quad (2)$$
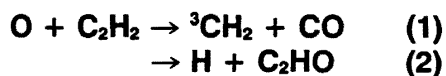
Thermodynamic Data

$\Delta H^\circ_{298} (1) = -200 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (1) = 31.2 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(1) = 7.31\cdot10^5 \ T^{-1.40} \exp(+23500/T)$

$\Delta H^\circ_{298} (2) = -80.4 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (2) = 6.9 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(2) = 1.17 \ T^{0.15} \exp(+9600/T)$

Rate Coefficient Data ($k = k_1 + k_2$)

k [cm^3 molecule^{-1} s^{-1}]	T [K]	Reference	Comments
Rate Coefficient Measurements			
$3.3\cdot10^{-11} \exp(-1600/T)$	230–450	Westenberg and de Haas (1969)[1]	(a)
$2.0\cdot10^{-11} \exp(-1500/T)$	243–673	Hoyermann, Wagner, and Wolfrum (1969)[2]	(b)
$k_2/k = 0.42$	404	Williamson (1971)[3]	(c)
$8.6\cdot10^{-11} \exp(-1860/T)$	1200–1700	Peeters and Mahnen (1973)[4]	(d)
$k_1/k = 0.95$	298	Blumenberg, Hoyermann,	
$k_2/k < 0.03$		and Sievert (1976)[5]	(e)
$1.2\cdot10^{-13}$	297	Westenberg and de Haas (1977)[6]	(f)
$1.1\cdot10^{-10} \exp(-2000/T)$	700–1430	Vandooren and Van Tiggelen (1977)[7]	(g)
$k_1 = 2.0\cdot10^{-10} \exp(-3300/T)$	1500–2570	Löhr and Roth (1981)[8]	(h)
$k_2 = 7.2\cdot10^{-10} \exp(-6100/T)$			
$3\cdot10^{-11} \exp(-1620/T)$	298–608	Aleksandrov, Arutyunov,	
$k_2/k = 0.5 \exp(-660/T)$		and Kozlov (1981)[9]	(i)
$2.7\cdot10^{-11} \exp(-1550/T)$	300–1300	Homann and Wellmann (1983)[10]	(j)
$k_2/k = 0.5$	1000	Homann and Wellmann (1983)[11]	(j)
$k_2/k = 0.6$	287 , 535	Peeters, Schaeker, and Vinckier (1986)[12]	(k)
$k_1 = 2.7\cdot10^{-10} \exp(-4975/T)$	1500–2500	Frank, Bhaskaran, and Just (1986)[13]	(l)
$k_2 = 6.6\cdot10^{-10} \exp(-5365/T)$			
$1.1\cdot10^{-19} \ T^{2.6} \exp(-330/T)$	290–1510	Mahmud and Fontijn (1987)[14]	(m)
$k_2/k = 0.8$	287	Peeters et al. (1987)[15]	(n)
$6.6\cdot10^{-11} \exp(-1900/T)$	370–876	Russell et al. (1988)[16]	(o)
Reviews and Evaluations			
$k_1 = 6.8\cdot10^{-16} \ T^{1.5} \exp(-850/T)$	300–2500	Warnatz (1984)[17]	(p)
$k_2 = 7.2\cdot10^{-10} \exp(-6100/T)$	1000–2500		
$2.9\cdot10^{-11} \exp(-1600/T)$	200–450	NASA (1985)[18]	(q)
$2.9\cdot10^{-11} \exp(-1600/T)$	200–700	Tsang and Hampson (1986)[19]	(r)
$2.7\cdot10^{-11} \exp(-1550/T)$	250–1300	Cvetanovic (1987)[20]	(s)
$k_1 = 3.5\cdot10^{12} \ T^{1.5} \exp(-850/T)$	300–2500		
$k_2 = 1.5\cdot10^{-11} \exp(-2300/T)$	300–600		
$= 7.0\cdot10^{-10} \exp(-6100/T)$	1000–2500		

Comments

(a) Discharge flow with ESR detection. Stoichiometry of 2 oxygen atoms consumed for each reaction with C_2H_2 determined from combined ESR/mass spectrometry experiments.

(b) Discharge flow with detection by ESR and mass spectrometry.

(c) Applies to O + C_2D_2. O generated from Hg photosensitized decomposition of N_2O. D yield determined from HD produced by scavenging with H_2. HD measured relative to N_2.

(d) Ethylene flame study using molecular beam sampling and mass spectrometry to determine molecular flux gradients.

(e) Mass spectrometric detection from a laval nozzle reactor. Ratios based on H, CO, and C_2H_2 signals although CH_2 and CHCO were also observed.

(f) Flash photolysis, resonance fluorescence. O generated from photolysis of O_2.

(g) Acetylene flame study using molecular beam sampling and mass spectrometry.

(h) Reflected shock wave in $N_2O/C_2H_2/Ar$. O and H monitored by atomic resonance absorption spectrometry.

(i) O generated by discharge through N_2O, admitted through movable nozzle. H and O detected by resonance fluorescence, absolute calibration being achieved via equilibrium concentrations of H and O in H_2 and O_2 at 1300–1500 K. k determined from decay of O signal, k_2/k from the absolute H signal.

(j) Discharge flow ($O/C_2H_2/He$), nozzle beam sampling with mass spectrometric detection.

(k) Flow reactor, O generated by discharge through O_2, molecular beam sampling with mass spectrometric detection.

(l) Reflected shock wave study on $N_2O/C_2H_2/Ar$. O, H, and CO detected by resonance absorption spectrometry. Channel (2) was essential if the initial shape of the H profile was to be reproduced.

(m) Flash photolysis, resonance fluorescence. O generated from photolysis of O_2 or CO_2.

(n) Flow reactor, O and H generated by discharge. k_2/k determined from the dependence of the CH_2 signal on $[H]/[O]$, based on secondary generation of CH_2 via H + HCCO.

(o) Laser flash photolysis, photoionisation mass spectrometry. O generated from photolysis of SO_2, C_2H_2 from photolysis of C_2H_3Br.

(p) Evaluation, based on the low temperature data summarised by Cvetanovic[20] and the high temperature data of Peeters and Mahnen[4], Vandooren and Van Tiggelen[7], Löhr and Roth[8], and Homann and Wellmann[10]. k_2 based on data of Löhr and Roth[8] and Homann and Wellmann[11].

(q) NASA panel evaluation based on low temperature data over the period 1965–1981.

(r) Accepted the NASA evaluation but extended range.

(s) Low temperature evaluation of data prior to 1986. Cvetanovic selected a dependence close to that of Homann and Wellmann[11].

Preferred Values

$k = 3.6 \cdot 10^{-20} \, T^{2.8} \exp(-250/T)$ cm^3 molecule^{-1} s^{-1} over range 300–2500 K

$k_2 / k = 0.5$ over range 300–2500 K

Reliability

$\Delta \log k = \pm 0.2$

$\Delta(k_2/k) = \pm 0.3$

Comments on Preferred Values

(i) Overall rate constant

The recommended rate coefficient is that proposed by Mahmud and Fontijn[14] from a fit to their own data and that published earlier. There is generally good agreement between the data sets although, especially in the intermediate temperature range, the discrepancies between different sets of direct measurements are surprisingly large. We have, accordingly, increased the uncertainty limits beyond the $\pm$ 35% value suggested by Mahmud and Fontijn.

(ii) Channel efficiencies

While it is difficult to recommend precise channel efficiencies, there is clear evidence that both channels are significant.

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$$O + C_2H_2 \rightarrow CH_2 + CO \qquad (1)$$
$$\rightarrow H + C_2HO \qquad (2)$$

$$O + C_2H_2 \rightarrow {}^3CH_2 + CO \qquad (1)$$
$$\rightarrow H + C_2HO \qquad (2)$$

$$O + C_2H_3 \rightarrow H + CH_2CO \quad (1)$$
$$\rightarrow CH_3 + CO \quad (2)$$
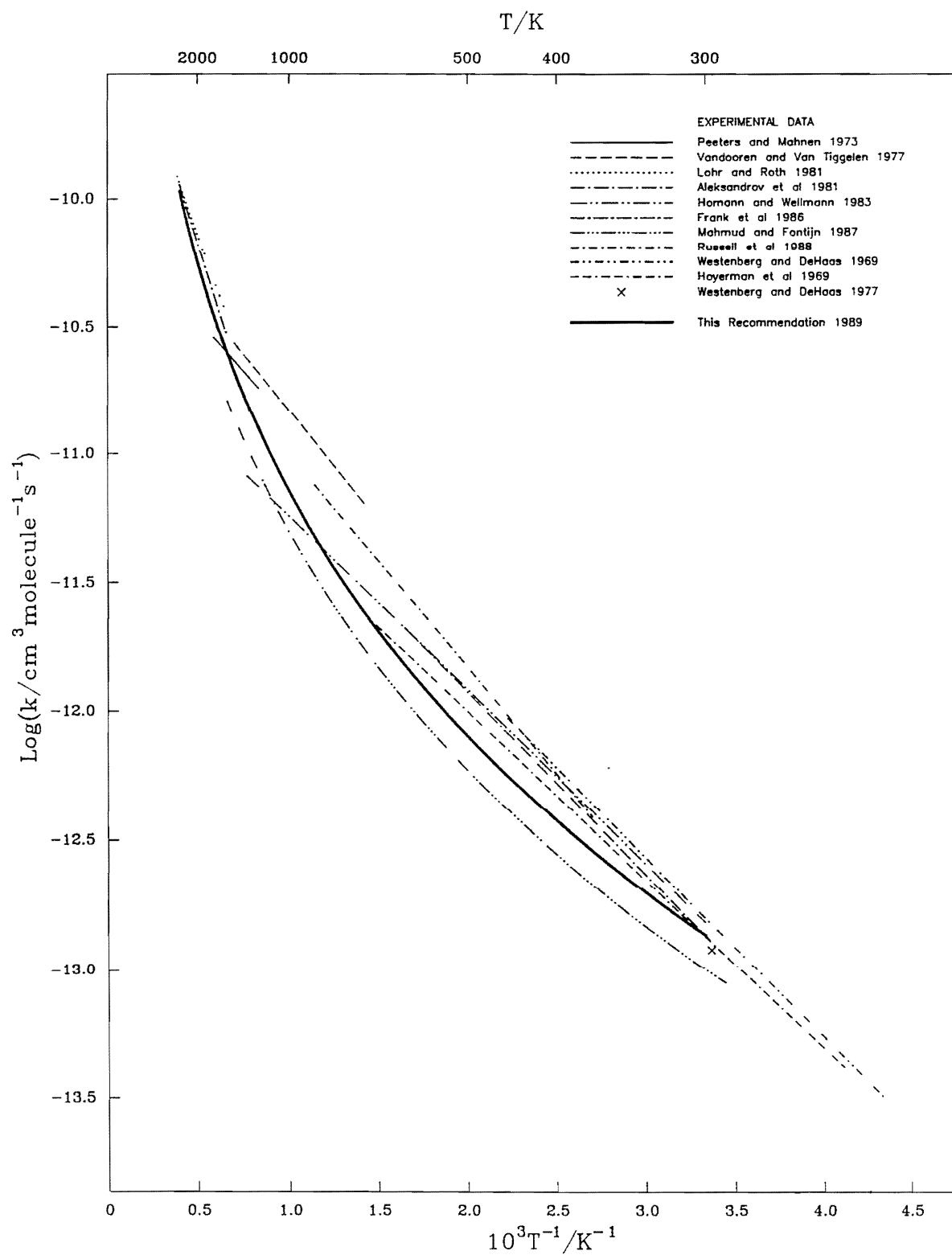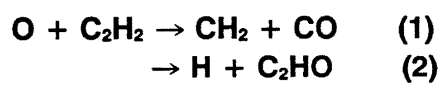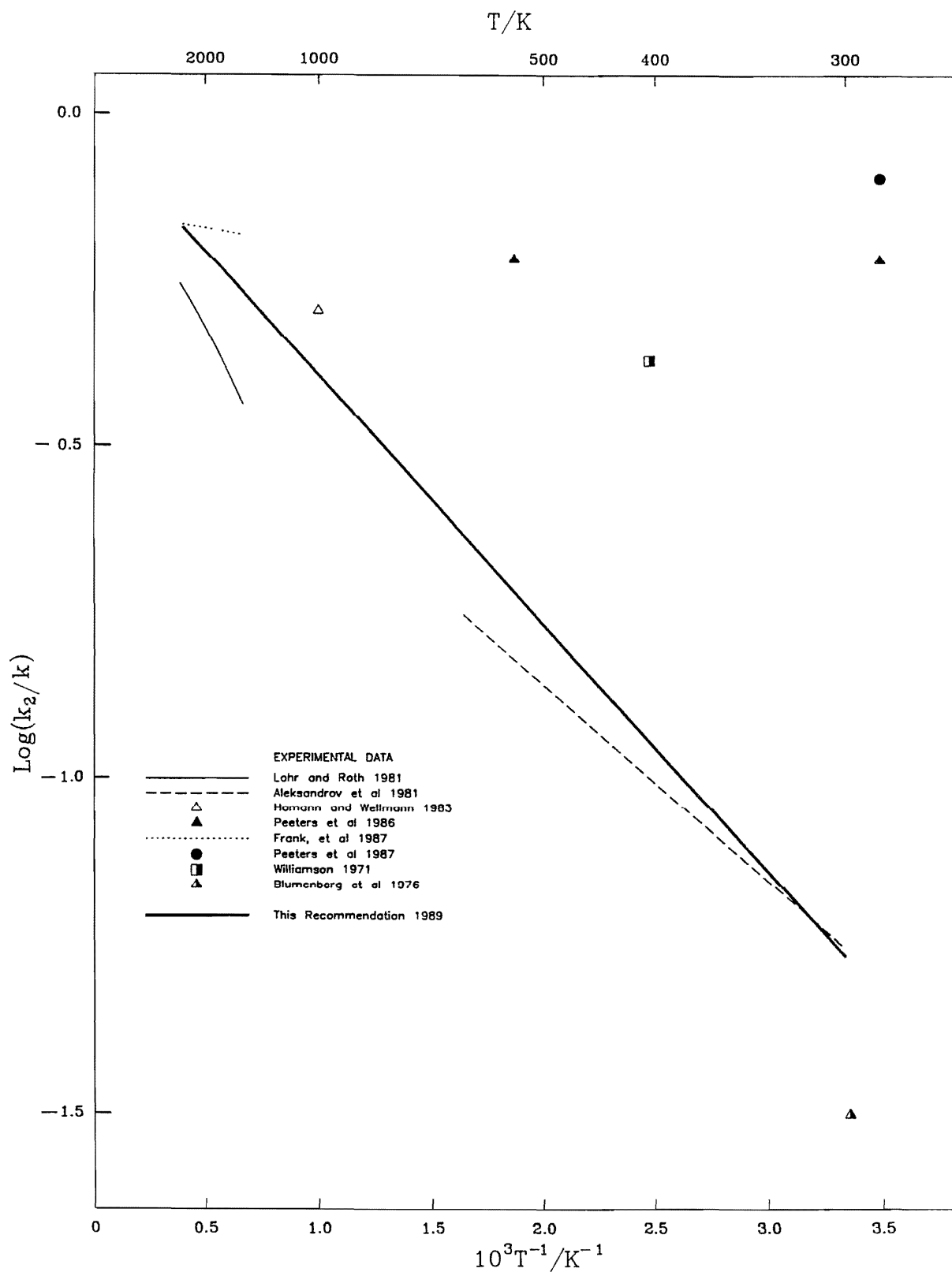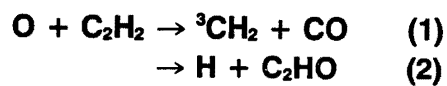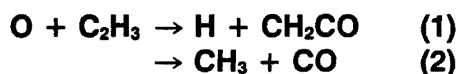
Thermodynamic Data

$\Delta H^{\circ}_{298} (1) = -369$ kJ mol^{-1}

$\Delta S^{\circ}_{298} (1) = -36.1$ J K^{-1}mol^{-1}

$K_p(1) = 7.9 \cdot 10^{-5} \, T^{0.816} \exp(+44600/T)$

$\Delta H^{\circ}_{298} (2) = -500$ kJ mol^{-1}

$\Delta S^{\circ}_{298} (2) = -0.87$ J K^{-1}mol^{-1}

$K_p(2) = 1.10 \cdot 10^2 \, T^{-0.636} \exp(+59800/T)$

Rate Coefficient Data ($k = k_1 + k_2$)

k [cm^3 molecule^{-1} s^{-1}]	T [K]	Reference	Comments
Rate Coefficient Measurements			
$3.3 \cdot 10^{-11}$	298	Homann and Schweinfurth (1981)[1]	(a)
$5 \cdot 10^{-11}$	≈ 200 (see comments)	Heinemann et al. (1986)[2]	(b)
Reviews and Evaluations			
$k = 5.0 \cdot 10^{-11}$	300–2000	Warnatz (1984)[3]	(c)
$k = 1.6 \cdot 10^{-10}$	–	Tsang and Hampson (1986)[4]	(d)

Comments

(a) Discharge flow – mass spectrometric detection study of O + C$_2$H$_2$ with and without added H. k was one of several rate coefficients determined by fitting a numerical model. The products were assumed to be H + CH$_2$ + CO.

(b) Low pressure (0.3–4 mbar) measurements in a laval nozzle reactor using mass-spectrometric detection. The rate coefficient was measured relative to that for O + (CH$_3$)$_3$C which in turn had been measured relative to that for O + CH$_3$. A value of $1.2 \cdot 10^{-10}$ cm^3 molecule^{-1} s^{-1} was assumed for k(CH$_3$ + O), in good agreement with the value recommended in this evaluation ($1.4 \cdot 10^{-10}$ cm^3 molecule^{-1} s^{-1}). Both products of channel (2) were detected and CH$_2$CO was also found showing that channel (1) also operates. It was not possible to determine a branching ratio. The authors commented that it is difficult to determine the temperature in the laval nozzle reactor, but a value of ≈ 200 K seems appropriate.

(c) Based on Ref. 1 and a preliminary, private communication from the authors of Ref. 2.

(d) Estimated by comparison with O + CH$_3$.

Preferred Values

$k = 5.0 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1} over range 300–2000 K

Reliability

$\Delta \log k = \pm 0.5$ over the whole range

Comments on Preferred Values

The value determined by Heinemann et al.[2] is preferred, because of the more direct nature of their experimental technique; large error limits have been assigned pending confirmatory measurements.

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$$O + C_2H_4 \rightarrow CH_2CHO + H \quad (1)$$
$$\rightarrow CHO + CH_3 \quad (2)$$
$$\rightarrow HCHO + CH_2 \quad (3)$$
$$\rightarrow CH_2CO + H_2 \quad (4)$$
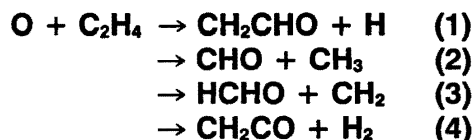
Thermodynamic Data

$\Delta H^\circ_{298}(1) = -58.5 \text{ kJ mol}^{-1}$
$\Delta S^\circ_{298}(1) = 2.3 \text{ J K}^{-1}\text{mol}^{-1}$
$K_p(1) = 0.127 \ T^{0.415} \exp(+7030/T)$

$\Delta H^\circ_{298}(2) = -112 \text{ kJ mol}^{-1}$
$\Delta S^\circ_{298}(2) = 38.5 \text{ J K}^{-1}\text{mol}^{-1}$
$K_p(2) = 4.5 \cdot 10^4 \ T^{-0.114} \exp(+13100/T)$

$\Delta H^\circ_{298}(3) = -30.5 \text{kJ mol}^{-1}$
$\Delta S^\circ_{298}(3) = 33.9 \text{ J K}^{-1}\text{mol}^{-1}$
$K_p(3) = 6.08 \cdot 10^4 \ T^{-0.948} \exp(+3210/T)$

$\Delta H^\circ_{298}(4) = -353.0 \text{ kJ mol}^{-1}$
$\Delta S^\circ_{298}(4) = -7.73 \text{ J K}^{-1}\text{mol}^{-1}$
$K_p(4) = 0.369 \ T^{0.143} \exp(+42280/T)$

Rate Coefficient Data ($k = k_1 + k_2 + k_3 + k_4$)

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	$T[\text{K}]$	Reference	Comments
Rate Coefficient Measurements			
$6.73 \cdot 10^{-13}$	298	Fonderie *et al.* (1983)[1]	(a)
$2.42 \cdot 10^{-12}$	552		
$4.61 \cdot 10^{-12}$	736		
$8.43 \cdot 10^{-12} \exp(-757/T)$	197–372	Browarzik and Stuhl (1984)[2]	(b)
$k_1/k = 0.27$	300	Smalley *et al.* (1986)[3]	(c)
$k_1/k = 0.37$	769		
$k_2/k_1 = 1.2$	298	Koda *et al.* (1987)[4]	(d)
$k_2/k_1 = 6.0$			
$1.3 \cdot 10^{-11} \exp(-830/T) +$			
$\quad 1.9 \cdot 10^{-9} \exp(-6940/T)$	290–1510	Mahmud *et al.* (1987)[5]	(e)
$1.02 \cdot 10^{-11} \exp(-753/T) +$			
$\quad 2.75 \cdot 10^{-10} \exp(-4220/T)$	244–1052	Klemm *et al.* (1987)[6]	(f)
Reviews and Evaluations			
$5.4 \cdot 10^{-12} \exp(-565/T)$	200–500	Herron and Huie (1973)[7]	(g)
$2.67 \cdot 10^{-15} \ T^{1.2} \exp(-370/T)$	300–2000	Warnatz (1984)[8]	(h)
$2.2 \cdot 10^{-16} \ T^{1.55} \exp(-215/T)$	230–940	Tsang and Hampson (1986)[9]	(i)
$1.07 \cdot 10^{-11} \exp(-800/T)$	200–500	Cvetanovic (1987)[10]	(j)

Comments

(a) Discharge flow–mass spectrometry with molecular beam sampling. Decay of C_2H_4 in large excess of O. Data in table obtained at 2 Torr; no effect of pressure between 0.5–5 Torr was found at any of the three temperatures investigated.

(b) Laser photolysis of NO to produce O which was monitored by O + NO chemiluminescence in excess C_2H_4.

(c) Branching ratio for the H + CH_2CHO product channel determined from measured H- and O-atom profiles in this flash photolysis–resonance fluorescence study. Relative detector sensitivities for O and H determined, giving accurate value of k_1/k. The branching ratio increased slightly with temperature, based on measurements at 300, 515, 608, 677, and 769 K.

(d) Branching ratio determined from measurement of CHO (CDO) and CH_2CHO (CD_2CDO) yields using time-resolved microwave spectroscopy in pulsed Hg-photosensitised reaction of N_2O/C_2H_4 mixtures. Pressure = 30 mTorr.

(e) High temperature flash photolysis of CO_2 to produce $O(^3P)$; resonance fluorescence detection. Pressure 60–500 Torr.

(f) Two techniques used: flash photolysis–resonance fluorescence (244–1052 K) and discharge flow–resonance fluorescence (298–1017 K). NO was used as photolytic source of $O(^3P)$ at $T > 600$ K to avoid problems from secondary reactions involving O_2.

(g) Recommendation based mainly on results reported by Davis *et al.*[11].

(h) Based on experimental data up to 1980, including high temperature data of Peeters and Mahnen[18].

(i) Fit to results of Davis *et al.*[11], Westenberg and de-Haas[12] for $T < 500$ K, Atkinson and Pitts[13], Singleton and Cvetanovic[14], Atkinson and Pitts[15], Nicovich and Ravishankara[16], and Perry[17]. Uncertainty of 20%.

(j) Considered 33 literature sources up to 1984. Assumed linear Arrhenius plot up to 500 K.

Preferred Values

$k = 5.75 \cdot 10^{-18} \ T^{2.08} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over range 300–2000 K

$k_1 / k = 0.35$ at p $\geq$ 3 Torr and $T \geq 300$ K
$k_2 / k = 0.60$

Reliability

$\Delta \log k = \pm 0.1$ for $T < 1000$ K increasing to ± 0.3 at
  2000 K

$\Delta k_1/k = \pm 0.05$

$\Delta k_2/k = \pm 0.10$

$\Delta k_4/k = \pm 0.10$

Comments on Preferred Values

There is a large amount of data on this reaction which has been reviewed regularly. Only those recent data not presented by Cvetanovic[10] are listed here. The recent direct studies at higher temperatures[1,5,6,16,17] show clear non-Arrhenius behaviour at temperatures > 500 K. The recent study of Browarzik and Stuhl[2] extends the temperature range down to 197 K. All the data are in excellent agreement, within the stated experimental uncertainty. Both recent studies at temperatures > 1000 K suggest a biexponential representation of the overall k. The expression given by Klemm *et al.*[6] does not include the higher temperature data of Mahmud *et al.*[5], but nevertheless gives a good fit to all the data over the range 250–1500 K. The preferred expression is derived by performing a 3 parameter $A T^n \exp(E/RT)$ fit to the curve generated from the expression of Klemm *et al.* over the range 250–1500 K. The exponential term was negligible, the curve being accurately described by an AT^n expression. The results from Ref. 1 show that k is independent of pressure at $T > 300$ K.

The recent determination of the branching ratio, k_1/k, confirms that H atom elimination is a major pathway in this reaction. Koda *et al.*[4] have rationalised these results, as well as their observed isotope effect, with a model involving unimolecular dissociation on a triplet biradical surface (channel 1) and a competitive triplet-to-singlet crossing. The small temperature effect may reflect an increase in rate of fragmentation of the initial adduct with increasing energy of the reactants, which is also consistent with the results of Buss *et al.*[19] who found $k_1/k = \approx 1.0$ at high kinetic energies of reactants in molecular beam experiments. The recommended values of the branching ratios are based on these studies. Earlier attempts to determine the branching ratios by mass spectrometry appear to have given an erronous picture.

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$$O + C_2H_4 \rightarrow CH_2CHO + H \quad (1)$$
$$\rightarrow CHO + CH_3 \quad (2)$$
$$\rightarrow HCHO + CH_2 \quad (3)$$
$$\rightarrow CH_2CO + H_2 \quad (4)$$

$$O + C_2H_5 \rightarrow CH_3CHO + H \quad (1)$$
$$\rightarrow HCHO + CH_3 \quad (2)$$
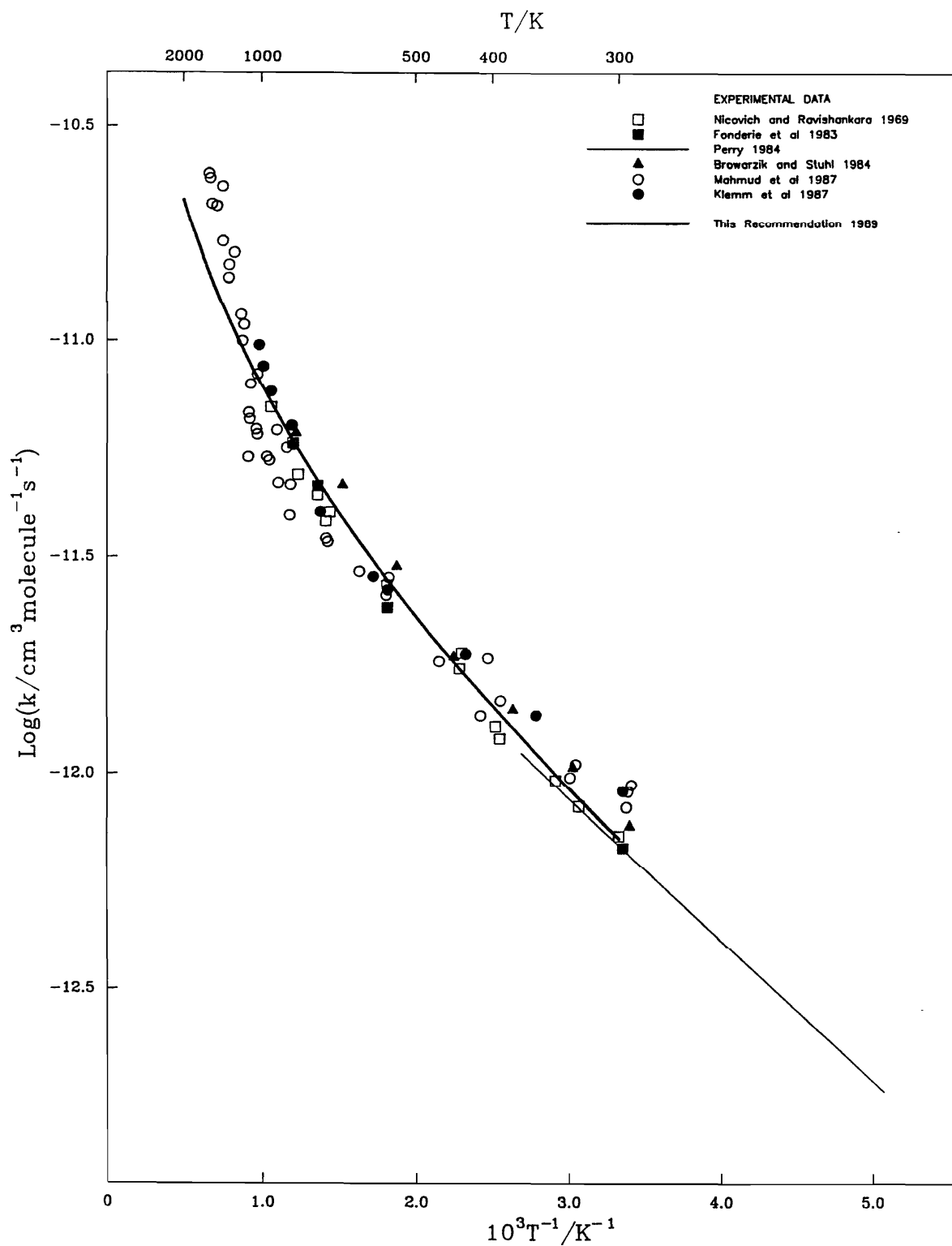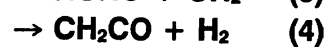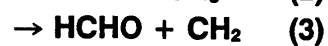
Thermodynamic Data

$\Delta H^\circ_{298} (1) = -314 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (1) = -34.2 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(1) = 1.30 \cdot 10^{-4} \, T^{0.750} \exp(+37900/T)$

$\Delta H^\circ_{298} (2) = -337 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (2) = -0.07 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(2) = 64.8 \, T^{-0.546} \exp(+40200/T)$

Rate Coefficient Data ($k = k_1 + k_2$)

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	$T[\text{K}]$	Reference	Comments
Rate Coefficient Measurements			
$k_1/k_2 = 5 \pm 1$	300	Hoyermann and Sievert (1979)[1]	(a)
$9.5 \cdot 10^{-11}$	720–785	Peeters and Caymax (*)[2]	(b)
Reviews and Evaluations			
$8.3 \cdot 10^{-11}$	700–2000	Warnatz (1984)[3]	(c)
$1.6 \cdot 10^{-10}$	300–2500	Tsang and Hampson (1986)[4]	(d)

Comments

(a) Low pressure flow system with nozzle reactor and mass spectrometric analysis. Products CH_3CHO and HCHO taken as confirmation for channels (1) and (2). Absence of OH and C_2H_2 products indicates that channel $O + C_2H_5 \rightarrow OH + C_2H_4$ does not occur in this system.

(b) Discharge-flow technique with molecular beam sampling for mass spectrometry. O atoms (microwave discharge) reacted with C_2H_6 at total pressures of 2 Torr. k derived from measurements of [O] (titration) and [C_2H_5] (mass spectrometry) at the approach to the stationary state of [C_2H_5].

(c) Estimated value.

(d) Assumed value taken to be equal to $k(O + CH_3)$.

Preferred Values

$k = 1 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over range 300–2500 K

$k_2/k = 0.17$ at 300 K

Reliability

$\Delta \log k = \pm 0.3$ over range 300–1000 K

$= \pm 0.5$ over range 1000–2500 K

$\Delta k_2/k = \pm 0.03$ at 300 K

Comments on Preferred Values

The recent measurement of this rate coefficient by Peeters and Caymax[2] are direct and should be free from major complications. We have recommended a rounded-off rate coefficient from this study, but this requires confirmation along with studies over a wider range of temperatures. The recommended branching ratio, k_2/k, is calculated from the experimental ratio $k_1/k_2 = 5$ as determined by Hoyermann and Sievert[1]. Here again confirmation plus a temperature dependence are both needed.

References

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[2] J. Peeeters and M. Caymax, awaiting publication.

[3] J. Warnatz, in "Combustion Chemistry", ed. W. C. Gardiner, Springer-Verlag, New York (1984).

[4] W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data 15, 1087 (1986).

O + C$_2$H$_6$ → OH + C$_2$H$_5$
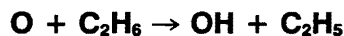
Thermodynamic Data
ΔH°_{298} = −9.1 kJ mol^{-1}
ΔS°_{298} = 45.3 J K^{-1}mol^{-1}
K_p = 5.29·10^4 $T^{-0.748}$ exp(+744/T)

Rate Coefficient Data

k [cm^3 molecule^{-1} s^{-1}]	Temperature [K]	Reference	Comments
Rate Coefficient Measurements			
1.39·10^{-10} exp(−3770 /T)	853–933	Azatayan, Nalbandyan, and Meng-yuan (1962)[1]	(a)
3.0·10^{-11} exp(−2650/T)	320–589	Westenberg and DeHaas (1967)[2]	(b)
3.0·10^{-11} exp(−2650/T)	272–615	Westenberg and DeHaas (1969)[3]	(c)
1.38·10^{-10} exp(−3620/T)	336–595	Herron and Huie (1969)[4]	(d)
4.6·10^{-11} exp(−3270/T)	303–364	Papadopoulos, Ashmore, and Tyler (1969)[5]	(e)
3.2·10^{-10} exp(−4806 /T)	600–1030	Caymax and Peeters (1983)[6]	(f)
Reviews and Evaluations			
4.2·10^{-11} exp(−3200/T)	298–650	Herron and Huie (1973)[7]	(g)
5.0·10^{-20} T^2 exp(−2575/T)	300–1500	Warnatz (1984)[8]	
1.55·10^{-20} $T^{2.2}$ exp(−2890/T)	–	Cohen (1986)[9]	(h)
2.0·10^{-12} $T^{0.6}$ exp(−3680/T)	500–1000	Tsang and Hampson (1986)[10]	(i)

Comments

(a) Effect of C$_2$H$_6$ on lower explosion limit of CO + O$_2$ mixtures.

(b) Discharge flow with ESR detection of O atoms.

(c) Reinvestigation using same technique; report same parameters. In both studies stoichiometry measured only at 500 K and assumed temperature independent.

(d) Discharge flow with mass spectrometric detection of reagents. Secondary reactions avoided by large [O]/[C$_2$H$_5$D] ratios.

(e) Flow discharge, [O] by NO titration. Detailed determination of stoichiometry at 310 K.

(f) Discharge flow, molecular beam sampling and mass spectrometric analysis.

(g) Details of early studies given.

(h) T range not given, but < 1000 K.

(i) Recommend Cohen's[11] expression determined from transition state theory.

Preferred Values

k = 1.66·10^{-15} $T^{1.5}$ exp(−2920/T) cm^3 molecule^{-1} s^{-1}
over range 300–1200 K

Reliability
Δlog k = ± 0.15 between 500 K and 1200 K rising to 0.3 at 300 K

Comments on Preferred Values

The rate constants are only reasonably reliable between 500 and 1000 K. Cohen[9] suggests that all the experimental values below 500 K are too high by factors rising up to 4 at 300 K due to incorrect stoichiometry used in the determination of k. The preferred value is based on Cohens[9] analysis of the low temperature data.

References

[1]V. V. Azatayan, A. B. Nalbandyan, and T. Meng-yuan, Doklad. Akad. Nauk. SSSR 147, 361 (1962).

[2]A. A. Westenberg and N. DeHaas, J. Chem. Phys. 46, 490 (1967).

[3]A. A. Westenberg and N. DeHaas, J. Chem. Phys. 50, 2512 (1969).

[4]J. T. Herron and R. E. Huie, J. Phys. Chem. 73, 3327 (1969).

[5]C. Papadopoulos, P. G. Ashmore, and B. J. Tyler, 13th Symp. (Int.) Combust., 281 (1969).

[6]M. Caymax and J. Peeters, 19th Symp. (Int.) Combust., 51 (1983).

[7]J. T. Herron and R. E. Huie, J. Phys. Chem. Ref. Data 2, 467 (1973).

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[9]N. Cohen, Int. J. Chem. Kin. 18, 59 (1986).

[10]W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data 15, 1087 (1986).

[11]N. Cohen, Aerospace Report. No. ATR–84(7073)–1, August 1984 (reported in Ref. 10).

O + C₂H₆ → OH + C₂H₅

EXPERIMENTAL DATA

Westenberg and de Haas 1967
Westenberg and de Haas 1969
Avramenko et al. 1963
Herron and Huie 1969
Azatyan et al 1962
Saunders and Heicklen 1966
Papadopoulos et al 1969
Azatyan et al 1961
Caymax and Peeters 1982
Smets and Peeters 1975
Tanzawa and Klemm 1980

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O + CHCO → 2 CO + H
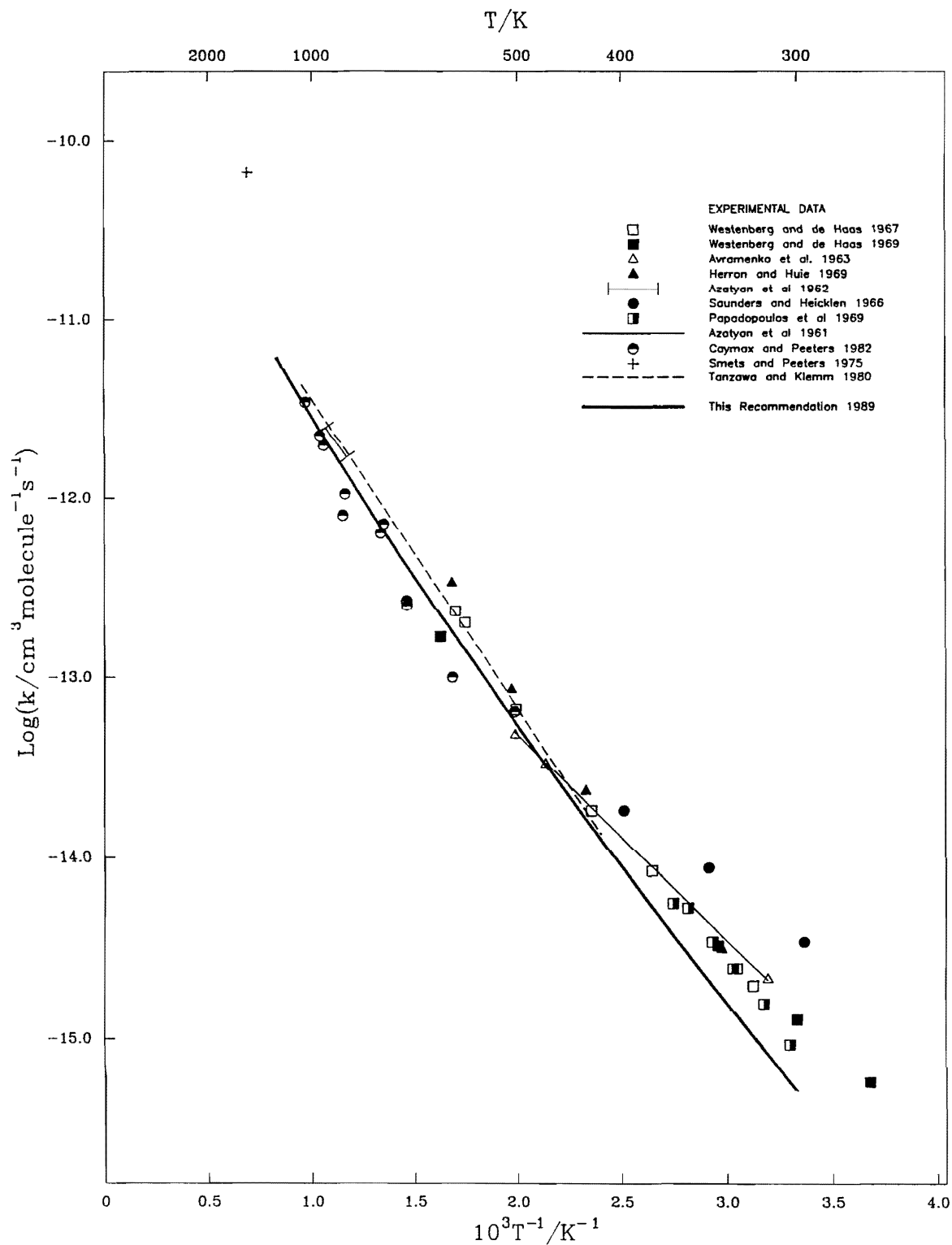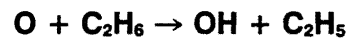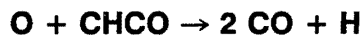
Thermodynamic Data

$\Delta H^{\circ}_{298} = -429.8 \text{ kJ mol}^{-1}$

$\Delta S^{\circ}_{298} = 94.6 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p = 2.38 \cdot 10^6 \, T^{-0.439} \exp(+51460/T)$

Rate Coefficient Data

k [cm^3 molecule^{-1} s^{-1}]	Temperature [K]	Reference	Comments
Rate Coefficient Measurements			
$2.0 \cdot 10^{-12}$	298	Jones and Bayes (1973)[1]	(a)
$3.2 \cdot 10^{-10} \exp(-300/T)$	285–535	Vinckier *et al.* (1985)[2]	(b)
$1.6 \cdot 10^{-10}$	1500–1700	Frank *et al.* (1986)[3]	(c)

Comments

(a) Discharge flow study with O atoms generated from N + NO. CHCO produced as an intermediate from O + C$_2$H$_2$ with [CHCO] and [O] measured by photo-ionisation mass spectroscopy. k measured from steady state value of [CHCO] at relatively long reaction times with simplifying assumptions concerning the mechanism.

(b) Flow study with O atoms generated by O$_2$ discharge, and measured by standard titration technique. Radical concentrations measured by molecular beam mass spectrometry. Conditions selected so that CHCO is effectively removed only by reaction with O atoms. Value of k at 535 K determined from best fit to [CHCO] profile at 535 K. Activation energy determined from measurements of [CHCO]$_{ss}$.

(c) Shock tube study, with simultaneous measurement of [H], [O], and [CO] by atomic and molecular absorption spectrometry. O + CHCO important in later stages of O + C$_2$H$_2$ system. k determined from [O] profile under optimised stoichiometry.

Preferred Values

$k = 1.6 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over range 300–2500 K

Reliability

$\Delta \log k = \pm 0.3$ over range 300–2500 K

Comments on Preferred Values

This reaction is very important in the oxidation of acetylene at combustion temperatures[4], but very little kinetic information is available. No other channels have been suggested, and alternatives are unlikely below about 2000 K. The two low temperature values of k differ by a factor of about 60 at 300 K. The Jones and Bayes value appears very low for a strongly exothermic atom + radical reaction. Further, as the activation energy will be effectively zero, the shock tube value obtained by Frank *et al.*[3] is in excellent agreement with a value of $1.6 \cdot 10^{-10}$ at 410 K obtained from the expression given by Vinckier *et al.*for the range 285–535 K.

References

[1] I. T. N. Jones and K. D. Bayes, 14th Symp. (Int.) Combust., 277 (1973).

[2] C. Vinckier, M. Schaekers, and J. Peeters, J. Phys. Chem. **89**, 508 (1985).

[3] P. Frank, K. A. Bhaskaran, and Th. Just, 21st Symp. (Int.) Combust., 885 (1986).

[4] K. H. Homann and Ch. Wellmann, Ber. Bunsenges. Phys. Chem. **87**, 609 (1983).

$$O + CH_2CO \rightarrow CH_2O + CO \quad (1)$$
$$\rightarrow CHO + H + CO \quad (2)$$
$$\rightarrow CHO + CHO \quad (3)$$
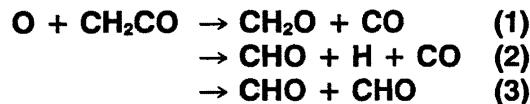
Thermodynamic Data

$\Delta H^\circ_{298} (1) = -424 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (1) = 13.4 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(1) = 2.0 \cdot 10^4 \, T^{1.26} \exp(+50600/T)$

$\Delta H^\circ_{298} (2) = -46.4 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (2) = 134 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(2) = 2.39 \cdot 10^8 \, T^{0.378} \exp(+5260/T) \text{ atm}$

$\Delta H^\circ_{298} (3) = -110 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (3) = 46.3 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(3) = 6.66 \cdot 10^5 \, T^{-1.15} \exp(+12900/T)$

Rate Coefficient Data ($k = k_1 + k_2 + k_3$)

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	$T[\text{K}]$	Reference	Comments
Rate Coefficient Measurements			
$8.8 \cdot 10^{-13}$	298	Carr, Glass, and Niki (1968)[1]	(a)
$5.67 \cdot 10^{-13}$	293	Mack and Thrush (1974)[2]	(b)
$2.92 \cdot 10^{-12} \exp(-680/T)$	230–449	Washida *et al.* (1983)[3]	(c)
Reviews and Evaluations			
$3.3 \cdot 10^{-11} \exp(-1155/T)$	300	Warnatz (1984)[4]	

Comments

(a) Discharge flow system. O atoms produced by reaction $N + NO \rightarrow O + N_2$. CH_2CO in excess. Analysis by mass spectrometry. CO_2, CO, H_2O, H_2, H and H_2CO observed in the products. Experiments using ^{18}O mixtures of CH_2CO and CD_2CO suggest channels (2) and (3) not of major importance.

(b) Discharge flow system, O atoms produced by reaction $N + NO \rightarrow O + N_2$. [O] followed by e.s.r.and chemiluminescence, product analysis by gas chromatography. Results suggested channels (1) and (2) not of major importance.

(c) Two experimental methods used.

(i) Pulse radiolysis; O produced by CO_2 decomposition in Ar bath gas. [O] monitored by resonance absorption.

(ii) Discharge flow system. O atoms generated by microwave discharge in O_2/He mixture. Product analysis by photoionization mass spectrometry. CH_2O observed in products indicating that channel (1) is of importance.

Preferred Values

$k = 3.8 \cdot 10^{-12} \exp(-680/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over range 230–500 K

Reliability

$\Delta\log k = \pm 0.3$ over range 230–500 K

Comments on Preferred Values

The recommended expression is for the overall rate constant; no measurements for the individual channels have yet been made. The expression is based upon the results of Washida *et al.*[3] and Mack and Thrush[2], the two most recent studies the results of which agree to within a factor of 2 at room temperature. The subsequent error limits reflect the scarcity of experimental data.

Carr *et al.*[1] concluded that the probable initial step is formation of $CH_2CO_2^*$, which may rapidly decompose. Results from the isotope study[1] and product analysis[2] by gas chromatography indicate that channels (2) and (3) may be dominant but more recently[3] CH_2O has been observed as a major product suggesting that reaction (1) is also of importance. No recommendations are made for the branching ratios.

References

[1] R. W. Carr, G. P. Glass, and H. Niki, J. Chem. Phys. **49**, 846 (1968).

[2] G. P. R. Mack and B. A. Thrush, J. Chem. Soc., Faraday Trans. I, **70**, 187 (1974).

[3] N. Washida, S. Hatakeyama, H. Takagi, T. Kyogoky, and S. Sato, J. Chem. Phys. **78**, 4533 (1983).

[4] J. Warnatz, in "Combustion Chemistry", ed. W. C. Gardiner, Springer-Verlag, New York (1984).

$$O + CH_2CO \rightarrow CH_2O + CO$$
$$\rightarrow CHO + H + CO$$
$$\rightarrow CHO + CHO$$

T/K

EXPERIMENTAL DATA

□   Curr et al 1966
■   Mack and Thrush 1974
△   Washida et al 1983

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$Log(k/cm^3 molecule^{-1}s^{-1})$

$10^3 T^{-1}/K^{-1}$

$$O + CH_3CHO \rightarrow OH + CH_3CO \quad (1)$$
$$\rightarrow OH + CH_2CHO \quad (2)$$
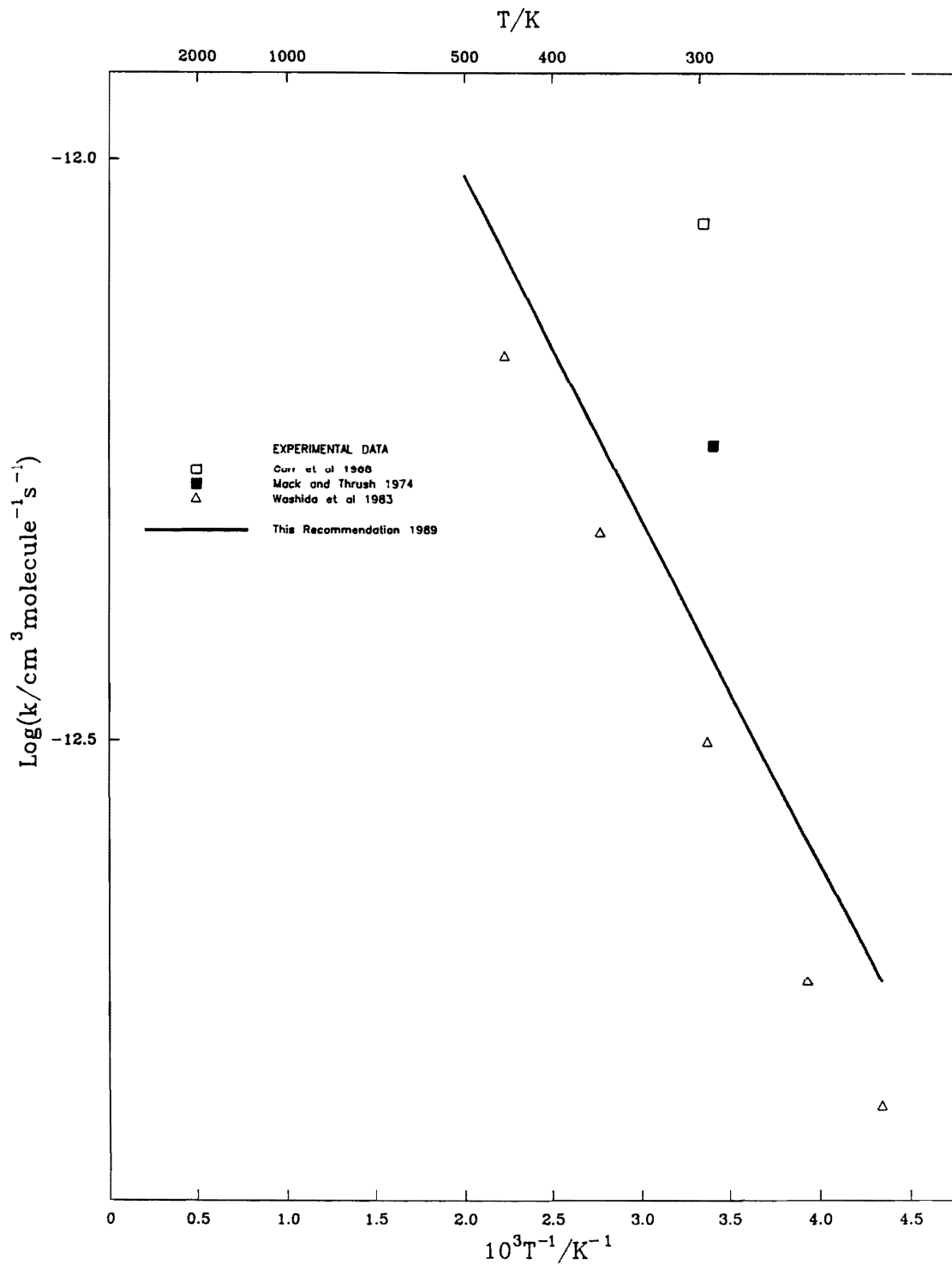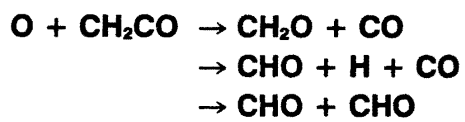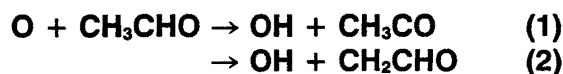
Thermodynamic Data

$\Delta H^{\circ}_{298} (1) = -67.5 \text{ kJ mol}^{-1}$

$\Delta S^{\circ}_{298} (1) = 25.6 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(1) = 2.18 \cdot 10^3 \, T^{-0.614} \exp(+7780/T)$

$\Delta H^{\circ}_{298} (2) = -19.8 \text{ kJ mol}^{-1}$

$\Delta S^{\circ}_{298} (2) = 26.6 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(2) = 9.6 \cdot 10^2 \, T^{-0.455} \exp(2050/T)$

Rate Coefficient Data ($k = k_1 + k_2$)

k [cm^3 molecule^{-1} s^{-1}]	T [K]	Reference	Comments
Rate Coefficient Measurements			
$4.8 \cdot 10^{-13}$	300	Mack and Thrush (1974)[1]	(a)
$1.7 \cdot 10^{-11} \exp(-2010/T)$	1550–1850	Beeley et al. (1977)[2]	(b)
$4.9 \cdot 10^{-13}$	298	Michael and Lee (1977)[3]	(c)
$1.2 \cdot 10^{-11} \exp(-990/T)$	298–472	Singleton et al. (1977)[4]	(d)
Reviews and Evaluations			
$8.3 \cdot 10^{-12} \exp(-900/T)$	300–2000	Warnatz (1984)[5]	

Comments

(a) Discharge flow system. Oxygen atoms monitored by EPR and air afterglow.

(b) Ignition of CH$_3$CHO/O$_2$/Ar mixtures behind incident shock waves. Stable and transient species monitored by UV and IR emission. k determined from modelling the system.

(c) Discharge flow system. Oxygen atoms monitored by resonance fluorescence.

(d) Modulated photolysis of N$_2$O/CH$_3$CHO. Oxygen atoms monitored by air afterglow.

Preferred Values

$k = 9.7 \cdot 10^{-12} \exp(-910/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over range 298–1500 K

Reliability

$\Delta \log k = \pm 0.5$ at 1500 K reducing to ± 0.05 at 298 K

Comments on Preferred Values

Preferred values are based on the low temperature data of Mack and Thrush[1], Michael and Lee[3], and Single-ton et al.[4]. Temperature dependence based on the data of Singleton et al.[4]. Although the data of Beeley et al.[2] agrees with the extrapolation based on a simple Arrhenius expression, the determination was indirect and subject to uncertainty. No information is available on the branching ratio. If it is assumed that $k_2 = 1/2 \, k_0 + C_2H_6$ then the second channel only becomes significant ($k_2/k > 0.1$) at $T > 700$ K. However the extrapolated value is a factor of 2 higher than the overall rate given by Beeley et al.[2]. The contribution of the second channel is negligible at $T < 500$ K, where the only reliable studies were conducted.

References

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[2] P. Beeley, J. F. Griffiths, B. A. Hunt, and A. Williams, 16th Symp. (Int.) Combust., 1013 (1976).

[3] J. V. Michael and J. H. Lee, Chem. Phys. Lett. **51**, 303 (1977).

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[6] R. D. Cadle and J. W. Powers, J. Phys. Chem. **71**, 1702 (1967).

$$O + CH_3CHO \rightarrow OH + CH_3CO$$
$$\rightarrow OH + CH_2CHO$$

T/K

EXPERIMENTAL DATA

☐   Mock and Thrush 1974
         Beeley et al 1977
△   Michael and Lee 1977
- - - - Singleton et al 1977
○   Cadle and Powers 1967

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$$O + C_2H_5OOH \rightarrow OH + C_2H_5OO \quad (1)$$
$$\rightarrow OH + C_2H_4OOH \quad (2)$$
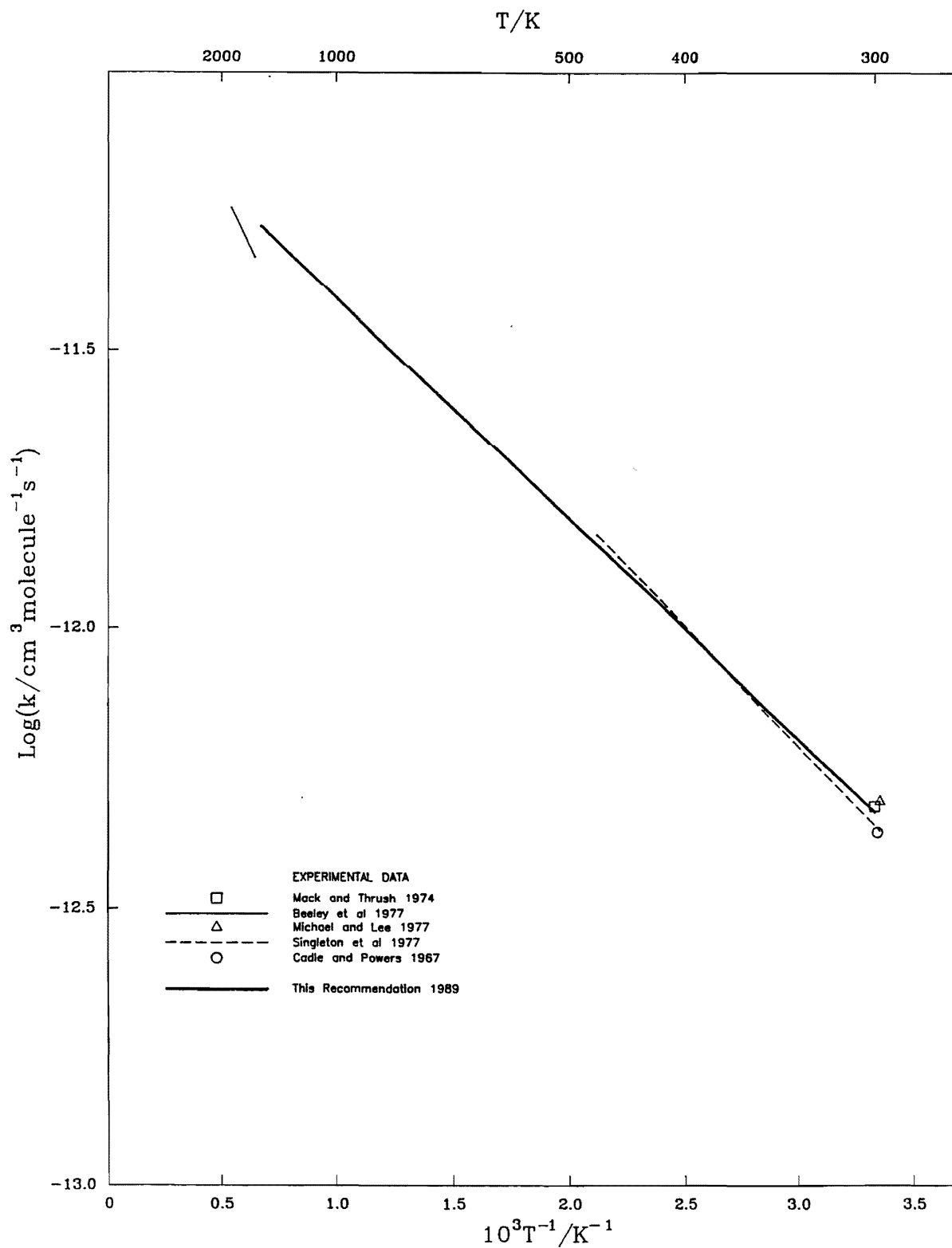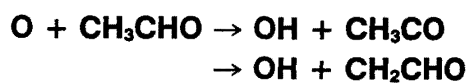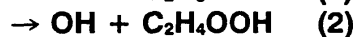
Thermodynamic Data

$\Delta H^{\circ}_{298} (1) = -60.15 \text{ kJ mol}^{-1}$

$\Delta H^{\circ}_{298} (2) = -20.7 \text{ kJ mol}^{-1}$

Comment

There are no experimental data for the reaction of $O(^3P)$ with C_2H_5OOH. As for CH_3OOH the rate expres-

sion $k = 6.85 \cdot 10^{-13} \ T^{0.57} \exp(-1390/T) \text{ cm}^3 \text{ molecule}^{-1}$ s^{-1} with channel (2) dominant, is recommended by analogy with H abstraction from HCHO and H_2O_2.

$$O + C_6H_6 \rightarrow OH + C_6H_5 \quad (1)$$
$$O + C_6H_6 \ (+ M) \rightarrow C_6H_5OH \ (+ M) \quad (2)$$
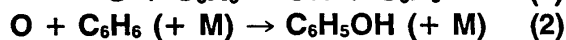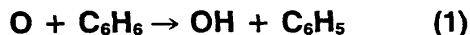
Thermodynamic Data

$\Delta H^{\circ}_{298} (1) = 35.3 \text{ kJ mol}^{-1}$
$\Delta S^{\circ}_{298} (1) = 41.7 \text{ J K}^{-1}\text{mol}^{-1}$
$K_p(1) = 9.8 \cdot 10^4 \ T^{-0.88} \exp(-4701/T)$

$\Delta H^{\circ}_{298} (2) = -428.5 \text{ kJ mol}^{-1}$
$\Delta S^{\circ}_{298} (2) = -115.4 \text{ J K}^{-1}\text{mol}^{-1}$
$K_p(2) = 4.3 \cdot 10^{-6} \ T^{-0.20} \exp(+51411/T) \text{ atm}^{-1}$

Rate Coefficient Data ($k = k_1 + k_2$)

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	$T[\text{ K}]$	Reference	Comments
Rate Coefficient Measurements			
$6.0 \cdot 10^{-14}$	298	Mani and Sauer (1968)[1]	(a)
$2.5 \cdot 10^{-10} \exp(-2768/T)$	883–963	Mkryan et al. (1971)[2]	(b)
$k_1 = 5.3 \cdot 10^{-10} \exp(-3019/T)$	1300–1700	Fujii and Asaba (1972)[3]	(c)
$k_2 = 6.3 \cdot 10^{-11} \exp(-2214/T)$	255–305	Bonnano et al. (1972)[4]	(d)
$2.4 \cdot 10^{-14}$	300	Atkinson and Pitts (1974)[5]	(e)
$1.8 \cdot 10^{-11} \exp(-2214/T)$	298–462	Colussi et al. (1975)[6]	(f)
$1.8 \cdot 10^{-11} \exp(-2003/T)$	299–392	Atkinson and Pitts (1975)[7]	(g)
$1.7 \cdot 10^{-11} \exp(-2010/T)$	299–440	Atkinson and Pitts (1979)[8]	(h)
$4.6 \cdot 10^{-11} \exp(-2470/T)$	298–867	Nicovich et al. (1982)[9]	(i)
$k_1 = 5.3 \cdot 10^{-10} \exp(-3020/T)$	1600–2300	Hsu et al. (1984)[10]	(j)
Reviews and Evaluations			
$2.5 \cdot 10^{-11} \exp(-2130/T)$	298–600	Cvetanovic (1987)[11]	(k)

Comments

(a) Pulsed radiolysis with product analysis by gas chromatography. O atoms originate from radiolysis of CO_2 and NO_2 at high pressures. Rate coefficient from absorption profiles of transient species.

(b) Evaluation of an overall rate coefficient from a flow reactor study.

(c) Single pulse shock tube with gas chromatographic analysis of stable products and absorption/emission measurements during the progress of the reaction were used to investigate the kinetic behaviour of benzene/argon mixtures containing small amounts of oxygen.

(d) Flow system study. The decrease of O atoms was monitored by ESR detection and changes in benzene concentration were followed by mass spectrometry. It was found that O atoms removal is much faster than benzene decrease. Therefore it was assumed that the O atoms react with radicals produced in the initiation reaction. The rate coefficient for channel (2) was

evaluated from the mass spectrometric measurements.

(e) Same method as in comment (a).

(f) Phase shift–O + NO chemiluminescence. O atoms are generated during Hg photosensitized decomposition of NO_2.

(g) Same method as in comment (f).

(h) Flash photolysis–resonance fluorescence. O atoms are generated by VUV photolysis of O_2 and NO.

(i) Flash photolysis–resonance fluorescence. O atoms are generated by VUV photolysis of O_2.

(j) The oxidation of benzene under fuel lean conditions was studied behind reflected shock waves using a stabilized cw CO laser to monitor CO production. The formed CO was modelled by a 25 step reaction mechanism. A rate coefficient for channel (1) was determined.

(k) Critical evaluation and compilation of chemical kinetic data of $O(^3P)$ atoms with unsaturated hydrocarbons.

Preferred Values

$$k = 1.2 \cdot 10^{-22} \, T^{3.68} \exp\left(-570/T\right) \, \text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1} \text{ over}$$
range 300–1000 K

Reliability

$\Delta \log k = \pm 0.5$ over range 300–1000 K

Comments on Preferred Values

There exists a large variety of studies on benzene pyrolysis in the lower temperature range up to $\approx$ 900 K. The shock tube data for the higher temperature range are evaluated from reaction systems with reduced sensitivity. From the present data a clear separation between addition and abstract channel is not possible, and therefore only a rate expression for the overall reaction is recommended.

References

[1] I. Mani and M. C. Sauer, Jr., Advanc. Chem. Ser. **82**, 142 (1968).
[2] T. G. Mkryan, K. T. Oganesyan, and A. B. Nalbandyan, Arm. Khim. Zh. **24**, 299 (1971).
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[6] A. J. Colussi, D. L. Singleton, R. S. Irwin, and R. J. Cvetanovic, J. Phys. Chem. **79**, 1900 (1975).
[7] R. Atkinson and J. N. Pitts, Jr., J. Phys. Chem. **79**, 295 (1975).
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[9] J. M. Nicovich, C. A. Gump, and A. R. Ravishankara, J. Phys. Chem. **86**, 1684 (1982).
[10] D. S. Y. Hsu, C. Y. Lin, and M. C. Lin, 20th Symp. (Int.) Combust., 623 (1984).
[11] R. J. Cvetanovic, J. Phys. Chem. Ref. Data **16**, 261 (1987).

$$O + C_6H_6 \rightarrow OH + C_6H_5$$
$$O + C_6H_6 \;(+ M) \rightarrow C_6H_5OH \;(+ M)$$

T/K

EXPERIMENTAL DATA

□　Mani and Sauer 1968
　　Mkyran et al 1971
　　Fujii and Asaba (k1) 1972
▲　Bonnano et al (k2) 1972
○　Atkinson and Pitts 1974
●　Colussi et al 1975
◨　Atkinson and Pitts 1975
△　Nicovich et al 1982
-- -- --　Hsu et al (k1) 1984
+　Atkinson and Pitts 1979

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$10^3 T^{-1}/K^{-1}$

$\mathrm{Log}(k/cm^3 molecule^{-1} s^{-1})$

$$O + C_6H_5CH_2 \rightarrow HCO + C_6H_6 \quad (1)$$
$$\rightarrow CH_2O + C_6H_5 \quad (2)$$
$$\rightarrow H + C_6H_5CHO \quad (3)$$
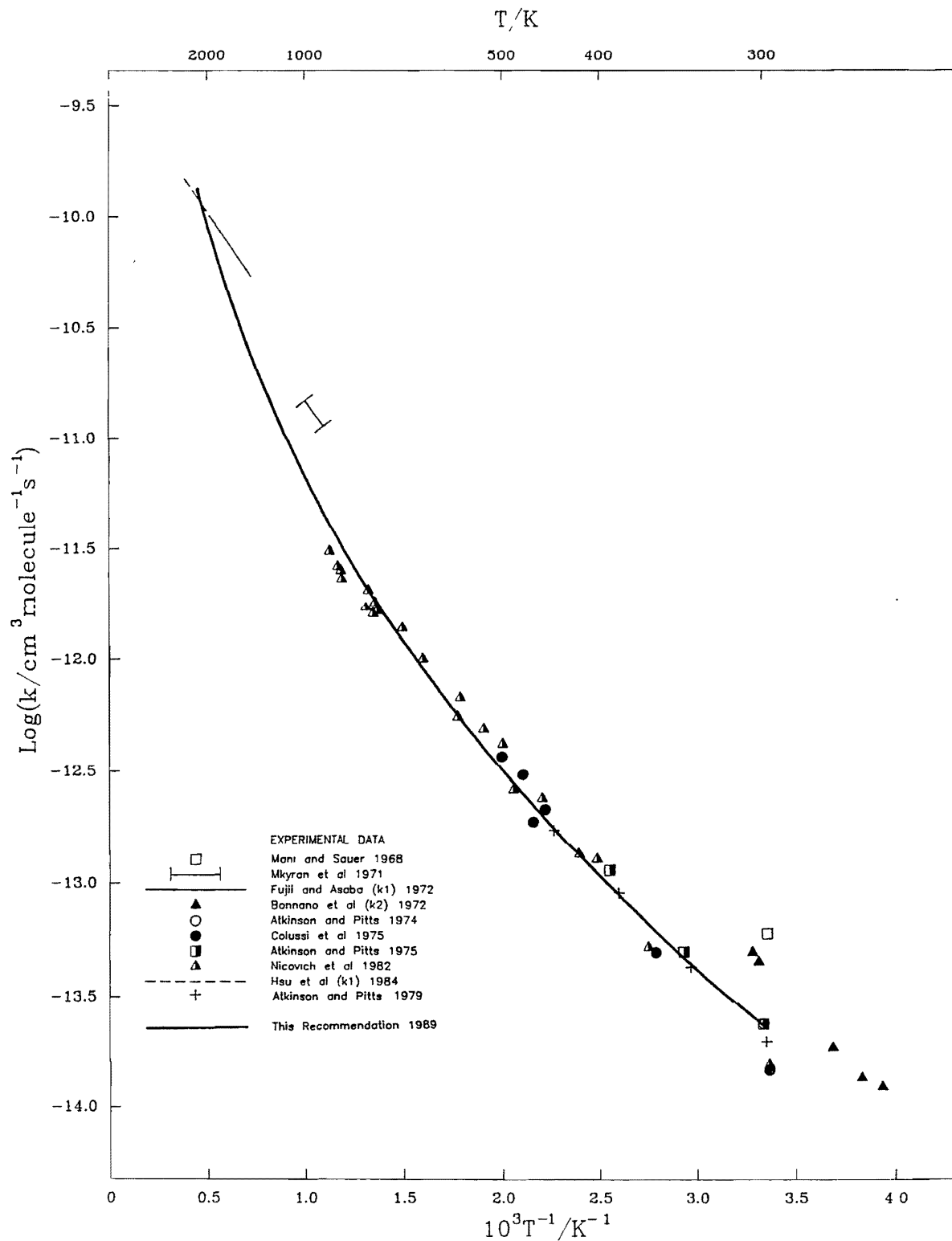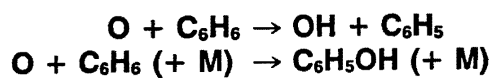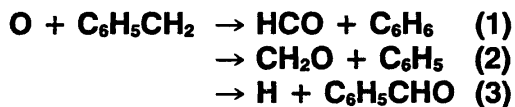
Thermodynamic Data

$\Delta H^\circ_{298} (1) = -322.8 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (1) = 16.7 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(1) = 3.5 \cdot 10^4 \ T^{-1.28} \exp(+38474/T)$

$\Delta H^\circ_{298} (2) = -236.7 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (2) = 29.9 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(2) = 8.0 \cdot 10^6 \ T^{-1.84} \exp(+27932/T)$

Rate Coefficient Data ($k = k_1 + k_2 + k_3$)

$k[\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}]$	$T[\text{K}]$	Reference	Comments
Rate Coefficient Measurements			
$k_2 = 1.7 \cdot 10^{-11}$	1700–2800	McLain *et al.* (1979)[1]	(a)
$k_1 + k_3 = 5.5 \cdot 10^{-10}$	298	Bartels *et al.* (1988)[2]	(b)

Comments

(a) Investigation of benzene and toluene/oxygen/argon mixtures behind incident shock waves by monitoring UV and IR emission of CO, CO$_2$, and the product [O]·[CO]. Rate constant for channel (2) estimated from reaction model.

(b) Reactions of benzyl with H, O, and O$_2$ were studied at low pressures (around 1 mbar) in a multiple discharge flow reactor by molecular beam sampling technique and mass spectrometric detection. The relative rate constants for channel (1) and (3) were determined with Ref. to the reaction of methyl radicals with oxygen atoms.

Preferred Values

$k_1 + k_3 = 5.5 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at room temperature

Reliability

$\Delta\log(k_1 + k_3) = \pm 0.3$

Comments on Preferred Values

The high temperature data have been obtained by an indirect method and do not allow a recommendation. The room temperature value has been measured under isolated conditions, which show that the two reaction pathways (1) and (3) are equally probable.

References

[1] D. C. McLain, C. J. Jachimowski, and C. H. Wilson, NASA TP–1472 (1979).

[2] M. Bartels, J. Edelbuettel-Einhaus, and K. Hoyermann, 22nd Symp. (Int.) Combust., 1041 (1988).

O + C$_6$H$_5$CH$_3$ → products

Rate Coefficient Data

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	$T[\text{K}]$	Reference	Comments
Rate Coefficient Measurements			
$2.4 \cdot 10^{-11}\exp(-1640/T)$	393–495	Jones and Cvetanovic (1961)[1]	(a)
$8.9 \cdot 10^{-14}$	303	Grovenstein and Mosher (1970)[2]	(b)
$2.3 \cdot 10^{-13}$	298	Mani and Sauer (1968)[3]	(c)
$7.5 \cdot 10^{-14}$	300	Atkinson and Pitts (1974)[4]	(d)
$3.8 \cdot 10^{-11}\exp(-1942/T)$	298–462	Colussi *et al.* (1975)[5]	(e)
$1.4 \cdot 10^{-11}\exp(-1560/T)$	299–392	Atkinson and Pitts (1975)[6]	(f)
$8.3 \cdot 10^{-12}\exp(-1359/T)$	373–648	Furuyama and Ebara (1975)[7]	(g)
$1.6 \cdot 10^{-11}\exp(-1535/T)$	299–440	Atkinson and Pitts (1979)[8]	(h)
$1.7 \cdot 10^{-10}\exp(-3625/T)$	1700–2800	McLain *et al.* (1979)[9]	(i)
$4.3 \cdot 10^{-11}\exp(-1910/T)$	298–932	Nicovich *et al.* (1982)[10]	(j)
Reviews and Evaluations			
$2.7 \cdot 10^{-11}\exp(-1720/T)$	298–932	Cvetanovic (1987)[11]	(k)

Comments

(a) O atoms from Hg photosensitized decomposition of N_2O. Ratio derived from relative k data in competing experiments. Reference reaction was O + cyclopentene → products. Evaluated by Cvetanovic[11].

(b) Same method as in (a). Reference reaction was O + benzene → products. Evaluated by Cvetanovic[11].

(c) O atoms from pulse radiolysis of CO_2 and N_2O at high pressures. Rate coefficient from absorption spectra of transient species.

(d) Phase shift–O + NO chemiluminescence. O atoms from Hg photosensitized decomposition of N_2O.

(e) Same method as in (d).

(f) Same method as in (d).

(g) Microwave discharge–fast flow reactor. O atoms from N + NO.

(h) Flash photolysis–resonance fluorescence. O atoms from VUV photolysis of O_2 and NO.

(i) Incident shock wave investigation of the oxidation mechanism of $C_6H_6/O_2/Ar$ and $C_6H_5CH_3/O_2/Ar$ mixtures by monitoring UV and IR emission of CO, CO_2, and the product [O]·[CO]. Arrhenius expression for the product channel $C_6H_5CH_2$ + OH estimated by comparison with data for benzene.

(j) Flash photolysis–resonance fluorescence. O atoms from VUV photolysis of O_2.

(k) Critical evaluation and compilation of chemical kinetic data of $O(^3P)$ atoms with unsaturated hydrocarbons.

Preferred Values

$k = 5.3 \cdot 10^{-15}\, T^{1\cdot 21} \exp(-1260/T)$ cm^3 molecule^{-1} s^{-1} over range 298–2800 K

Reliability

$\Delta \log k = \pm\ 0.4$ at 2800 K reducing to ± 0.1 at 300 K

Comments on Preferred Values

The results of 8 studies concerning the determination of the rate coefficient for total O consumption by toluene are in excellent agreement for the range from room temperature up to about 1000 K. The temperature dependence of the rate coefficient at higher temperatures is difficult to define because the only available rate expression has not been measured directly, but has been estimated from modelling a relatively complex reaction system. It has been assumed that at higher temperatures the reaction proceeds predominantly by direct abstraction of a H atom. The reliability at 2800 K has been estimated by comparing the shock tube values with the values obtained by linear extrapolation of the k values in the T-range 300–1000 K.

References

[1] G. R. H. Jones and R. J. Cvetanovic, Can. J. Chem. **39**, 2444 (1961).

[2] E. Grovenstein, Jr. and A. J. Mosher, J. Am. Chem. Soc. **92**, 3810 (1970).

[3] M. C. Sauer and I. Mani, Advanc. Chem. Ser. No. 82, 142 (1968).

[4] R. Atkinson and J. N. Pitts, Jr., J. Phys. Chem. **78**, 1780 (1974).

[5] A. J. Colussi, D. L. Singleton, R. S. Irwin, and R. J. Cvetanovic, J. Phys. Chem. **79**, 1900 (1975).

[6] R. Atkinson and J. N. Pitts, Jr., J. Phys. Chem. **79**, 295 (1975).

[7] S. Furuyama and N. Ebara, Int. J. Chem. Kin. **7**, 689 (1975).

[8] R. Atkinson and J. N. Pitts, Jr., Chem. Phys. Lett. **63**, 485 (1979).

[9] A. G. McLain, C. J. Jachimowski, and C. H. Wilson, NASA TP-1472 (1979).

[10] J. M. Nicovich, C. A. Gump, and A. R. Ravishankara, J. Phys. Chem. **86**, 1648 (1982).

[11] R. J. Cvetanovic, J. Phys. Chem. Ref. Data **16**, 261 (1987).
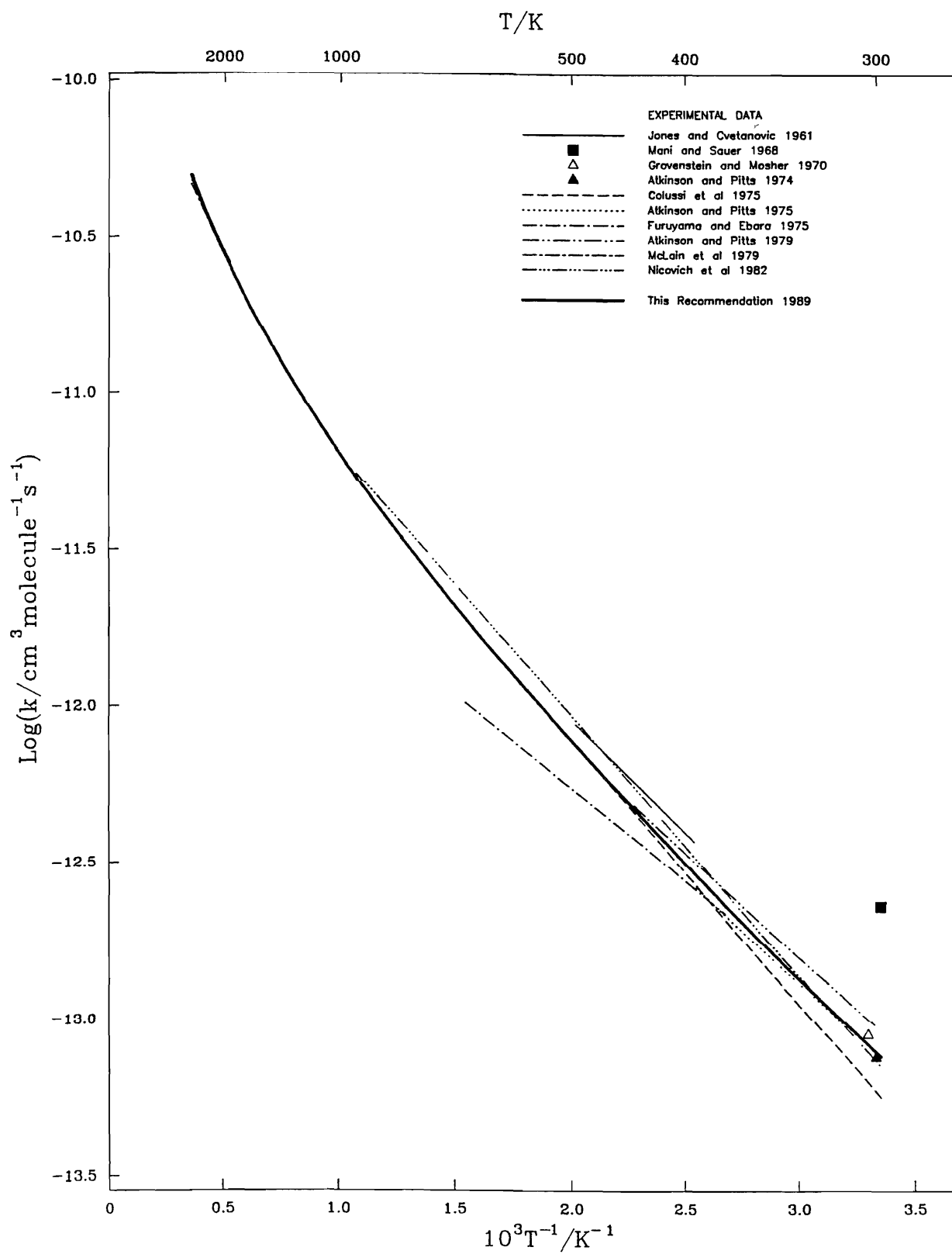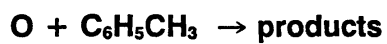
O + $C_6H_5CH_3$ → products

T/K

O + p-$C_6H_4(CH_3)_2$ → products

Rate Coefficient Data

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$7.5 \cdot 10^{-13}$	298	Mani and Sauer (1968)[1]	(a)
$1.8 \cdot 10^{-13}$	300	Atkinson and Pitts, Jr. (1974)[2]	(b)
$1.3 \cdot 10^{-11} \exp(-1280/T)$	299–392	Atkinson and Pitts, Jr. (1975)[3]	(c)
$3.9 \cdot 10^{-11} \exp(-1540/T)$	298–600	Nicovich *et al.* (1982)[4]	(d)
Reviews and Evaluations			
$2.0 \cdot 10^{-13}$	298	Cvetanovic (1987)[5]	(e)
$2.6 \cdot 10^{-11} \exp(-1409/T)$	298–600		

Comments

(a) O from pulse radiolysis of CO_2 or N_2O. k from absorption spectra of transients (not positively identified). p ~ 60 bar.

(b) Phase shift–O + NO chemiluminescence. O-atoms from Hg-photosensitized decomposition of N_2O. p ≈ 72 mbar.

(c) Same method as in (b).

(d) Flash photolysis–resonance fluorescence. O-atoms from VUV photolysis of O_2. Density range $2 \cdot 10^{10}$–$2 \cdot 10^{12}$ cm^{-3}.

(e) Critical evaluation and compilation of chemical kinetic data of O(^{3}P) atoms with unsaturated hydrocarbons.

Preferred Values

k = $2.6 \cdot 10^{-11} \exp(-1409/T)$ cm^3 molecule^{-1} s^{-1} over range 298–600 K
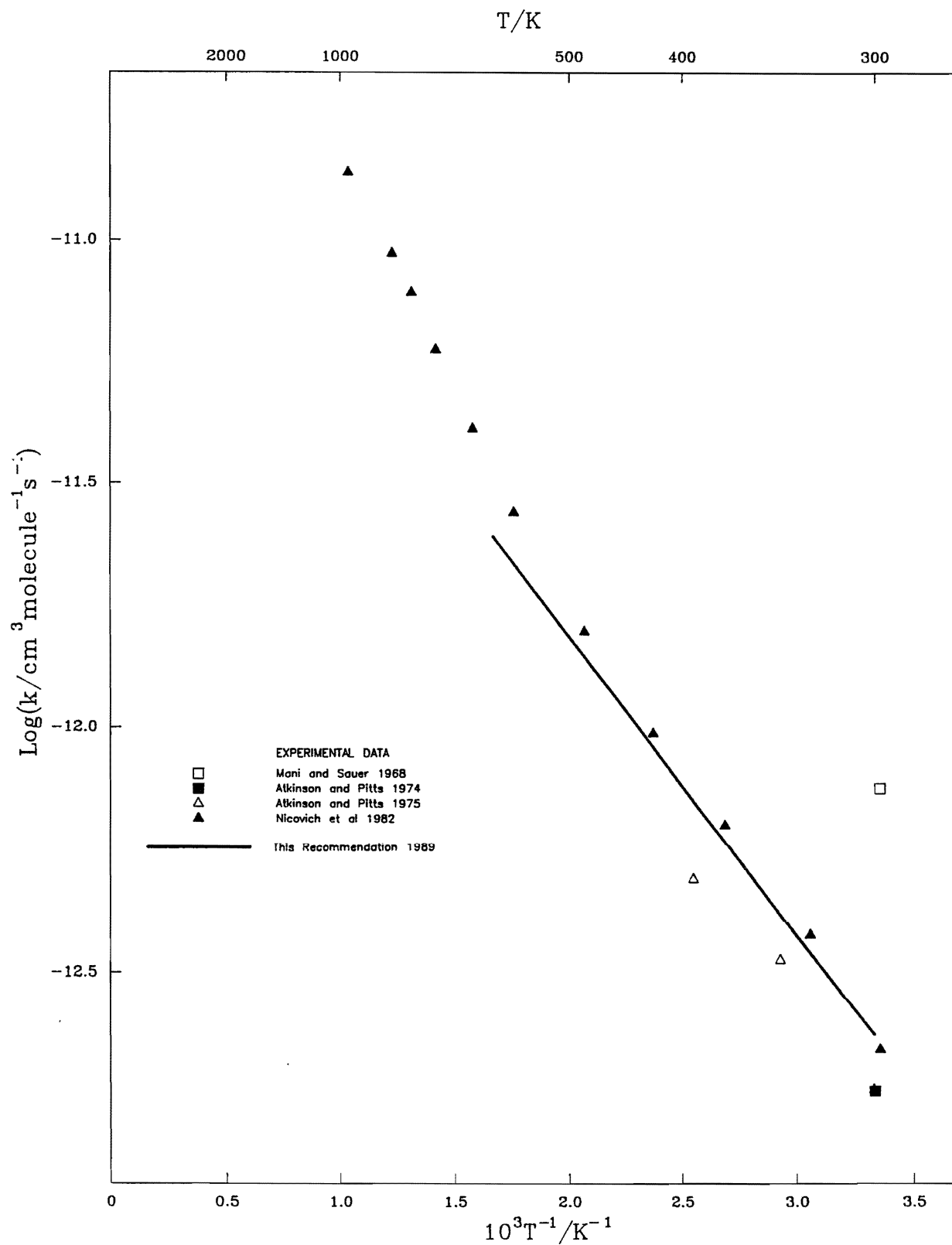
Reliability
$\Delta \log k$ = ± 0.3

Comments on Preferred Values
The preferred value is based on the evaluation of Cvetanovic[5].

References

[1] I. Mani and M. C. Sauer, Jr., Advanc. Chem. Ser. No. 82, 142 (1968).
[2] R. Atkinson and J. N. Pitts, Jr., J. Phys. Chem. **78**, 1780 (1974).
[3] R. Atkinson and J. N. Pitts, Jr., J. Phys. Chem. **79**, 295 (1975).
[4] J. M. Nicovich, C. A. Gump, and A. R. Ravishankara, J. Phys. Chem. **86**, 1690 (1982).
[5] R. J. Cvetanovic, J. Phys. Chem. Ref. Data **16**, 261 (1987).

O + *p*-C₆H₄ (CH₃)₂ → products

O + $C_6H_5C_2H_5$ → products

Rate Coefficient Data

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$5.3 \cdot 10^{-13}$	298	Mani and Sauer (1968)[1]	(a)
$1.0 \cdot 10^{-13}$	303	Grovenstein and Mosher (1970)[2]	(b)
Reviews and Evaluations			
$1.0 \cdot 10^{-13}$	298	Cvetanovic (1987)[3]	(c)

Comments

(a) O from pulse radiolysis of CO_2 or N_2O. k from absorption spectra of transients (not positively identified). $p \approx 53$ bar.

(b) Ratio derived from relative k data in competing experiments. Reference reaction was O + benzene → products. $p \approx 1$ bar. Evaluated by Cvetanovic[3].

(c) Critical evaluation and compilation of chemical kinetic data of O(^{3}P) atoms with hydrocarbons.

Preferred Values

$k = 1.0 \cdot 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar

Reliability
$\Delta \log k = \pm 0.3$

Comments on Preferred Values
The preferred value is based on the evaluation of Cvetanovic[3].

References

[1] I. Mani and M. C. Sauer, Jr., Advanc. Chem. Ser. **82**, 142 (1968).
[2] E. Grovenstein, Jr., and A. J. Mosher, J. Am. Chem. Soc. **92**, 3810 (1970).
[3] R. J. Cvetanovic, J. Phys. Chem. Ref. Data **16**, 261 (1987).

O_2 + CH_4 → HO_2 + CH_3
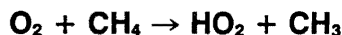
Thermodynamic Data
$\Delta H_{298} = 231.0$ kJ mol^{-1}
$\Delta S_{298} = 31.9$ J K^{-1}mol^{-1}
$K_p = 39.6\ T^{-0.105} \exp(-27930/T)$

Rate Coefficient Data

k [cm^3 molecule^{-1} s^{-1}]	Temperature [K]	Reference	Comments
Rate Coefficient Measurements			
No experimental measurements have been made.			
Reviews and Evaluations			
$6.6 \cdot 10^{-11} \exp(-28630/T)$	500–2000	Walker (1974)[1]	(a)

Comments

(a) Based on experimental value[2] for HCHO + O_2 → HO_2 + HCO, which is effectively $3.3 \cdot 10^{-11} \exp(-\Delta H /R\ T)$ cm^3 molecule^{-1} s^{-1}. Assuming equal A factors per C−H bond $k = 6.6 \cdot 10^{-11} \exp(-\Delta H / R\ T)$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

$k = 6.6 \cdot 10^{-11} \exp(-28630/T)$ cm^3 molecule^{-1} s^{-1} over range 500–2000 K

Reliability
$\Delta \log k = \pm 0.5$ between 500 and 1000 K, rising to ± 1.0 at 2000 K

Comments on Preferred Values
See comment (a) above.

References

[1] R. W. Walker, in "Reaction Kinetics", Specialist Periodical Reports, Chemical Society, London, Vol. **1**, 161 (1974).
[2] R. R. Baldwin, A. R. Fuller, D. Longthorn, and R. W. Walker, J. Chem. Soc., Faraday Trans. 1, **70**, 1257 (1974).

$O_2 + C_2H_6 \rightarrow HO_2 + C_2H_5$
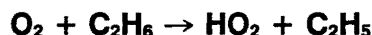
Thermodynamic Data
$\Delta H^\circ_{298} = 211.5 \text{ kJ mol}^{-1}$
$\Delta S^\circ_{298} = 46.6 \text{ J K}^{-1}\text{mol}^{-1}$
$K_p = 6.39 \cdot 10^3 \, T^{-0.445} \exp(-25630/T)$

Rate Coefficient Data

k [cm^3 molecule^{-1} s^{-1}]	Temperature [K]	Reference	Comments
Rate Coefficient Measurements			
No experimental measurements have been made.			
Reviews and Evaluations			
$6.7 \cdot 10^{-11} \exp(-25620/T)$	500–2000	Walker (1974)[1]	(a)

Comments

(a) Based on experimental value[2] for $HCHO + O_2 \rightarrow$ $HO_2 + CHO$, which is effectively $3.3 \cdot 10^{-11} \exp(-\Delta H/R \, T)$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

$k = 1.0 \cdot 10^{-10} \exp(-26100/T)$ cm^3 molecule^{-1} s^{-1} over range 500–2000 K

Reliability

$\Delta\log k = \pm 0.5$ between 500 and 1000 K rising to ± 1.0 at 2000 K

Comments on Preferred Values

The value given in the Walker review has been modified slightly to allow for the higher heat of formation of the C_2H_5 radical now recommended[3] and for an assumed equal A factor per C—H bond in HCHO + O_2 and C_2H_6 + O_2.

References

[1]R. W. Walker, in "Reaction Kinetics", Specialist Periodical Reports, Chemical Society, London, Vol. 1, 161 (1974).
[2]R. R. Baldwin, A. R. Fuller, D. Longthorn, and R. W. Walker, J. Chem. Soc., Faraday Trans. 1, 70, 1257 (1974).
[3]R. R. Baldwin, G. R. Drewery, and R. W. Walker, J. Chem. Soc. Faraday Trans. I, 80, 2827 (1984).

$O_2 + HCHO \rightarrow HO_2 + CHO$
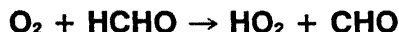
Thermodynamic Data
$\Delta H^\circ_{298} = 170 \text{ kJ mol}^{-1}$
$\Delta S^\circ_{298} = 29.9 \text{ J K}^{-1}\text{mol}^{-1}$
$K_p = 0.083 \, T^{-0.071} \exp(-20600/T)$

Rate Coefficient Data

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$3.4 \cdot 10^{-11}\exp(-19580/T))$	713–813	Baldwin *et al.* (1974)[1]	(a)
$7.5 \cdot 10^{-11}\exp(-20630/T)$	878–952	Vardanyan *et al.* (1975)[2]	(b)
Reviews and Evaluations			
$6.7 \cdot 10^{-11}\exp(-20100/T)$	650–900	Walker (1975)[3]	(c)
$3.4 \cdot 10^{-11}\exp(-19600/T)$	300–2000	Tsang and Hampson (1986)[4]	(d)

Comments

(a) Oxidation of HCHO in KCl coated vessels under conditions where the chain length is near unity.

(b) Thermal oxidation of HCHO; expression for k cited from earlier work published in Armenian Chemical Journal[5].

(c) Based on Ref. 1; recommended Arrhenius parameters for general reaction RH + $O_2 \rightarrow$ R + HO_2 are $E =$

ΔH° and $A = 6.7 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1}. Accuracy estimated to be $\pm$ a factor of 2–4 in the temperature range 650–900 K.

(d) Accepts the value in Ref. 1.

Preferred Values

$k = 1.0 \cdot 10^{-10} \exp(-20460/T)$ cm^3 molecule^{-1} s^{-1} over range 700–1000 K

Reliability

$\Delta \log k = \pm 0.5$ over range 700–1000 K

Comments on Preferred Values

The results of Baldwin *et al.*[1] appear reliable and are confirmed by the rate parameters cited from the Russian work. The preferred value is obtained using the approach of Walker[3], using the currently accepted ΔH° and the A factor adjusted to fit the value of $k = 3.4 \cdot 10^{-22}$ cm^3 molecule^{-1} s^{-1} at 773 K from Ref. 2.

References

[1]R. R. Baldwin, A. R. Fuller, D. Longthorn, and R. W. Walker, J. Chem. Soc. Faraday Trans. 1, **70**, 1257 (1974).

[2]I. A. Vardanyan, G. A. Sachyan, and A. B. Nalbandyan, Int. J. Chem. Kin. **7**, 23 (1975).

[3]R. W. Walker, in "Reaction Kinetics", ed. P. G. Ashmore (Spec. Per. Reports), The Chemical Society, London, **1**, 161 (1975).

[4]W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data **15**, 1087 (1986).

[5]I. A. Vardanyan, G. A. Sachyan, and A. B. Nalbandyan, Arm. Chim. J. **25**, 281 (1972).

O_2 + CH_3CHO → HO_2 + CH_3CO
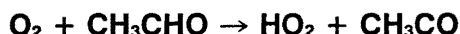
Thermodynamic Data

$\Delta H^\circ_{298} = 153$ kJ mol^{-1}

$\Delta S^\circ_{298} = 26.8$ J K^{-1}mol^{-1}

$K_p = 2.63\ T^{-0.31}\ \exp(-18600/T)$

Rate Coefficient Data

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$3.32 \cdot 10^{-11} \exp(-21240/T)$	700–1100	Colket *et al.* (1977)[1]	(a)
Reviews and Evaluations			
$6.7 \cdot 10^{-11} \exp(-20100/T)$	650–900	Walker (1975)[2]	(b)

Comments

(a) Flow reactor study of high temperature oxidation of CH$_3$CHO (1030–1115 K). k based on an assumed value of $3.3 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1} for the reaction CH$_3$ + HO$_2$ → CH$_3$O + OH and analysis of a complex mechanism. Arrhenius parameters determined using value of k(C$_2$H$_5$CHO + O$_2$) = $1.27 \cdot 10^{-21}$ cm^3 molecule^{-1} s^{-1} at 713 K (erroneously quoted from Baldwin *et al.*[3]) together with experimental results on CH$_3$CHO + O$_2$.

(b) Recommended expression using $E = \Delta H^\circ = 167$ kJ mol^{-1} and $A = 6.7 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1}, based on work of Baldwin *et al.*[3].

Preferred Values

$k = 5.0 \cdot 10^{-11} \exp(-19700/T)$ cm^3 molecule^{-1} s^{-1} over range 600–1100 K

Reliability

$\Delta \log k = \pm 0.5$ at 600 K rising to ± 1.0 at 1100 K

Comments on Preferred Values

The only reported experimental values of k are obtained from analysis of a complex mechanism and are therefore subject to considerable uncertainty. The Arrhenius expression reported by Colket *et al.* is apparently based on an erroneously quoted value of k(C$_2$H$_5$CHO + O$_2$) from the work of Baldwin *et al.* The value employed was 0.760 l mol s^{-1} at 713 K instead of 0.076 l mol s^{-1} at 753 K obtained in the study of Baldwin *et al.* Using the latter the following Arrhenius parameters are obtained: $A = 6.2 \cdot 10^{-8}$ cm^3 molecule^{-1} s^{-1} and $E/R = 25450$ K. The activation energy thus obtained is significantly greater than the reaction enthalpy $\Delta H/R = 19700$ K and the A factor unreasonably large. Clearly the experimental data in the two temperature regions are incompatible. For this evaluation we prefer the approach of Walker and the recommended value is based on the best current ΔH°_{298} value (= 163.8 kJ mol^{-1} using ΔH°_f(CH$_3$CO) = 11.0 kJ mol^{-1} and ΔH°_f(HO$_2$) = 14.6 kJ mol^{-1}). and $A = 5.0 \cdot 10^{-11}$ cm^3 molecule^{-1}s^{-1}.

References

[1]M.B.Colket, D.W.Naegeli, and I.Glassman, 16th Symp.(Int.) Combust., 1023 (1976).

[2]R.W.Walker, in "Gas Kinetics", ed. P.G.Ashmore, (Specialist Periodic Reports), The Chemical Society, London (1975).

[3]R.R.Baldwin, D.H.Langford, and R.W.Walker, Trans.Faraday Soc. **65**, 792, 806, and 2116 (1969).

$H + O_2 \rightarrow O + OH$
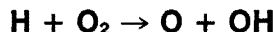
Thermodynamic Data

$\Delta H^\circ_{298} = 70.2$ kJ mol^{-1}

$\Delta S^\circ_{298} = 24.9$ J K^{-1}mol^{-1}

$K_p = 3.02 \cdot 10^2 \ T^{-0.374} \exp(-8620/T)$

Rate Coefficient Data

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$4.5 \cdot 10^{-10} \exp(-8354/T)$	910–1470	Kochubei and Moin (1973)[1]	(a)
$2.0 \cdot 10^{-7} \ T^{-0.91} \exp(-8369/T)$	1250–2500	Schott (1973)[2]	(b)
$1.0 \cdot 10^{-9} \exp(-8450/T)$	1875–2240	Bowman (1975)[3]	(c)
$1.8 \cdot 10^{-10} \exp(-8107/T)$	925–1825	Chiang and Skinner (1979)[4]	(d)
$2.0 \cdot 10^{-10} \exp(-8107/T)$	1000–2500	Pamidimukkala and Skinner (1982)[5]	(e)
$4.1 \cdot 10^{-10} \exp(-8696/T)$	1700–2500	Frank and Just (1985)[6]	(f)
$2.8 \cdot 10^{-10} \exp(-8118/T)$	962–1705	Klemm et al.(1989)[7]	(g)
Reviews and Evaluations			
$3.7 \cdot 10^{-10} \exp(-8456/T)$	700–2500	Baulch et al. (1972)[8]	
$2.8 \cdot 10^{-7} \ T^{-0.9} \exp(-8744/T)$	300–1250	Cohen and Westberg (1983)[9]	
$2.0 \cdot 10^{-7} \ T^{-0.91} \exp(-8310/T)$	300–2500	Warnatz (1984)[10]	

Comments

(a) Oxidation of H_2 in $O_2/CO_2/N_2$ mixtures; static system. Product analysis by gas chromatography. Total pressures 80–900 Torr.

(b) Shock heating of lean and rich $H_2/CO/O_2/Ar$ mixtures, time-resolved chemiluminescence in the visible and ultraviolet region ($\lambda > 340$ nm). Total pressures 20–350 Torr.

(c) Shock heating of stoichiometric and rich $CH_4/O_2/Ar$ mixtures, [OH] by absorption at 308 nm, [O] from chemiluminescence near 370 nm, [CO] and [CO$_2$] from infrared emission at 4.8 mu and 6.3 mu. Total densities $(1.4–2.3) \cdot 10^{-5}$ mol cm^{-3}. Numerical modelling of 23 reaction mechanism of methane oxidation and adjusting of sensitive rates.

(d) Shock tube; $H_2/O_2/Ar$ mixtures; [H] by Lyman α-resonance absorption. Total pressure ≈ 2 atm.

(e) Shock heating of rich and stoichiometric $H_2/O_2/Ar$ mixtures; [O] by resonance absorption. Total pressures $\approx 1.5–2.5$ atm.

(f) Shock heating of $N_2O/H_2/O_2/Ar$ mixtures; [H] and [O] by time-resolved atomic resonance absorption. Total densities ($6 \cdot 10^{-6} – 1.3 \cdot 10^{-5}$) mol cm^{-3}. Numerical modelling of 10 reaction mechanism and adjusting of rate parameters.

(g) Shock tube; H atoms produced by flash photolysis of either NH_3 or H_2O in the reflected shock regime; [H] by atomic resonance absorption. Total pressures 10–30 Torr.

Preferred Values

$k = 3.3 \cdot 10^{-10} \exp(-8456/T)$ cm^3 molecule^{-1} s^{-1} over range 300–2500 K

Reliability

$\Delta \log k = \pm 0.1$ at low temperatures rising to ± 0.2 at 2500 K

Comments on Preferred Values

The preferred value is similar to the recommendation of Baulch et al.[8], but a little smaller in agreement with new results of Frank and Just[6] and Klemm et al.[7]. The negative temperature dependence measured by Schott[2] is not taken into consideration.

References

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H + O₂ → O + OH

$H + O_2 (+ M) \rightarrow HO_2 (+ M)$
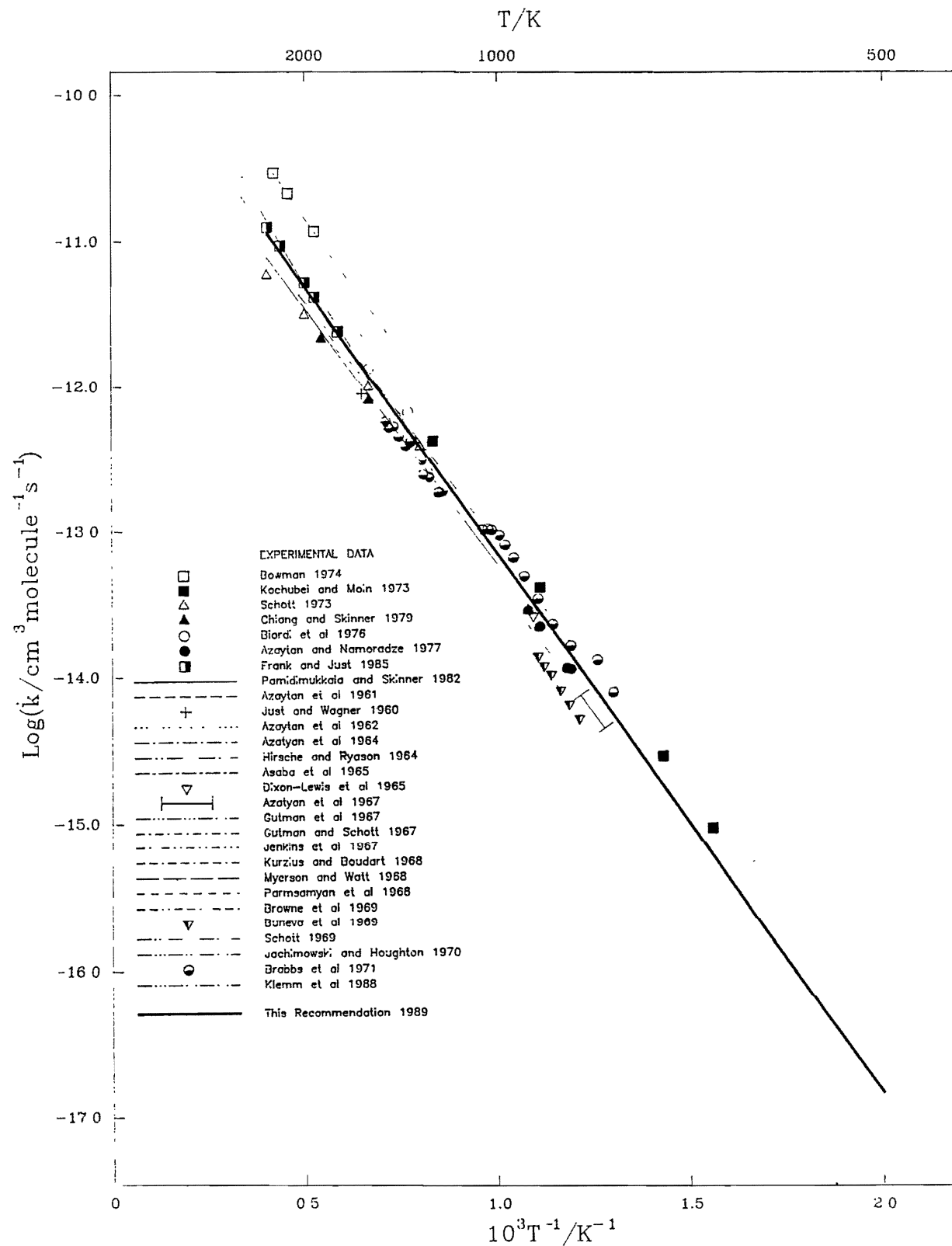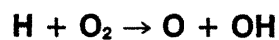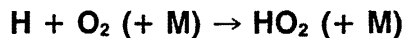
Thermodynamic Data

$\Delta H^{\circ}_{298} = -208 \text{ kJ mol}^{-1}$

$\Delta S^{\circ}_{298} = -90.6 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p = 6.9 \cdot 10^{-3} \, T^{-0.95} \exp(+24800/T) \text{ atm}^{-1}$

Rate Coefficient Data

$k[\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}]$	$T[\text{K}]$	$p[\text{Torr}]$	M	Reference	Comments
Rate Coefficient Measurements					
$0.6 \cdot 10^{-32}$	298	10–600	Ar	Ahumada et al. (1972)[1]	(a)
$1.2 \cdot 10^{-32}$	298	10–600	H_2		
$0.75 \cdot 10^{-32}$	298	10–600	He		
$1.9 \cdot 10^{-32}$	300		Ar, He	Westenberg and deHaas (1972)[2]	(b)
$6.7 \cdot 10^{-33} \exp(+238/T)$	203–404	10–400	Ar, He	Kurylo (1972)[3]	(c)
$8.9 \cdot 10^{-33} \exp(+770/T)$	913–1473	80–900	H_2	Kochubei and Moin (1973)[4]	(d)
$6.8 \cdot 10^{-33} \exp(+345/T)$	220–360	10–500	Ar	Wong and Davis (1974)[5]	(e)
$1.4 \cdot 10^{-32}$	300	2–30	He	Hack et al. (1974)[6]	(f)
$2.5 \cdot 10^{-32}$	773		H_2	Dixon-Lewis et al. (1975)[7]	(g)
$2.1 \cdot 10^{-32}$	1500				
$1.2 \cdot 10^{-32}$	2130				
$2.5 \cdot 10^{-32}$	293		Ar	Hack (1977)[8]	(h)
$9.1 \cdot 10^{-33}$	980–1176	1520	N_2	Slack (1977)[9]	(i)
$1.2 \cdot 10^{-33} \exp(+505/T)$	925–1825	≈ 1520	Ar	Chiang and Skinner (1979)[10]	(j)
$6.0 \cdot 10^{-32}$	298	760	H_2	Nielsen et al. (1982)[11]	(k)
$1.2 \cdot 10^{-33} \exp(+505/T)$	1000–2500	1140–1900	Ar	Pamidimukkala and Skinner (1982)[12]	(l)
$7.9 \cdot 10^{-34} \exp(+796/T)$	231–512	2–10	Ar	Pratt and Wood (1983)[13]	(m)
$2.8 \cdot 10^{-32}$	298		Ar	Troe et al. (1985)[14]	(n)
$6.5 \cdot 10^{-32}$	298		N_2		
$1.5 \cdot 10^{-31}$	298		CH_4		
$k_\infty = 7.5 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}\text{s}^{-1}$	298				
F_{cent} (Ar) ≈ 0.45					
F_{cent} (N_2) ≈ 0.50					
F_{cent} (CH_4) ≈ 0.54					
$2.6 \cdot 10^{-32}$	298	4.8–30	He	Kaufman et al. (1987)[15]	(o)
$6.1 \cdot 10^{-32}$	298	4.8–30	N_2		
$6.4 \cdot 10^{-31}$	298	4.8–30	H_2O		
$7.1 \cdot 10^{-33}$	746–987		Ar	Klemm et al. (1989)[16]	(p)
Reviews and Evaluations					
$4.1 \cdot 10^{-33} \exp(+505/T)$	300–2000		Ar	Baulch et al. (1972)[17]	
$1.4 \cdot 10^{-32} \exp(+505/T)$	300–2000		H_2		
$1.7 \cdot 10^{-30} \, T^{-0.8}$	200–2000		Ar	Baulch et al. (1980)[18]	
$5.8 \cdot 10^{-30} \, T^{-0.8}$	200–400		N_2		
$1.8 \cdot 10^{-29} \, T^{-1}$	300–2500		O_2, N_2	Tsang and Hampson (1986)[19]	

Comments

(a) Hg sensitized photodecomposition of H_2; [H] monitored by Lyman α spectroscopy. Reaction was found to be third order over total pressure range. Relative efficiencies H_2 : Kr : He : Ar : Ne = 2.0 : 1.8 : 1.2 : 1.0 : 0.2.

(b) Discharge-flow system; [H], [OH], and [O] measured by ESR.

(c) Flash photolysis of CH_4 or $C_3H_8/O_2/He$, Ar, or N_2 mixtures. [H] monitored by Lyman α resonance fluorescence. Relative collision efficiencies CH_4 : N_2 : He : Ar = 15.7 : 3.4 : 1.0 : 1.0.

(d) Oxidation of H_2 in $O_2/CO_2/N_2$ mixtures; product analysis by gas chromatography. H_2 in excess.

(e) VUV flash photolysis of $CH_4/O_2/M$ mixtures. [H] by Lyman α resonance fluorescence. Relative efficiencies Ar : He : H_2 : N_2 : CH_4 = 1.0 : 0.93 : 2.8 : 22 at 300 K.

(f) Discharge-flow study; [H] and [OH] by ESR.

(g) Numerical simulation of $H_2/O_2/N_2$ flames. Relative efficiencies H_2 : O_2 : N_2 : H_2O = 1.0 : 0.35 : 0.44 : 6.5.

(h) Discharge-flow study; [H], [O], and [OH] by ESR.

(i) Shock heating of H_2/air mixtures. OH and H_2O observed by emission at 307 nm and 2.7 μm, respectively. Modelling of induction times near to the second explosion limit; results very sensitive to k.

(j) Decomposition of $H_2/O_2/Ar$ mixtures behind reflected shock waves; [H] by Lyman α resonance absorption.

(k) Pulse radiolysis of H_2 with small amounts of O_2; [HO_2] monitored by absorption at 230 nm.

(l) Shock heating of rich and stoichiometric $H_2/O_2/Ar$ mixtures. [O] by resonance absorption.

(m) Discharge-flow system; [HO_2] by gas chromatography, other products by mass spectrometry.

(n) Laser flash photolysis of NH_3 in the presence of excess O_2. Total pressures between 1 and 200 bar. HO_2 monitored by absorption at 220 nm. Reaction found to be in the fall-off range; extrapolation to limiting low- and high-pressure rate coefficients.

(o) Flow reactor; H generated by microwave discharge or by thermal decomposition on a W filament. [H] by resonance absorption, [OH] by resonance fluorescence.

(p) Flash photolysis of either NH_3 or H_2O in the reflected shock regime. [H] monitored by atomic resonance absorption spectroscopy.

Preferred Values

$k = 1.7 \cdot 10^{-30} \, T^{-0.8} \, cm^6 \, molecule^{-2} \, s^{-1}$ over range 300–2000 K for M = Ar

$k = 5.8 \cdot 10^{-30} \, T^{-0.8} \, cm^6 \, molecule^{-2} \, s^{-1}$ over range 300–2000 K for M = H_2

$k = 3.9 \cdot 10^{-30} \, T^{-0.8} \, cm^6 \, molecule^{-2} \, s^{-1}$ over range 300–2000 K for M = N_2

$k = 4.3 \cdot 10^{-30} \, T^{-0.8} \, cm^6 \, molecule^{-2} \, s^{-1}$ over range 300–2000 K for M = H_2O

Reliability

$\Delta \log k = \pm 0.5$ over range 300–2000 K

Comments on Preferred Values

The value preferred by Baulch *et al.*[2] has been adopted.

For clarity, rate data measured before 1972 are included in the Arrhenius plot (see Baulch *et al.*[17] for Ref.).

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H + O₂ + Ar → HO₂ + Ar

H + O₂ + H₂ → HO₂ + H₂

H + H (+M) → H₂ (+M)
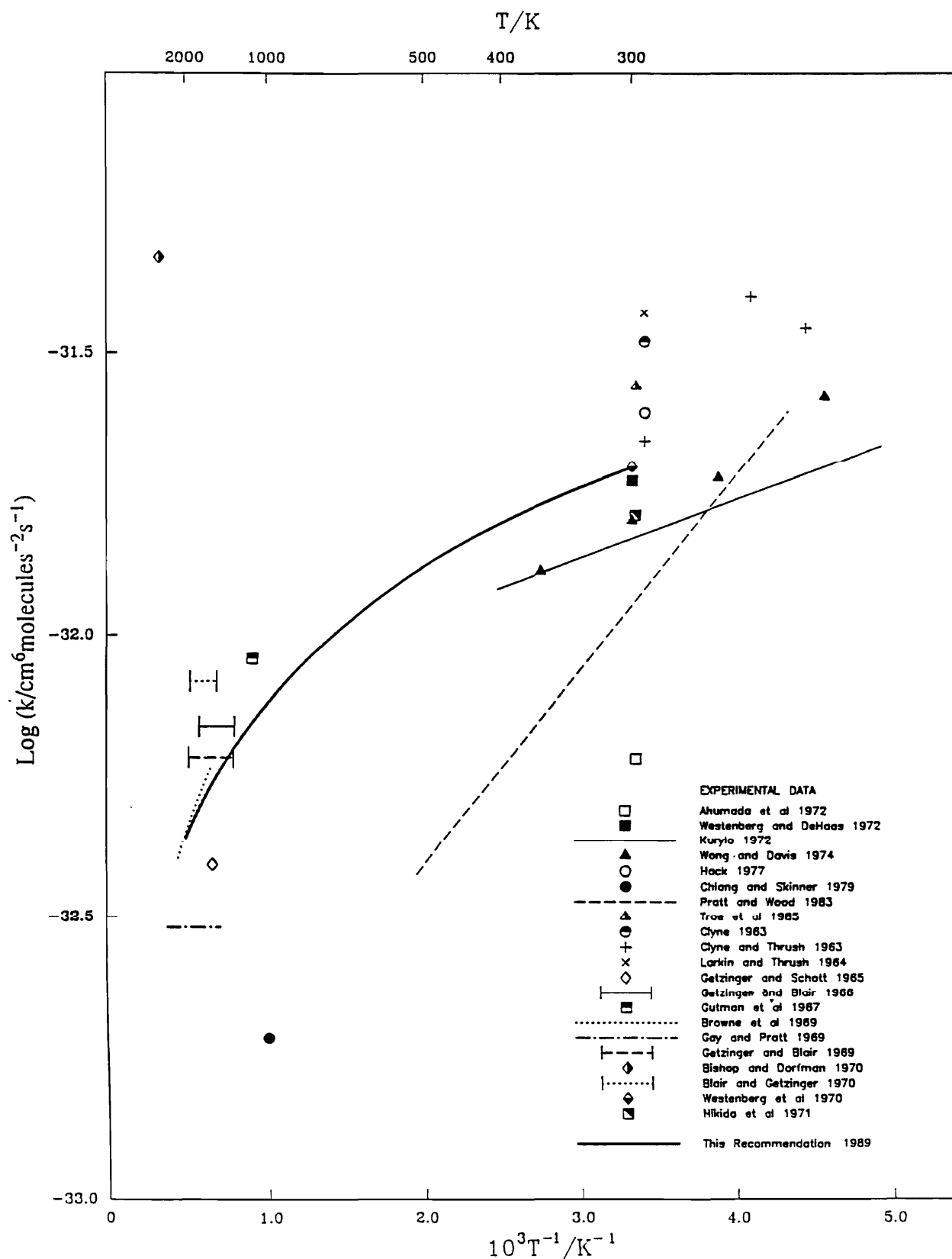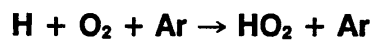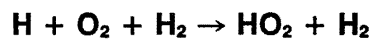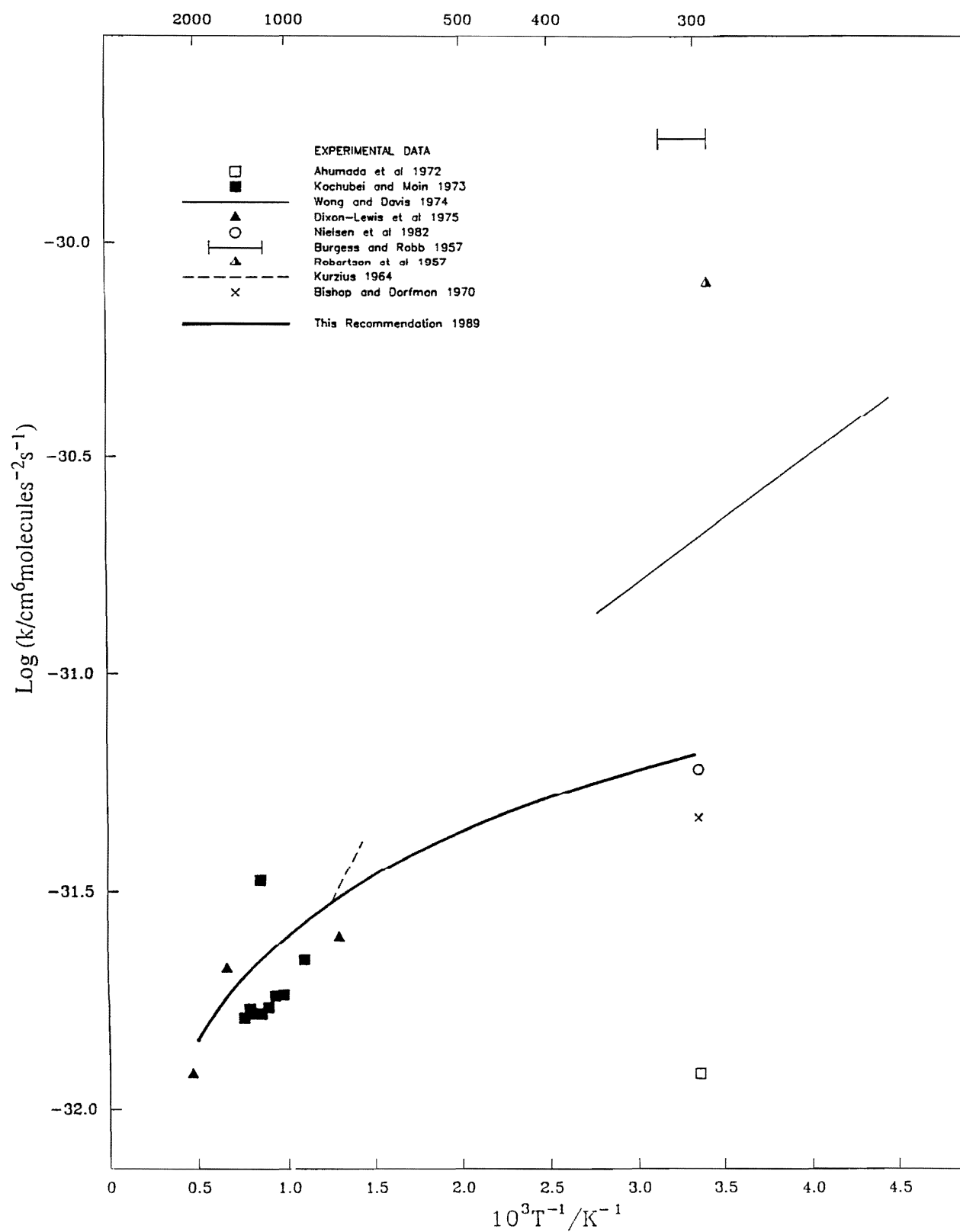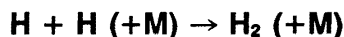
Thermodynamic Data

$\Delta H^\circ_{298} = -436$ kJ mol^{-1}

$\Delta S^\circ_{298} = -98.6$ J K^{-1}mol^{-1}

$K_p = 3.19 \cdot 10^{-2} \, T^{-1.28} \exp(+52100/T)$ atm^{-1}

Rate Coefficient Data

k[cm⁶ molecule^{-2} s^{-1}]	T[K]	M	Reference	Comments
Rate Coefficient Measurements				
$8.1 \cdot 10^{-33}$	298	H₂	Trainor, Ham, and Kaufman (1973)[1]	(a)
$7.0 \cdot 10^{-33}$	298	He		
$9.2 \cdot 10^{-33}$	298	Ar		
$1.6 \cdot 10^{-32}$	298	He	Azatyan *et al.* (1973)[2]	(b)
$1.2 \cdot 10^{-32}$		Ar		
$2.8 \cdot 10^{-33}$	1300–1700	Ar	Mallard and Owen (1974)[3]	(c)
$2.5 \cdot 10^{-31} \, T^{-0.6}$	77–295	H₂	Walkauskas and Kaufman (1975)[4]	(a)
$9.2 \cdot 10^{-31} \, T^{-0.81}$	77–295	Ar		
$1.8 \cdot 10^{-29} \, T^{-1.33}$	77–295	N₂		
$5.6 \cdot 10^{-32} \, T^{-0.31}$	300–1800		Dixon-Lewis *et al.* (1975)[5]	(d)
$3.3 \cdot 10^{-32}$	300	H₂	Haraguchi (1975)[6]	(e)
$1.9 \cdot 10^{-32}$	300	He		
$8.5 \cdot 10^{-33}$	298	H₂	Lynch, Schwab, and Michael (1976)[7]	(f)
$6.9 \cdot 10^{-33}$	298	He		
$8.0 \cdot 10^{-33}$	298	Ar		
$9.6 \cdot 10^{-33}$	298	N₂		
$1.5 \cdot 10^{-32}$	300	H₂	Haraguchi and Kumagai (1978)[8]	(e)
$2.8 \cdot 10^{-31}$	297	H₂O	Grigoryan (1980)[9]	(g)
$1.3 \cdot 10^{-32}$	297	He		
$2.2 \cdot 10^{-32}$	297	Ar		
Reviews and Evaluations				
$1.8 \cdot 10^{-30} \, T^{-1.0}$	2500–5000	Ar	Baulch *et al.* (1972)[10]	
$7.2 \cdot 10^{-30} \, T^{-1.0}$		H₂		
$8.3 \cdot 10^{-33}$	300	H₂		
$1.5 \cdot 10^{-29} \, T^{-1.3}$	77–2000	N₂	Tsang and Hampson (1986)[11]	

Comments

(a) Flow tube; H atoms generated thermally on a heated W filament. [H] monitored by energy release of catalytic recombination. Total pressures 2–15 Torr.

(b) Jet system; H generated by microwave discharge and monitored by ESR.

(c) Shock initiated combustion of rich H₂/O₂/Ar mixtures. [OH] monitored by resonance absorption at 306.7 nm. Computer simulation of a 16 reaction mechanism sensitive to k.

(d) Numerical simulation of H₂/O₂/N₂ flames. Equal collision efficiencies for all molecules assumed.

(e) Discharge-flow system. [H] by use of a hot wire detector or isothermal calorimeter.

(f) H atoms generated by Hg photosensitization of H₂ and monitored by Lyman α absorption spectroscopy. Total pressures 500–1500 Torr.

(g) Flow tube, EPR detection.

Preferred Values

$k = 1.8 \cdot 10^{-30} \, T^{-1.0}$ cm⁶ molecule^{-2} s^{-1} over range 300–2500 K for M = Ar

$k = 2.7 \cdot 10^{-31} \, T^{-0.6}$ cm⁶ molecule^{-2} s^{-1} over range 100–5000 K for M = H₂

Reliability

$\Delta \log k = \pm 0.5$ over whole temperature range

Comments on Preferred Values

The value preferred by Baulch *et al.*[10] has been adopted. The arguments given there are accepted, and the values measured after 1972 do not contradict this recommendation.

For clarity, rate data measured before 1972 are included in the Arrhenius plot (see Baulch *et al.*[10] for Ref.).

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H + H + Ar → H₂ + Ar

T/K

EXPERIMENTAL DATA

■ (with error bar)	Mallard and Owen 1974
■	Walkauskas and Kaufman 1975
△	Trainor et al 1973
▲	Lynch et al 1976
○	Grigoryan 1980
●	Schott 1960
⊢ — — ⊣	Patch 1962
——	Rink 1962
— — —	Sutton 1962
+	Larkin and Thrush 1964
×	Russo et al 1964
◇	Schott and Bird 1964
⊢········⊣	Jacobs et al 1965
▣	Larkin and Thrush/Larkin 1968
▽	Getzinger and Blair 1966
·········	Jacobs et al 1967
▼	Azatyan et al 1968
—·—·—	Gay and Pratt 1969
◆	Getzinger and Blair 1969
◇	Halstead and Jenkins 1969
—··—··—	Hurle et al 1969
▯	Roberts et al 1969
——————	This Recommendation 1989

$10^3 T^{-1} / K^{-1}$

Log (k/cm⁶molecules⁻²s⁻¹)

H + H + H$_2$ → H$_2$ + H$_2$

H + OH (+ M) → H$_2$O (+ M)

Thermodynamic Data

$\Delta H^\circ_{298} = -499$ kJ mol^{-1}
$\Delta S^\circ_{298} = -109$ J K^{-1}mol^{-1}
$K_p = 3.6 \cdot 10^{-3}\ T^{-1.2}\ \exp(+59800/T)$ atm^{-1}

Rate Coefficient Data

k[cm^6 molecule^{-2} s^{-1}]	T[K]	M	Reference	Comments
Rate Coefficient Measurements				
$2.1 \cdot 10^{-24}\ T^{-2.6}$	2570–3290	Ar	Homer and Hurle (1969)[1]	(a)
$4.1 \cdot 10^{-23}\ T^{-2.6}$	2570–3290	H$_2$O		
$8.8 \cdot 10^{-33}$	1900	Ar	Halstead	(b)
$2.2 \cdot 10^{-32}$	1900	He	and Jenkins (1969,70)[2,3]	
$8.8 \cdot 10^{-33}$	1900	N$_2$		
$7.5 \cdot 10^{-32}$	1900	H$_2$O		
$< 1 \cdot 10^{-32}$	1900	CO, CO$_2$		
$2.1 \cdot 10^{-32}$	2130		Friswell and Sutton (1972)[4]	(c)
$8.3 \cdot 10^{-33}\ \exp(+750/T)$	300–1800	N$_2$	Dixon-Lewis *et al.* (1975)[5]	(d)
$4.3 \cdot 10^{-25}\ T^{-2.6}$	220–300	He	Zellner *et al.* (1977)[6]	(e)
$1.0 \cdot 10^{-28}\ T^{-1}$			Goodings and Hayhurst (1988)[7]	(f)
Reviews and Evaluations				
$2.3 \cdot 10^{-26}\ T^{-2.0}$	1000–3000	Ar	Baulch *et al.* (1972)[8]	
$6.1 \cdot 10^{-26}\ T^{-2.0}$	1000–3000	N$_2$		
$3.9 \cdot 10^{-25}\ T^{-2.0}$	1000–3000	H$_2$O		
$6.1 \cdot 10^{-26}\ T^{-2.0}$	300–3000	N$_2$	Tsang and Hampson (1986)[9]	

Comments

(a) Dissociation of water vapour in Ar behind shock waves; [OH] measured by flash absorption near 310 nm. k_{-1} obtained, k calculated from thermodynamic equilibrium.

(b) Study of rich premixed H$_2$/O$_2$ flames; [H] monitored by Li/LiOH technique. Experimental data reanalysed in Ref. 3.

(c) Fuel-lean H$_2$/O$_2$/N$_2$ flames at atmospheric pressure; [H] by Li/LiOH method.

(d) Numerical simulation of H$_2$/O$_2$/N$_2$ flames; assumed equal collision efficiencies for H$_2$, N$_2$, and O$_2$. k(H$_2$O) = 5 k(N$_2$). Results not very sensitive to the chosen values of k.

(e) Discharge-flow system; [OH] by resonance fluorescence. Total pressures 3–11 Torr. Relative third body efficiencies at 300 K He : Ar : N$_2$: CO$_2$ = 1 : 1.5 : 3.2 : 6.

(f) Modelling study of premixed lean H$_2$/O$_2$/N$_2$ flames.

Preferred Values

$k = 2.3 \cdot 10^{-26}\ T^{-2.0}$ cm^6 molecule^{-2} s^{-1} over range 300–3000 K for M = Ar

$k = 6.1 \cdot 10^{-26}\ T^{-2.0}$ cm^6 molecule^{-2} s^{-1} over range 300–3000 K for M = N$_2$

$k = 3.9 \cdot 10^{-25}\ T^{-2.0}$ cm^6 molecule^{-2} s^{-1} over range 300–3000 K for M = H$_2$O

Reliability

$\Delta \log k = \pm 0.3$ for M = Ar
$\Delta \log k = \pm 0.5$ for M = N$_2$
$\Delta \log k = \pm 0.5$ for M = H$_2$O

Comments on Preferred Values

The value preferred by Baulch *et al.*(1972)[8] has been taken. The arguments given there are accepted, and the values measured after 1972 do not contradict this recommendation.

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H + OH + H₂O → H₂O + H₂O

H + OH + N$_2$ → H$_2$O + N$_2$

T/K

EXPERIMENTAL DATA

☐	Halstead and Jenkins 1970
——	Dixon–Lewis 1975
△	Black and Porter 1962
▲	Dixon–Lewis et al 1962
○	McAndrew and Wheeler 1962
●	Rosenfeld and Sugden 1964
⊢——⊣	Schott and Bird 1964
▲	Dixon–Lewis et al 1965
⊖	Zeegers and Alkemade 1965
⊢ – – ⊣	Getzinger and Blair 1969
– – – –	Gay and Pratt 1969
——	This Recommendation 1989

$$H + HO_2 \rightarrow H_2 + O_2 \quad (1)$$
$$\rightarrow OH + OH \quad (2)$$
$$\rightarrow O + H_2O \quad (3)$$
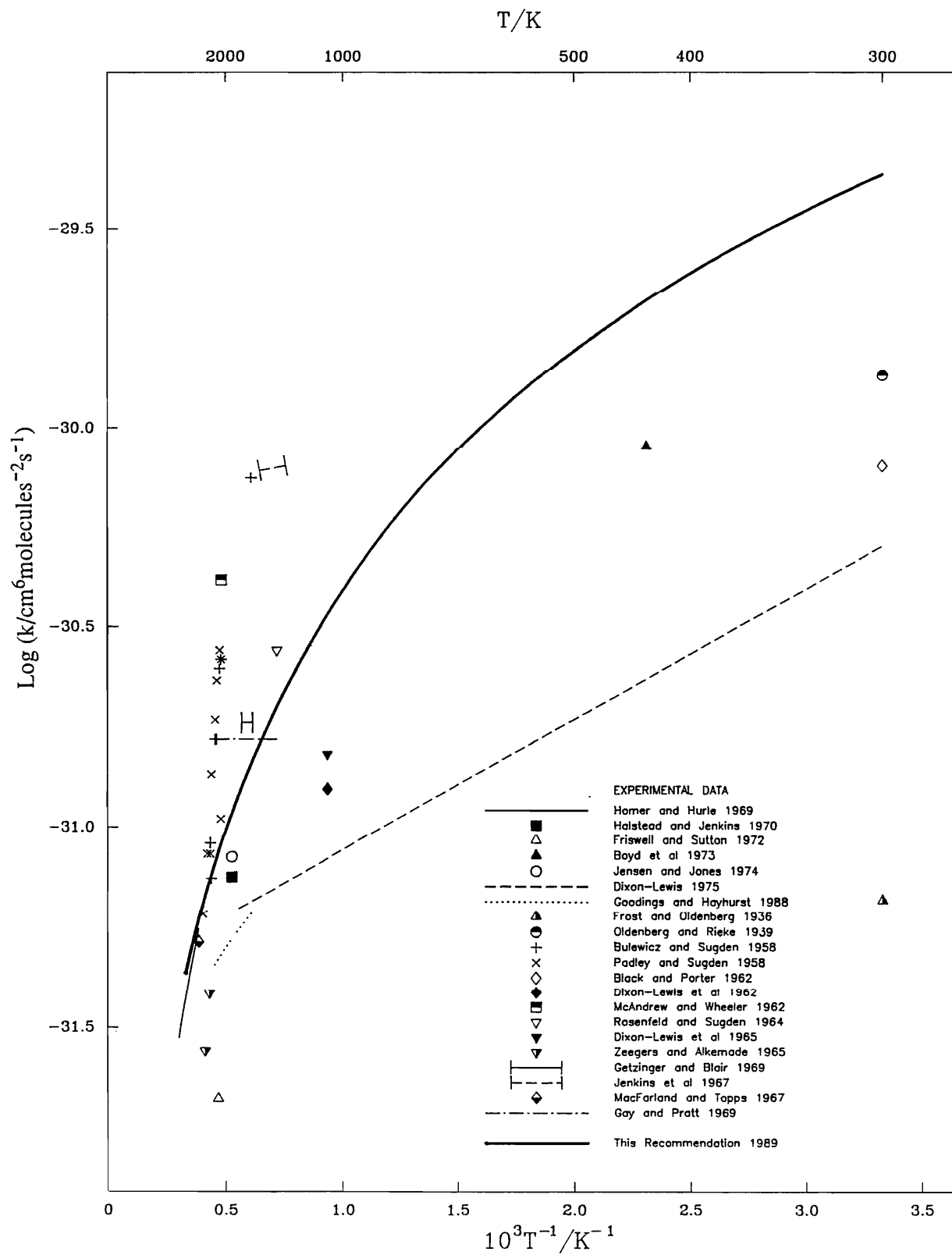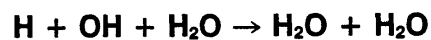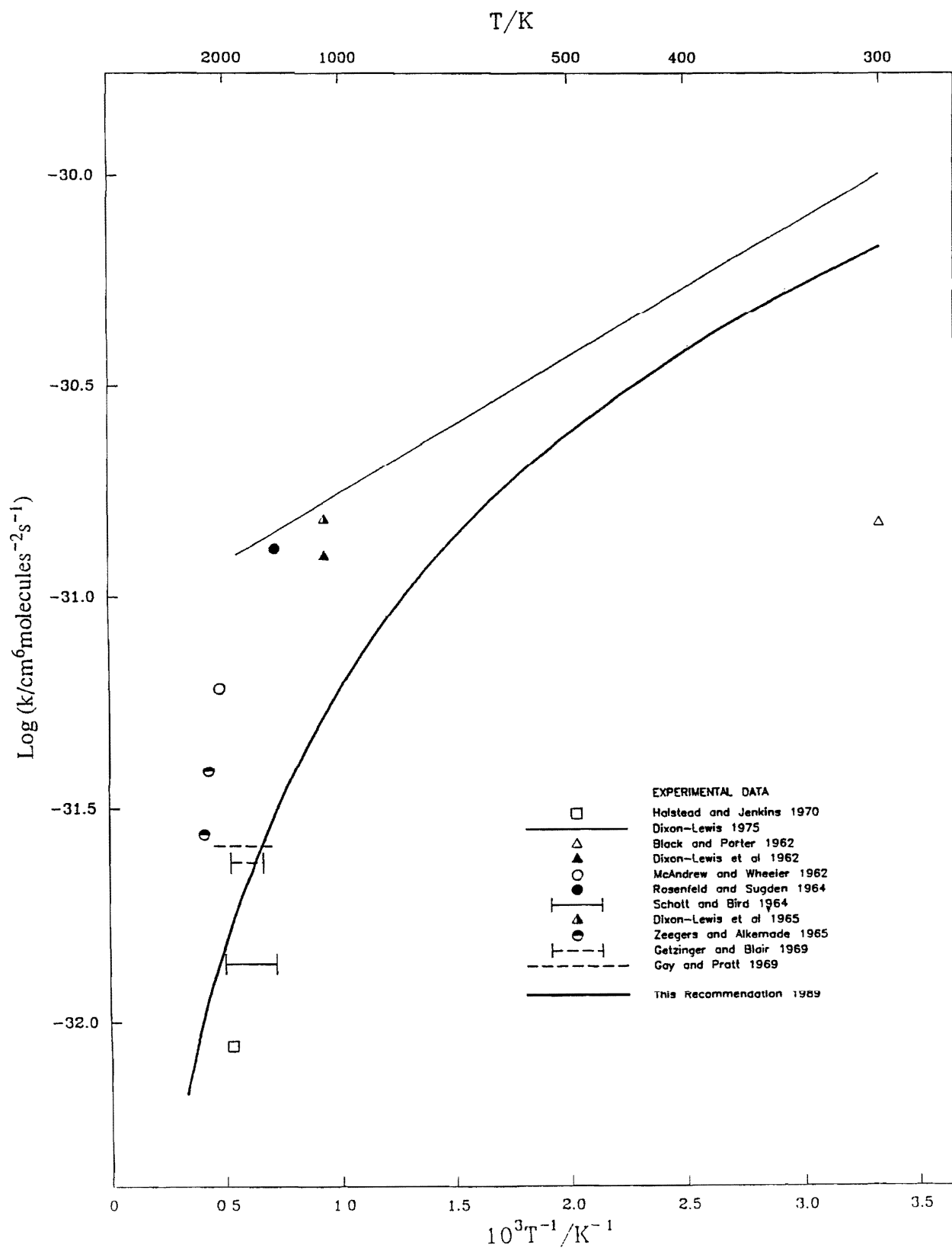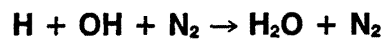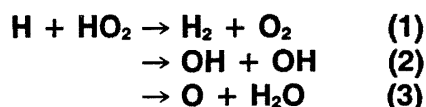
Thermodynamic Data

ΔH°_{298} (1) = -228 kJ mol^{-1}

ΔS°_{298} (1) = -7.96 J K^{-1}mol^{-1}

$K_p(1)$ = $4.58\ T^{-0.331} \exp(+27300/T)$

ΔH°_{298} (2) = -150 kJ mol^{-1}

ΔS°_{298} (2) = 23.6 J K^{-1}mol^{-1}

$K_p(2)$ = $2.5 \cdot 10^3\ T^{-0.678} \exp(+17800/T)$

ΔH°_{298} (3) = -221 kJ mol^{-1}

ΔS°_{298} (3) = 6.06 J K^{-1}mol^{-1}

$K_p(3)$ = $1.56 \cdot 10^2\ T^{-0.621} \exp(+26300/T)$

Rate Coefficient Data

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$k_1 / k_2 / k_3$ = 0.62 : 0.27 : 0.11	298	Westenberg and deHaas (1972)[1]	(a)
k_1 = $2.7 \cdot 10^{-11} \exp(-180/T)$	300–1000	Day et al. (1973)[2]	(b)
k_2 = $3.8 \cdot 10^{-10} \exp(-930/T)$			
$k_3 / k_2 \approx 0.1$			
k_1 / k = 0.29	293	Hack, Wagner, and Hoyermann (1978)[3]	(c)
k_2 / k = 0.02			
k_3 / k = 0.69			
$4.7 \cdot 10^{-11}$	293	Hack, Preuss, and Wagner (1979)[4]	(d)
k_1 = $4.6 \cdot 10^{-11}$	758–850	Baldwin and Walker (1979)[5]	(e)
k_2 = $9.0 \cdot 10^{-10} \exp(-915/T)$			
k_3 = $8.3 \cdot 10^{-11} \exp(-915/T)$			
k_2 = $3.3 \cdot 10^{-11}$	349	Pagsberg et al. (1979)[6]	(f)
$5.0 \cdot 10^{-11}$	298	Thrush and Wilkinson (1981)[7]	(g)
k_1 = $6.7 \cdot 10^{-12}$	296	Sridharan, Qiu, and Kaufman (1982)[8]	(h)
k_2 = $6.4 \cdot 10^{-11}$			
k_3 = $3.0 \cdot 10^{-12}$			
k_2 / k_1 = $27.54 \exp(-737/T)$	231–464	Pratt and Wood (1983)[9]	(i)
k_1 = $7 \cdot 10^{-12}$	245–300	Keyser (1986)[10]	(j)
k_2 = $7.8 \cdot 10^{-11}$			
k_3 = $2 \cdot 10^{-12}$			
Reviews and Evaluations			
k_1 = $4.2 \cdot 10^{-11} \exp(-349/T)$	290–800	Baulch et al. (1972)[11]	
k_2 = $4.2 \cdot 10^{-10} \exp(-950/T)$			
k_1 = $1.4 \cdot 10^{-11}$	298	Baulch et al. (1980)[12]	
k_2 = $3.2 \cdot 10^{-11}$			
$k_3 \leq 9.5 \cdot 10^{-13}$			
k_2 = $4.8 \cdot 10^{-11}$	298	Kaufman and Sherwell (1983)[13]	
$k_1 / k_2 / k_3$ = 0.42 : 1 : 0.03			
k_1 = $4.2 \cdot 10^{-11} \exp(-350/T)$	300–1000	Warnatz (1984)[14]	
k_2 = $2.5 \cdot 10^{-10} \exp(-505/T)$	300–1000		
k_1 = $1.1 \cdot 10^{-10} \exp(-1070/T)$	300–2500	Tsang and Hampson (1986)[15]	
k_2 = $2.8 \cdot 10^{-10} \exp(-440/T)$			

Comments

(a) Discharge-flow system; absolute [H] and steady-state [OH] and [O] by electron spin resonance.

(b) Numerical modelling of burning velocities of rich H_2/O_2/N_2 flames. Parameters not very accurate.

(c) Discharge-flow system; HO_2 from H + O_2 recombination. [H], [O], and [OH] monitored by electron spin resonance. Total pressure near $5 \cdot 10^2$ Pa. k estimated to lie in the range $(3.3–7.3) \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

(d) Discharge-flow system; HO_2 from F + H_2O_2 reaction or from H + O_2 + M recombination. [OH] and [HO$_2$] observed by laser magnetic resonance. Total pressures 500–800 Pa and 130 Pa.

(e) Recalculated because of a revised value for k(H + O_2) $\rightarrow$ OH + O.

(f) Pulse radiolysis of gaseous ammonia – oxygen mixtures at atmospheric pressure; [NH$_2$], [NH], and [OH] measured by UV absorption spectroscopy. Numerical integration of 23 reaction mechanism and fitting of unknown rate parameters to experimental results.

(g) Discharge-flow system; HO_2 steady-state concentration measured by laser magnetic resonance. Total pressures 2.5–3.2 Torr. Given rate based on a relative collision efficiency of O_2/Ar = 3 : 1 in H + O_2 + M recombination.

(h) Flow system; HO_2 from F + H_2O_2 reaction. [HO_2] monitored by conversion to OH with excess NO, [H] and [O] by VUV resonance fluorescence, [OH] by laser induced fluorescence. Total pressures near 2.5 Torr He.

(i) Discharge-flow system; HO_2 from H + O_2 + M recombination. Product analysis by mass spectrometry and gas chromatography. Total pressures 2–10 Torr Ar.

(j) Flow system; HO_2 from F + H_2O_2 reaction. [OH], [O], and [H] monitored by resonance fluorescence, [HO_2] by quantitatively converting it to OH with an excess of NO.

Preferred Values

k_1 = $7.1 \cdot 10^{-11}$ exp($-710/T$) cm^3 molecule^{-1} s^{-1} over range 300–1000 K

k_2 = $2.8 \cdot 10^{-10}$ exp($-440/T$) cm^3 molecule^{-1} s^{-1} over range 300–1000 K

k_3 = $5.0 \cdot 10^{-11}$exp($-866/T$) cm^3 molecule^{-1} s^{-1} over range 300–1000 K

Reliability

Δlog k = ± 0.3 for total rate coefficient over range 300–1000 K

20 % error on branching ratios for (1) and (2), 100 % for (3)

Comments on Preferred Values

For the reaction leading to H_2 and O_2 the recommendation is based on the relatively small rate coefficients at low temperature measured with modern methods and on

the spare high temperature values. For the reaction leading to OH + OH, the recommendation of Tsang and Hampson[15] is adopted which is similar to the recommendation of Warnatz[14].

For clarity, rate data measured before 1972 are included in the Arrhenius plot (see Baulch *et al*.[11] for Ref.).

References

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[14]J. Warnatz, in "Combustion Chemistry", ed. W. C. Gardiner, Springer-Verlag, New York (1984).

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H + HO₂ → H₂ + O₂

H + HO$_2$ → H$_2$ + O$_2$

T/K

Log(k/cm^{3}molecule^{-1}s^{-1})

10^3T^{-1}/K^{-1}

EXPERIMENTAL DATA

Sridharan et al 1982
Hack et al 1978
Day et al 1973
Baldwin et al 1974
Westenberg and DeHaas 1972
Keyser 1972
Pratt and Wood 1983
Baldwin and Walker 1979
Clyne and Thrush 1963
Albers 1969
Browne et al 1969
Dodonov et al 1969
Dixon–Lewis et al 1970
Bennet and Blackmore 1971

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H + HO₂ → OH + OH

H + HO₂ → H₂O + O

H + H₂O → OH + H₂

$$\text{H} + \text{H}_2\text{O} \rightarrow \text{OH} + \text{H}_2$$
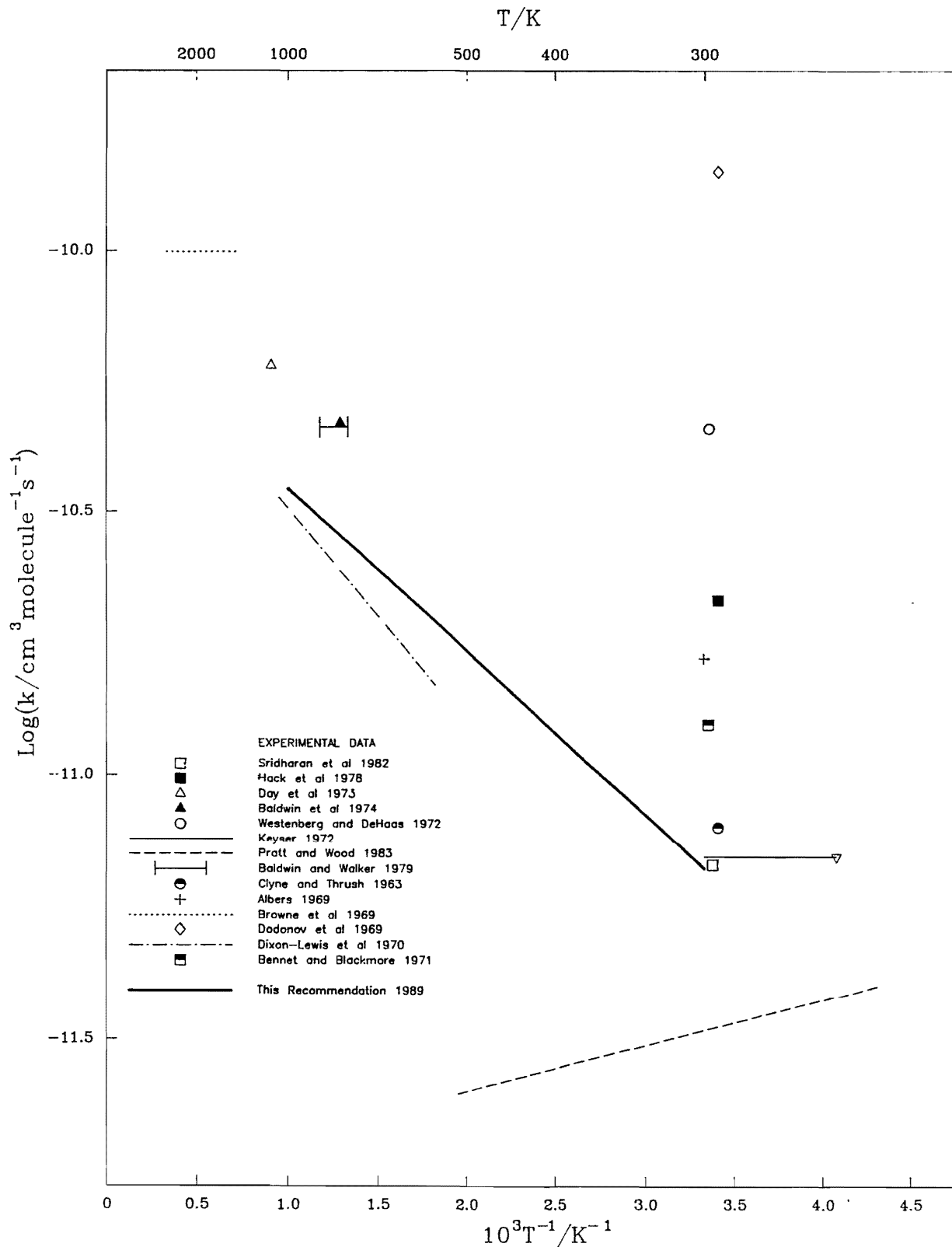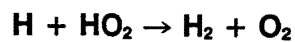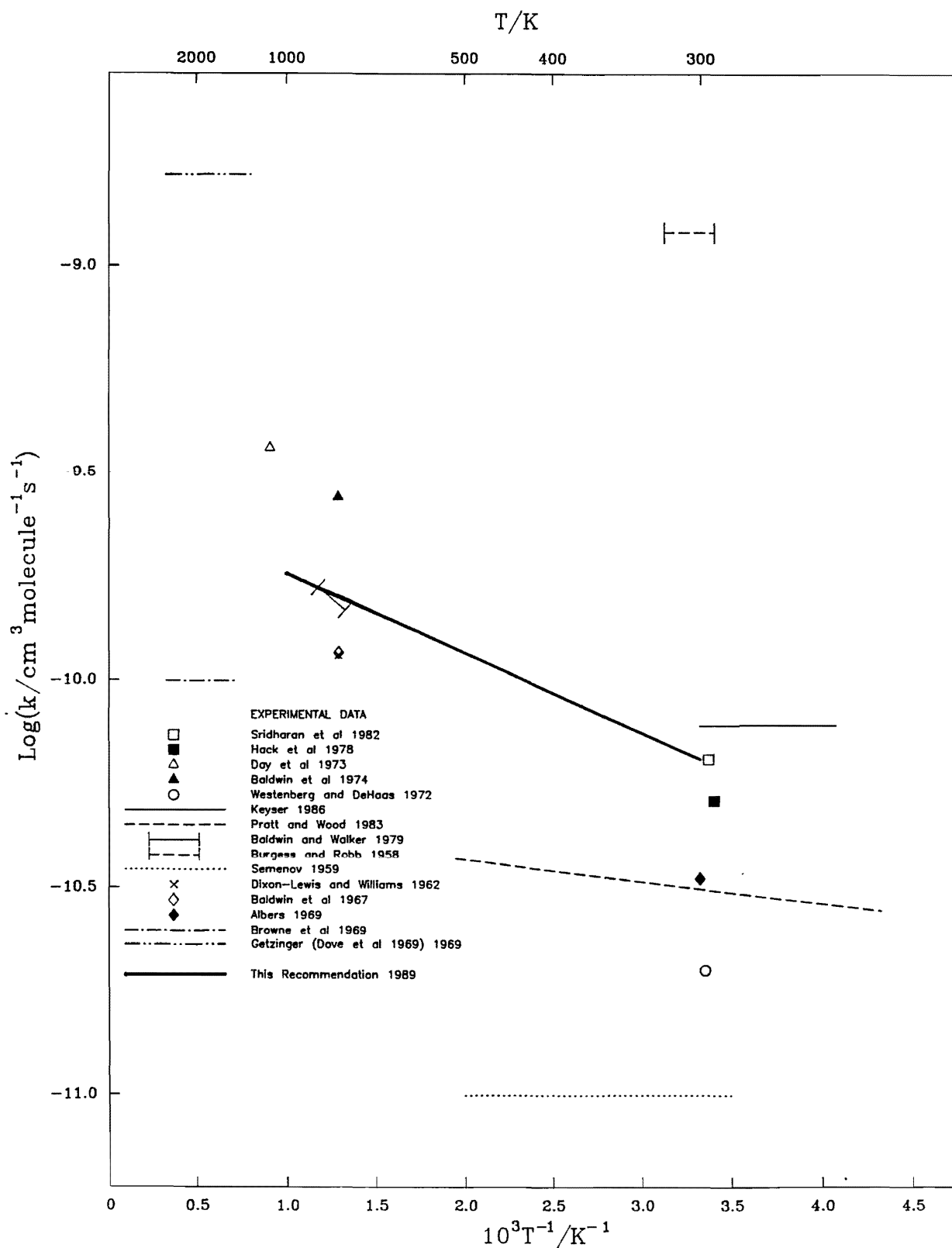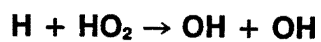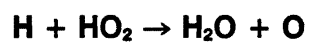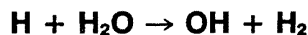
Thermodynamic Data

$\Delta H^\circ_{298} = 62.9 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} = 10.9 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p = 8.85 \ T^{-0.084} \exp(-7680/T)$

Rate Coefficient Data

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	$T[\text{K}]$	Reference	Comments
Rate Coefficient Measurements			
$5.2{\cdot}10^{-10} \exp(-11100/T)$	1160–1390	Madronich and Felder (1984)[1]	(a)
$4.6{\cdot}10^{-10} \exp(-11558/T)$	1246–2297	Michael and Sutherland (1988)[2]	(b)
Reviews and Evaluations			
$1.5{\cdot}10^{-10} \exp(-10248/T)$	300–2500	Baulch *et al*. (1972)[3]	
$1.0{\cdot}10^{-16} \ T^{1.9} \exp(-9260/T)$	400–2400	Tsang and Hampson (1986)[4]	

Comments

(a) Flash photolysis of H₂O; [OH] by time resolved resonance fluorescence. Total pressures near 200 Torr. Experimental difficulties due to H atom diffusion.

(b) Shock tube; H atoms produced by flash photolysis of H₂O/Ar mixtures. [H] as a function of time by atomic resonance absorption spectroscopy.

Preferred Values

$k = 7.5{\cdot}10^{-16} \ T^{1.6} \exp(-9270/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over range 300–2500 K

Reliability

$\Delta \log k = \pm 0.2$ over range 300–2500 K

Comments on Preferred Values

The recommended rate coefficient is based on the spare high temperature measurements and rate data of the reverse reaction combined with the equilibrium constant.

For clarity, rate data measured before 1972 are included in the Arrhenius plot (see Baulch *et al*.[3] for Ref.).

References

[1]S. Madronich and W. Felder, J. Phys. Chem. **88**, 1857 (1984).

[2]J. V. Michael and J. W. Sutherland, J. Phys. Chem. **92**, 3853 (1988).

[3]D. L. Baulch, D. D. Drysdale, D. G. Horne, and A. C. Lloyd, "Evaluated Kinetic Data for High Temperature Reactions", Vol. 1: "Homogeneous Gas Phase Reactions of the H₂-O₂System", London, Butterworths (1972).

[4]W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data **15**, 1087 (1986).

H + H₂O → OH + H₂

$$H + H_2O_2 \rightarrow HO_2 + H_2 \quad (1)$$
$$\rightarrow OH + H_2O \quad (2)$$
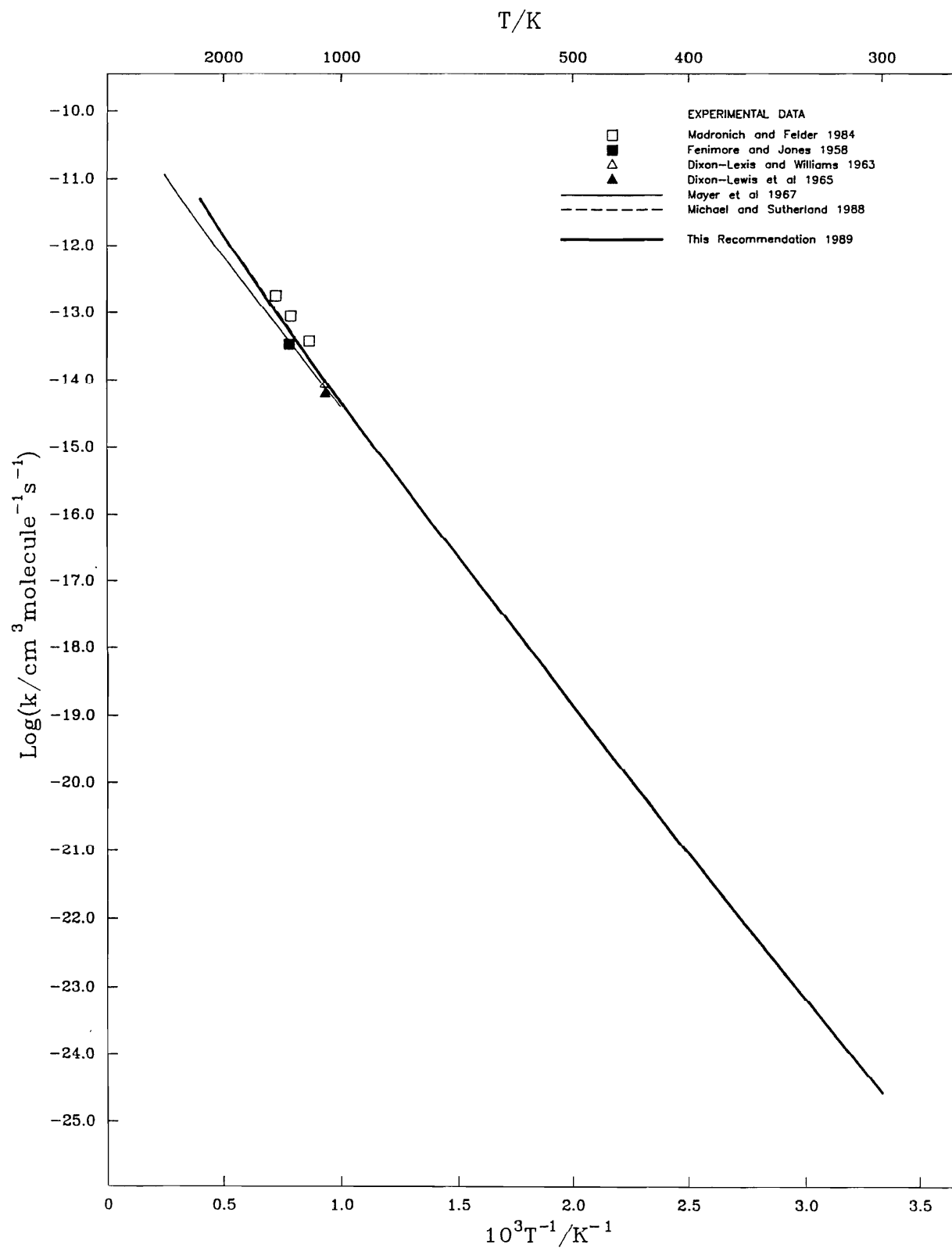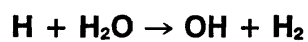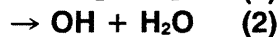
Thermodynamic Data

$\Delta H^\circ_{298} (1) = -71.4 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (1) = 12.1 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(1) = 5.65 \cdot 10^2 \, T^{-0.694} \exp(+8310/T)$

$\Delta H^\circ_{298} (2) = -285 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (2) = 24.8 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(2) = 1.59 \cdot 10^5 \, T^{-1.29} \exp(+33700/T)$

Rate Coefficient Data ($k = k_1 + k_2$)

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	$T[\text{K}]$	Reference	Comments
Rate Coefficient Measurements			
$k_2 / k_1 \approx 10$	870–1000	Kijewski and Troe (1971)[1]	(a)
$k_2 / k_1 = 3.0$	298	Gorse and Volman (1974)[2]	(b)
$k_2 / k_1 = 1.3$	298	Heicklen and Meagher (1974)[3]	(c)
$(E_2-E_1)/R = 2030 \text{ K}$	294–753	Baldwin *et al.* (1974)[4]	(d)
$A_2 / A_1 = 100$			
$5.2 \cdot 10^{-12} \exp(-1400/T)$	283–353	Klemm *et al.* (1975)[5]	(e)
Reviews and Evaluations			
$k_1 = 2.8 \cdot 10^{-12} \exp(-1890/T)$	300–800	Baulch *et al.* (1972)[6]	
$k_2 = 3.7 \cdot 10^{-9} \exp(-5906/T)$	400–800		
$k_1 = 2.8 \cdot 10^{-12} \exp(-1890/T)$	300–800	Warnatz (1984)[7]	
$k_2 = 1.7 \cdot 10^{-11} \exp(-1805/T)$	300–1000		
$k_1 = 8.0 \cdot 10^{-11} \exp(-4005/T)$	300–2500	Tsang and Hampson (1986)[8]	
$k_2 = 4.0 \cdot 10^{-11} \exp(-2000/T)$	300–2500		

Comments

(a) Thermal decomposition of H_2O_2 behind reflected shock waves in Ar carrier gas (density $\approx 5 \cdot 10^{-5}$ mol cm^{-3}) with added H_2. $[H_2O_2]$ by absorption measurements at 280 nm, $[HO_2]$ by absorption at 230 nm. Relative rate estimated from the maximum HO_2 yield in the quasi-stationary period of the reaction. Computer simulations of the system were only successful with k_1 > $1.7 \cdot 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

(b) Photolysis of H_2O_2 at 254 nm in the presence of CO; mass spectrometric analysis. k_2 / k_1 derived from relative yields of CO_2 and H_2.

(c) Photolysis of H_2O_2 at 253.7 nm in the presence of CO. Rate of CO_2 production monitored by quadrupole mass spectrometry. Total pressure near 50 Torr N_2.

(d) Combination of the results of Baldwin *et al.*[9] with those of Albers *et al.*[10] for H_2O_2 + D assuming small isotopic effects.

(e) VUV flash photolysis of H_2O_2/He to yield H. [H] monitored by Lyman-α resonance fluorescence. Below 1000 K channel (2) was found to be predominant.

Preferred Values

$k_1 = 2.8 \cdot 10^{-12} \exp(-1890/T)$ cm^3 molecule^{-1} s^{-1} over range 300–1000 K

$k_2 = 1.7 \cdot 10^{-11} \exp(-1800/T)$ cm^3 molecule^{-1} s^{-1} over range 300–1000 K

Reliability

$\Delta \log k_1 = \pm 0.3$ over range 300–1000 K

$\Delta \log k_2 = \pm 0.3$ over range 300–1000 K

Comments on Preferred Values

The values preferred by Warnatz[7] have been adopted. The arguments given there are accepted, and the values measured after 1984 do not contradict this recommendation.

For clarity, rate data measured before 1972 are included in the Arrhenius plot (see Baulch *et al.*[6] for Ref.).

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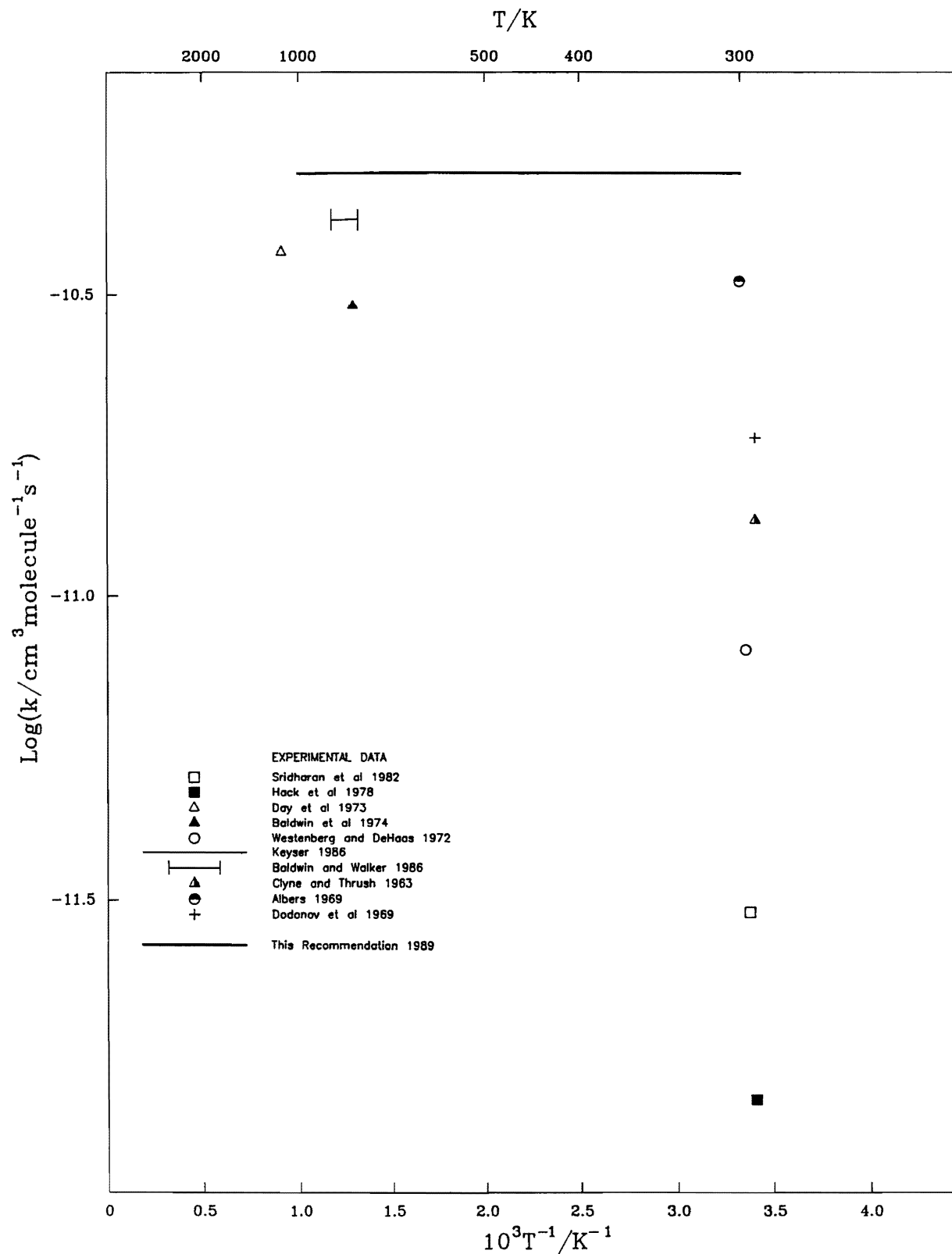
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H + H₂O₂ → H₂ + HO₂

$$H + H_2O_2 \rightarrow H_2 + HO_2$$

T/K

EXPERIMENTAL DATA

□	Gorse and Volman 1974
■	Baldwin and Walker 1979
△	Heicklen and Meagher 1974
▲	Foner and Hudson 1962
○	Baldwin et al 1970
●	Albers et al 1971
——	Kijewski and Troe 1971
▬▬	This Recommendation 1989

H + H₂O₂ → H₂O + OH

T/K

H + NH → H₂ + N
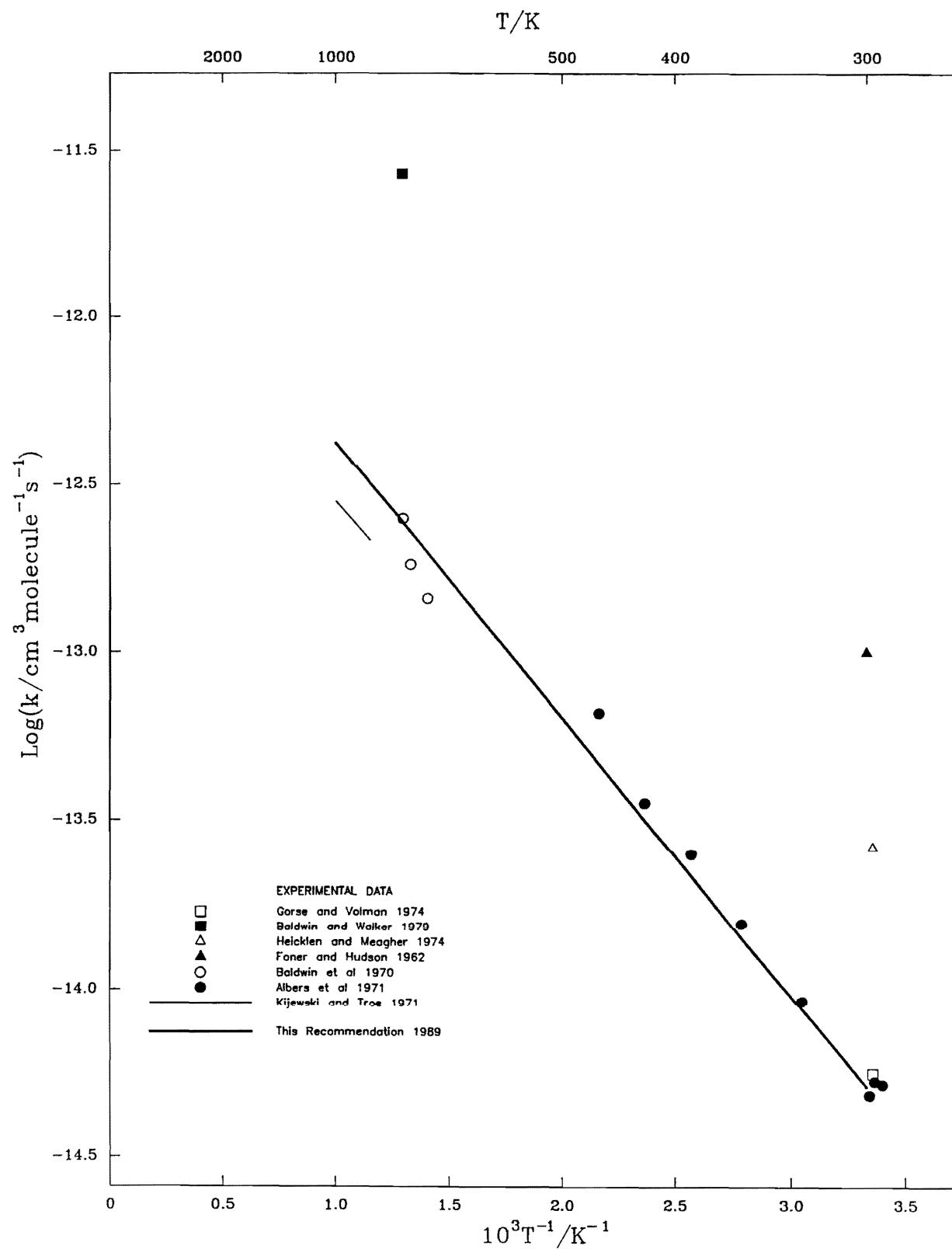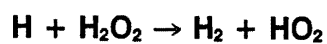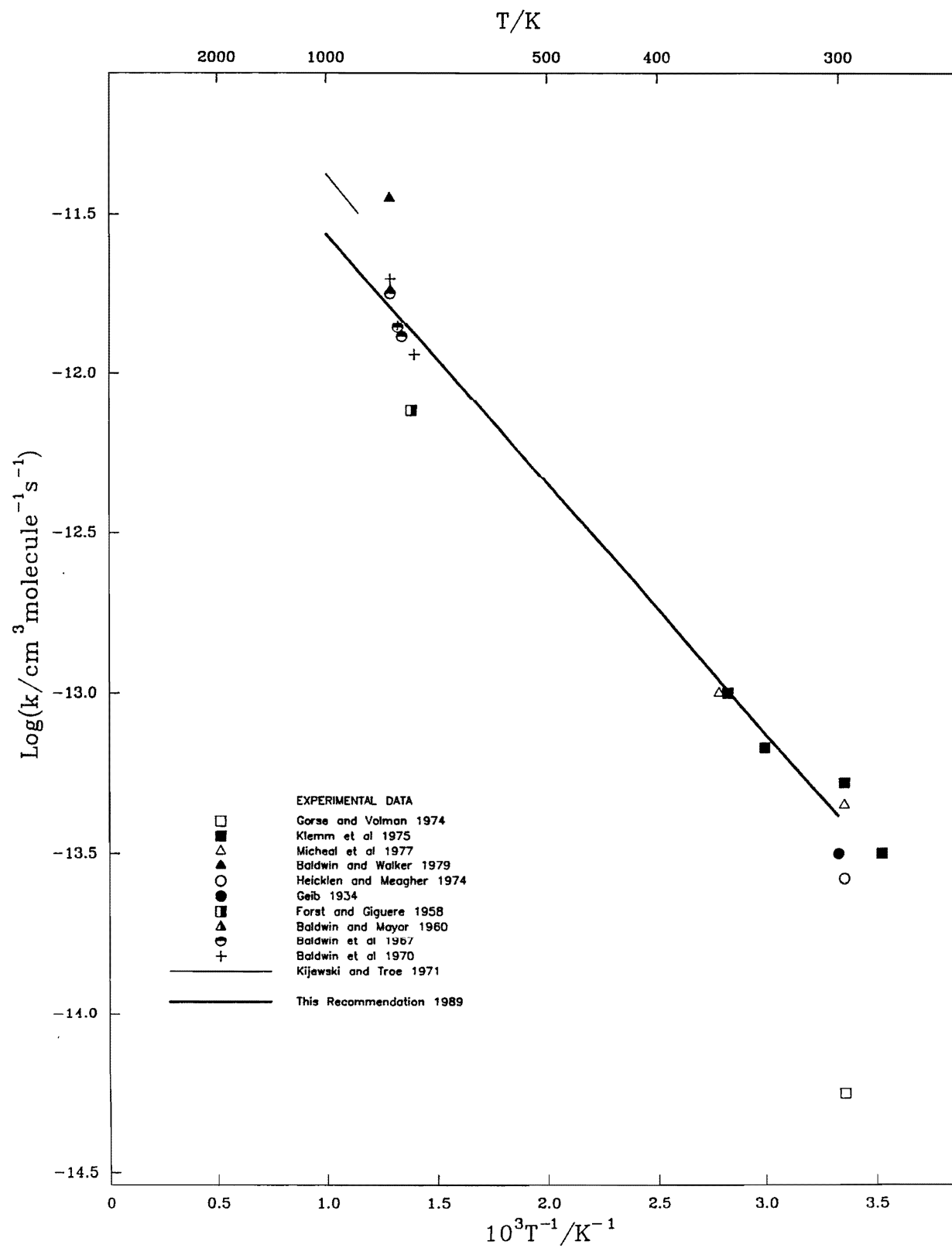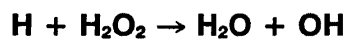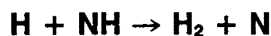
Thermodynamic Data (See Comments on Preferred Values)
$\Delta H^\circ_{298} = -102 \text{kJ mol}^{-1}$
$\Delta S^\circ_{298} = -12.0 \text{ J K}^{-1}\text{mol}^{-1}$
$K_p = 0.497 \, T^{-0.102}\exp(+12200/T)$

Rate Coefficient Data

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	$T[\text{K}]$	Reference	Comments
Rate Coefficient Measurements			
$\approx 1.7 \cdot 10^{-11}$	1790–2200	Morley (1981)[1]	(a)
Reviews and Evaluations			
$\sim 5 \cdot 10^{-11}$	1790–2200	Hanson and Salimian (1984)[2]	(b)

Comments

(a) $H_2/O_2/Ar$ flames doped with CH_3CN. [NH] monitored by laser induced fluorescence. Accuracy limited by calibration for NH. k also calculated from the results of Haynes[3] assuming mole fraction of $H_2 = 5.7 \cdot 10^{-2}$ and $K = 3$ in his conditions.
(b) Review of experimental measurements. Recommends value of Morley[1].

Preferred Values

$k = 1.7 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over range 1500–2500 K

Reliability
$\Delta \log k = \pm 1.0$ over the range 1500–2500 K

Comments on Preferred Values

The only experimental determinations are those of Morley[1] and of Haynes[3] recalculated by Morley[1].

The value of Morley is recommended and, since the rate coefficient is expected to have only a small temperature coefficient, the recommendation is made for a wider temperature range than that of the measurements but with substantial error limits to accomodate any error introduced by this extrapolation.

The thermodynamic data should be used with caution. There are significant uncertainties associated with the data on NH.

References

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H + NH₂ → H₂ + NH
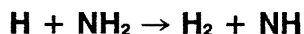
Thermodynamic Data (See Comments on Preferred Values)
$\Delta H^\circ_{298} = -51.9 \text{kJ mol}^{-1}$
$\Delta S^\circ_{298} = 2.54 \text{ J K}^{-1}\text{mol}^{-1}$
$K_p = 5.24 \, T^{-0.156}\exp(+6090/T)$

Rate Coefficient Data

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	$T[\text{K}]$	Reference	Comments
Reviews and Evaluations			
	–	Baulch et al. (1974)[1]	(a)
$5.0 \cdot 10^{-11} \exp(-4600/T)$	1800–3000	Lesclaux (1984)[2]	(b)
$3.16 \cdot 10^{-11}$	2400–3000	Hanson and Salimian (1985)[3]	(c)

Comments

(a) Review of data to 1973. Alternative addition channel yielding NH_3 assumed dominant.
(b) Evaluation. Value of k based on Yumura et al.[6].
(c) Review of data.

Preferred Values

$k = 1.0 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over range 2000–3000 K

Reliability
$\Delta \log k = \pm 1.0$ over the range 2000–3000 K

Comments on Preferred Values

All of the available data have been reviewed[1,2,3].
At low temperatures there are two measurements of k differing by a factor of 4. There is an alternative channel $(H + NH_2 + M \rightarrow NH_3 + M)$ which may be important at low temperatures (see data sheet on $NH_3 + M$). We make no recommendation for this temperature regime.

At high temperatures (1800–3000 K) the results from three studies[5,6,7] of shock tube pyrolysis of NH_3 scatter over an order of magnitude. Two of these[5,7] depend upon measurements of k_{-1} and equilibrium data. The value of Roose[5] plotted is a value which supersedes an older value from the same laboratory[9]. The recommended value is based on the values from all three studies with substantial error limits.

The thermodynamic data should be used with caution. There may be significant errors in the data on NH.

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H + $^3CH_2$ → H$_2$ + CH
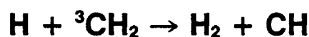
Thermodynamic Data

$\Delta H^\circ_{298} = -10.8kJ \ mol^{-1}$
$\Delta S^\circ_{298} = 3.44 \ J \ K^{-1}mol^{-1}$
$K_p = 3.64 \ T^{-0.11} \ exp(+1220/T)$

Rate Coefficient Data

k [cm^3 molecule^{-1} s^{-1}]	T [K]	Reference	Comments
Rate Coefficient Measurements			
$2.7 \cdot 10^{-10}$	298	Böhland and Temps (1984)[1]	(a)
$1.3 \cdot 10^{-11}$	2000–2800	Frank, Bhaskaran, and Just (1986)[2]	(b)
$1.8 \cdot 10^{-10}$	298	Böhland, Temps, and Wagner (1987)[3]	(a)
Reviews and Evaluations			
$2.7 \cdot 10^{-10}$	298	Tsang and Hampson (1986)[4]	(c)

Comments

(a) Discharge flow with LMR detection of $^3CH_2$. H produced from discharge through H_2, $^3CH_2$ by discharge through ketene.

(b) Absorption spectroscopy study of H and CO following thermal dissociation of dilute ketene in argon behind reflected shocks.

(c) Based on Ref. 1.

Preferred Values

$k = 1.0 \cdot 10^{-11} \ exp(+900/T) \ cm^3 \ molecule^{-1} \ s^{-1}$ over range 300–3000 K

Reliability

$\Delta log \ k = \pm 0.7$

Comments on Preferred Values

Böhland *et al.*[3] demonstrated that, when their value is combined with the reverse rate coefficient of Zabarnick *et al.*[5], an estimate of 389 kJ mol^{-1} is obtained for $\Delta H^\circ_{f,298}(^3CH_2)$, in good agreement with the accepted value.

Frank *et al.*[2] argue that the rate coefficient must decrease with temperature and that a value as high as that of Böhland *et al.*[3] is not compatible with their high temperature data. Löhr and Roth[6] found some evidence for a high temperature value of $5 \cdot 10^{-11} \ cm^3 \ molecule^{-1} \ s^{-1}$ but the technique was less direct than that of Frank *et al.*, and subject to significant uncertainty. In view of the large discrepancy between the estimates of Refs. 2 and 3, a negative temperature dependence is proposed, compatible with a mechanism involving a CH_3 association complex. Large uncertainties are attached.

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$$H + CH_3 \rightarrow H_2 + {}^1CH_2 \qquad (1)$$
$$H + CH_3 (+ M) \rightarrow CH_4 (+ M) \qquad (2)$$
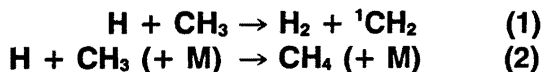
Thermodynamic Data

$\Delta H^2_{298} (1) = 61.0 \text{ kJ mol}^{-1}$

$\Delta S^2_{298} (1) = 10.7 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(1) = 23.7 \ T^{-0.57} \exp(-7640/T)$

$\Delta H^2_{298} (2) = -439 \text{ kJ mol}^{-1}$

$\Delta S^2_{298} (2) = -123 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(2) = 1.76 \cdot 10^{-4} \ T^{-1.06} \exp(+52700/T) \text{ atm}^{-1}$

Rate Coefficient Data

k [cm^3 molecule^{-1} s^{-1}]	T [K]	Reference	Comments
Rate Coefficient Measurements			
$k_1 = 3.0 \cdot 10^{-10} \exp(-7580/T)$	1700–2300	Bhaskaran *et al.* (1979)[1]	(a)

Comments

(a) Shock tube study using atomic resonance absorption spectroscopy.

Preferred Values

$k = 1.0 \cdot 10^{-10} \exp(-7600/T)$ cm^3 molecule^{-1} s^{-1} over range 300–2500 K

Reliability

$\Delta \log k = \pm 1.0$

Comments on Preferred Values

Combining the well established low temperature rate coefficient for the reverse reaction ($1.2 \cdot 10^{-10}$ cm^3

molecule^{-1} s^{-1}, this evaluation) with K_p gives $k = 2.8 \cdot 10^{-9}$ $T^{-0.5}\exp(-7640/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 300–1000 K, a factor, at 1000 K, of 6 below that predicted by extrapolation of the Arrhenius expression of Bhaskaran *et al.*[1]. It is possible, although unlikely, that the rate coefficient for the reverse reaction increases with temperature. A preferred rate coefficient midway between the thermodynamic value and that of Bhaskaran *et al.*[1] has been adopted to accommodate this possibility.

Reference

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H + CH₃(+M) → CH₄(+M)
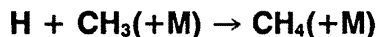
Thermodynamic Data

$\Delta H^{\circ}_{298} = -439$ kJ mol^{-1}

$\Delta S^{\circ}_{298} = -123$ J K^{-1}mol^{-1}

$K_p = 1.76 \cdot 10^{-4} \, T^{-1.06} \exp(+52700/T)$ atm^{-1}

Rate Coefficient Data

k[cm³ molecule^{-1} s^{-1}]	T[K]	[M][molecule cm^{-3}]	Reference	Comments
Rate Coefficient Measurements				
Low Pressure Range				
[He] $3.2 \cdot 10^{-29}$	504	$(4.8-76.7) \cdot 10^{17}$ (He)	Brouard *et al.* (1985)[1]	(a)
[He] $4.0 \cdot 10^{-29}$	300–600	$(4.8-163.5) \cdot 10^{17}$ (He)	Brouard *et al.* (1989)[2]	(a)
Intermediate Fall-off Range				
$6.6 \cdot 10^{-12}$	298	$(5.2-10.0) \cdot 10^{16}$ (Ar)	Brown *et al.* (1966)[3]	(b)
$1.7 \cdot 10^{-11}$	293	$2.2 \cdot 10^{17}$ (He)	Dodonov *et al.* (1969)[4]	(c)
$3.9 \cdot 10^{-12}$	290	$2.7 \cdot 10^{17}$ (Ar)	Halstead *et al.* (1970)[5]	(d)
$6.6 \cdot 10^{-12}$		$5.4 \cdot 10^{17}$		
$1.8 \cdot 10^{-12}$	303–603	$2.0 \cdot 10^{16}$ (H₂)	Teng and Jones (1972)[6]	(e)
$2.0 \cdot 10^{-12}$	300	$2.4 \cdot 10^{16}$ (He)	Michael *et al.* (1973)[7]	(f)
$5.5 \cdot 10^{-12}$		$8.1 \cdot 10^{16}$		
$8.0 \cdot 10^{-12}$		$11.1 \cdot 10^{16}$		
$1.8 \cdot 10^{-12}$	503–753	$1.3 \cdot 10^{17}$ (Ar)	Camilleri *et al.* (1974)[8]	(g)
$3.6 \cdot 10^{-12}$		$2.6 \cdot 10^{17}$		
$3.0 \cdot 10^{-12}$	295	$2.0 \cdot 10^{17}$ (He)	Pratt and Veltmann (1974)[9]	(h)
$7.4 \cdot 10^{-12}$		$4.9 \cdot 10^{17}$		
$6.7 \cdot 10^{-12}$	321	$2.4 \cdot 10^{17}$ (He)	Pratt and Veltmann (1976)[10]	(h)
$5.2 \cdot 10^{-12}$	415	$1.9 \cdot 10^{17}$		
$3.4 \cdot 10^{-12}$	521	$1.5 \cdot 10^{17}$		
$0.53 \cdot 10^{-10}$	308	$0.94 \cdot 10^{18}$ (C₂H₆)	Cheng and Yeh (1977)[11]	(i)
$1.8 \cdot 10^{-10}$		$3.1 \cdot 10^{18}$		
$2.5 \cdot 10^{-10}$		$9.4 \cdot 10^{18}$		
$2.8 \cdot 10^{-10}$		$25.1 \cdot 10^{18}$		
$3.0 \cdot 10^{-10}$		$72.1 \cdot 10^{18}$		
$2.6 \cdot 10^{-12}$	640–818	$9.8 \cdot 10^{16}$ (Ar)	Sepehrad *et al.* (1979)[12]	(j)
$4.7 \cdot 10^{-12}$		$18.5 \cdot 10^{16}$		
$2.0 \cdot 10^{-10}$	296	$2.5 \cdot 10^{17}$ (N₂, H₂)	Sworski *et al.* (1980)[13]	(k)
$1.52 \cdot 10^{-11}$	504	$4.8 \cdot 10^{17}$ (He)	Brouard *et al.* (1985)[1]	(a)
$1.86 \cdot 10^{-11}$		$9.6 \cdot 10^{17}$		
$3.44 \cdot 10^{-11}$		$19.3 \cdot 10^{17}$		
$5.31 \cdot 10^{-11}$		$38.5 \cdot 10^{17}$		
$7.75 \cdot 10^{-11}$		$76.7 \cdot 10^{17}$		
$2.26 \cdot 10^{-11}$	301	$0.81 \cdot 10^{18}$ (He)	Brouard *et al.* (1989)[2]	(a)
$3.52 \cdot 10^{-11}$		$1.6 \cdot 10^{18}$		
$6.36 \cdot 10^{-11}$		$3.3 \cdot 10^{18}$		
$14.0 \cdot 10^{-11}$		$9.8 \cdot 10^{18}$		
$18.2 \cdot 10^{-11}$		$16.3 \cdot 10^{18}$		
$1.35 \cdot 10^{-11}$	401	$0.61 \cdot 10^{18}$		
$2.52 \cdot 10^{-11}$		$1.2 \cdot 10^{18}$		
$4.44 \cdot 10^{-11}$		$2.4 \cdot 10^{18}$		
$10.1 \cdot 10^{-11}$		$8.4 \cdot 10^{18}$		
$14.4 \cdot 10^{-11}$		$14.7 \cdot 10^{18}$		
$2.11 \cdot 10^{-11}$	601	$1.7 \cdot 10^{18}$		
$3.78 \cdot 10^{-11}$		$4.9 \cdot 10^{18}$		
$6.18 \cdot 10^{-11}$		$11.4 \cdot 10^{18}$		
High Pressure Range				
$1.5 \cdot 10^{-10}$	300	$(1.6-32.2) \cdot 10^{18}$ (Ar, SF₆)	Patrick *et al.* (1980)[14]	(l)
$3.5 \cdot 10^{-10}$	504	$(4.8-76.7) \cdot 10^{17}$ (He)	Brouard *et al.* (1985)[1]	(a)
$4.7 \cdot 10^{-10}$	300	$(8.1-16.4) \cdot 10^{18}$ (He)	Brouard and Pilling (1986)[15]	(a)
$4.7 \cdot 10^{-10}$	300–600	$(8.1-16.4) \cdot 10^{18}$ (He)	Brouard *et al.* (1989)[2]	(a)
Reviews and Evaluations				
$k_0 = [\text{Ar}] \, 2.2 \cdot 10^{-21} \, T^{-3}$	300–2500		Warnatz (1984)[16]	(m)
$k_{\infty} = 1.0 \cdot 10^{-7} \, T^{-1}$				
$k_{\infty} = 2.0 \cdot 10^{-9} \, T^{-0.4}$	300–1100		Tsang and Hampson (1986)[17]	(n)

Rate Coefficient Data — Continued

k[cm^3 molecule^{-1} s^{-1}]	T[K]	[M][molecule cm^{-3}]	Reference	Comments
$k_\infty = 4.23 \cdot 10^{-8} \, T^{-0.82} \exp(-159/T)$	300–2500		Stewart et al. (1989)[18]	(o)
$k_\infty = 2.0 \cdot 10^{-9} \, T^{-0.4}$	300–1100		Tsang (1989)[19]	(p)
$k_0 = [\text{He}] \, 6.2 \cdot 10^{-29} \, (T/300)^{-1.8}$	300–1000		Cobos and Troe (1990)[20]	(q)
$k_0 = [\text{C}_2\text{H}_6] \, 3.0 \cdot 10^{-28} \, (T/300)^{-1.8}$	300–1000			
$F_c(\text{He}) = \exp(-0.45 - T/3231)$	300–1000			
$F_c(\text{C}_2\text{H}_6) = \exp(-0.34 - T/3035)$	300–1000			
$k_\infty = 3.5 \cdot 10^{-10}$	300–1000			

Comments

(a) 193 nm photolysis of acetone, [CH$_3$] and [H] by time-resolved UV absorption and resonance fluorescence respectively. [CH$_3$] $\gg$ [H]. k_∞ by RRKM/master equation fit.

(b) Discharge flow study of H + C$_2$H$_4$ system. CH$_3$ generated by H + C$_2$H$_5$ → 2 CH$_3$. ESR detection of H. Relied on Toby and Schiff's[24] product yield analysis to interpret data.

(c) Mass spectrometric study of species distribution in diffusion cloud; CH$_3$ generated from H + C$_2$H$_4$, H + C$_3$H$_6$; H generated in discharge.

(d) Discharge flow study of H + C$_2$H$_4$ system; used GC analysis of CH$_4$, C$_2$H$_6$, C$_3$H$_8$, and C$_4$H$_{10}$.

(e) Discharge flow study of H + C$_2$H$_4$ system, products analysed by GC and simulated by numerical integration.

(f) Comparison of H + C$_2$H$_4$ data from high pressure pulsed Hg photosensitization–resonance absorption and low pressure discharge flow–mass spectrometry. Radical – atom reactions make greater contribution in latter study. Numerical integration.

(g) Discharge flow study of H + C$_2$H$_6$ system. GC detection of CH$_4$, C$_2$H$_4$, and C$_3$H$_8$. Rate coefficients from fitting the reaction scheme using numerical integration. Assumed k_1 independent of temperature.

(h) Discharge flow study of H + C$_2$H$_4$ system. Products detected by mass spectrometry. Rate coefficients by fitting 7 reaction scheme using numerical integration.

(i) Steady-state Hg photosensitisation of C$_2$H$_6$. Products detected by mass spectrometry. k_∞ by Lindemann plot.

(j) Discharge flow study of H + CH$_4$ system. Products detected by gas chromatography. Rate coefficients from numerical integration of 14 reaction scheme.

(k) 160 nm photolysis of H$_2$O/CH$_4$ mixtures. CH$_3$ detected as function of time at 216 nm. Rate coefficient determined by fitting to 11 reaction scheme with H$_2$ and N$_2$ diluent.

(l) Flash photolysis of azomethane/ethene mixtures. Products analysed by gas chromatography. Rate coefficient determined by numerical integration of 9 reaction scheme, but probably low because (i) reaction (1) competes primarily with CH$_3$ + CH$_3$ and low rate coefficient was used for CH$_3$ recombination, (ii) H + azomethane was neglected. k_∞ by RRKM fit.

(m) Review of literature prior to 1980.

(n) The results of Cheng et al.[11], Sworski et al.[13], and Patrick et al.[14] have been combined with the reverse rate determination of Chen et al.[25] to derive the recommended expression. A tabulation of log k/k_∞ over the temperature range 300–2500 K from RRKM calculations is also given.

(o) Single-channel hindered Gorin model RRKM calculations of the CH$_4$ decomposition with a fit to experimental results. Conversion to k_∞ via the equilibrium constant.

(p) The results of Cheng et al.[11], Sworski et al.[13], and Patrick et al.[14] have been combined with the reverse rate determination of Chen et al.[25] to derive the recommended expression.

(q) Theoretical calculation based on k_0 calculations from Ref. 21, the representation of fall-off curves from Ref. 22, and the k_∞ treatment from Ref. 23. Collision efficiencies β_c at 300 K of 0.07 for M = He and of 0.15 for M = C$_2$H$_6$ point to particularly inefficient energy transfer for which $<\Delta E>$ values may increase proportional to the temperature. Therefore, the temperature coefficient of k_0 at $T \leq 1000$ K was chosen as in the strong collision limit, i.e., assuming β_c to be temperature independent. The temperature coefficient of k_∞ was derived from SACM-modified PST calculations of Ref. 23 which also predicts the absolute value of k_∞ to be as recommended. The broadening factors contain a considerable weak collision contribution, strong collision broadening factors being given by $F_c^{sc} = \exp(-0.09 - T/3316)$.

Preferred Values

$k_0 = [\text{He}] \, 6.2 \cdot 10^{-29} \, (T/300)^{-1.8}$ cm^3 molecule^{-1} s^{-1} over range 300–1000 K

$k_0 = [\text{Ar}] \, 6.0 \cdot 10^{-29} \, (T/300)^{-1.8}$ cm^3 molecule^{-1} s^{-1} over range 300–1000 K

$k_0 = [\text{C}_2\text{H}_6] \, 3.0 \cdot 10^{-28} \, (T/300)^{-1.8}$ cm^3 molecule^{-1} s^{-1} over range 300–1000 K

$k_\infty = 3.5 \cdot 10^{-10}$ cm^3 molecule^{-1} s^{-1} over range 300–1000 K

$F_c = \exp(-0.45 - T/3231)$ for M = He, Ar

$F_c = \exp(-0.34 - T/3053)$ for M = C$_2$H$_6$

Reliability

$\Delta \log k_0 = \pm 0.3$ for M = He over range 300–1000 K

$\Delta \log k_0 = \pm 0.5$ for M = Ar, C_2H_6 over range 300–1000 K

$\Delta \log k_\infty = \pm 0.3$ over range 300 1000 K

$\Delta F_c = \pm 0.1$ over range 300–1000 K

Comments on Preferred Values

The preferred values are chosen from a comparison of a recent theoretical modelling by Cobos and Troe[20] with the most extensive experimental data from Pilling and coworkers[1,2] for the bath gas He. This model points to comparably low β_c and $< \Delta E >$ values such that a positive temperature coefficient of $< \Delta E >$ and a temperature independent β_c in agreement with the fit to the experiments appears not unconceivable. The high pressure limit is based mainly on the data by Cheng and Yeh[11] in accord with the theoretical prediction from Ref. 23. The values for $M = Ar$ are uncertain, Ref. 3 indicating a larger k_0 value than for $M = He$ which is in contrast to the more detailed results from Ref. 5. More experiments close to the low and high pressure limits are required to arrive at a conclusive picture.

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CH₃ + H + He → CH₄ + He

H + CH$_4$ → H$_2$ + CH$_3$
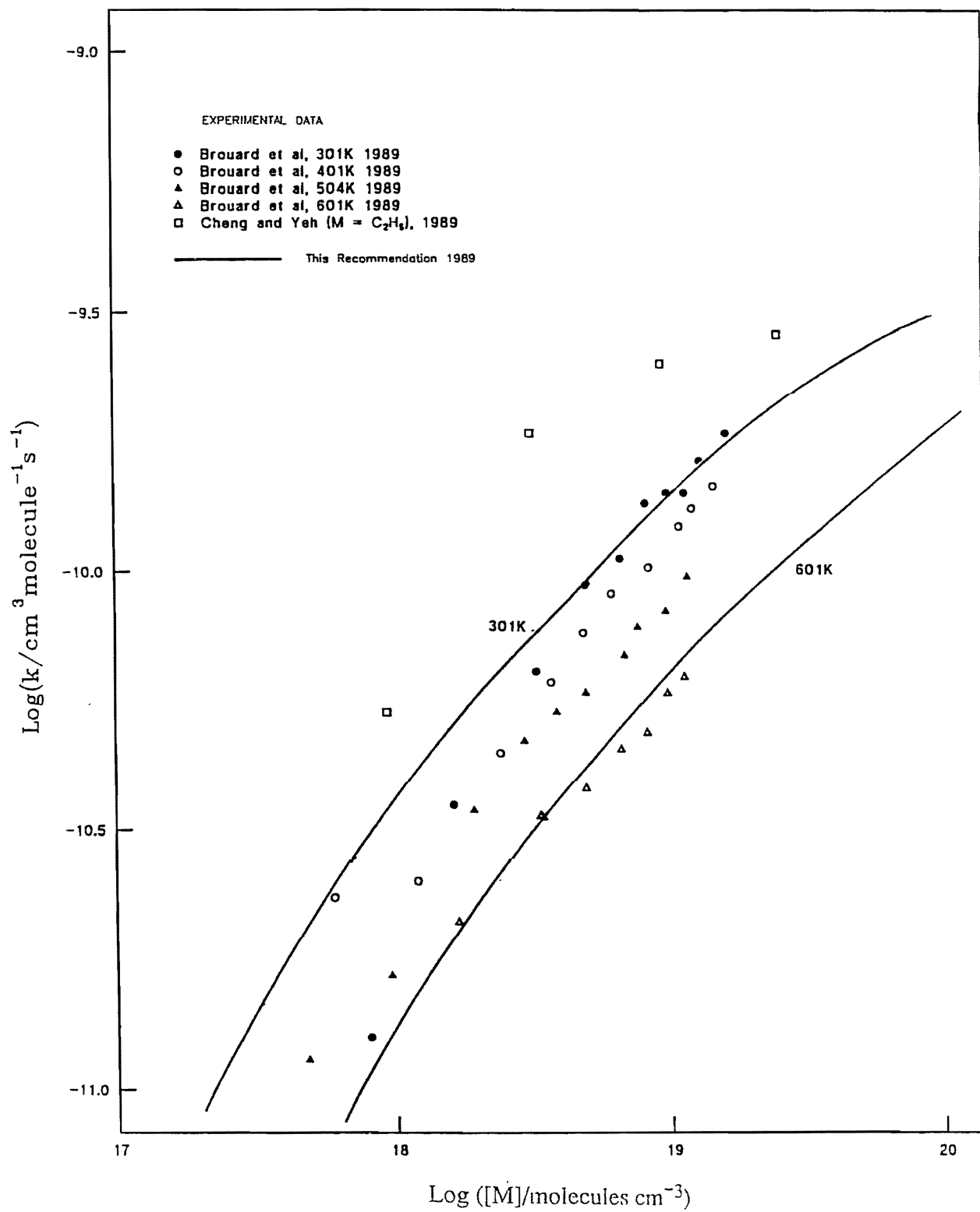
Thermodynamic Data
$\Delta H^\circ_{298} = 2.6$ kJ mol^{-1}
$\Delta S^\circ_{298} = 24.0$ J K^{-1}mol^{-1}
$K_p = 1.81 \cdot 10^2 \, T^{-0.225} \exp(-638/T)$

Rate Coefficient Data

k [cm^3 molecule^{-1} s^{-1}]	Temperature [K]	Reference	Comments
Rate Coefficient Measurements			
$1.7 \cdot 10^{-14} \exp(-2265/T)$	372–436	Berlie and LeRoy (1954)[1]	(a)
$6.3 \cdot 10^{-11} \exp(-5185/T)$	1150–1900	Fenimore and Jones (1961)[2]	(b)
$1.15 \cdot 10^{-10} \exp(-5539/T)$	426–747	Kurylo and Timmons (1969)[3]	(c)
$1.04 \cdot 10^{-10} \exp(-5838/T)$	500–732	Kurylo, Hollinden, and Timmons (1970)[4]	(d)
$5.33 \cdot 10^{-12}$	1600	Peeters and Mahnen (1973)[5]	(e)
$3.55 \cdot 10^{-19} \, T^3 \exp(-8889/T)$	1300–1750	Biordi, Papp, and Lazzara (1974)[6]	(f)
$1.02 \cdot 10^{-11}$	1700	Biordi, Papp, and Lazzara (1975)[7]	(g)
$1.2 \cdot 10^{-9} \exp(-7580/T)$	1700–2300	Roth and Just (1975)[8]	(h)
$3.02 \cdot 10^{-10} \exp(-6627/T)$	640–818	Sepehrad, Marshall, and Purnell (1979)[9]	(i)
Reviews and Evaluations			
$2.1 \cdot 10^{-10} \exp(-5990/T)$	370–1800	Walker (1968)[10]	(j)
$3.73 \cdot 10^{-20} \, T^3 \exp(-4405/T)$	300–1800	Clark and Dove (1973)[11]	(k)
$2.35 \cdot 10^{-17} \, T^2 \exp(-4449/T)$	370–1800	Shaw (1978)[12]	(l)
$1.26 \cdot 10^{-10} \exp(-6002/T)$	400–1800	Sepehrad, Marshall, and Purnell (1979)[9]	(m)
$3.73 \cdot 10^{-20} \, T^3 \exp(-4405/T)$	300–2500	Warnatz (1984)[13]	(n)
$3.73 \cdot 10^{-20} \, T^3 \exp(-4405/T)$	300–2000	Tsang and Hampson (1986)[14]	(o)

Comments

(a) Only low temperature data available; k values more reliable than A and E. H atoms measured by catalytic recombination.

(b) Low pressure flames. k determined relative to k(H + N$_2$O) for which $1.26 \cdot 10^{-10} \exp(-7600/T)$ cm^3 molecule^{-1} s^{-1} is used[15].

(c) Flow discharge; ESR detection of H atoms.

(d) Flow discharge; ESR detection of H atoms; excellent agreement with authors' earlier results.

(e) Flame study; molecular beam sampling, mass spectrometric detection of all species.

(f) Low pressure flames, modulated molecular beam with mass spectrometric detection. Authors do not quote k values; Arrhenius parameters determined from published graph.

(g) CF$_3$Br–inhibited CH$_4$ flames, techniques as in (f).

(h) Shock tube–resonance fluorescence study of CH$_4$ pyrolysis.

(i) Discharge flow; computer fit to C$_2$H$_6$ yields determined by gas chromatography.

(j) Reviews early work critically and discusses reliability of data.

(k) Simplified BEBO form of calculating k values. Gave good fit to reliable data between 300 and 1800 K.

(l) Non-critical review of rate constants; useful coverage of data up to 1978.

(m) Argues for Arrhenius expression, but ignores high temperature data.

(n) Recommends Clark and Dove expression without comment.

(o) Carried out further BEBO calculations and Clark and Dove's results are confirmed; same parameters recommended.

Preferred Values

$k = 2.18 \cdot 10^{-20} \, T^{3.0} \exp(-4045/T)$ cm^3 molecule^{-1} s^{-1} over range 300–2000 K

Reliability
$\Delta \log k - \pm 0.05$ over range 500–1000 K rising to ± 0.1 at 2000 K and ± 0.2 at 2500 K
$= \pm 0.2$ at 300 K

Comments on Preferred Values
Extensive literature on this reaction is available. Walker[10] has shown that a number of early studies are unreliable. The value of k is defined very accurately between 500 and 2000 K, but no reliable data are available at room temperature. The preferred expression gives a slightly better fit to the high temperature data than Clark and Dove's, but the two expressions give very similar rate constants at all temperatures and both involve a T^3 term.

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H + CH$_4$ → CH$_3$ + H$_2$

H + CHO → CO + H₂
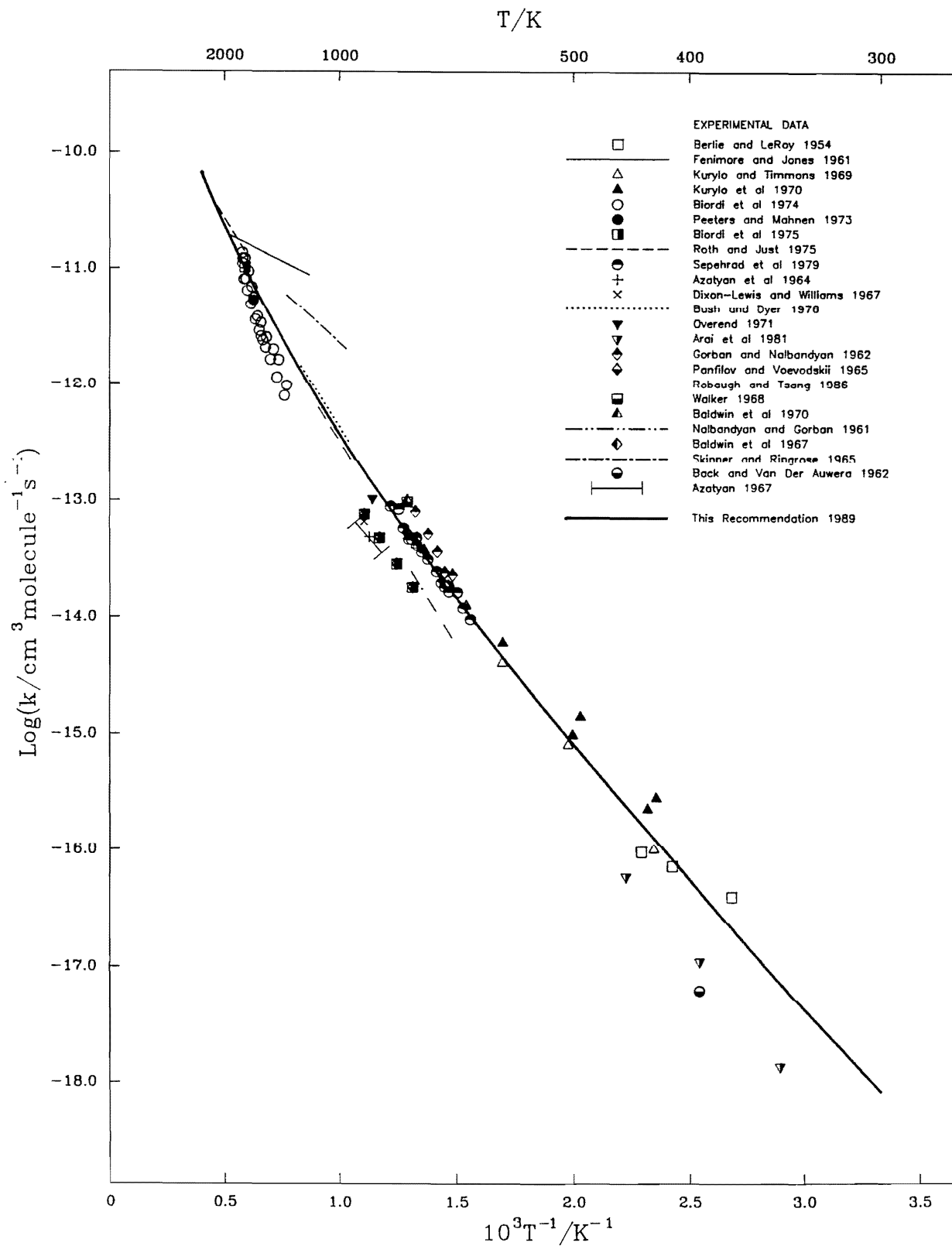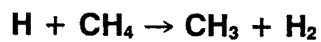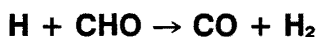
Thermodynamic Data
$\Delta H^{\circ}_{298} = -372$ kJ mol⁻¹
$\Delta S^{\circ}_{298} = -11.0$ J K⁻¹mol⁻¹
$K_p = 11.4\ T^{-0.509} \exp(+44500/T)$

Rate Coefficient Data

k[cm³ molecule⁻¹ s⁻¹]	T[K]	Reference	Comments
Rate Coefficient Measurements			
3.3·10⁻¹¹	1000–1700	Browne *et al.* (1969)[1]	(a)
$k / k_{CHO + O} = 3$	300	Niki, Daby, and Weinstock (1969)[2]	(b)
$k / k_{CHO + O} = 4.0$	298	Mack and Thrush (1973)[3]	(c)
$k / k_{CHO + O} = 2.1$	425	Campbell and Handy (1978)[4]	(d)
≈ 5.5·10⁻¹⁰	298	Reilly *et al.* (1978)[5] (e)	
2.0·10⁻¹⁰	298	Nadtochenko, Sarkisov, and Vedeneev (1979)[6]	(f)
1.2·10⁻¹⁰	298	Hochanadel, Sworsky, and Ogren (1980)[7]	(g)
6.6·10⁻¹¹	≈ 1100	Cherian *et al.* (1981)[8]	(h)
1.4·10⁻¹⁰	296	Timonen, Ratajczak, and Gutman (1987)[9]	(i)
1.3·10⁻¹⁰	350		
9.6·10⁻¹¹	418		
Reviews and Evaluations			
3.3·10⁻¹⁰	300–2500	Warnatz (1984)[10]	
2.0·10⁻¹⁰	300–2500	Tsang and Hampson (1986)[11]	

Comments

(a) Modelling of lean and rich acetylene flames at low pressures. Species profiles by gas chromatography, [OH], [CH], and [C₂] by absorption measurements.

(b) C₂H₄/O discharge-flow system; mass spectrometry. Total pressure 1–2.3 Torr.

(c) Discharge-flow system; CH₂O/O reaction; gas chromatography, air afterglow chemiluminescence observed, [O] and [H] by electron spin resonance. Total pressure ≈ 1.5–3 Torr.

(d) Stirred flow reactor, microwave discharge of N₂; CHO formed by addition of various amounts of CO to O/H₂ mixtures. [O] from O + CO chemiluminescence. Total densities ≈ (1–3)·10⁻⁴ mol cm⁻³ Ar or N₂.

(e) Near-UV pulsed photolysis of CH₂O; intracavity dye laser spectroscopy of CHO absorption at either 613.8 nm or 614.5 nm. Total pressure 10 Torr pure CH₂O. Numerical solution of a kinetic scheme and fitting of rates to experimental data; results are rather insensitive to k.

(f) Pulsed photolysis of CH₃CHO/Ar at 10–200 Torr; intracavity dye laser spectroscopy of CHO absorption.

(g) Flash photolysis of H₂O or H₂O/CO (/CH₄ or H₂) mixtures at 1–3 atm; UV absorption of CHO at 230 nm and of CH₃ at 213 nm monitored. Numerical integration of 17 reaction mechanism.

(h) Numerical modelling of burning velocities of flat H₂/O₂/N₂ flames at atmospheric pressure using a 27 reaction mechanism and assuming zero activation energy for k.

(i) Pulsed laser photolysis of CH₃CHO/H/He mixtures at 308 nm; H atoms from microwave discharge. Mass spectrometry, [H] monitored by NO titration.

Preferred Values

$k = 1.5·10⁻¹⁰$ cm³ molecule⁻¹ s⁻¹ over range 300–2500 K
Reliability
$\Delta \log k = \pm 0.3$ over range 300–2500 K
Comments on Preferred Values

The preferred values are based on the expectation that the rate coefficient will have a negligibly small temperature coefficient and on the reasonable concordant values of $k^{6,7,9}$ at 298 K. The assumption of a small temperature coefficient is supported by the high value found for k at 298 K and the few high temperature values indicating little change with temperature.

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H + CHO → CO + H₂

H + HCHO → H₂ + CHO
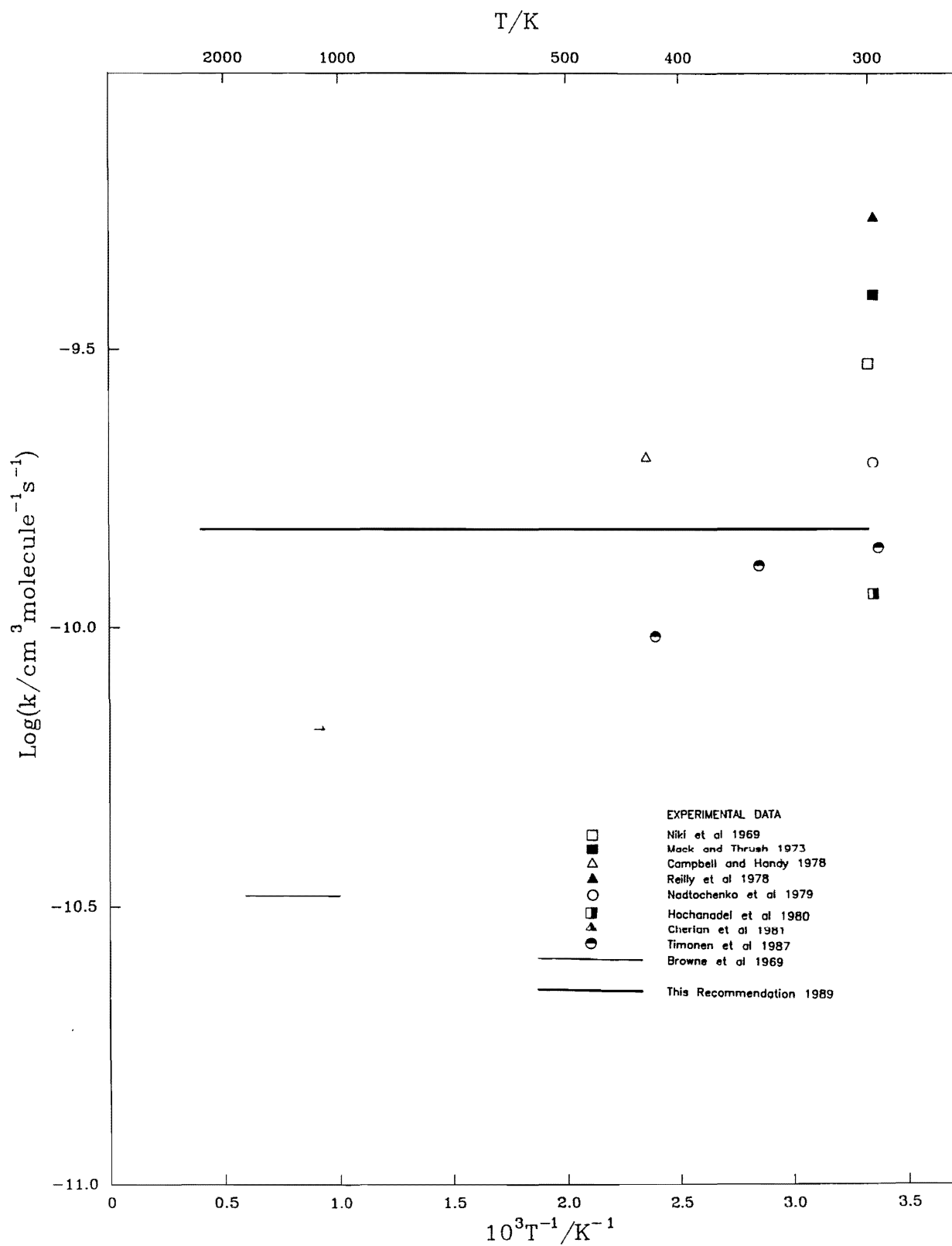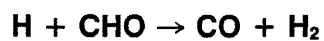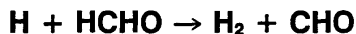
Thermodynamic Data
$\Delta H^\circ_{298} = -58.5 \text{ kJ mol}^{-1}$
$\Delta S^\circ_{298} = 21.9 \text{ J K}^{-1}\text{mol}^{-1}$
$K_p = 3.8 \cdot 10^2 \ T^{-0.4} \exp(+6730/T)$

Rate Coefficient Data

k [cm³ molecule⁻¹ s⁻¹]	T [K]	Reference	Comments
Rate Coefficient Measurements			
$3.3 \cdot 10^{-11} \exp(-1660/T)$	1400–2200	Schecker and Jost (1969)[1]	(a)
$2.2 \cdot 10^{-11} \exp(-1892/T)$	297–652	Westenberg and deHaas (1972)[2]	(b)
$5.4 \cdot 10^{-14}$	297	Ridley *et al.* (1972)[3]	(c)
$3.3 \cdot 10^{-11} \exp(-1847/T)$	264–479	Klemm (1979)[4]	(d)
$5.5 \cdot 10^{-10} \exp(-5280/T)$	1700–2500	Dean *et al.* (1980)[5]	(e)
Reviews and Evaluations			
$4.2 \cdot 10^{-11} \exp(-2009/T)$	300–2500	Warnatz (1984)[6]	(f)
$3.64 \cdot 10^{-16} \ T^{1.77} \exp(-1510/T)$	264–2500	Tsang and Hampson (1986)[7]	(g)

Comments

(a) Thermal dissociation of HCHO/Ar in a shock tube; species monitored by UV absorption and IR emission.

(b) Microwave discharge of H₂/He; behaviour of H atoms in the presence of excess HCHO determined by ESR.

(c) Pulsed vacuum UV photolysis of HCHO; behaviour of H atoms in the presence of excess HCHO determined by Lyman α resonance fluorescence.

(d) Flash photolysis; resonance fluorescence detection of H atoms.

(e) HCHO/O₂/Ar and HCHO/N₂O/Ar mixtures investigated in reflected shock waves; HCHO detected by IR emission.

(f) Based on low temperature data of Westenberg and deHaas[2], Ridley *et al.*[3], and Klemm[4], which are in good agreement, and the high temperature data of Schecker and Jost[1].

(g) Based on the data of Westenberg and deHaas[2], Ridley *et al.*[3], Klemm[4], and Dean *et al.*[5], and fitted using transition state frequencies as defined from BEBO calculations.

Preferred Values

$k = 3.8 \cdot 10^{-14} \ T^{1.05} \exp(-1650/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over range 250–2200 K

Reliability
$\Delta \log k = \pm 0.5$ at 2000 K reducing to ± 0.1 at 300 K

Comments on Preferred Values

The preferred values are based on the low temperature data of Ridley *et al.*[3], Klemm[4], and the high temperature data of Dean *et al.*[5].

References

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H + HCHO → H₂ + HCO

H + CH₃O → H₂ + HCHO
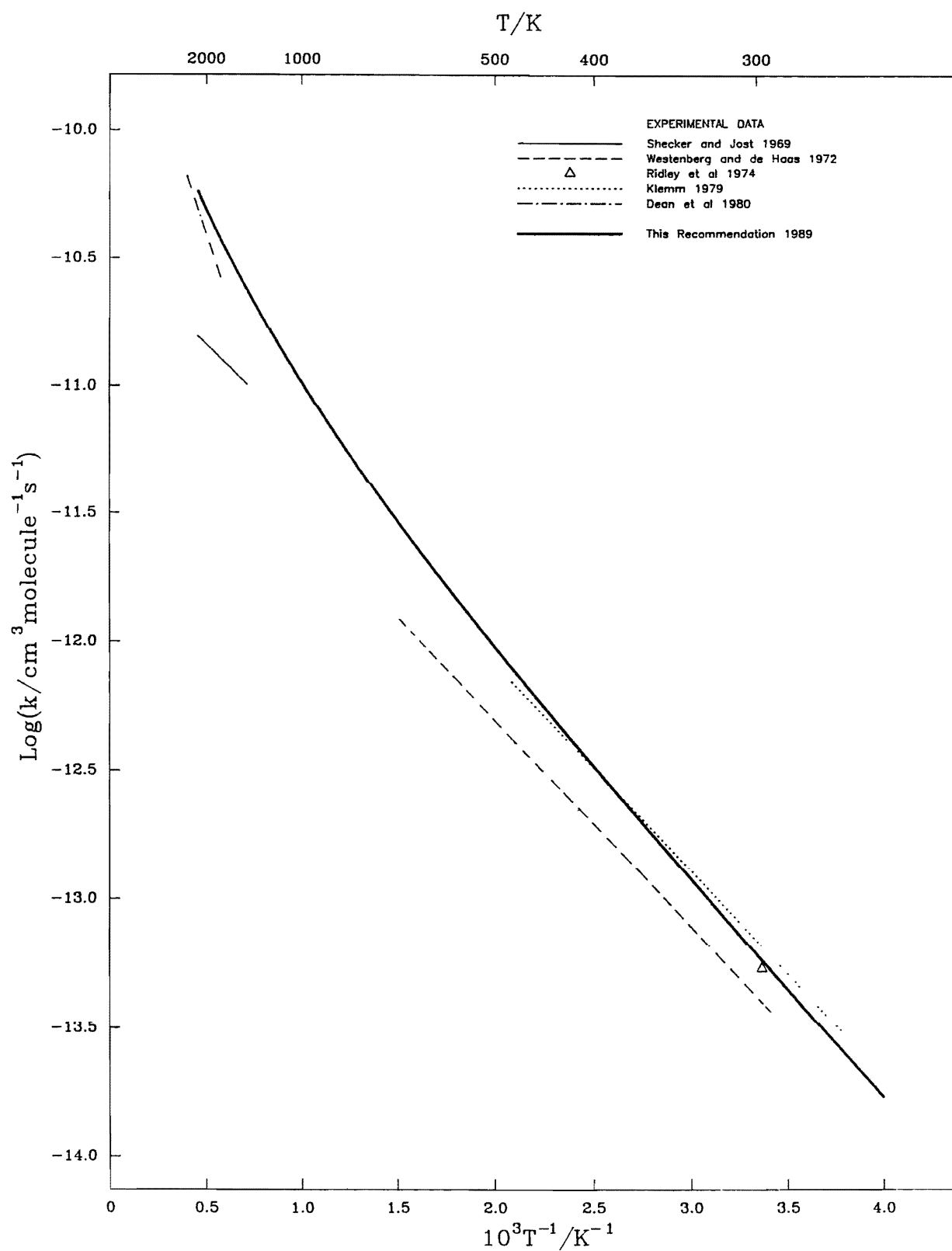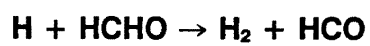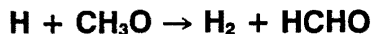
Thermodynamic Data
$\Delta H^\circ_{298} = -350$ kJ mol⁻¹
$\Delta S^\circ_{298} = 6.1$ J K⁻¹mol⁻¹
$K_p = 2.12\ T^{-0.61}\ \exp(+41800/T)$

Rate Coefficient Data

k[cm³ molecule⁻¹ s⁻¹]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$2.8 \cdot 10^{-11}$	300	Hoyermann *et al.* (1981)[1]	(a)
Reviews and Evaluations			
$3.3 \cdot 10^{-11}$	300–2000	Warnatz (1984)[2]	(b)
$3.3 \cdot 10^{-11}$	300	Tsang and Hampson (1986)[3]	(b)

Comments

(a) Discharge flow–mass spectrometric detection. Rate
determined relative to $k(C_2H_5 + H)$ for which this
evaluation gives $6 \cdot 10^{-11}$ cm³ molecule⁻¹ s⁻¹. Pressure
= 1 Torr.

(b) Based on the work of Hoyermann *et al.*[1]; uncertainty
is a factor 3.

Preferred Values

$k = 3.0 \cdot 10^{-11}$ cm³ molecule⁻¹ s⁻¹ over range 300–1000 K

Reliability
$\Delta \log k = \pm 0.5$ over range 300–1000 K

Comments on Preferred Values

No new data have been reported on this reaction. Hoy-
ermann *et al.* showed that the direct H-abstraction reac-
tion accounts for 75% of the total reaction at 300 K, with
about 25% proceeding by complex formation to give ex-
cited CH₃OH. The latter pathway is expected to be less
important at high temperatures.

References

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(1986).
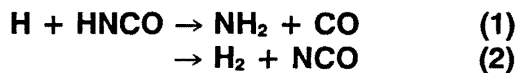
H + HNCO → NH₂ + CO (1)
→ H₂ + NCO (2)

Thermodynamic Data
ΔH°_{298} (1) = −34.0 kJ mol⁻¹
ΔS°_{298} (1) = −38.8 J K⁻¹mol⁻¹
$K_p(1) = 1.58 \cdot 10^6\ T^{-1.41}\ \exp(+3610/T)$

ΔH°_{298} (2) = 45.6 kJ mol⁻¹
ΔS°_{298} (2) = 9.39 J K⁻¹mol⁻¹
$K_p(2) = 23.6\ T^{-0.272}\ \exp(-5640/T)$

Rate Coefficient Data ($k = k_1 + k_2$)

k[cm³ molecule⁻¹ s⁻¹]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$k_1 = 2.3 \cdot 10^{-11}$	1700–1800	Beer *et al.* (1981)[1]	(a)
$k_2 = 5.3 \cdot 10^{-13}$	1700–1800		

Comments

(a) Combustion of a 0.7% N No. 6 Fuel Oil with air in a
furnace assembly, with on line gas analysis instru-
ments (unspecified) for CO, CO₂, and O₂ measure-
ment and a chemiluminescent analyser for NO
analysis. The results were fitted to a 34 reaction
mechanism from which the quoted values resulted.

Preferred Values

$k_2 = 3.4 \cdot 10^{-10}\ T^{-0.27}\ \exp(-10190/T)$ cm³ molecule⁻¹ s⁻¹
over range 500–1000 K

Reliability
$\Delta \log k = \pm 1.0$ over range 500–1000 K

Comments on Preferred Values

There are no direct experimental measurements of rate constants for either of the channels or the total reaction. The values tabulated are of doubtful quality.

Values of both $k_1^{4,5}$ and k_2^2 have been used in modelling high temperature systems (1600–1800 K) but all are from unpublished sources. In all cases k_1 has been assumed to be much larger than k_2.

Perry et al.[3] have obtained a value for k_{-2} over the range 591–913 K which may be combined with the equilibrium data to give the expression for k_2 quoted above.

References

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H + NCO → NH + CO   (1)
→ HCN + O   (2)

Thermodynamic Data (See Comments on Preferred Values)

$\Delta H^\circ_{298} (1) = -131 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (1) = 32.0 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(1) = 3.52 \cdot 10^5 \ T^{-1.29} \exp(+15300/T)$

$\Delta H^\circ_{298} (2) = 6.95 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (2) = 16.0 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(2) = 2.62 \cdot 10^2 \ T^{-0.546} \exp(-995/T)$

Rate Coefficient Data ($k = k_1 + k_2$)

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	$T[\text{K}]$	Reference	Comments
Rate Coefficient Measurements			
$1.74 \cdot 10^{-10} \exp(-1000/T)$	1400–1500	Louge and Hanson (1984)[1]	(a)

Comments

(a) Shock tube study of $C_2N_2/O_2/N_2O$ mixtures. [NCO] monitored as a function of time by absorption spectroscopy at 440.5 nm.

Preferred Values

$k = 8.7 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over range 1400–1500 K

Reliability

$\Delta \log k = \pm 0.5$ over range 1400–1500 K

Comments on Preferred Values

There is only one direct determination of k, that of Louge and Hanson[1]. Although they derive a temperature coefficient for the reaction the temperature range covered is small and we therefore recommend a constant value of k over the range 1400–1500 K with substantial error limits.

A number of other values of k have been quoted in the literature and used in modelling a range of reaction systems[2,3,4,5]. However, none of the systems studied was sufficiently sensitive to the chosen value of k for these values to be considered in this evaluation.

There are no data on the branching ratios. Channel (1) is usually assumed to be more important than (2); the available data on k_{-2} and $K_p(2)$ support this. There are other channels possible leading to OH + CN and HCO + N but both are substantially endothermic.

The thermodynamic data given for channel (1) should be used with caution. There may be significant errors in the data for NH.

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[5] J. M. Beer, M. -T. Jacques, W. Farmayan, and B. R. Taylor, 18th Symp. (Int.) Combust., 101 (1981).

$$H + C_2H_2 \rightarrow H_2 + C_2H \qquad (1)$$
$$H + C_2H_2(+ M) \rightarrow C_2H_3(+ M) \qquad (2)$$
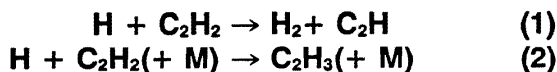
Thermodynamic Data

$\Delta H^\circ_{298}(1) = 116 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298}(1) = 22.5 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(1) = 7.24 \cdot 10^3 \, T^{-0.866} \exp(-14300/T)$

$\Delta H^\circ_{298}(2) = -158 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298}(2) = -84 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(2) = 0.412 \, T^{-1.5} \exp(+18900/T) \text{ atm}^{-1}$

Rate Coefficient Data ($k = k_1$)

k [cm^3 molecule^{-1}s^{-1}]	T [K]	Reference	Comments
Rate Coefficient Measurements			
$5 \cdot 10^{-12}$	1600	Porter et al. (1967)[1]	(a)
$9 \cdot 10^{-10} \exp(-9600/T)$	1000–1700	Browne et al. (1969)[2]	(b)
$8 \cdot 10^{-11} \exp(-8300/T)$	1023–1700	Yampolskii et al. (1974)[3]	(c)
$1.3 \cdot 10^{-23} T^{3.2} \exp(-240/T)$	1700–3400	Tanzawa and Gardiner (1978)[4]	(d)
$1.7 \cdot 10^{-10} \exp(-9600/T)$	2000	Warnatz et al. (1982)[5]	(e)
Reviews and Evaluations			
$1.3 \cdot 10^{-9} \exp(-12900/T)$	1850–3000	Frank and Just (1980)[6]	(f)
$1 \cdot 10^{-10} \exp(-11900/T)$	300–3000	Warnatz (1984)[7]	(g)
$1 \cdot 10^{-10} \exp(-11200/T)$		Tsang and Hampson (1986)[8]	(h)

Comments

(a) Acetylene and methane flames probed in absorption and emission. Assumed O_2 removed exclusively by $H + O_2 \rightarrow OH + O$.

(b) Probing of concentration, by absorption and emission spectroscopy, and temperature in acetylene flames. Numerical integration of complex mechanism.

(c) Pyrolysis of acetylene in presence of D_2, CD_4. Analysis by mass spectrometry. Assumed reaction (1) was sole mechanism for H_2 production.

(d) Thermal decomposition of acetylene behind shock wave. Laser schlieren, computer modelling.

(e) Burner stabilised laminar flat $C_2H_2/O_2/Ar$ flame. Sampling nozzle with mass spectrometric detection. Studied the formation of C_4H_2.

(f) Reflected shock waves in C_2H_2/Ar; atomic resonance absorption on H. Data not sensitive to k, but they review earlier data.

(g) Based on reverse reaction and thermodynamics. Took $\Delta H^\circ(1) = 87 \text{ kJ mol}^{-1}$ and $k_{-1} = 2.5 \cdot 10^{-11} \exp(-1560/T)$ cm^3 molecule^{-1}s^{-1}.

(h) Based on thermodynamics and $k_{-1} = 1.9 \cdot 10^{-11} \exp(-1450/T)$ cm^3 molecule^{-1}s^{-1}.

Preferred Values

$k_1 = 1 \cdot 10^{-10} \exp(-14000/T)$ cm^3 molecule^{-1}s^{-1} over range 1000– 3000 K

Reliability

$\Delta \log k_1 = \pm 1.0$

Comments on Preferred Values

The experimental investigations are very indirect, with the possible exception of that of Tanzawa and Gardiner[4], and make sweeping assumptions. The most direct approach is to use thermodynamic data and k_{-1}. The preferred value is based on $k_{-1} = 2.5 \cdot 10^{-11} \exp(-1560/T)$ cm^3 molecule^{-1}s^{-1}.

The value used for $\Delta H^\circ_{298}(1)$ corresponds to $\Delta H^\circ_{f,298}(C_2H) = 560 \text{ kJ mol}^{-1}$, which is consistent, within experimental error, with the value quoted by McMillen and Golden[9]($564 \pm 4 \text{ kJ mol}^{-1}$) and with more recent spectroscopic data[10].

References

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H + C$_2$H$_2$ → H$_2$ + C$_2$H

H + C₂H₂ (+ M) → C₂H₃ (+ M)

$$H + C_2H_2 (+ M) \rightarrow C_2H_3 (+ M)$$
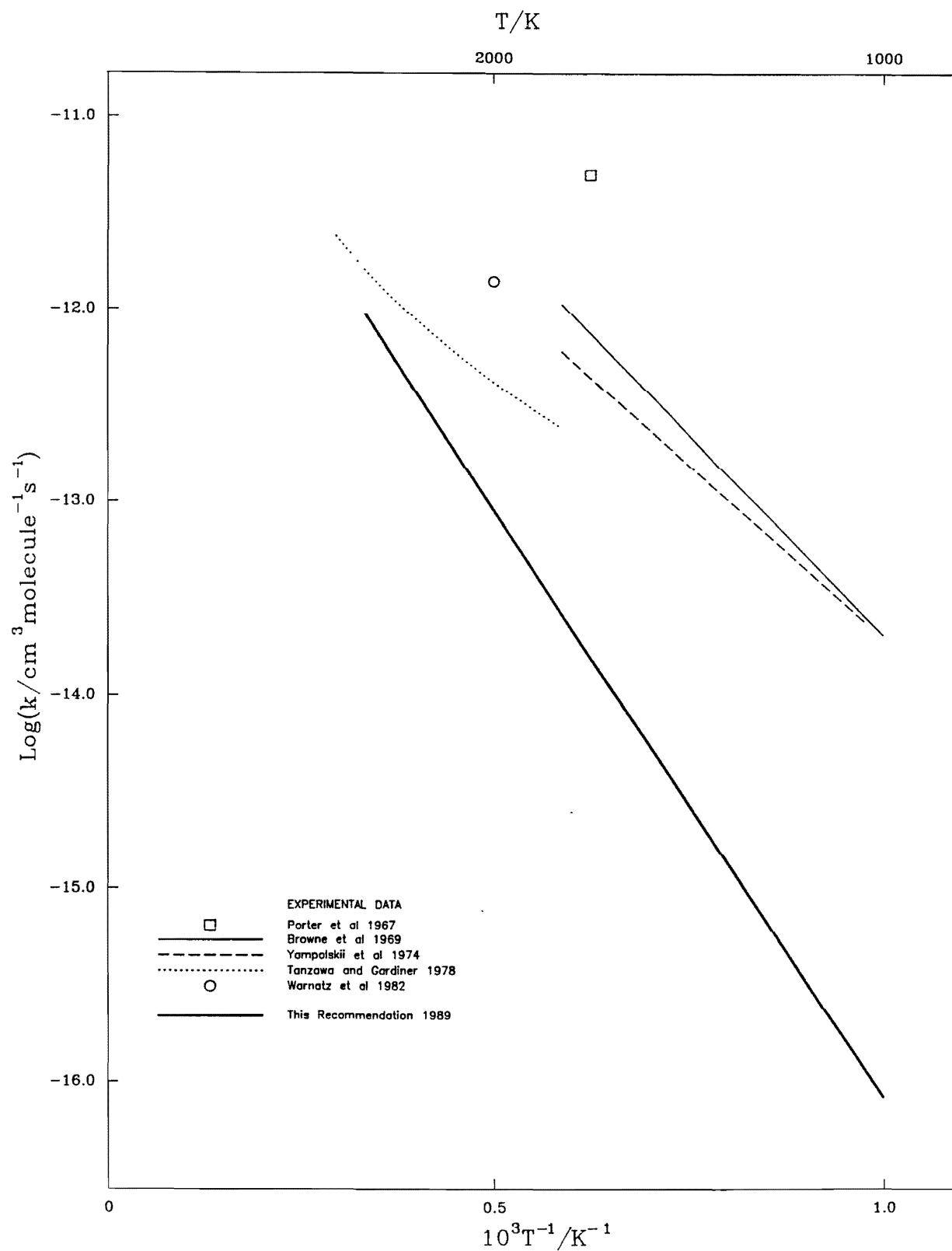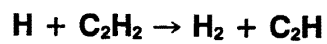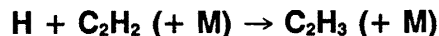
Thermodynamic Data

$\Delta H^\circ_{298} = -158 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} = -84 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p = 0.412 \ T^{-1.50} \exp(18900/T) \text{ atm}^{-1}$

Rate Coefficient Data

k [molecule^{-1} cm^{-3} s^{-1}]	T[K]	[M][molecule cm^{-3}]	Reference	Comments
Rate Coefficient Measurements				
Intermediate Fall-off Range				
$2.3 \cdot 10^{-14}$	298	$1.7 \cdot 10^{16}$ (He)	Michael and Niki (1967)[1]	(a)
$3.9 \cdot 10^{-14}$		$5.4 \cdot 10^{16}$		
$2 \cdot 10^{-14}$	243	$4.5 \cdot 10^{16}$ (He)	Hoyermann *et al.* (1968)[2]	(b)
$4 \cdot 10^{-14}$		$5.1 \cdot 10^{17}$		
$2 \cdot 10^{-14}$	303	$3.0 \cdot 10^{16}$		
$1 \cdot 10^{-13}$		$8.4 \cdot 10^{17}$		
$4 \cdot 10^{-14}$	373	$5.9 \cdot 10^{16}$		
$2 \cdot 10^{-13}$		$7.5 \cdot 10^{17}$		
$7 \cdot 10^{-14}$	463	$7.2 \cdot 10^{16}$		
$3 \cdot 10^{-13}$		$5.8 \cdot 10^{17}$		
$2.1 \cdot 10^{-14}$	298	$3.1 \cdot 10^{16}$ (He)	Keil *et al.* (1976)[3]	(c)
$6.9 \cdot 10^{-14}$		$1.6 \cdot 10^{18}$		
$1.8 \cdot 10^{-13}$		$2.4 \cdot 10^{19}$		
$1.1 \cdot 10^{-14}$	193	$1.0 \cdot 10^{18}$ (He)	Payne and Stief (1976)[4]	(d)
$1.4 \cdot 10^{-14}$		$6.0 \cdot 10^{18}$		
$1.9 \cdot 10^{-14}$	228	$4.2 \cdot 10^{17}$		
$3.7 \cdot 10^{-14}$		$4.2 \cdot 10^{18}$		
$5.1 \cdot 10^{-14}$		$2.1 \cdot 10^{19}$		
$3.2 \cdot 10^{-14}$	298	$3.2 \cdot 10^{17}$		
$1.1 \cdot 10^{-13}$		$3.2 \cdot 10^{18}$		
$1.6 \cdot 10^{-13}$		$2.3 \cdot 10^{19}$		
$5.0 \cdot 10^{-14}$	400	$2.4 \cdot 10^{17}$		
$2.3 \cdot 10^{-13}$		$2.4 \cdot 10^{18}$		
$4.2 \cdot 10^{-13}$		$1.7 \cdot 10^{19}$		
High Pressure Range				
$3.8 \cdot 10^{-11} \exp(-1374/T)$	207–451		Sugawara *et al.* (1981)[5]	(e)
$1.4 \cdot 10^{-11} \exp(-1363/T)$	298–473	$2.5 \cdot 10^{19}$ (H₂,D₂,He)	Ellul *et al.* (1981)[6]	(f)
Reviews and Evaluations				
$k_0 = $ [Ar] $1.2 \cdot 10^{-30} \exp(-350/T)$	300–500		Warnatz (1984)[7]	(g)
$k_\infty = 9.1 \cdot 10^{-12} \exp(-1200/T)$	300–2000			
$k_0 = $ [N₂] $1.05 \cdot 10^{-7} \ T^{-7.27} \exp(-3632/T)$	700–2500		Tsang and Hampson (1986)[8]	(h)

Comments

(a) The reaction was studied in a fast discharge-flow system coupled to a time-of-flight mass spectrometer. The reaction mechanism was confirmed by an isotopic study.

(b) The reaction was investigated in a fast flow-system coupled to ESR and mass spectrometer.

(c) The reaction was studied in a conventional discharge flow reactor coupled to a time-of-flight mass spectrometer. RRKM treatment of the results.

(d) The technique of flash photolysis coupled with time resolved detection of H via resonance fluorescence was employed in this investigation.

(e) The reaction was investigated using the pulse radiolysis/resonance absorption technique.

(f) Pulsed photolysis/resonance absorption study. The reaction was followed monitoring 121.6 nm Lyman α absorption.

(g) Data evaluation and simplified fall-off construction.

(h) Construction of RRKM fall-off curves.

Preferred Values

$k_\infty = 1.4 \cdot 10^{-11} \exp(-1300/T) \text{ cm}^{-3} \text{ molecule}^{-1} \text{ s}^{-1}$ over range 200–400 K

$k_0 = $ [He] $3.3 \cdot 10^{-30} \exp(-740/T) \text{ cm}^{-3} \text{ molecule}^{-1} \text{ s}^{-1}$ over range 200–400 K

$F_c \cong 0.44$ over range 200–400 K

Reliability

$\Delta \log k_\infty = \pm 0.3$ over range 200–400 K

$\Delta \log k_0 = \pm 0.5$ for over range 200–400 K

$\Delta \log F_c = \pm 0.1$ over range 200–400 K

Comments on Preferred Values

The preferred values are based on the experimental data from Ref. 4 and a construction of the corresponding fall-off curve from the present evaluation.

References

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$$H + C_2H_3 \rightarrow H_2 + C_2H_2 \qquad (1)$$
$$H + C_2H_3 (+ M) \rightarrow C_2H_4 (+ M) \qquad (2)$$
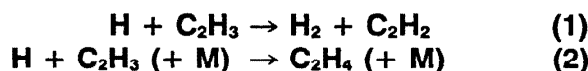
Thermodynamic Data

$\Delta H^{\circ}_{298} (1) = -277 \text{ kJ mol}^{-1}$

$\Delta S^{\circ}_{298} (1) = 14.6 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(1) = 7.75 \cdot 10^{-2} T^{0.217} \exp(+33200/T)$

$\Delta H^{\circ}_{298} (2) = -452 \text{ kJ mol}^{-1}$

$\Delta S^{\circ}_{298} (2) = 127 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(2) = 6.83 \cdot 10^{-5} T^{-0.608} \exp(+54400/T) \text{ atm}^{-1}$

Rate Coefficient Data

k [cm³ molecule⁻¹ s⁻¹]	T [K]	Reference	Comments
Rate Coefficient Measurements			
$k_1 = 7 \cdot 10^{-12}$	1170–1780	Benson and Haugen (1967)[1]	(a)
$k_1 = 3 \cdot 10^{-11}$	1100–1500	Skinner, Sweet, and Davis (1971)[2]	(b)
$k_1 = 1 \cdot 10^{-11}$	298	Keil et al. (1976)[3]	(c)
$k_1 = 1.7 \cdot 10^{-11}$	1300–2500	Olson, Tanzawa, and Gardiner (1979)[4]	(d)
Reviews and Calculations			
$k_1 = 3 \cdot 10^{-11}$	300–2500	Warnatz (1984)[5]	(e)
$k_1 = 1.6 \cdot 10^{-10}$	–	Tsang and Hampson (1986)[6]	(f)

Comments

(a) Steady state analysis of the shock tube data of Skinner and Sokolski[7] on H and H/D exchange with C_2H_4 and its isotopomers.

(b) Shock tube study at 3 atm of H and H/D exchange with C_2H_4, C_2H_2, and their isotopomers. Steady state analysis.

(c) Analysis of effects of atom/radical reactions on H + C_2H_2 system. Simulation by numerical integration and comparison of discharge flow – mass spectrometry, flash photolysis – resonance fluorescence and flash photolysis – resonance fluorescence experiments.

(d) Shock tube study of ethane dissociation in argon by laser schlieren. Numerical integration of a 14 reaction scheme.

(e) Evaluation based on tabulated data plus a privately communicated value from Hoyermann at 298 K of $7 \cdot 10^{-11}$ cm³ molecule⁻¹ s⁻¹.

(f) Estimate.

Preferred Values

$k_1 = 2 \cdot 10^{-11}$ cm³ molecule⁻¹ s⁻¹ over range 300–2500 K

Reliability

$\Delta \log k_1 = \pm 0.5$

Comments on Preferred Values

All of the determinations are very indirect, hence the wide error limits. The large exothermicity of reaction (1) suggests that there is a negligible probability of forming stabilised C_2H_4 except under conditions of very high pressure.

References

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$$H + C_2H_4 \rightarrow H_2 + C_2H_3 \qquad (1)$$
$$H + C_2H_4 \ (+ \ M) \rightarrow C_2H_5 \ (+ \ M) \qquad (2)$$
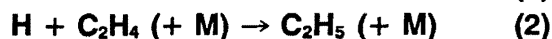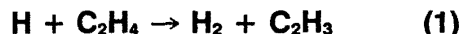
Thermodynamic Data

$\Delta H^\circ_{298} (1) = 15.8 \ kJ \ mol^{-1}$
$\Delta S^\circ_{298} (1) = 28.3 \ J \ K^{-1}mol^{-1}$
$K_p(1) = 4.67 \cdot 10^3 \ T^{-0.673} \exp(-2270/T)$

$\Delta H^\circ_{298} (2) = -153 \ kJ \ mol^{-1}$
$\Delta S^\circ_{298} (2) = -82.1 \ J \ K^{-1}mol^{-1}$
$K_p(2) = 5.83 \cdot 10^{-2} \ T^{-1.13} \exp(+18300/T) \ atm^{-1}$

Rate Coefficient Data ($k = k_1$)

k [cm^3 molecule^{-1} s^{-1}]	T [K]	Reference	Comments
Rate Coefficient Measurements			
$4.2 \cdot 10^{-13}$	813	Baldwin, Simmons, and Walker (1966)[1]	(a)
$1.0 \cdot 10^{-10}\exp(-3000/T)$	1170–1780	Benson and Haugen (1967)[2]	(b)
$2.6 \cdot 10^{-10}\exp(-7000/T)$	1100–1500	Skinner, Sweet, and Davis (1971)[3]	(c)
$1.8 \cdot 10^{-10}\exp(-4300/T)$	1200–1700	Peeters and Mahnen (1974)[4]	(d)
$8.3 \cdot 10^{-9}\exp(-11500/T)$	1700–2000	Just, Roth, and Damm (1977)[5]	(e)
$7 \cdot 10^{-14}$	773	Baldwin *et al.* (1984)[6]	(f)
$1.5 \cdot 10^{-13}$	900	Jayaweera and Pacey (1988)[7]	(g)
Reviews and Evaluations			
$2.5 \cdot 10^{-10}\exp(-5100/T)$	700–2000	Warnatz (1984)[8]	(h)
$2.2 \cdot 10^{-18} \ T^{2.53}\exp(-6160/T)$	–	Tsang and Hampson (1986)[9]	(i)

Comments

(a) Inhibition of first and second limits of $H_2 + O_2$ reaction by C_2H_4. Assuming 'reasonable' A factor, they give $k_2 = 1.7 \cdot 10^{-10}\exp(-4900/T)$.

(b) Reinterpretation of the data of Skinner and Sokolski[8] on hydrogen, deuterium exchange in C_2H_4 and its isotopomers.

(c) Shock tube study of H, D exchange in C_2H_4 and its isotopomers. GC/MS analysis.

(d) Molecular beam – mass spectrometer sampling of C_2H_4/O_2 flames.

(e) Thermal decomposition of C_2H_4 in reflected shock waves. H atom profile by atomic resonance absorption spectroscopy.

(f) Addition of C_2H_4 to slowly reacting mixtures of $H_2 + O_2$ and observation of pressure change corresponding to 50% loss of additive. k was measured relative to $H + O_2 \rightarrow OH + O$ ($k(H + C_2H_4)/k(H + O_2) = 12 \pm 4$) and the value of $k(H + O_2)$ recommended in this evaluation ($5.8 \cdot 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 773 K) has been assumed.

(g) Pyrolysis of ethene in a flow system and measurement of H_2 formation. The value of k depends on the equilibrium constant for $H + C_2H_4 \rightleftharpoons C_2H_5$ and the rate coefficient for $C_2H_5 + C_2H_4 \rightarrow C_2H_6 + C_2H_3$, previously measured by McKenzie *et al.*[11].

(h) Approximate representation of Refs. 1–5.

(i) Based on a BEBO fit to the data of Ref. 5.

Preferred Values

$k = 9 \cdot 10^{-10}\exp(-7500/T)$ cm^3 molecule^{-1} s^{-1} over range 700–2000 K

Reliability
$\Delta \log k = \pm 0.5$

Comments on Preferred Values

With the exception of the data of Skinner *et al.*[3], there is good agreement in the magnitude of the high temperature values, although the temperature dependencies are not well defined. Similarly the more recent and more reliable lower temperature value of Baldwin *et al.*[6] is compatible with that of Jayaweera and Pacey[7]. The recommended rate coefficient expression is a compromise between the high and low temperature data. The high A factor may indicate a curved Arrhenius plot, but the data only permit a linear expression with wide error limits.

References

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$$H + C_2H_4 \rightarrow C_2H_3 + H_2$$

T/K

2000   1000

Log(k/cm³ molecule⁻¹ s⁻¹)

$10^3 T^{-1}/K^{-1}$

EXPERIMENTAL DATA
Baldwin et al 1966
Benson and Haugen 1967
Skinner et al 1971
Peeters and Mahnen 1973
Just et al 1977
Baldwin et al 1984
Jayaweera and Pacey 1988

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$$H + C_2H_5 \rightarrow 2\ CH_3 \qquad (1)$$
$$H + C_2H_5\ (+\ M) \rightarrow C_2H_6\ (+\ M) \qquad (2)$$
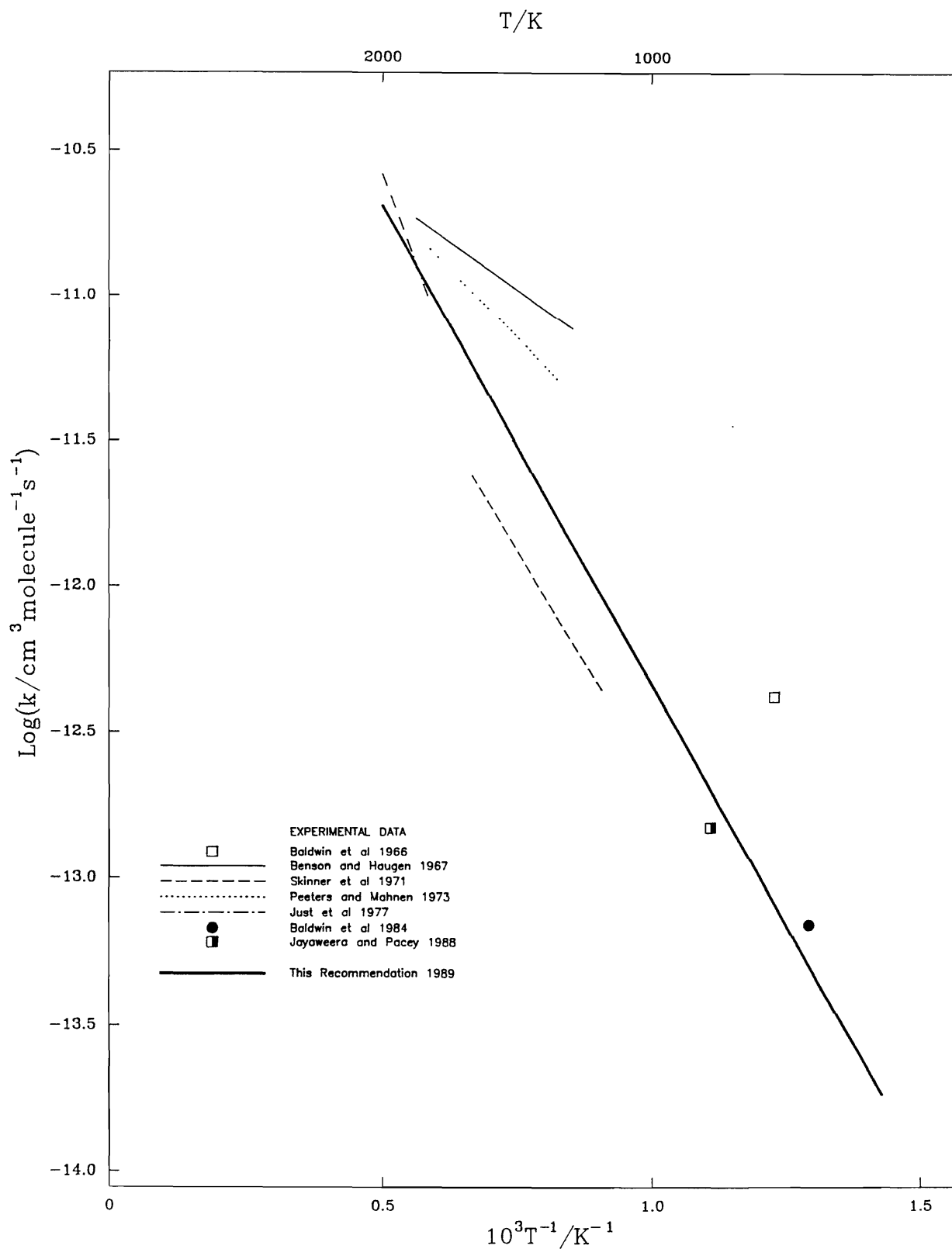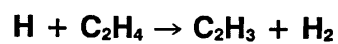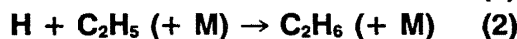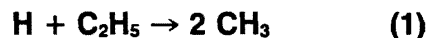
Thermodynamic Data

$\Delta H^\circ_{298}\ (1) = -43.8\ \text{kJ mol}^{-1}$

$\Delta S^\circ_{298}\ (1) = 21.9\ \text{J K}^{-1}\text{mol}^{-1}$

$K_p(1) = 4.52 \cdot 10^3\ T^{-0.74}\ \exp(+4790/T)$

$\Delta H^\circ_{298}\ (2) = -419\ \text{kJ mol}^{-1}$

$\Delta S^\circ_{298}\ (2) = -137\ \text{J K}^{-1}\text{mol}^{-1}$

$K_p(2) = 1.09 \cdot 10^{-6}\ T^{-0.505}\ \exp(+50400/T)\ \text{atm}^{-1}$

Rate Coefficient Data ($k = k_1 + k_2$)

k [cm^3 molecule^{-1} s^{-1}]	T [K]	Reference	Comments
Rate Coefficient Measurements			
$k_2 = 6 \cdot 10^{-11}$	298	Kurylo, Peterson, and Braun (1970)[1]	(a)
$k_1 = (4-9) \cdot 10^{-11}$	303–603	Teng and Jones (1972)[2]	(b)
$k_1 = 2.5 \cdot 10^{-11}$	298	Michael, Osborne, and Suess (1973)[3]	(c)
$k_1 = 6 \cdot 10^{-11}$	503–753	Camilleri, Marshall, and Purnell (1974)[4]	(d)
$k_1 = 1.1 \cdot 10^{-10} \exp(-50/T)$	321–521	Pratt and Veltmann (1976)[5]	(e)
$k_1 = 1.2 \cdot 10^{-11}$	1950–2770	Tabayashi and Bauer (1979)[6]	(f)
$k_1 = 8 \cdot 10^{-11} \exp(-127/T)$	230–568	Pratt and Wood (1984)[7]	(g)
Reviews and Evaluations			
$k_1 = 5.0 \cdot 10^{-11}$	300–1500	Warnatz (1984)[8]	(h)
$k_1 = 6.0 \cdot 10^{-11}$		Tsang and Hampson (1986)[9]	(i)

Comments

(a) Flash photolysis – resonance fluorescence study of H + C$_2$H$_4$. Computer simulation of increase in apparent rate constant as [H]/[C$_2$H$_4$] was increased. Suggested they were measuring k_2.

(b) Discharge flow study of H + C$_2$H$_4$; products analysed by GC. Computer simulation of product yields.

(c) Pulsed Hg photosensitized decomposition of H$_2$ – resonance absorption, discharge flow – time-of-flight mass spectrometry studies of H + C$_2$H$_4$ system. k_1 from analysis of stoichiometry.

(d) Discharge flow study of H + C$_2$H$_6$. Products by gas chromatography. Numerical integration.

(e) Discharge flow study of H + C$_2$H$_4$. Mass spectrometric detection. Numerical integration.

(f) Shock tube study of CH$_4$/Ar, CH$_4$/O$_2$/Ar. Laser schlieren.

(g) Discharge flow study of CH$_3$ + O$_2$. CH$_3$ formed from H + C$_2$H$_4$. Products analysed by GC and simulated by numerical integration.

(h) Evaluation, mean of low temperature data.

(i) Evaluation based on Refs. 1, 3, and 4. A strong collision analysis of k_1/k_2 is presented.

Preferred Values

$k_1 = 6.0 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1} over range 300–2000 K

Reliability

$\Delta\log k = \pm\ 0.3$ at 300 K rising to $\pm\ 0.7$ at 2000 K

Comments on Preferred Values

Channel (1) almost certainly dominates at room temperature and at the low pressures of the discharge flow experiments. It is favoured by low pressures and high temperatures. There have been no realistic studies of the k_1/k_2 ratio, and Tsang and Hampson's strong collision analysis is probably inadequate. A modelling (RRKM/master equation) study would be of value.

References

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$$H + C_2H_5 \rightarrow CH_3 + CH_3$$
$$\rightarrow C_2H_6$$

EXPERIMENTAL DATA

□   Teng and Jones (k1) 1972
■   Michael et al (k1) 1973
———   Camilleri et al (k1) 1974
▲   Pratt and Veltmann (k1) 1976
|—| Tabayashi and Bauer (k1) 1979
— — —   Pratt and Wood (k1) 1984
▣   Kurylo et al (k2) 1970

━━━   This Recommendation (k1) 1989

H + C$_2$H$_6$ → H$_2$ + C$_2$H$_5$
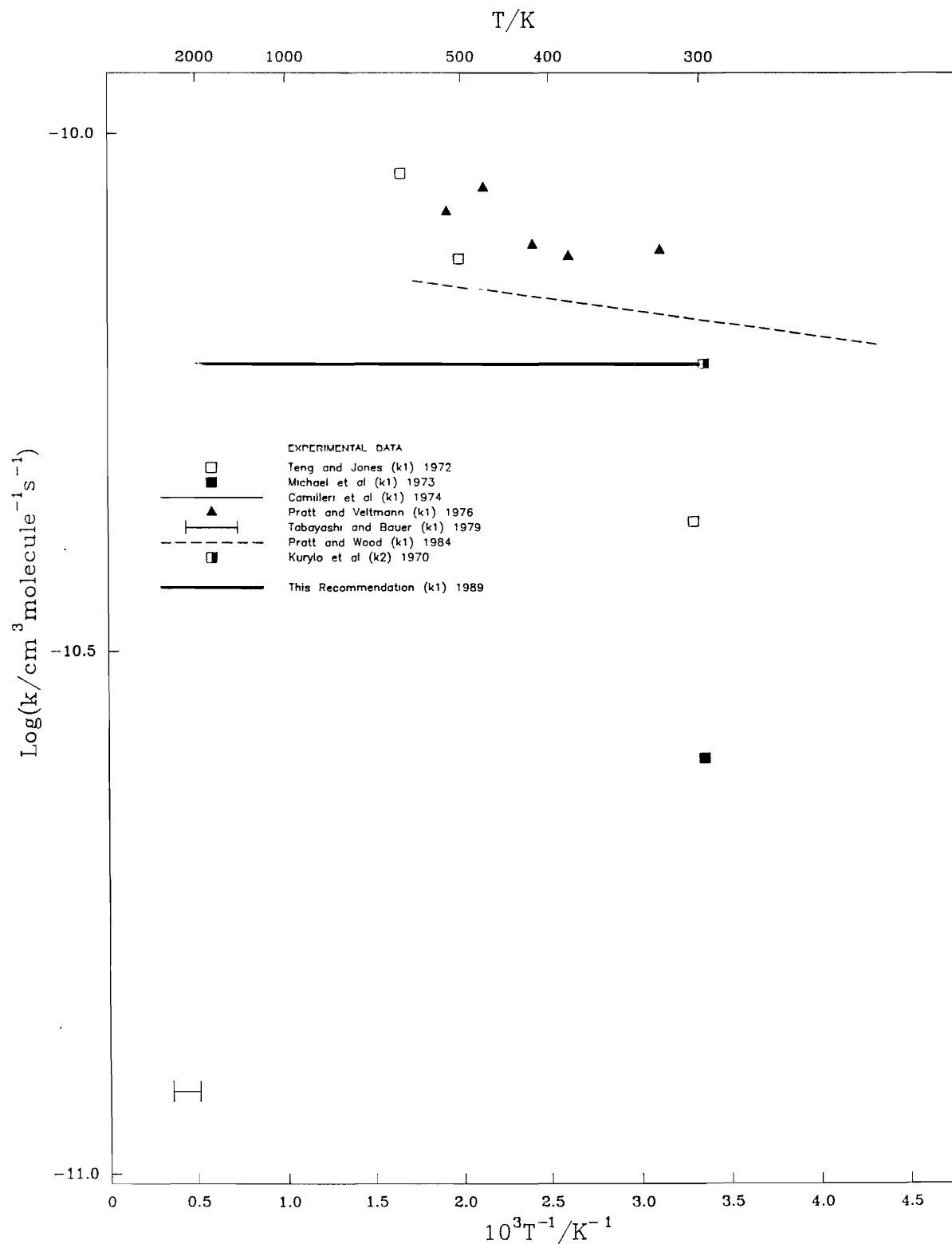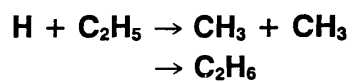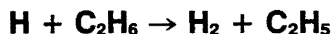
Thermodynamic Data

$\Delta H^\circ_{298} = -16.9 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} = 38.6 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p = 2.92 \cdot 10^4 \, T^{-0.775} \exp(+1660/T)$

Rate Coefficient Data

k [cm^3 molecule^{-1} s^{-1}]	Temperature [K]	Reference	Comments
Rate Coefficient Measurements			
$5.65 \cdot 10^{-12} \exp(-3420/T)$	353–436	Berlie and LeRoy (1953)[1]	(a)
$7.94 \cdot 10^{-11} \exp(-4310/T)$	990–1500	Fenimore and Jones (1961)[2]	(b)
$8.3 \cdot 10^{-11} \exp(-3960/T)$	853–953	Parsamyan et al. (1968)[3]	(c)
$3.09 \cdot 10^{-10} \exp(-4920/T)$	503–753	Purnell et al. (1974)[4]	(d)
$1.78 \cdot 10^{-10} \exp(-4643/T)$	385–544	Purnell et al. (1977)[5]	(e)
$8.3 \cdot 10^{-11} \exp(-4580/T)$	281–347	Lede and Villermaux (1978)[6]	(f)
$4.06 \cdot 10^{-13}$	773	Baldwin and Walker (1979)[7]	(g)
$8.7 \cdot 10^{-10} \exp(-6440/T)$	876–1016	Cao and Back (1984)[8]	(h)
Reviews and Evaluations			
$2.17 \cdot 10^{-10} \exp(-4885/T)$	300–1500	Baldwin and Melvin (1964)[9]	(i)
$8.9 \cdot 10^{-22} \, T^{3.5} \exp(-2615/T)$	300–1800	Clark and Dove (1973)[10]	(j)
$2.19 \cdot 10^{-10} \exp(-4715/T)$	300–1300	Purnell et al. (1974)[4]	(k)
$8.9 \cdot 10^{-22} \, T^{3.5} \exp(-2615/T)$	300–2000	Warnatz (1984)[11]	(l)
$8.9 \cdot 10^{-22} \, T^{3.5} \exp(-2615/T)$	300–1800	Tsang and Hampson (1986)[12]	(m)

Comments

(a) H atom concentration determined by catalytic recombination. Constant stoichiometry assumed at all temperatures, but (Ref. 5) k values not seriously in error.

(b) Low pressure C$_2$H$_6$ + H$_2$ + O$_2$ flames; effectively measured k/k(H + O$_2$ → OH + O). Results recalculated[11] using k(H + O$_2$) = $2.0 \cdot 10^{-7} \, T^{-0.91} \exp(-8310/T)$ cm^3 molecule^{-1} s^{-1}.

(c) Inhibition of H$_2$ + O$_2$ limit by C$_2$H$_6$. Results recalculated using k(H + O$_2$) in (b).

(d) Flow discharge, computer fit of all products.

(e) Flow discharge, mass spectrometry. Both excess C$_2$H$_6$ and excess H atom used, and stoichiometry measured over temperature range used.

(f) Discharge flow, H atoms formed Hg from HgO target, and released Hg vapour measured spectrophotometrically.

(g) Addition of C$_2$H$_6$ to H$_2$ + O$_2$ reaction gives k/k(H + O$_2$). Value of k(H + O$_2$) given in (b).

(h) H$_2$ ⇌ 2 H equilibrium used to control and effectively measure H atom concentration.

(i) Review of early measurements of k.

(j) Simplified BEBO calculation of rate constants.

(k) Recalculated assumed stoichiometry of earlier workers; argue strongly for Arrhenius expression between 300 and 1300 K.

(l) Recommends Clark and Dove's expression without comment.

(m) Recommend Clark and Dove's expression, but emphasize that it may overestimate k above 1500 K.

Preferred Values

$k = 2.35 \cdot 10^{-15} \, T^{1.5} \exp(-3725/T)$ cm^3 molecule^{-1} s^{-1} over range 300–2000 K

Reliability

$\Delta \log k = \pm 0.15$ between 300 K and 1500 K rising to ± 0.3 at 2000 K

Comments on Preferred Values

The agreement between the various sets of experimental values of k is less good than might be expected. No particular temperature dependence of the pre-exponential term is dictated by the results. Between 300 and 1300 K, the Arrhenius expression $(1.89 \pm 0.60) \cdot 10^{-10} \exp(-4635 \pm 200/T)$ cm^3 molecule^{-1} s^{-1} fits the results as well as the preferred values, but is unlikely to give relatively accurate values of k above 2000 K. The rate constant expression suggested by Clark and Dove, and recommended by Warnatz and by Tsang and Hampson, gives values of k too high at 300 and above 1300 K. Above 2000 K, the Clark and Dove expression is recommended.

References

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[11]J. Warnatz, in "Combustion Chemistry", ed. W. C. Gardiner, Springer-Verlag, New York (1984).

[12]W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data **15**, 1087 (1986).

H + C₂H₆ → C₂H₅ + H₂

$$H + C_2H_6 \rightarrow C_2H_5 + H_2$$

EXPERIMENTAL DATA

□	Berlie and LeRoy 1953
▲	Gorban and Nalbandyan 1960
——	Gorban and Nalbandyan 1962
△	Baldwin and Melvin 1964
⊢——⊣	Parsamyan et al 1968
– – –	Azatyan et al 1969
◆	Baldwin et al 1070
⊢– –⊣	Azatyan and Romanovich 1971
▽	Azatyan 1971
▼	Camilleri et al 1974
▼	Kalinenko et al 1974
◈	Jones et al 1977
◈	Lede and Villermaux 1977
◇	Lede and Villermaux 1978
⊟	Clark et al 1971
▲	Baldwin and Walker 1979
▼	Azatyan 1967
◈	Yang and Gant 1961
⊖	Davis and Williamson 1959
⋯⋯	Cao and Back 1984
——	This Recommendation 1989

$$H + CHCO \rightarrow CH_2 + CO \quad (1)$$
$$\rightarrow C_2O + H_2 \quad (2)$$
$$\rightarrow HCCOH \quad (3)$$

Thermodynamic Data

$\Delta H^\circ_{298} (1) = -175.3 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (1) = 24.3 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(1) = 6.23 \cdot 10^5 \, T^{-1.55} \exp(+13865/T)$

$\Delta H^\circ_{298} (2) = -108.9 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (2) = -5.2 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(2) = 5.39 \, T^{-0.337} \exp(+12990/T)$

$\Delta H^\circ_{298} (3) = -310.1 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (3) = -123.1 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(3) = 3.26 \cdot 10^{-5} \, T^{-0.765} \exp(-37270/T)$

Rate Coefficient Data ($k = k_1 + k_2 + k_3$)

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	Temperature [K]	Reference	Comments
Rate Coefficient Measurements			
$5 \cdot 10^{-11}$	1600–2000	Löhr and Roth (1981)[1]	(a)
$5 \cdot 10^{-12}$	1000	Homann and Wellmann (1983)[2]	(b)
$2.5 \cdot 10^{-10}$	535	Vinckier et al. (1985)[3]	(c)
$2.5 \cdot 10^{-10}$	1500–1700	Frank et al. (1986)[4]	(d)

Comments

(a) Direct measurement of [H] and [O] in reaction zone behind shock waves generated in O + C_2H_2 mixtures. Reaction H + CHCO needed to give good fit to [O] and [H] time profiles. Derived k is best-fit value and assumed to be k_1.

(b) High temperature flow reactor coupled to a quadrupole mass spectrometer. Value of k obtained from best fit to [CO]-time profiles. However, value of k is based partly on the Jones and Bayes[5] value for k(O + CHCO) which is almost certainly too low by a factor of at least 50 (see comment on O + CHCO reaction).

(c) Discharge flow study of O + C_2H_2, radical concentrations being monitored by molecular beam mass spectrometry. Value of k determined from best fit to [CHCO]-time profile at 535 K and determined from ratio k/k(O + CHCO) = 1.4 with k(O + CHCO) = $1.8 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Value of k(O + CHCO) is effectively indistinguishable from recommended value = $1.6 \cdot 10^{-10}$, see comment on O + CHCO reaction).

(d) Shock tube study, with simultaneous measurement of [H], [O], and [CO] by atomic and molecular absorption spectrometry. H + CHCO important in later stages of O + C_2H_2 reactions. k determined from [O] and [H] profiles under optimised stoichiometry.

Preferred Values

$k = 2.5 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over range 300–2500 K

Reliability

$\Delta \log k = \pm 0.4$ over range 300–2500 K

Comments on Preferred Values

Based on computer fitting of intermediate products, reaction (1) is the preferred path[2,3]. Faubel and Wagner[6] have suggested, however, that reaction (2) could be an important route for C_2O formation in the O + C_2H_2 system. The values of k differ by a factor of 50, but that obtained by Homann and Wellmann is almost certainly too low by a factor of at least 10 (see comments). With an activation energy of effectively zero the values obtained by Frank et al. and by Vinckier et al. are in excellent agreement, and are the bases of the preferred value of k.

References

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[6] C. Faubel and H. Gg. Wagner, Ber. Bunsenges. Phys. Chem. **81**, 684 (1977).

H + CH₂CO → CH₃ + CO (1)
→ CH₂CHO (2)

$$H + CH_2CO \rightarrow CH_3 + CO \quad (1)$$
$$\rightarrow CH_2CHO \quad (2)$$
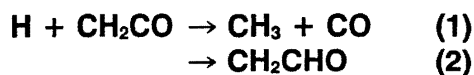
Thermodynamic Data

ΔH°_{298} (1) = -131 kJ mol^{-1}
ΔS°_{298} (1) = 35.2 J K^{-1}mol^{-1}
$K_p(1)$ = $1.4 \cdot 10^6 \, T^{-1.45} \exp(+15300/T)$

ΔH°_{298} (2) = -141 kJ mol^{-1}
ΔS°_{298} (2) = -88.6 J K^{-1}mol^{-1}
$K_p(2)$ = $1.1 \cdot 10^{-2} \, T^{1.01} \exp(+16900/T)$

Rate Coefficient Data ($k = k_1 + k_2$)

k[cm³ molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$1.3 \cdot 10^{-13}$	298	Carr *et al*. (1968)[1]	(a)
$6.0 \cdot 10^{-12} \exp(-1176/T)$	218–363	Slemr and Warnek (1975)[2]	(b)
$1.88 \cdot 10^{-11} \exp(-1725/T)$	298–500	Michael *et al*. (1979)[3]	(c)
$7.3 \cdot 10^{-14}$	298		
$6.48 \cdot 10^{-12} \exp(-975/T)$	240–440	Umemoto *et al*. (1985)[4]	(d)
$3.0 \cdot 10^{-11}$	1650–1850	Frank *et al*. (1986)[5]	(e)
Reviews and Evaluations			
$7.0 \cdot 10^{-13} \exp(-1515/T)$	300–500	Warnatz (1984)[6]	(f)

Comments

(a) Discharge flow system. H atoms produced from H₂/He mixtures flowing through a microwave discharge. CH₂CO in excess. Analysis by mass spectrometer. CH₄ and CO observed to be major products. C₂H₄, C₂H₆ and CH₂O also observed.

(b) Discharge flow system, H atoms in excess. H generated from H₂/He mixtures flowing through a microwave discharge, ketene produced by continuous pyrolysis of diketene. Analysis by mass spectrometer.

(c) Two techniques used.
   (i) Flash photolysis of CH₄/CH₂Cl/Ar mixtures, analysis by resonance fluorescence for [H].
   (ii) Discharge flow system, analysis by resonance fluorescence for [H], CH₂CO in excess. Results at 298 K only.

(d) Pulse radiolysis of H₂/ketene mixtures, ketene in excess. [H] decay measured by resonance absorption.

(e) Shock tube study, CH₂CO/Ar mixtures. [H] and [CO] measured with respect to time by atomic and molecular resonance absorption spectroscopy.

(f) Only low temperature results available.

Preferred Values

$k_1 = 3.0 \cdot 10^{-11} \exp(-1700/T)$ cm³ molecule^{-1} s^{-1} over range 200–2000 K

Reliability

$\Delta \log k_1 = \pm 0.5$ at 200 K rising to ± 1.0 at 2000 K

Comments on Preferred Values

All the experimental data available is for the total rate constant ($k = k_1 + k_2$). No determination of the importance of the separate channels has yet been made. However, it has been assumed[2,3,4] that channel (1) is dominant and channel (2) is of negligible importance.

The absolute values of the rate constants obtained in the different low temperature studies[1,2,3,4] are in good agreement but there are significant differences in the temperature coefficients obtained. Use of the largest temperature coefficient[3] to extrapolate to high temperatures still leaves the extrapolated value of k slightly lower at 1800 K than the experimental results of Frank *et al*.[5]. This may imply curvature of the Arrhenius plot or merely reflect the errors in the measurements.

The preferred values are based on the temperature coefficient of k of Michael *et al*.[3] and a value of $k = 1.0 \cdot 10^{-13}$ cm³ molecule^{-1} s^{-1} at 298 K.

References

[1] R. W. Carr, I. D. Gay, G. P. Glass, and H. Niki, J. Chem. Phys. 49, 846 (1968).

[2] F. Slemr and P. Warnek, Ber. Bunsenges. Phys. Chem. 79, 152 (1975).

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H + CH₂CO → CH₃ + CO

$$\text{H} + \text{CH}_3\text{CHO} \rightarrow \text{H}_2 + \text{CH}_3\text{CO} \qquad (1)$$
$$\rightarrow \text{H}_2 + \text{CH}_2\text{CHO} \qquad (2)$$
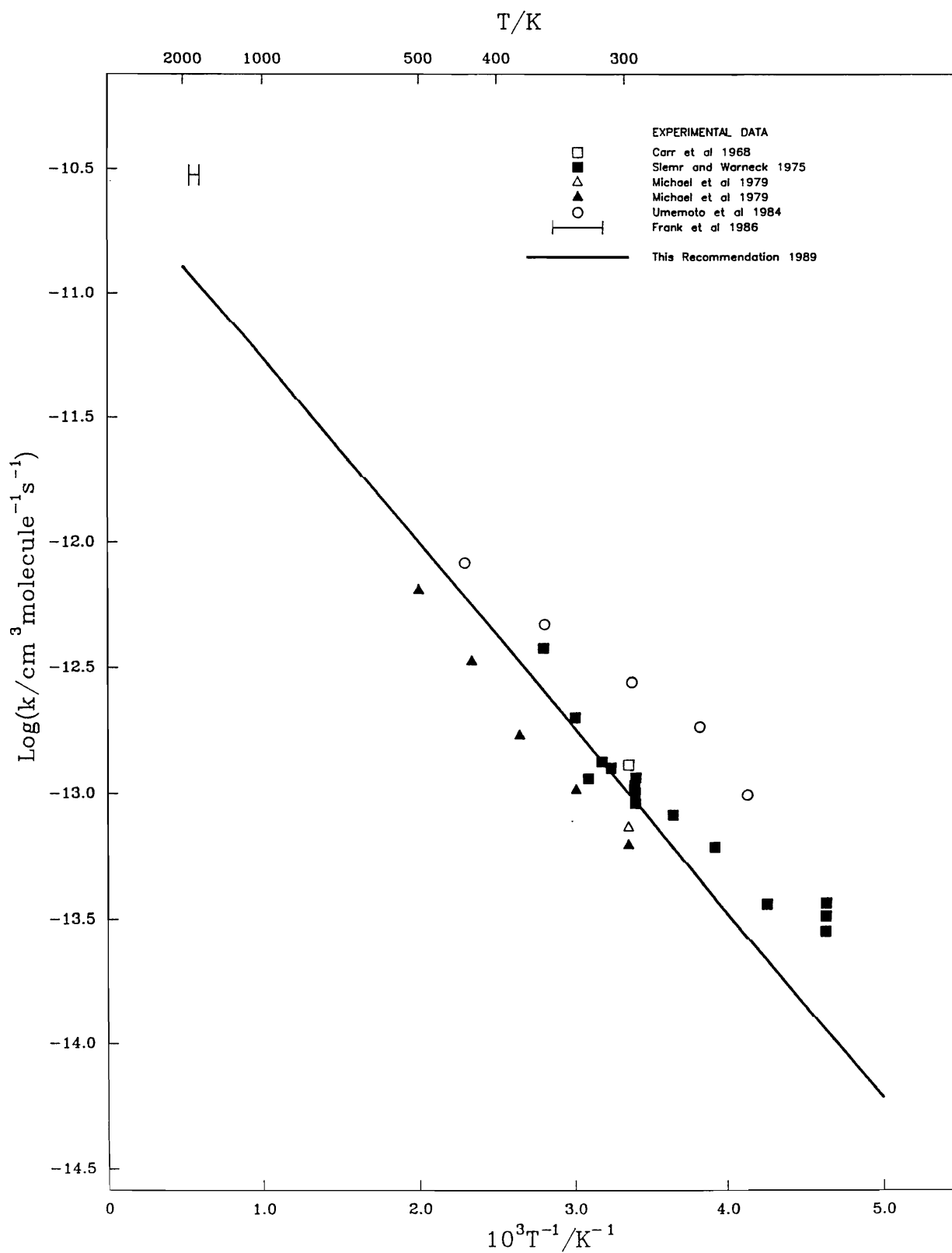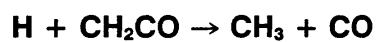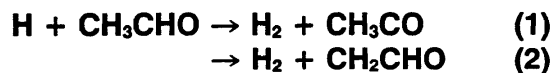
Thermodynamic Data

$\Delta H^{\circ}_{298} (1) = -75.3 \text{ kJ mol}^{-1}$

$\Delta S^{\circ}_{298} (1) = 18.9 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(1) = 1.21 \cdot 10^3 \, T^{-0.641} \exp(+8690/T)$

$\Delta H^{\circ}_{298} (2) = -27.6 \text{ kJ mol}^{-1}$

$\Delta S^{\circ}_{298} (2) = 20.0 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(2) = 53.2 \, T^{-0.48} \exp(+2967/T)$

Rate Coefficient Data ($k = k_1 + k_2$)

k [cm^3 molecule^{-1} s^{-1}]	T [K]	Reference	Comments
Rate Coefficient Measurements			
$4.3 \cdot 10^{-12} \exp(-1310/T)$	295–389	Aders and Wagner (1973)[1]	(a)
$5.3 \cdot 10^{-14}$	298	Slemr and Warneck (1975)[2]	(b)
$2.2 \cdot 10^{-11} \exp(-1660/T)$	298–500	Whytock et al. (1976)[3]	(c)
$1.4 \cdot 10^{-11} \exp(-3490/T)$	1550–1850	Beeley et al. (1977)[4]	(d)
$9.8 \cdot 10^{-14}$	298	Michael and Lee (1977)[5]	(e)
Reviews and Evaluations			
$6.6 \cdot 10^{-11} \exp(-2120/T)$	300–2000	Warnatz (1984)[6]	

Comments

(a) Fast flow reactor. Transients and products measured by ESR and mass spectroscopy.

(b) Discharge flow mass spectroscopic measurement of stable species. k measured relative to the reaction of hydrogen atoms with ketene.

(c) Flash photolysis – resonance fluorescence (Lyman α).

(d) Ignition of CH$_3$CHO/O$_2$/Ar mixtures behind incident shock waves. Stable and transient species monitored by UV and IR emission. k determined from modelling the system.

(e) Discharge flow – resonance fluorescence (Lyman α).

Preferred Values

$k = 6.8 \cdot 10^{-15} \, T^{1.16} \exp(-1210/T) \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$ over range 300–2000 K

Reliability

$\Delta \log k = \pm 0.4$ at 2000 K reducing to ± 0.1 at 300 K

Comments on Preferred Values

Preferred values are based on the data of Whytock et al.[3] and Michael and Lee[5] at low temperature. Arrhenius plot curved to fit the data of Beeley et al.[4] at high temperature. Temperature dependence data of Whytock et al.[3] indicates possibility of curvature. No experimental information is available on the contribution of the second channel. Assuming $k_2 = 0.5 \, k(\text{H} + \text{C}_2\text{H}_6)$, k_2/k increases from 0.04 at 700 K to 0.5 at 1700 K. The contribution at lower temperatures where most of the measurements have been made is negligible.

References

[1]W. K. Aders and H. Gg. Wagner, Ber. Bunsenges. Phys. Chem. **77**, 332 (1973).

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$$H + CH_3CHO \rightarrow H_2 + CH_3CO$$
$$\rightarrow H_2 + CH_2CHO$$

T/K

EXPERIMENTAL DATA
Aders and Wagner 1973
■ Slemr and Warneck 1975
Whytock et al 1976
Beeley et al 1977
O Michael and Lee 1977

This Recommendation 1989

$Log(k/cm^3molecule^{-1}s^{-1})$

$10^3T^{-1}/K^{-1}$

H + C$_6$H$_5$ (+ M) → C$_6$H$_6$ (+ M)
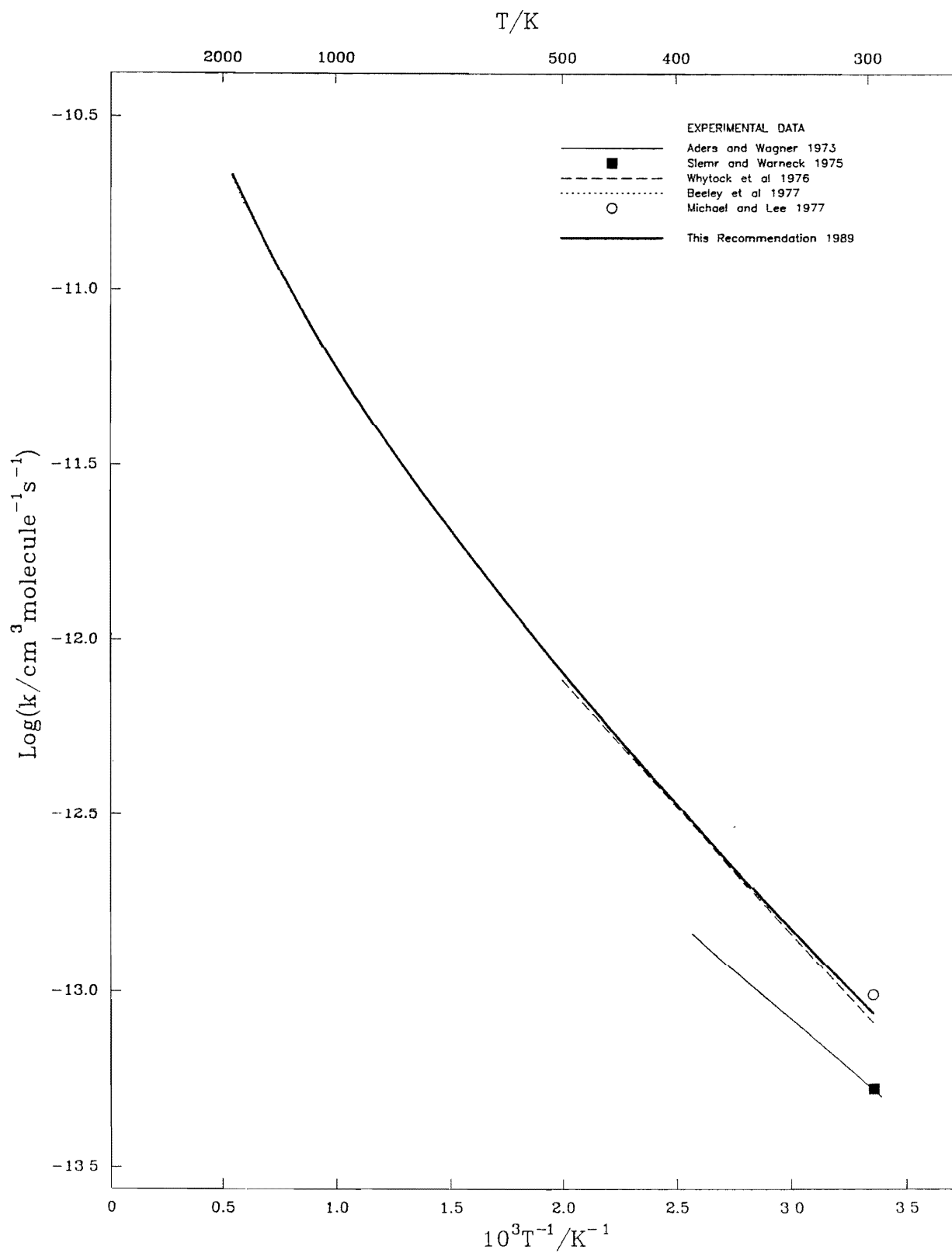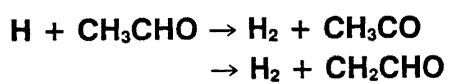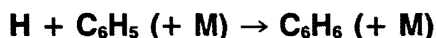
Thermodynamic Data

ΔH°_{298} (1) = −463.5 kJ mol^{-1}
ΔS°_{298} (1) = −133.7 J K^{-1}mol^{-1}
K_p(1) = 1.0·10^{-6}$T^{-0.45}$exp($+$55840/T) atm^{-1}

Rate Coefficient Data

k[cm^{3}molecule^{-1}s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
1.7·10^{-11}	1500–2000	Frenklach et al. (1985)[1]	(a)
1.3·10^{-10}	1380–1700	Braun-Unkhoff et al. (1989)[2]	(b)

Comments

(a) Modelling of soot formation under the conditions in shock tube pyrolysis. Initial concentrations of about 1% acetylene in argon were used at post shock pressures of 5–7 bar. No sensitivity of the rate constant value with respect to the measured profiles is presented.

(b) Dissociation of phenyl radicals behind reflected shock waves was investigated by monitoring H atoms with ARAS. Nitrosobenzene served as thermal source for the phenyl radicals. The test gas mixtures consisted of argon with relative concentrations of 1–100 ppm nitrosobenzene. It was found that besides the dissociation reaction sequence of phenyl, the recombination step has strongest influence on the measured H atom concentration level.

Preferred Values

k = 1.3·10^{-10} cm^3 molecule^{-1} s^{-1} over range 1400–1700 K

Reliability
Δlog k = ± 0.5

Comments on Prefered Values
The recommended value is based on the only experimental study of phenyl pyrolysis and is actually dependent upon the rate of the phenyl recombination reaction.

References

[1] M. Frenklach, D. W. Clary, W. C. Gardiner, Jr., and S. E. Stein, 20th Symp. (Int.) Combust., 887 (1985).
[2] M. Braun-Unkhoff, P. Frank, and Th. Just, 22nd Symp. (Int.) Combust., 1053 (1989).

H + C$_6$H$_6$ → H$_2$ + C$_6$H$_5$ (1)
H + C$_6$H$_6$ (+ M) → C$_6$H$_7$ (+ M)   (2)
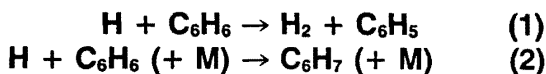
Thermodynamic Data

ΔH°_{298} (1) = 27.2 kJ mol^{-1}
ΔS°_{298} (1) = 35.1 J K^{-1}mol^{-1}
K_p(1) = 5.3·10^4 $T^{-0.90}$ exp($-$3780/T)

ΔH°_{298} (2) = 112.3 kJ mol^{-1}
ΔS°_{298} (2) = −78.9 J K^{-1}mol^{-1}
K_p(?) = 6.4·10^{-1} $T^{-1.27}$ exp($-$14060/T) atm^{-1}

Rate Coefficient Data ($k = k_1 + k_2$)

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
1.3·10^{-11} exp($-$1661/T)	300–357	Sauer and Ward (1967)[1]	(a)
9.8·10^{-11} exp($-$2164/T)	298–393	Sauer and Mani (1970)[2]	(b)
k_1 = 3.40·10^{-11} exp($-$4378/T)	883–963	Mkryan et al. (1971)[3]	(c)
k_1 = 6.6·10^{-10} exp($-$3623/T)	1400–1900	Asaba and Fujii (1971)[4]	(d)
k_2 = 3.0·10^{-14}	303	Knutti and Buehler (1972)[5]	(e)
k_2 = 1.7·10^{-11}exp($-$2013/T)	540	Louw and Lucas (1973)[6]	(f)
k_2 = 1.2·10^{-11} exp($-$1864/T)	296–493	Hoyermann et al. (1975)[7]	(g)
k_1 = 1.3·10^{-10} exp($-$5032/T)	1200–1900	Fujii and Asaba (1977)[8]	(h)
k_1 = 1.1·10^{-11} exp($-$4780/T)	1273–2073	Smith (1979)[9]	(i)
6.7·10^{-11} exp($-$2170/T)	298–1000	Nicovich and Ravishankara (1984)[10]	(j)
k_1 = 4.7·10^{-11} exp($-$8052/T)	1630–1940	Rao and Skinner (1984)[11]	(k)
k_1 = 4.2·10^{-10} exp($-$8052/T)	1900–2200	Kiefer et al. (1985)[12]	(l)

Comments

(a) Pulsed radiolysis with product analysis by gas chromatography. Transient species were monitored as function of time by absorption in the wavelength range 260–340 μm. The results are close to the high pressure limiting rate coefficient.

(b) H atom reactions with a series of monosubstituted benzenes, naphthalene, the xylenes, and pyridine were investigated using the pulsed-radiolysis method. Optical absorption changes occurring after the electron pulses were monitored for the wavelength range 260–400 μm. Measurements of the overall reaction are close to the high pressure limits.

(c) Evaluation of an overall rate coefficient from a flow reactor study.

(d) Mixtures of 10–20% benzene with argon were pyrolyzed in a single pulse shock tube at 2–8 atm. The products formed were analyzed by gas chromatography. Additionally absorption spectroscopy was applied. A complex mechanism was used for modelling the experimental data.

(e) Low pressures study (mbar range) in a fast gas flow system. The time dependence of adducts, transient species, and of products were measured by mass spectroscopy. The rate expression is deduced from a kinetic model.

(f) The conversion of benzene and of deuterated benzene mixtures into biphenyl was examined in a tank flow reactor at atmospheric pressure. Formation of biphenyl was detected by gas chromatography.

(g) The experiments were carried out in an isothermal flow reactor using ESR, MS, and GC detection techniques. The reactions of H atoms with cyclohexene and cyclohexadiene have also been measured.

(h) The high temperature pyrolysis of benzene was studied in a single pulse shock. Gas samples were heated by reflected shock waves; the products were analyzed by GC. The reaction rate was also followed by light absorption at 200–600 nm (benzene, biphenyl). The experimental data are interpreted by a chain mechanism consisting of 7 elementary reactions.

(i) The pyrolysis of mixtures of toluene and benzene were studied in a high temperature Knudsen cell by using modulated molecular beam mass spectrometric methods.

(j) Observed rate coefficient for the consumption of H atoms using the flash photolysis–resonance fluorescence technique for $p = 10$–200 Torr. H-atoms were produced by photolysis of benzene or H_2O. Time-de-

pendent detection of H-resonance fluorescence at 121.5 nm (channel (2)). An estimated rate coefficient for channel (1) ($k_1 = 5 \cdot 10^{-12} \exp(-4076/T)$ cm³ molecule⁻¹ s⁻¹) gives negligible contribution to the overall rate at any temperature less than 1000 K. Consequently a limiting high pressure rate expression for channel (2) is evaluated for temperature range below 1000 K.

(k) Dilute mixtures of deuterated benzene and of chlorobenzene were pyrolyzed behind reflected shock waves at total pressures of 2–3 atm. The formation of D or H atoms was monitored by a time resolved ARAS.

(l) The shock tube–laser schlieren technique was used to investigate the high temperature pyrolsis of benzene in mixtures with krypton. The measured density gradient profiles were modelled by a 26 step mechanism (channel (1)).

Preferred Values

$k_{2,\infty} = 6.7 \cdot 10^{-11} \exp(-2170/T)$ cm³ molecule⁻¹ s⁻¹ over range 300–1000 K

Reliability

$\Delta \log k_2 = \pm 0.2$

Comments on Preferred Values

The present data do not allow an evaluation of a rate expression for the abstraction channel (1) because of the scattering of the experimental data at high temperatures.

For the adduct reaction channel (2) a high pressure limiting rate coefficient is evaluated based on the data of Ref. 10.

References

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[2] M. C. Sauer, Jr., and I. Mani, J. Phys. Chem. **74**, 59 (1970).

[3] T. G. Mkryan, K. T. Oganesyan, and A. B. Nalbandyan, Arm. Khim. Zh. **24**, 299 (1971).

[4] T. Asaba and N. Fujii, 13th Symp. (Int.) Combust., 155 (1971).

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[7] K. Hoyermann, A. W. Preuss, and H. Gg. Wagner, Ber. Bunsenges. Phys. Chem. **79**, 156 (1975).

[8] N. Fujii and T. Asaba, J. Fac. Eng., Univ. Tokyo, Ser. B **34**, 189 (1977).

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[11] V. S. Rao and G. B. Skinner, J. Phys. Chem. **88**, 5990 (1984).

[12] J. H. Kiefer, L. J. Mizerka, M. R. Patel, and H. C. Wei, J. Phys. Chem. **89**, 2013 (1985).

$$H + C_6H_6 \rightarrow H_2 + C_6H_5$$
$$\rightarrow C_6H_7$$

H + C₆H₅O (+ M) → C₆H₅OH (+ M)
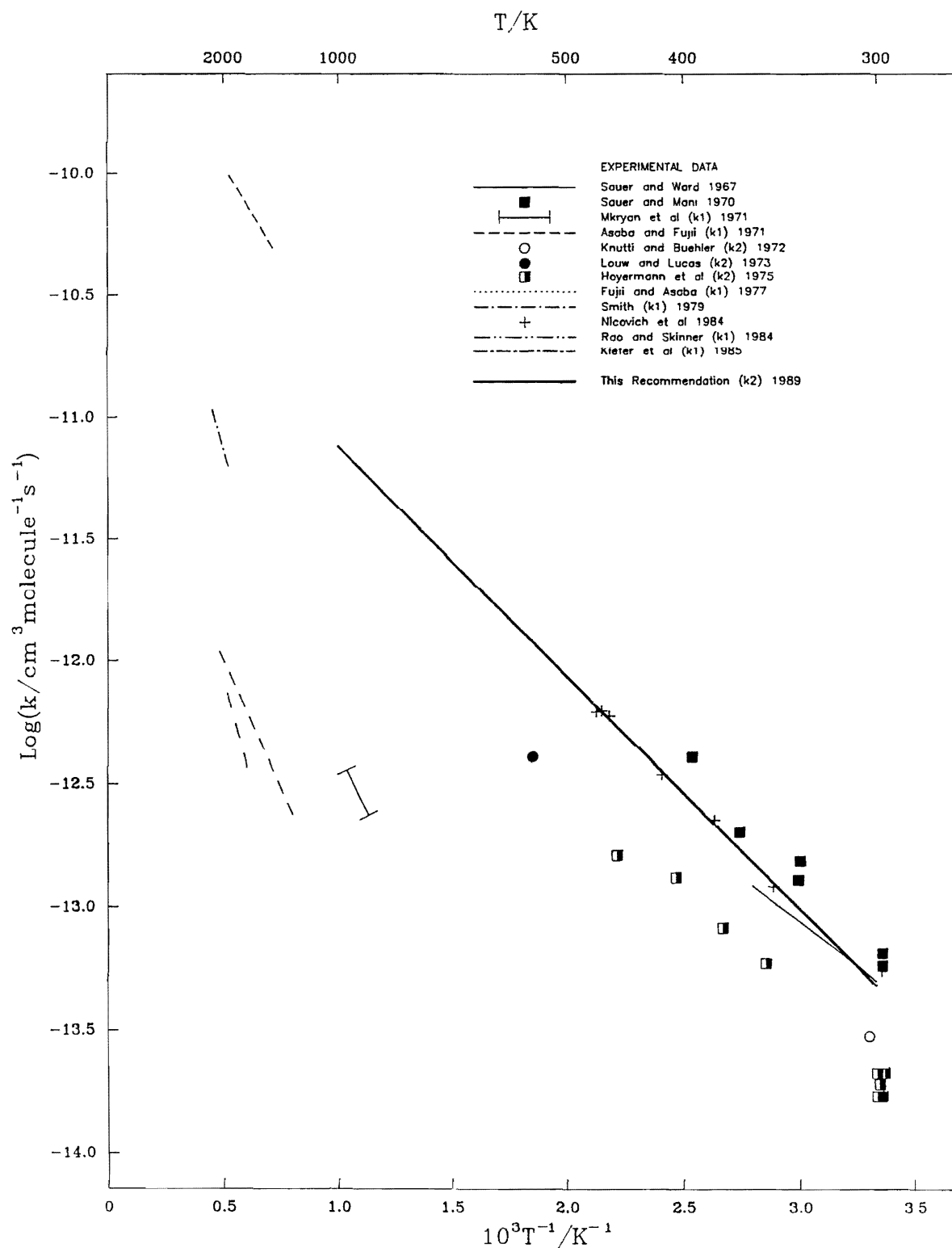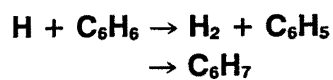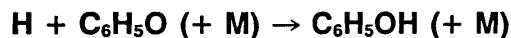
Thermodynamic Data

$\Delta H^\circ_{298} = -362.1$ kJ mol^{-1}

$\Delta S^\circ_{298} = -107.6$ J K^{-1}mol^{-1}

$K_p = 4.6 \cdot 10^{-4} T^{-0.813} \exp(+43373/T)$ atm^{-1}

Rate Coefficient Data

$k[\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}]$	$T[\text{K}]$	Reference	Comments
Rate Coefficient Measurements			
$4.2 \cdot 10^{-10}$	≈ 1000	He *et al*. (1988)	(a)

Comments

(a) Obtained solely by computer simulation of the system phenol + H (see appropriate data sheet), based on GC measurements of the two stable end products isobutene and benzene.

No literature is found on the potential role of bimolecular channels.

Preferred Values

In the absence of any other measurements the rate coefficient of He *et al*.is recommended.

References

[1]Y. Z. He, W. G. Mallard, and W. Tsang, J. Phys. Chem. **92**, 2196 (1988).
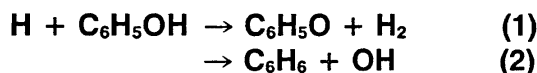
H + C₆H₅OH → C₆H₅O + H₂   (1)
→ C₆H₆ + OH   (2)

Thermodynamic Data

ΔH°_{298} (1) $= -73.9$ kJ mol^{-1}

ΔS°_{298} (1) $= 8.9$ J K^{-1}mol^{-1}

$K_p(1) = 1.1 \cdot 10^2 T^{-0.528} \exp(+8693/T)$

ΔH°_{298} (2) $= 0.3$ kJ mol^{-1}

ΔS°_{298} (2) $= 23.5$ J K^{-1}mol^{-1}

$K_p(2) = 2.1 \cdot 10^4 T^{-1.112} \exp(-262/T)$

Rate Coefficient Data ($k = k_1 + k_2$)

$k[\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}]$	$T[\text{K}]$	Reference	Comments
Rate Coefficient Measurements			
$k_1 = 1.9 \cdot 10^{-10} \exp(-6240/T)$	1000–1150	He *et al*. (1988)	(a)
$k_2 = 3.7 \cdot 10^{-11} \exp(-3990/T)$	1000–1150	He *et al*. (1988)	(a)

Comments

(a) Shock tube; 2.5–5 atm of Ar. H source is the decomposition of C₈H₁₈ to H atoms and isobutene. Phenol is in large excess over C₈H₁₈ and is thus the main H sink. Benzene is produced via reaction (2) and measured by GC, together with isobutene yields. This establishes the branching ratio for reactions (1) and (2). Absolute rate data are obtained by using CH₄ + H as an internal standard, i.e., by observing the change of benzene yields under addition of several percent of

CH₄. Kinetic complications were investigated by varying the stoichiometry and by computer simulation.

Preferred Values

In the absence of any other study the expressions of He *et al*.are preferred.

References

Y. Z. He, W. G. Mallard, and W. Tsang, J. Phys. Chem. **92**, 2196 (1988).

H + C₆H₅CH₂ (+ M) → C₆H₅CH₃ (+ M)

Thermodynamic Data
$\Delta H^\circ_{298} = -368.0 \text{ kJ mol}^{-1}$
$\Delta S^\circ_{298} = -110.9 \text{ J K}^{-1}\text{mol}^{-1}$
$K_p = 1.8 \cdot 10^{-2} \ T^{-1.49} \exp(+44028/T) \text{ atm}^{-1}$

Rate Coefficient Data

$k[\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}]$	$T[\text{K}]$	Reference	Comments
Rate Coefficient Measurements			
$1.3 \cdot 10^{-10}$-$1.3 \cdot 10^{-9}$	1450–1900	Brouwer *et al.* (1988)[1]	(a)
$5.5 \cdot 10^{-10}$	298	Bartels *et al.* (1989)[2]	(b)

Comments

(a) The thermal decomposition of toluene has been rein-vestigated in shock wave experiments. The absorption signals of toluene, benzyl, and assumed benzyl fragments were monitored. The rate coefficient was determined from modelling studies.

(b) The reaction of benzyl radicals with H and O atoms were studied in a flow reactor at room temperature and at pressures around 1 mbar. Molecular beam sampling and mass spectrometric detection were applied. The rate for the recombination was measured with reference to the reaction of methyl radicals with deuterium atoms.

Preferred Values

$k = 5.5 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the range 300–2000 K

Reliability
$\Delta \log k = \pm 0.2$ at room temperature increasing to ± 0.7 at 2000 K

Comments on Preferred Values

The only direct measurements performed at room temperature provide evidence for the recombination channel to toluene. Owing to the high exothermicity of this reaction no barrier is expected to be involved, and the recommendation has been extended to the range up to 2000 K.

References

[1]L. D. Brouwer, W. Mueller-Markgraf, and J. Troe, J. Phys. Chem. **92**, 4905 (1988).

[2]M. Bartels, J. Edelbuettel-Einhaus, and K. Hoyermann, 22nd Symp. (Int.) Combust., 1041 (1989).

$$H + C_6H_5CH_3 \rightarrow H_2 + C_6H_5CH_2 \quad (1)$$
$$\rightarrow H_2 + C_6H_4CH_3 \quad (2)$$
$$\rightarrow CH_3 + C_6H_6 \quad (3)$$
$$H + C_6H_5CH_3 (+ M) \rightarrow C_6H_6CH_3 (+ M) \quad (4)$$

Thermodynamic Data

$\Delta H^\circ_{298} (1) = -68.0$ kJ mol^{-1}

$\Delta S^\circ_{298} (1) = 12.3$ J K^{-1}mol^{-1}

$K_p(1) = 2.4 \ T^{0.171} \exp(+8060/T)$

$\Delta S^\circ_{298} (3) = -39.4$ J K^{-1}mol^{-1}

$\Delta H^\circ_{298} (3) = 28.9$ kJ mol^{-1}

$K_p(3) = 2.1 \cdot 10^4 \ T^{-0.940} \exp(+4400/T)$

$\Delta H^\circ_{298} (2) = 37.5$ kJ mol^{-1}

$\Delta S^\circ_{298} (2) = 12.1$ J K^{-1}mol^{-1}

$K_p(2) = 2.5 \ T^{0.158} \exp(-4630/T)$

Rate Coefficient Data ($k = k_1 + k_2 + k_3 + k_4$)

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$k_3 = 3.3 \cdot 10^{-12}\exp(-755/T)$	633	Benson and Shaw (1967)[1]	(a)
$k_4 = 1.7 \cdot 10^{-13}$	298	Sauer and Ward (1967)[2]	(b)
$k_1 = 1.4 \cdot 10^{-10}\exp(-4630/T)$	863–963	Mkryan *et al.* (1972)[3]	(c)
$k_4 = 8.5 \cdot 10^{-14}$	303	Knutti and Buehler (1975)[4]	(d)
$k_1 = 8.3 \cdot 10^{-11}\exp(-1864/T)$	1500–1800	Astholz *et al.* (1981)[5]	(e)
$k_1 = 1.3 \cdot 10^{-28} \ T^{5.5} \exp(-171/T)$	600–1700	Rao and Skinner (1984)[6]	(f)
$k_1 = 5.4 \cdot 10^{-9}\exp(-7548/T)$	1600–2150	Pamidimukkala and Kern (1985)[7]	(g)
$k_2 = 5.4 \cdot 10^{-9}\exp(-9561/T)$	1600–2150		
$k_3 = 2.1 \cdot 10^{-12}\exp(-1862/T)$	1600–2150		
$k_1 = 1.8 \cdot 10^{-20} \ T^{3.0}\exp(-1183/T)$	950–1100	Robaugh and Tsang (1986)[8]	(h)
$k_3 = 1.1 \cdot 10^{-21} \ T^{3.0}\exp(+377/T)$	950–1100		
$k_1 = 7.3 \cdot 10^{-24} \ T^{4.0}\exp(-1057/T)$	1300–1800	Mizerka and Kiefer (1986)[9]	(i)
$k_3 = 5.0 \cdot 10^{-13}$	773	Baldwin *et al.* (1987)[10]	(j)
$9.7 \cdot 10^{-13}$	773		
$k_2 = 4.2 \cdot 10^{-10} \exp(-8052/T)$	1600–2100	Pamidimukkala *et al.* (1987)[12]	(k)
$k_1 = 8.3 \cdot 10^{-10} \exp(-6290/T)$	1380–1700	Braun-Unkhoff *et al.* (1989)[13]	(l)

Comments

(a) Static system. Detection by gas chromatography and mass spectrometry. Rate expression for channel (3) deduced by comparison with H addition to benzene.

(b) Pulsed radiolysis with product analysis by gas chromatography. Transient species were monitored as function of time by absorption in the wavelength range 260–340 μm. A k-value for the overall reaction (4) at room temperature was deduced.

(c) Evaluation of a k-expression for channel (1) from a flow reactor study.

(d) Fast flow reactor with product analysis by mass spectrometry. H atoms produced in microwave discharge. Rate expression evaluated for the overall reaction (channel (4)).

(e) Shock tube study with toluene/Ar mixtures. Toluene and benzyl were monitored as function of time by absorption in the 200–350 nm range. A rate expression for channel (1) was derived on the assumption that the benzyl radical exhibits sufficient thermal stability.

(f) Shock tube study with initial mixtures of toluene-d_8/Ar and neopentane/toluene-d_8/Ar mixtures. D and H atoms were monitored as function of time by ARAS. Investigation covered a temperature range from 1200–1460 K for neopentane/toluene, and from

1410–1730 K for toluene experiments. Together with unpublished results of Ravishankara and Nicovich a non-Arrhenius expression for $T = 600$–1700 K was deduced for channel (1).

(g) Shock tube study with mixtures of toluene and ethylbenzene, respectively. Products were monitored as function of time by time-of-flight mass spectrometry. The rate expression for formation of benzyl radicals and hydrogen (channel (1)) is reevaluated from the data of Ref. 6. Rate expressions for the formation of methyl phenyl radicals and hydrogen (channel (2)) and of benzene and methyl radicals (channel (3)) are deduced from experiments.

(h) Single pulse shock tube. The source of H atoms was the thermal decay of small quantities of hexamethylethane. The k-values have been derived on the basis of competive process H + CH$_4$ → CH$_3$ + H$_2$ with $k = 2.2 \cdot 10^{-20} \ T^{3.0}\exp(-4045/T)$. Rate expressions for the formation of benzene and methyl radicals (channel (3)) and of benzyl radicals and hydrogen (channel (1)) were obtained.

(i) Small amounts of toluene (0.05–0.5%) have been added to slowly reacting mixtures of hydrogen and oxygen at 773 K. Under the experimental conditions the H$_2$ + O$_2$ system provides a reproducible source of H, O, and OH radicals. The measurements of the rel-

ative consumption of H_2 and of the additive permits the evaluation of rate constants for the reaction of H, O, and OH with toluene.

(j) Shock tube study on high temperature pyrolysis of ethylbenzene with the laser schlieren technique. Rate expression for channel (1).

(k) Two independent shock tube techniques (time-of-flight mass spectrometry and laser schlieren densitometry) were used to investigate the high temperature pyrolysis of toluene in mixtures with Kr and Ne, respectively. A rate coefficient for the formation of methyl phenyl (channel (2)) was obtained.

(l) Shock tube study with very low initial concentrations of toluene in Ar. Hydrogen atom formation is monitored by ARAS. The measured H profiles were sensitive to k_1 in the later stage of observation time. A rate coefficient for channel (1) was deduced which is slightly smaller than the rate constant of Rao and Skinner[6].

Preferred Values

$k_1 = 6.6 \cdot 10^{-22} \, T^{3.44} \, \exp(-1570/T) \, \text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1}$
over range 600–2800 K

$k_4 = 1.2 \cdot 10^{-13} \, \text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1}$ at $T = 298$ K

Reliability

$\Delta \log k_1 = \pm 0.5$ at 2800 K reducing to ± 0.3 at 600 K

$\Delta \log k_4 = \pm 0.2$ at 298 K

Comments on Preferred Values

Most of the available measurements give evidence for the product channel (1) leading to benzyl radicals and molecular hydrogen. It has to be noted that only a few

experiments permit a discrimination between the channels at elevated temperatures. Therefore from the majority of the data, the different product pathways have been deduced not by direct measurement of product distribution and concentration but by modelling with the aid of plausible reaction systems. By combining the few room temperature data with the rate constant values at elevated temperatures, it has to be assumed that a change in the reaction mechanism occurs, possibly from channel (4) at room temperature to channel (1) dominating at temperatures above 1000 K[11]. The data are insufficient to permit a recommendation of a rate expression for the overall H-consuming reaction over the whole temperature range. For the adddition reaction (4) it is only possible to evaluate a room temperature value.

References

[1]S. W. Benson and R. Shaw, J. Phys. Chem. **47**, 4052 (1967); S. W. Benson and R. Shaw, J. Am. Chem. Soc. **89**, 5351 (1967).

[2]M. C. Sauer and B. Ward, J. Phys. Chem. **71**, 3971 (1967).

[3]T. G. Mkryan, K. T. Oganesyan, and A. B. Nalbandyan, Arm. Khim. Zh. **25**, 893 (1972).

[4]K. Knutti and R. Buehler, Chem. Phys. **7**, 229, (1975).

[5]D. C. Astholz, J. Durant, and J. Troe, 18th Symp. (Int.) Combust., 885 (1981).

[6]V. S. Rao, and G. B. Skinner, J. Phys. Chem. **88**, 4362 (1984).

[7]K. M. Pamidimukkala and R. D. Kern, Poster Paper, Int. Conf. on Chem. Kinetics, Gaithersburg, MD (1985).

[8]D. Robaugh and W. Tsang, J. Phys. Chem. **90**, 4159 (1986).

[9]J. H. Kiefer and L. J. Mizerka, Int. J. Chem. Kin. **18**, 363 (1984).

[10]R. R. Baldwin, M. Scott and R. W. Walker, 21st Symp. (Int.) Combust., 991 (1986).

[11]A. Amano, O. Horie, and N. H. Hank, Int. J. Chem. Kin. **8**, 321 (1976).

[12]K. M. Pamidimukkala, R. D. Kern, M. R. Patel, H. C. Wei, and J. H. Kiefer, J. Phys. Chem. **91**, 2148 (1987).

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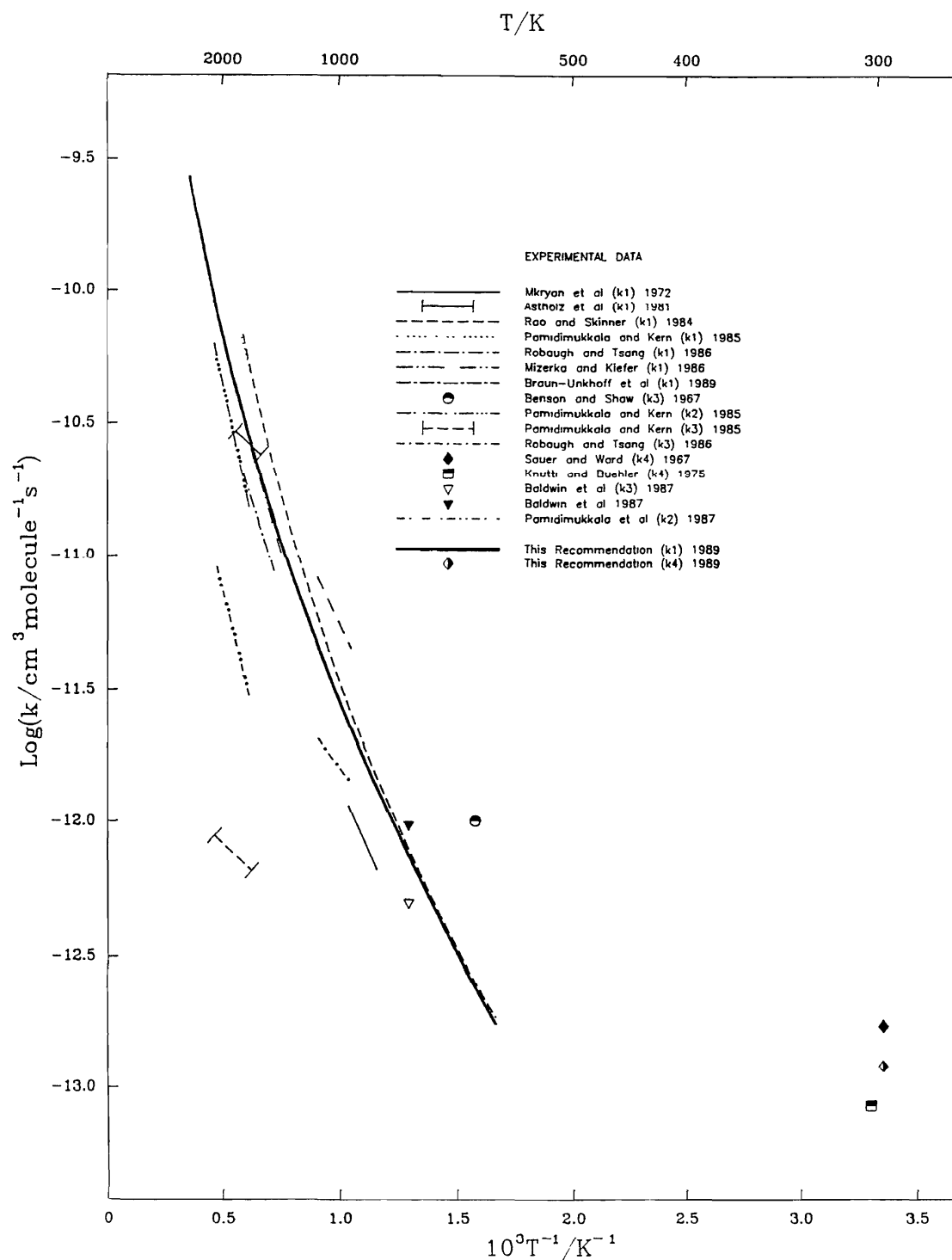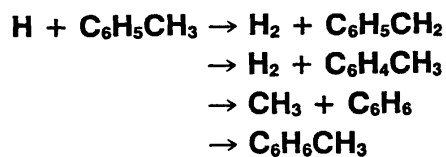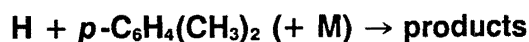
$$H + C_6H_5CH_3 \rightarrow H_2 + C_6H_5CH_2$$
$$\rightarrow H_2 + C_6H_4CH_3$$
$$\rightarrow CH_3 + C_6H_6$$
$$\rightarrow C_6H_6CH_3$$

H + p-C$_6$H$_4$(CH$_3$)$_2$ (+ M) → products

Rate Coefficient Data

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$5.8 \cdot 10^{-13}$	298	Sauer, Jr., and Mani (1970)[1]	(a)

Comments

(a) Pulse-radiolysis study at pressures around 75 bar. Analysis from transient spectra.

Preferred Values

$k = 5.8 \cdot 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K

Reliability
$\Delta \log k = \pm 0.1$

Comments on Preferred Values

In the absence of other experimental data we recommend the rate coefficient reported by Sauer, Jr., and Mani[1].

Reference

[1] M. C. Sauer, Jr., and I. Mani, J. Phys. Chem. **74**, 59 (1970).

H + C$_6$H$_5$C$_2$H$_5$ → C$_6$H$_5$C$_2$H$_4$ + H$_2$ (1)
H + C$_6$H$_5$C$_2$H$_5$ (+ M) → C$_6$H$_6$C$_2$H$_5$ (+ M) (2)
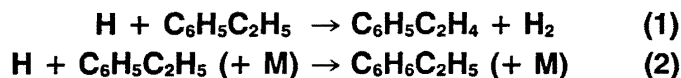
Thermodynamic Data
ΔH°_{298} (1) = -94.6 kJ mol^{-1}
ΔS°_{298} (1) = 11.7 J K^{-1}mol^{-1}
K_p(1) = $2.4 \cdot 10^1\ T^{-0.199}$ exp($+11180/T$)

Rate Coefficient Data ($k = k_1 + k_2$)

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$3.3 \cdot 10^{-13}$	298	Sauer, Jr., and Mani (1970)[1]	(a)

Comments

(a) Pulse-radiolysis study at pressures around 75 bar. Analysis from transient spectra.

Preferred Values

$k = 3.3 \cdot 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K

Reliability
$\Delta \log k = \pm 0.1$

Comments on Preferred Values

In the absence of other experimental data we recommend for the addition channel the rate coefficient k given by Sauer, Jr., and Mani[1].

Reference

[1] M. C. Sauer, Jr., and I. Mani, J. Phys. Chem. **74**, 59 (1970).

H_2 (+ M) $\rightarrow$ H + H (+ M)
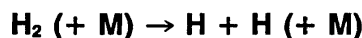
Thermodynamic Data
$\Delta H^o_{298} = 436 \text{ kJ mol}^{-1}$
$\Delta S^o_{298} = 98.6 \text{ J K}^{-1}\text{mol}^{-1}$
$K_p = 31.3 \ T^{1.28} \exp(-52100/T) \text{ atm}$

Rate Coefficient Data

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	$T[\text{K}]$	M	Reference	Comments
Rate Coefficient Measurements				
$1.6 \cdot 10^{-10} \exp(-44740/T)$	3500–8000	Ar	Breshears and Bird (1973)[1]	(a)
$5.5 \cdot 10^{-9} \exp(-52990/T)$	3500–8000	H_2		
Reviews and Evaluations				
$3.7 \cdot 10^{-10} \exp(-48350/T)$	2500–5000	Ar	Baulch *et al*. (1972)[2]	
$1.5 \cdot 10^{-9} \exp(-48350/T)$	2500–5000	H_2		
$7.6 \cdot 10^{-5} \ T^{-1.4} \exp(-52525/T)$	600–2000	N_2	Tsang and Hampson (1986)[3]	

Comments

(a) Dissociation of H_2 in Ar behind incident shock waves. Postshock density gradients measured by laser schlieren technique.

Preferred Values

$k = 3.7 \cdot 10^{-10} \exp(-48350/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over range 2500–8000 K for M = Ar

$k = 1.5 \cdot 10^{-9} \exp(-48350/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over range 2500–8000 K for M = H_2

Reliability
$\Delta \log k = \pm 0.3$ for M = Ar
$\Delta \log k = \pm 0.5$ for M = H_2

Comments on Preferred Values

The value preferred by Baulch *et al*.[2] has been adopted. The arguments given there are accepted, and the values measured after 1972 do not contradict this recommendation.

For clarity, rate data measured before 1972 are included in the Arrhenius plot (see Baulch *et al*.[2] for Ref.).

References

[1]W. D. Breshears and P. F. Bird, 14th Symp. (Int.) Combust., 211 (1973).

[2]D. L. Baulch, D. D. Drysdale, D. G. Horne, and A. C. Lloyd, "Evaluated Kinetic Data for High Temperature Reactions", Vol. 1: "Homogeneous Gas Phase Reactions of the H_2–O_2System", London, Butterworths (1972).

[3]W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data **15**, 1987 (1986).

$H_2 + Ar \rightarrow H + H + Ar$

T/K

OH + H$_2$ → H + H$_2$O

Thermodynamic Data
ΔH°_{298} = − 62.9 kJ mol^{-1}
ΔS°_{298} = − 10.9 J K^{-1}mol^{-1}
K_p = 0.113 $T^{0.0839}$ exp(7680/T)

Rate Coefficient Data

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
7.1·10^{-15}	300	Stuhl and Niki (1972)[1]	(a)
8.6·10^{-11} exp(−3271/T)	1200–1800	Gardiner *et al*. (1973)[2]	(b)
4.6·10^{-12}	1050	Day, Thompson, and Dixon-Lewis (1973)[3]	(c)
7.6·10^{-15}	298	Westenberg and deHaas (1973)[4]	(d)
1.8·10^{-14}	352		
3.3·10^{-14}	403		
1.4·10^{-13}	518		
3.7·10^{-13}	628		
6.6·10^{-13}	745		
1.8·10^{-11} exp(−2333/T)	210–460	Smith and Zellner (1974)[5]	(e)
8.6·10^{-11} exp(−3248/T)	1350–1600	Gardiner, Mallard, and Owen (1974)[6]	(f)
5.3·10^{-15}	300	Trainor and von Rosenberg (1975)[7]	(g)
5.9·10^{-12} exp(−2008/T)	297–434	Atkinson. Hansen. and Pitts (1975)[8]	(h)
5.8·10^{-15}	295	Overend *et al*. (1975)[9]	(i)
1.2·10^{-11} exp(−2214/T)	600–1300	Vandooren, Peeters, and van Tiggelen (1975)[10]	(j)
8.5·10^{-15}	296	Sworsky, Hochanadel, and Ogren (1980)[11]	(k)
4.1·10^{-19} $T^{2.44}$ exp(−1281/T)	250–1050	Tully *et al*. (1980,1981)[12,13]	(l)
7.9·10^{-11} exp(−3067/T)	1700–2500	Frank and Just (1985)[14]	(m)
5.8·10^{-15}	295	Schmidt *et al*. (1985)[15]	(n)
1.05·10^{-10} exp(−4045/T)	1246–2297	Michael and Sutherland (1988)[16]	(o)
Reviews and Evaluations			
3.7·10^{-11}exp(−2586/T)	300–2500	Baulch *et al*. (1972)[17]	
·5.3·10^{-17} $T^{1.77}$ exp(−1528/T)		Gardiner, Mallard, and Owen (1974)[6]	
1.7·10^{-16} $T^{1.6}$ exp(−1660/T)	300–2000	Zellner (1979)[18]	
1.8·10^{-11} exp(−2333/T)	210–300	Baulch *et al*. (1980)[19]	
1.1·10^{-17} $T^{2.0}$ exp(−1491/T)	240–2400	Cohen and Westberg (1983)[20]	
1.7·10^{-16} $T^{1.6}$ exp(−1660/T)	300–2500	Warnatz (1984)[21]	

Comments

(a) Pulsed VUV photolysis of H$_2$O; [OH] by resonance fluorescence. Total pressure 20 Torr He.

(b) Combustion of rich H$_2$/O$_2$/Ar mixtures behind incident shock waves; [OH] by absorption spectroscopy, [CO$_2$] by emission at 4.2 μm, CO + O chemiluminescence. Numerical integration of 12 reaction mechanism.

(c) Calculation of burning velocities and concentration profiles in rich H$_2$/D$_2$/O$_2$/N$_2$ flames.

(d) Discharge-flow reactor; [OH] by ESR. Total pressures 1–3 Torr.

(e) Flash photolysis of either H$_2$O or N$_2$O/H$_2$ mixtures; time-resolved resonance absorption of OH. Total pressures at least 10 Torr.

(f) Shock-initiated combustion of rich H$_2$/O$_2$/Ar mixtures; [OH] by resonance absorption. Numerical integration of 12 reaction mechanism; k adjusted to fit the experimental OH concentration profiles.

(g) Flash photolysis of H$_2$O/H$_2$/N$_2$ mixtures; [OH] by time-resolved resonance UV absorption spectroscopy. Total pressures near 100 Torr.

(h) Pulsed VUV photolysis of H$_2$O; [OH] by resonance fluorescence at 306.4 nm. Total pressures 15–25 Torr Ar.

(i) Flash photolysis of H$_2$O/H$_2$ of N$_2$O/H$_2$ mixtures; [OH] by time-resolved resonance absorption. Total pressures 40–760 Torr.

(j) Lean CO/H$_2$/O$_2$ flames on a flat burner; molecular beam sampling coupled with mass spectrometry. Total pressure 40 Torr. k determined from mole flux of H$_2$O.

(k) Flash photolysis of H$_2$O/CH$_4$ mixtures with and without H$_2$ or N$_2$ at atmospheric pressures; [CH$_3$] by absorption at 216 nm. Numerical integration of 11 reaction mechanism.

(l) Flash photolysis of H$_2$O/H$_2$/Ar mixtures; [OH] by resonance fluorescence.

(m) Shock heating of $N_2O/H_2/O_2/Ar$ mixtures; [H] and [O] by time-resolved atomic resonance absorption. Total densities $(6\cdot10^{-6}-1.3\cdot10^{-5})$ mol cm^{-3}. Numerical integration of 10 reaction mechanism.

(n) Excimer laser photolysis of H_2O_2 or HNO_3 in synthetic air at a total pressure of 1 atm; [OH] by laser induced fluorescence near 300 nm.

(o) Flash photolysis – shock tube study of k_{-1}; [H] by atomic resonance absorption. k calculated from equilibrium data.

Preferred Values

$k = 1.7\cdot10^{-16}\ T^{1.6}\ \exp(-1660/T)\ cm^3\ molecule^{-1}\ s^{-1}$
over range 300–2500 K

Reliability
$\Delta\log k = \pm\ 0.3$ at 2500 K reducing to $\pm\ 0.1$ below 1000 K

Comments on Preferred Values

The rate coefficient recommended by Zellner[18] is adopted, which represents the ample experimental material very well.

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OH + H₂ → H₂O + H

OH + OH → O + H$_2$O
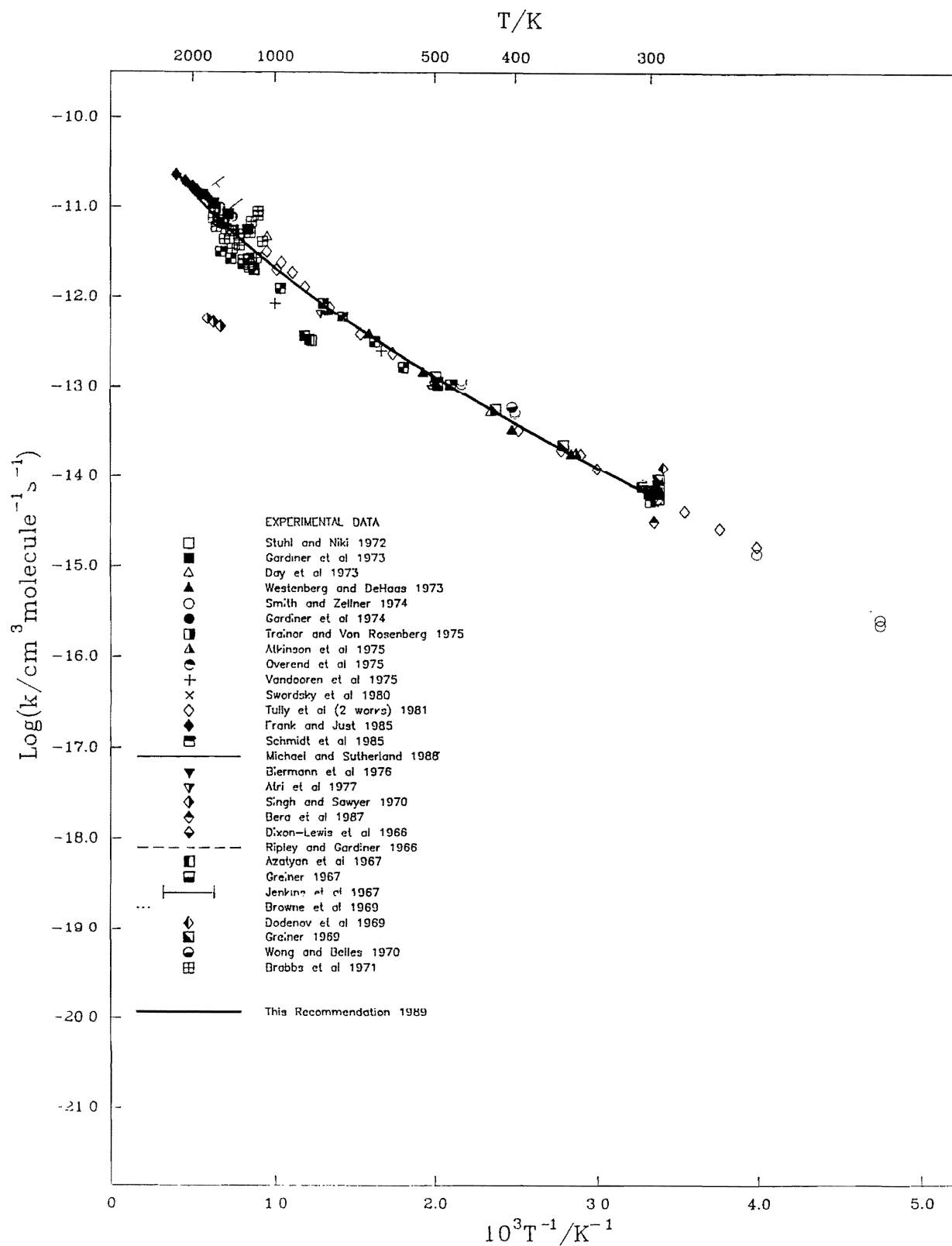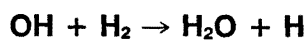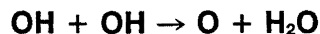
Thermodynamic Data

$\Delta H^\circ_{298} = -70.6 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} = -17.5 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p = 6.24 \cdot 10^{-2} \ T^{0.057} \exp(+8600/T)$

Rate Coefficient Data

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	$T[\text{K}]$	Reference	Comments
Rate Coefficient Measurements			
$9.1 \cdot 10^{-11} \exp(-3523/T)$	1500–2000	Gardiner et al. (1973)[1]	(a)
$2.2 \cdot 10^{-12}$	298	McKenzie, Mulcahy, and Steven (1973)[2]	(b)
$2.3 \cdot 10^{-12}$	298	Westenberg and deHaas (1973)[3]	(c)
$1.4 \cdot 10^{-12}$	300	Clyne and Down (1974)[4]	(d)
$2.1 \cdot 10^{-12}$	298	Trainor and von Rosenberg (1974)[5]	(e)
$5.6 \cdot 10^{-11} \exp(-2526/T)$	1180–1820	Ernst, Wagner, and Zellner (1977)[6] and Zellner (1979)[7]	(f)
$3.2 \cdot 10^{-12} \exp(-277/T)$	250–380	Zellner and Wagner (1980)[8]	(g)
$3.2 \cdot 10^{-12} \exp(-242/T)$	250–580	Wagner and Zellner (1981)[9]	(g)
Reviews and Evaluations			
$1.0 \cdot 10^{-11} \exp(-553/T)$	300–2000	Baulch et al. (1972)[10]	
$1.8 \cdot 10^{-12}$	298	Baulch et al. (1980)[11]	
$2.5 \cdot 10^{-15} T^{1.14}$	300–2000	Ernst, Wagner, and Zellner (1977)[6]	
$9.1 \cdot 10^{13} \exp(1.49 \cdot 10^{3} T)$	250–2000	Wagner and Zellner (1981)[9]	
$2.5 \cdot 10^{-15} T^{1.14}$	300–2500	Warnatz (1984)[12]	
$3.5 \cdot 10^{-16} T^{1.4} \exp(+200/T)$	300–2000	Tsang and Hampson (1986)[13]	

Comments

(a) Combustion of lean H$_2$/O$_2$/Ar mixtures behind incident shock waves; [OH] by absorption spectroscopy, [CO$_2$] by IR emission, chemiluminescence from CO + O reaction. Numerical integration of 12 reaction mechanism.

(b) Discharge-flow system; OH from H + NO$_2$ reaction; [OH] monitored by ESR. Total pressure 1 Torr He or Ar.

(c) Discharge-flow system; OH radicals from H + NO$_2$ reaction; [OH] monitored by ESR. Total pressures ≈ 1 – 3 Torr He.

(d) Discharge-flow system; OH radicals from H + NO$_2$ reaction; [OH] by resonance fluorescence. Total pressure ≈ 120 nm^{-2}.

(e) Flash photolysis of water vapor; [OH] by time-resolved absorption spectroscopy at 308 nm. Total pressures 0 – 400 Torr N$_2$.

(f) Thermal decomposition of HNO$_3$ in Ar behind reflected shock waves; time-resolved resonance absorption of OH at 308 nm. From transition-state theory (BEBO): $k = 1.1 \cdot 10^{-15} T^{1.23} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

(g) Flash photolysis of H$_2$O/N$_2$ mixtures; [OH] by time-resolved resonance absorption. Total pressures below 80 Torr.

Preferred Values

$k = 2.5 \cdot 10^{-15} T^{1.14} \exp(-50/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over range 250–2500 K

Reliability

$\Delta \log k = \pm 0.2$ over total range

Comments on Preferred Values

The rate coefficient preferred by Ernst, Wagner, and Zellner[6] is taken as the recommendation due to the fact that it is based on experimental work over a large temperature range and careful evaluation of literature data.

For clarity, rate data measured before 1972 are included in the Arrhenius plot (see Baulch et al.[10] for reference).

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OH + OH (+ M) → H₂O₂ (+ M)
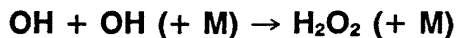
Thermodynamic Data

$\Delta H^{\circ}_{298} = -214 \text{ kJ mol}^{-1}$

$\Delta S^{\circ}_{298} = -134 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p = 2.26 \cdot 10^{-8} \, T^{0.091} \exp(+26000/T) \text{ atm}^{-1}$

Rate Coefficient Data

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	$T[\text{K}]$	$[\text{M}] [\text{molecule cm}^{-3}]$	Reference	Comments
Rate Coefficient Measurements				
Low Pressure Range				
$[\text{N}_2] \, 9.1 \cdot 10^{-31}$	253	$(0.06–2.7) \cdot 10^{19}$	Zellner *et al.* (1988)[1]	(a)
$[\text{N}_2] \, 6.9 \cdot 10^{-31}$	298			
$[\text{N}_2] \, 6.2 \cdot 10^{-31}$	353			
$[\text{H}_2\text{O}] \, 4.0 \cdot 10^{-30}$	298			
$[\text{H}_2\text{O}] \, 4.1 \cdot 10^{-30}$	353			
Intermediate Fall-off Range				
$5.6 \cdot 10^{-12}$	253	$3.1 \cdot 10^{19}$ (N_2)	Zellner *et al.* (1988)[1]	(b)
$5.9 \cdot 10^{-12}$	298	$2.9 \cdot 10^{19}$		
$3.4 \cdot 10^{-12}$	353	$1.4 \cdot 10^{19}$		
Reviews and Evaluations				
$k_0 = [\text{N}_2] \, 1.6 \cdot 10^{-23} \, T^{-3}$	500–2500		Tsang and Hampson (1986)[2]	(c)
$k_0 = [\text{N}_2] \, 8.0 \cdot 10^{-31} \, (T/300)^{-0.76}$	250–1400		Brouwer *et al.* (1987)[3]	(d)
$k_\infty = 1.5 \cdot 10^{-11} \, (T/300)^{-0.37}$	200–1500			
$F_c(\text{N}_2) = 0.5$	200–1500			

Comments

(a) Flash photolysis of H₂O vapour in N₂. Detection of OH by laser induced fluorescence. Discussion of earlier more scattered data.

(b) As comment (a). Extrapolation to $k_\infty = 1.5 \cdot 10^{-11} \text{ cm}^3$ molecule^{-1} s^{-1} using $F_c = 0.6$.

(c) Based on results of the reverse dissociation of H₂O₂ and RRKM calculations.

(d) Theoretical construction of fall-off curves for the forward and reverse reaction based on the experimental results from Ref. 1 and consistent with non-thermal H₂O₂ dissociation lifetime measurements.

Preferred Values

$k_0 = [\text{N}_2] \, 8.0 \cdot 10^{-31} \, (T/300)^{-0.76} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over range 250–1400 K

$k_0 = [\text{H}_2\text{O}] \, 4.0 \cdot 10^{-30} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over range 300–400 K

$k_\infty = 1.5 \cdot 10^{-11} \, (T/300)^{-0.37} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over range 200–1500 K

$F_c = 0.5$ for M = N₂ over range 200–1500 K

Reliability

$\Delta \log k_0 = \pm 0.4$ over range 250–1400 K for M = N₂

$\Delta \log k_\infty = \pm 0.5$ over range 200–1500 K

$\Delta F_c = \pm 0.2$ over range 200–1500 K

Comments on Preferred Values

The preferred values are from the analysis in Ref. 3 of theoretical modelling and experimental results from Ref. 1. Since the earlier experimental data scatter considerably, new experiments are required before safe recommendations can be made.

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OH + OH → H₂O + O
→ H₂O₂

OH + HO$_2$ → H$_2$O + O$_2$

Thermodynamic Data

$\Delta H^\circ_{298} = -291 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} = -18.8 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p = 0.517 \, T^{-0.247} \exp(35000/T)$

Rate Coefficient Data

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
≈ 10^{-11}–10^{-12}	1400	Troe (1969)[1]	(a)
2.0·10^{-11}	2130	Friswell and Sutton (1972)[2]	(b)
2.0·10^{-10}	298	Hochanadel, Ghormley, and Ogren (1972)[3]	(c)
6.6·10^{-12}	1050	Day, Thompson, and Dixon-Lewis (1973)[4]	(d)
8.3·10^{-11}	1400–1800	Peeters and Mahnen (1973)[5]	(e)
1.6·10^{-10}	298	DeMore and Tschuikow-Roux (1974)[6]	(f)
< 3.0·10^{-11}	298	Hack, Hoyermann, and Wagner (1975)[7]	(g)
1.4·10^{-11}	900–1100	Dixon–Lewis and Rhodes (1975)[8]	(h)
5.1·10^{-11}	293	Burrows, Harris, and Thrush (1977)[9]	(i)
2.2·10^{-11}	293	Hack, Preuss, and Wagner (1978)[10]	(j)
(2.0–3.0)·10^{-11}	295	Chang and Kaufman (1978)[11]	(k)
(1.2–1.3)·10^{-10}	230–334	DeMore (1979)[12]	(l)
1.0·10^{-10}	298	Burrows *et al.* (1979)[13]	(m)
1.0·10^{-10}	308	Lii *et al.* (1980)[14]	(n)
1.2·10^{-10}	296	Hochanadel, Sworski, and Ogren (1980)[15]	(o)
9.9·10^{-11}	308	Cox, Burrows, and Wallington (1981)[16]	(p)
6.2·10^{-11}	288–348	Burrows, Cox, and Derwent (1981)[17]	(q)
7.5·10^{-11}	298	Sridharan, Qiu, and Kaufman (1981)[18]	(r)
5.8·10^{-11}	298	Thrush and Wilkinson (1981)[19]	(s)
6.4·10^{-11}	299	Keyser (1981)[20]	(t)
≈ 1.1·10^{-10}	298	Braun, Hofzumahaus, and Stuhl (1982)[21]	(u)
1.2·10^{-10}	298	DeMore (1982)[22]	(v)
6.6·10^{-11}	296	Temps and Wagner (1982)[23]	(w)
5.2·10^{-11}	298	Rozenshtein *et al.* (1984,85)[24,25]	(x)
1.7·10^{-11} exp(+416/T)	252–420	Sridharan, Qiu, and Kaufman (1984)[26]	(y)
4.8·10^{-11} exp(+250/T)		Keyser (1988)[27]	(z)
Reviews and Evaluations			
3.5·10^{-11}	298	Baulch *et al.* (1980)[28]	
3.3·10^{-11}	300–2000	Warnatz (1984)[29]	
2.3·10^{-8} T^{-1}	300–1400	Tsang and Hampson (1986)[30]	

Comments

(a) Thermal decomposition of H$_2$O$_2$ in Ar behind reflected shock waves. [H$_2$O$_2$] by UV absorption at 290 nm. Total densities 10^{-5}−2·10^{-4} mol cm^{-3} Ar.

(b) Flat premixed lean H$_2$/O$_2$/N$_2$ flames; [H] measured by Li/LiOH method. k derived under the assumption of partial equilibrium for H + O$_2$ and OH + OH reactions.

(c) Flash photolysis of water vapour at atmospheric pressure. [OH] and [HO$_2$] monitored by absorption measurements. Rate parameter adjusted by numerical simulation of a reaction mechanism.

(d) Computer simulation of burning velocities of rich H$_2$/O$_2$/N$_2$ flames. No great accuracy.

(e) Lean and stoichiometric CH$_4$/O$_2$ flat flames at 40 Torr; molecular beam sampling and mass spectrometric analysis.

(f) Photolysis of O$_2$/H$_2$O mixtures at 184.9 nm until a steady-state was reached. Total pressure 700 Torr.

[O$_3$] monitored by absorption at 253.7 nm. Relative measurements with O$_2$/H$_2$O and O$_2$/H$_2$O/CO mixtures. Given value for k based on k(OH + O$_2$) = 6·10^{-14} cm^3 molecule^{-1} s^{-1} and k(HO$_2$ + HO$_2$) = 3.6·10^{-12} cm^3 molecule^{-1} s^{-1}.

(g) Discharge-flow reactor; [OH] by electron spin resonance. Total pressures around 2 Torr He. Computer modelling of the reaction system.

(h) Flat flame study; evaluation of existing experimental data.

(i) Fast-flow study of OH + H$_2$O$_2$ or H + H$_2$O$_2$ reaction at a few Torr. [OH] and [HO$_2$] monitored by laser magnetic resonance

(j) Discharge-flow reactor. [OH] and [HO$_2$] monitored by laser magnetic resonance. Total pressures around 250 Pa He. Original value 3.0·10^{-11} cm^3 molecule^{-1} s^{-1}, corrected by Keyser[20] due to a new value for k(OH + H$_2$O$_2$)[31,32].

(k) Discharge-flow reactor. Total pressures 2.1–3.7 Torr. [OH] by resonance fluorescence at 309 nm, [O$_3$] by absorption at 253.7 nm. Given range of k derived by computer modelling of a 12 reaction mechanism.

(l) As in (f), but smaller reaction cell and absorption spectrum scanned over the range 180–200 nm to monitor also H_2O_2.

(m) Discharge-flow system [OH] and [HO$_2$] monitored by laser magnetic resonance. Total pressure 2 Torr. Original value $5.1 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1}, corrected by Keyser[20] due to a new value for k(OH + H$_2$O$_2$)[31,32]. Result based on k(OH + H$_2$O$_2$) $= 8 \cdot 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

(n) Pulse-irradiation of H$_2$O/O$_2$/Ar mixtures. Total pressures up to 1200 Torr. Absorption measurements of HO$_2$ (230 nm) and OH (308.7 nm). Computer modelling of a 14 reaction mechanism and parameter fitting to experimental concentrations.

(o) Flash photolysis of H$_2$O in a H$_2$O/O$_2$/He system at atmospheric pressure. [HO$_2$] monitored by absorption at 220 nm. Computer modelling of a 21 reaction mechanism.

(p) Low-frequency square-wave modulated photolysis of O$_3$/H$_2$O mixtures monitoring the steady-state absorption of HO$_2$ at 210 nm. Total pressure 1 atm. Experimental upper limit for k adjusted to a lower value by computer modelling of a 17 reaction mechanism.

(q) Modulated photolysis of O$_3$ / H$_2$O / O$_2$ / N$_2$ or O$_3$ / H$_2$O / O$_2$ / He mixtures at atmospheric pressure. [HO$_2$] monitored by absorption at 210 nm, [OH] by resonance absorption at 308.2 nm. Modelling of a 15 reaction mechanism. The time dependence of [HO$_2$] could not be accurately described throughout a photolysis cycle by a single value of k.

(r) Discharge-flow system. [OH] by laser-induced fluorescence, [H] and [O] by VUV resonance fluorescence; [HO$_2$] measured by rapid conversion to OH with excess NO. Total pressure near 3 Torr.

(s) Discharge-flow tube. [OH] and [HO$_2$] by laser magnetic resonance. Given value of k based on k(HO$_2$ + HO$_2$) $= 1.6 \cdot 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

(t) Discharge-flow system. [OH], [O], and [H] monitored by resonance fluorescence. Total pressure 1 Torr. Computer simulation of 9 reaction mechanism.

(u) VUV flash photolysis of small amounts of H$_2$O diluted in N$_2$ at atmospheric pressure under slow-flow conditions. [OH] by resonance absorption at 308.2 nm. Computer simulation of a 16 reaction mechanism.

(v) Photolysis of H$_2$O at 184.9 nm in He or Ar diluent with trace amounts of O$_2$. Total pressures 75–730 Torr. Steady-state concentration of OH monitored by laser induced fluorescence. Computer simulation of a 7 reaction mechanism with a given value of k for atmospheric pressure. The authors observed a decline of k at lower pressures and support the hypothesis of a pressure-dependent radical – radical association in addition to the abstraction path of the reaction.

(w) Discharge-flow reactor. Total pressures 2.13 – 6.34 mbar He. [OH], [HO$_2$], and [O] by laser magnetic resonance. Computer simulation of a 15 reaction mechanism. The results of Hack *et al.*[10] are shown to be too low because of leaks in their apparatus; the former

measurements were reproduced and the results were now consistent with new data.

(x) Discharge-flow system. Total pressures 8–10 Torr He. [OH] by electron paramagnetic resonance, [HO$_2$] by laser magnetic resonance.

(y) Discharge-flow tube. [OH] monitored by laser induced fluorescence, [HO$_2$] by rapid conversion to OH with excess NO. The authors suggest the formation of a bound H$_2$O$_3$ complex as pressure-dependent reaction component.

(z) Discharge-flow system; [OH] by resonance fluorescence, [HO$_2$] by converting to OH with an excess of NO. NO$_2$ used to remove O and H atoms. Total pressure 1 Torr. The author concludes little or no pressure dependence of k over the range 1–1000 Torr because of the good agreement with measurements at 1 atm.

Preferred Values

$k = 4.8 \cdot 10^{-11} \exp(+250/T)$ cm^3 molecule^{-1} s^{-1} over range 300–2000 K

Reliability
$\Delta \log k = \pm 0.2$ at 300 K rising to ± 0.5 at 2000 K.

Comments on Preferred Values
The value of Keyser[27] is adopted as it is one of the few temperature dependent values and consistent with most of the low temperature material.

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OH + HO₂ → H₂O + O₂

$OH + HO_2 \rightarrow H_2O + O_2$

T/K

2000   1000   500   400   300

$Log(k/cm^3molecule^{-1}s^{-1})$

$10^3T^{-1}/K^{-1}$

EXPERIMENTAL DATA

□	Troe 1969
■	Friswell and Sutton 1972
△	Hochanadel et al 1972
▲	Day et al 1973
○	Peeters and Mahnen 1973
●	DeMore and Tschuikow–Roux 1974
◨	Hack et al 1975
	Dixon–Lewis and Rhodes 1975
◓	Burrows et al 1977
+	Hack et al 1978
×	Chang and Kaufman 1978
——	DeMore 1979
◆	Burrows et al 1979
▣	Lii et al 1980
▽	Hochanadel et al 1980
▼	Cox et al 1981
– – –	Burrows et al 1981
◈	Kurylo et al 1981
◈	Sridharan et al 1981
◇	Thrush and Wilkinson 1981
◪	Keyser 1981
◫	Braun et al 1982
▤	Demore et al 1982
▲	Temps and Wagner 1982
▼	Rozenshtein et al 1985
◇	Sridharan et al 1984
◪	Keyser 1988
⋯⋯	Goodings and Hayhurst 1988
——	This Recommendation 1989

OH + H₂O₂ → HO₂ + H₂O

Thermodynamic Data

$\Delta H^\circ_{298} = -134 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} = 1.23 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p = 63.7 \ T^{-0.61} \exp(16000 \ / \ T)$

Rate Coefficient Data

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	$T[\text{K}]$	Reference	Comments
Rate Coefficient Measurements			
$4.1 \cdot 10^{-13} \ T^{0.5} \exp(-604/T)$	300–458	Greiner (1968)[1]	(a)
$1.2 \cdot 10^{-12}$	298	Gorse and Volman (1972)[2]	(b)
$8.0 \cdot 10^{-12} \exp(-670/T)$	298–670	Hack et al. (1974)[3]	(c)
$6.8 \cdot 10^{-13}$	298	Harris and Pitts (1979)[4]	(d)
$2.5 \cdot 10^{-12} \exp(-126/T)$	245–423	Keyser (1980)[5]	(e)
$3.0 \cdot 10^{-12} \exp(-164/T)$	250–459	Sridharan et al. (1980)[6]	(f)
$1.6 \cdot 10^{-12}$	295	Nelson et al. (1981)[7]	(g)
$3.7 \cdot 10^{-12} \exp(-260/T)$	273–410	Wine et al. (1981)[8]	(h)
$1.7 \cdot 10^{-12}$	296	Temps and Wagner (1982)[9]	(i)
$1.2 \cdot 10^{-12}$	298	Marinelli and Johnston (1982)[10]	(j)
$2.9 \cdot 10^{-12} \exp(-158/T)$	250–370	Kurylo et al. (1982)[11]	(k)
$7.0 \cdot 10^{-20} \ T^{2.5} \exp(+838/T)$	241–413	Lamb et al. (1983)[12]	(l)
Reviews and Evaluations			
$1.7 \cdot 10^{-11} \exp(-902/T)$	300–800	Baulch et al. (1972)[13]	
$7.6 \cdot 10^{-12} \exp(-674/T)$	200–700	Baulch et al. (1980)[14]	
$1.2 \cdot 10^{-11} \exp(-722/T)$	300–1000	Warnatz (1984)[15]	
$2.8 \cdot 10^{-12} \exp(-156/T)$	300–2500	Tsang and Hampson (1986)[16]	

Comments

(a) Flash photolysis of H₂O₂; [OH] by absorption at 306.4 nm. Total pressure 100 Torr Ar.

(b) Photolysis of H₂O₂ at 254 nm in the presence of CO and O₂; mass spectrometric analysis. Total pressures 10–40 Torr. $k/k(\text{OH} + \text{CO}) = 8.13$; given value of k based on $k(\text{OH} + \text{CO}) = 1.5 \cdot 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

(c) Isothermal flow reactor; microwave discharge of H₂/He; OH produced by H + NO₂ reaction. [H] and [OH] monitored by ESR. k probably underestimated; OH is more rapidly regenerated by HO₂ + NO → OH + NO₂[6].

(d) VUV flash photolysis of mixtures of H₂O₂ and H₂O; [OH] monitored by resonance fluorescence near 306 nm. Result is too low due to the formation of H by H₂O₂ photolysis and the fast back reaction H + HO₂ → 2 OH[6].

(e) Flow tube; microwave discharge of H₂/He and H + NO₂ reaction; [OH] by resonance fluorescence near 308 nm. No pressure dependence between 1 and 4 Torr.

(f) Flow tube; microwave discharge of H₂ or F₂/He mixtures. [OH] monitored by laser induced fluorescence at 308.6 nm, [H] and [O] by resonance fluorescence at 121.6 nm or 130.2 nm, [H₂O₂] by absorption measurements at 213.9 nm.

(g) Laser flash photolysis of HNO₃ at 249 nm under slow flow conditions. [OH] monitored by resonance fluorescence, [H₂O₂] by absorption at 200 nm. Total pressure 10 Torr Ar.

(h) Pulsed laser photolysis of H₂O₂ at 266 nm. [OH] monitored by resonance fluorescence, [H₂O₂] by absorption at 228.8 nm. Total pressure 100 Torr He or 40 Torr SF₆.

(i) Isothermal flow reactor; microwave discharge of F₂/He. [OH] and [HO₂] by laser magnetic resonance. Total pressures 2–6 mbar He.

(j) Laser flash photolysis of H₂O₂ at 248 nm. [OH] by resonance fluorescence, [H₂O₂] by absorption at 200 nm. Total pressure 10 Torr Ar.

(k) Flash photolysis of H₂O₂/H₂O/Ar mixtures over a wide pressure range. [H₂O₂] by absorption at 213.9 nm, [OH] by resonance fluorescence.

(l) Flash photolysis of H₂O₂. [OH] by resonance fluorescence near 308 nm, [H₂O₂] by absorption measurements in the 205–220 nm range and by Fourier transform infrared spectroscopy. Total pressure 760 Torr He.

Preferred Values

$k = 1.3 \cdot 10^{-11} \exp(-670/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over range 300–1000 K

Reliability

$\Delta \log k = \pm 0.2$ over total range.

Comments on Preferred Values

The preferred value is based on the activation energy recommended by Baulch et al.[14]; the preexponential factor has been increased to represent new experimental data.

For clarity, rate data measured before 1972 are included in the Arrhenius plot (see Baulch *et al.*[13] for reference).

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[16]W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data **15**, 1087 (1986).

OH + H$_2$O$_2$ → HO$_2$ + H$_2$O

EXPERIMENTAL DATA

□	Gorse and Volman 1972
——	Hack et al 1974
△	Meagher and Heicklen 1974
▲	Hack et al 1975
○	Vardanyan et al 1974
●	Harris and Pitts 1979
◨	Baldwin and Walker 1979
▲	Keyser 1980
◓	Sridharan et al 1980
+	Hack et al 1980
×	Temps and Wagner 1982
◇	Kaufman 1981
◆	Wine et al 1981
▣	Sridharan et al 1981
▽	Keyser et al 1981
▼	Marinelli and Johnston 1982
▼	Nelson et al 1981
◈	Kurylo et al 1982
◈	Molina et al 1982
– – –	Lamb et al 1983
⊢——⊣	Baldwin et al 1970
◨	Frost and Oldenberg 1936
▤	Forst and Gigeure 1958
▲	Baldwin and Mayor 1960
▼	Baldwin and Bratten 1962
◈	Foner and Hudson 1962
◣	Baldwin et al 1965
◓	Greiner 1966
⊞	Hoare 1966
◪	Baldwin et al 1967
⊞	Greiner 1968
——	This Recommendation 1989

$$\text{OH} + \text{NH} \rightarrow \text{NO} + \text{H}_2 \qquad (1)$$
$$\rightarrow \text{N} + \text{H}_2\text{O} \qquad (2)$$

Thermodynamic Data (See Comments on Preferred Values)

ΔH°_{298} (1) = -305 kJ mol^{-1}

ΔS°_{298} (1) = -23.5 J K^{-1}mol^{-1}

$K_p(1)$ = $1.52 \cdot 10^{-2} T^{-0.193}$ exp($+36800/T$)

ΔH°_{298} (2) = -164 kJ mol^{-1}

ΔS°_{298} (2) = -22.8 J K^{-1}mol^{-1}

$K_p(2)$ = $5.61 \cdot 10^{-2} T^{-0.018}$ exp($+19890/T$)

Rate Coefficient Data ($k = k_1 + k_2$)

k[cm^3 molecule^{-1}s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$8.3 \cdot 10^{11}$	300	Hack and Kurzke (1985)[1]	(a)

Comments

(a) Discharge-flow system; NH$_2$ generated by the sequence F + NH$_3$ → HF + NH$_2$, O$_2$ added downstream. [NH$_2$], [NH], [OH] monitored by laser induced fluorescence. Measured concentration profiles simulated.

Preferred Values

k = $8.0 \cdot 10^{-11}$cm^3 molecule^{-1}s^{-1}over range 300–1000 K

Reliability

$\Delta \log k$ = $\pm$ 0.5 over range 300–1000 K

Comments on Preferred Values

The only measurement is indirect and although we accept it as our recommended value we assign large error limit. The reaction is likely to have a low activation energy and at high temperatures (2000 K) the rate constant is likely to be no more than an order of magnitude larger. However, the branching ratio may vary considerably with temperature. The thermodynamic data should be used with caution. There are significant uncertainties associated with the data on NH.

Reference

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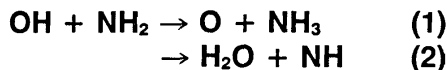
$$\text{OH} + \text{NH}_2 \rightarrow \text{O} + \text{NH}_3 \qquad (1)$$
$$\rightarrow \text{H}_2\text{O} + \text{NH} \qquad (2)$$

Thermodynamic Data (See Comments on Preferred Values)

ΔH°_{298} (1) = -26.1 kJ mol^{-1}

ΔS°_{298} (1) = -24.6 J K^{-1}mol^{-1}

$K_p(1)$ = $2.09 \cdot 10^{-3} T^{0.405}$ exp($+3420/T$)

ΔH°_{298} (2) = -115 kJ mol^{-1}

ΔS°_{298} (2) = -8.3 J K^{-1}mol^{-1}

$K_p(2)$ = $0.591 \ T^{-0.072}$ exp($+13800/T$)

Rate Coefficient Data

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Reviews and Evaluations			
k_1 = $1 \cdot 10^{-13}$ exp($-2500/T$)	300–1000	Baulch *et al*. (1973)[1]	(a)
k_1 = $1 \cdot 10^{-13}$	300–1000	Hampson (1980)[2]	(b)
	–	CODATA (1982)[3]	(c)

Comments

(a) Calculated from k_{-1} and a value for the equilibrium constant now known to be incorrect.

(b) Calculated from Baulch *et al*.'s k_{-1} and revised equilibrium data.

(c) Review of low temperature data; no recommendation.

Preferred Values

k_1 = $3.3 \cdot 10^{-14} \ T^{0.405}$ exp($-250/T$) cm^3 molecule^{-1} s^{-1} over range 500–2500 K

Reliability

$\Delta \log k_1$ = $\pm$ 0.5 over range 500–2500 K

Comments on Preferred Values

There are no experimental data for k or the branching ratio.

However, the reverse of reaction (1) has been extensively studied. We have evaluated the available data (Refs. 4–18) and obtain $k_{-1} = 1.6 \cdot 10^{-11} \exp(-3670/T)$ cm^3 molecule^{-1}s^{-1} over the range 500–2500 K. Combining this with the thermodynamic data gives the recommended value for k_1. There is no information on the relative importance of the two possible channels. There are significant uncertainties associated with the thermodynamic data on NH.

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OH + CO → H + CO₂
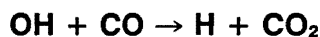
Thermodynamic Data

$\Delta H^{\circ}_{298} = -104 \text{ kJ mol}^{-1}$

$\Delta S^{\circ}_{298} = -52.8 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p = 4.24 \cdot 10^{-7} T^{1.18} \exp(13000/T)$

Rate Coefficient Data

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$2.7 \cdot 10^{-13}$	296	Cox, Derwent, and Holt (1976)[1]	(a)
$1.5 \cdot 10^{-13}$	299	Atkinson, Perry, and Pitts (1976,1977)[2,3]	(b)
$3.0 \cdot 10^{-13}$	298	Chan *et al.* (1977)[4]	(c)
$1.6 \cdot 10^{-13}$	773	Atri *et al.* (1977)[5]	(d)
$2.0 \cdot 10^{-13}$	296	Overend and Paraskevopoulos (1977)[6]	(e)
$2.7 \cdot 10^{-13}$	304	Butler, Solomon, and Snelson (1978)[7]	(f)
$\approx 1.5 \cdot 10^{-13}$	300	Biermann, Zetzsch, and Stuhl (1978)[8]	(g)
$2.2 \cdot 10^{-13} \exp(-88/T)$	293–430	Clyne and Holt (1979)[9]	(h)
$1.5 \cdot 10^{-13}$	300	Husain, Plane, and Slater (1981)[10]	(i)
$9.1 \cdot 10^{-14} \exp\{(1.22 \cdot 10^{-3} T)\}$	250–1040	Ravishankara and Thompson (1983)[11]	(j)
$2.1 \cdot 10^{-13}$	298	Paraskevopoulos and Irwin (1984)[12]	(k)
$1.5 \cdot 10^{-13}$	298	DeMore (1984)[13]	(l)
$2.3 \cdot 10^{-13}$	298	Hofzumahaus and Stuhl (1984)[14]	(m)
$2.4 \cdot 10^{-13}$	299	Niki *et al.* (1984)[15]	(n)
$1.5 \cdot 10^{-13}$	298	Smith and Williams (1985)[16]	(o)
Reviews and Evaluations			
$2.5 \cdot 10^{-17} T^{1.3} \exp(+385/T)$	250–2000	Baulch *et al.* (1976)[17]	
$7.3 \cdot 10^{-18} T^{1.5} \exp(+373/T)$	300–2000	Warnatz (1979,84)[18]	
$1.2 \cdot 10^{-13} \exp(9.2 \cdot 10^{-4} T)$	300–2000	Zellner (1979)[19]	
$1.5 \cdot 10^{-13}$	200–300	Baulch *et al.* (1980)[20]	
$1.2 \cdot 10^{-13} \exp(9.2 \cdot 10^{-4} T)$	300–2500	Tsang and Hampson (1986)[21]	

Comments

(a) Flow tube: photolysis of gaseous nitrous acid (HONO) at atmospheric pressure. [HONO], [NO], and [NO$_2$] by the ozone-NO chemiluminescence technique. k measured relative to k(OH + HONO) $\rightarrow$ H$_2$O + NO$_2$ and based on k(OH + H$_2$ $\rightarrow$ H$_2$O + H) = 7.0·10^{-15} cm^3 molecule^{-1}s^{-1}.

(b) Pulsed vacuum ultraviolet photolysis of H$_2$O (λ > 105 nm); slow flow conditions. [OH] by time-resolved resonance fluorescence at 306.4 nm. No effect of total pressure in the range 25–654 Torr Ar; when SF$_6$ is used as diluent gas, k rises from 1.5·10^{-13} cm^3 molecule^{-1} s^{-1} at 25 Torr to 3.4·10^{-13} cm^3 molecule^{-1}s^{-1} at 604 Torr.

(c) Photolysis of dilute mixtures of HONO, CO, i-C$_4$H$_{10}$, and NO$_x$ in synthetic air; Fourier transform infrared spectroscopy. k measured relative to k(OH + i-C$_4$H$_{10}$). Given value of k for p = 700 Torr, reducing to 1.4·10^{-13} cm^3 molecule^{-1}s^{-1} at 100 Torr.

(d) Small amounts of CO added to slowly reacting H$_2$/O$_2$/N$_2$ mixtures; relative H$_2$O and CO$_2$ yields by gas chromatography. Numerical integration of 19 reaction mechanism.
k(CO + OH)/k(OH + H$_2$) = 0.235; based on k(OH + H$_2$) = 6.8·10^{-13} cm^3 molecule^{-1} s^{-1}. Total pressure 500 Torr.

(e) VUV photolysis (λ < 160 nm) of H$_2$O in the presence of CO; [OH] by time-resolved resonance absorption. Given value of k for p = 50 Torr He. k = 3.2·10^{-13} cm^3 molecule^{-1}s^{-1} for 200 and 350 Torr SF$_6$.

(f) Photolysis of H$_2$O$_2$ in O$_2$/N$_2$/CO or O$_2$/N$_2$/CO/i-butane mixtures; [CO] by gas chromatography. Rate of Ref. reaction k(OH + i-C$_4$H$_{10}$) = 1.6·10^{-12} cm^3 molecule^{-1} s^{-1} at 100 Torr based on a low pressure value of k(CO + OH) = 1.5·10^{-13} cm^3 molecule^{-1}s^{-1} and assumed to be pressure-independent. Given value of k is the high-pressure limit for p $\geq$ 300 Torr; depends also on the rate of the H$_2$O$_2$ + OH reaction (set to 8.0·10^{-13} cm^3 molecule^{-1} s^{-1}).

(g) Pulsed VUV photolysis of H$_2$O in the presence of CO and N$_2$ or He; [OH] by time-resolved resonance absorption near 308 nm. Total pressures 25–750 Torr. No pressure effect of N$_2$ at pressures below 1 atm, but a strong increasing effect of O$_2$ at high N$_2$ pressures; at high O$_2$ concentrations constant value of k; at 0.28 Torr O$_2$ linear dependence of k on N$_2$ pressure. Observations explained by a complex reaction mechanism involving formation of an excited HOCO adduct decomposing to H + CO$_2$ or reacting after stabilization with O$_2$ to give HO$_2$ + CO$_2$. The authors recommend a linear extrapolation from 1.4·10^{-13} cm^3 molecule^{-1}s^{-1} near 0 Torr to 2.8·10^{-13} cm^3 molecule^{-1} s^{-1} at 760 Torr.

(h) Flow system; microwave discharge of H$_2$, OH from H + NO$_2$; [OH] by resonance fluorescence near 307 nm. Total pressure 200–260 Pa.

(i) VUV photolysis of water vapour (λ > 105 nm); [OH] by time-resolved resonance fluorescence at 307 nm. Slow flow conditions: total pressure 3.2 kPa He.

(j) Flash photolysis of H$_2$O (λ > 165 nm); [OH] by time-resolved resonance fluorescence. Slow flow conditions; total pressure 100 Torr Ar.

(k) VUV flash photolysis of H$_2$O; [OH] by time-resolved resonance absorption at 308.2 nm. Given value of k for p = 600 Torr N$_2$, reducing to k = 1.4·10^{-13} cm^3 molecule^{-1} s^{-1} at 20 Torr. Addition of small amounts of O$_2$ (0.1–0.2 Torr) resulted in non-exponential and slower decays of [OH]. Relative efficiencies in the deactivation of HOHO*: H$_2$O : SF$_6$: CF$_4$: N$_2$: He = 1.0 : 0.5 : 0.3 : 0.1 : 0.02.

(l) Photolysis of H$_2$O/CO mixtures at 184.9 nm: [OH] by laser-induced fluorescence near 309 nm. Slow flow conditions. k given for total pressures of 200–730 Torr Ar; similar result at 200 Torr N$_2$. With SF$_6$ as diluent k increases reaching a factor of 2 at 730 Torr SF$_6$. Within the experimental accuracies no dependence on Ar pressure, for N$_2$ enhancement of 30–50%; results according to the normal third-body efficiencies of these gases. No influence of added O$_2$ on the pressure enhancement. Recommendation for pressure dependence: k = 1.5·10^{-13} (1 + 0.4 p[atm]) cm^3 molecule^{-1} s^{-1}.

(m) VUV photolysis of H$_2$O in the presence of N$_2$; [OH] by resonance absorption. Total pressure 980–1000 mbar. Reinterpretation of the data of Biermann, Zetzsch, and Stuhl[8]; effects of O$_2$ addition explained by radical – radical reactions not considered there.

(n) Photolysis of mixtures containing RONO (R = CH$_3$, C$_2$H$_5$), NO, isotopic CO, and C$_2$H$_4$; Fourier transform infrared spectroscopy. Total pressure 700 Torr purified air. k(OH + C$_2$H$_4$)/k(OH + CO) = 35.95 and 36.30 for ^{13}C^{16}O and ^{12}C^{18}O, respectively. k(OH + CO) based on k(OH + C$_2$H$_4$) = 8.5·10^{-12} cm^3 molecule^{-1} s^{-1}.

(o) Pulsed photolysis of H$_2$O or HNO$_3$ (λ > 185 nm); [OH] by laser induced fluorescence. Total pressure 18 Torr Ar.

Preferred Values

k = 1.05·10^{-17} $T^{1.5}$ exp(+ 250/T) cm^3 molecule^{-1} s^{-1} over range 300–2000 K

Reliability

Δlog k = ± 0.2 at 300 K rising to ± 0.5 at 2000 K

Comments on Preferred Values

The large scatter of the high temperature measurements does not allow exact assignment of a rate coefficient. Thus, a relatively high value has been chosen compatible with flame simulations which are very sensitive to the rate of this reaction[22].

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OH + CO → H + CO₂

$$\text{OH} + \text{CO} \rightarrow \text{H} + \text{CO}_2$$

T/K

EXPERIMENTAL DATA

▢	Cox et al 1976
■	Atkinson et al 1976
△	Atri et al 1977
▲	Overend and Paraskevopoulos 1977
○	Butler et al 1978
●	Biermann et al 1978
▣	Clyne and Holt 1979
△	Husain et al 1981
◑	Ravishankara and Thompson 1983
+	Paraskevopolous and Irwin 1984
×	DeMore 1984
◇	Hofzumahaus and Stuhl 1984
◆	Niki et al 1984
▤	Smith and Williams 1985
▽	Chan et al 1977
▼	Brabbs et al 1971
——	Kijewski and Troe 1971
◈	Mulcahy and Smith 1971
├─┤	Singh and Sawyer 1971
◇	Dixon-Lewis 1972
◪	Stuhl and Niki 1972
— — —	Bonne and Wilson 1972
······	Gardiner et al 1973
▲	Peeters and Manhen 1973
▽	Smith and Zellner 1973
◈	Westenberg and DeHaas 1973
◪	Davies et al 1974
◑	Howard and Evenson 1974
⊞	Trainor and Von Rosenberg 1975
◪	Vandooren et al 1975
⊞	Hynes et al 1986
——	This Recommendation 1989

$$\text{OH} + \text{CH}_3 \rightarrow \text{CH}_3\text{OH} \qquad (1)$$
$$\rightarrow \text{H} + \text{CH}_2\text{OH} \qquad (2)$$
$$\rightarrow \text{H} + \text{CH}_3\text{O} \qquad (3)$$
$$\rightarrow \text{H}_2\text{O} + {}^1\text{CH}_2 \qquad (4)$$

Thermodynamic Data

ΔH°_{298} (1) = -386 kJ mol^{-1}

ΔS°_{298} (1) = -138 J K^{-1}mol^{-1}

K_p(1) = $1.26 \cdot 10^{-5}$ $T^{-0.289}$ exp($+46700/T$)

ΔH°_{298} (3) = 49.6 kJ mol^{-1}

ΔS°_{298} (3) = -34.6 J K^{-1}mol^{-1}

K_p(3) = $3.73 \cdot 10^{-5}$ $T^{0.778}$ exp($- 5470/T$)

ΔH°_{298} (2) = 16.1 kJ mol^{-1}

ΔS°_{298} (2) = -16.7 J K^{-1}mol^{-1}

K_p(2) = $1.50 \cdot 10^{-4}$ $T^{0.974}$ exp($-1570/T$)

ΔH°_{298} (4) = -1.8 kJ mol^{-1}

ΔS°_{298} (4) = -0.21 J K^{-1}mol^{-1}

K_p(4) = 26.7 $T^{-0.481}$ exp($+ 46.7$ /T)

Rate Coefficient Data ($k = k_1 + k_2 + k_3 + k_4$)

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$k_3 = 3.3 \cdot 10^{-8}$ exp($-13800/T$)	1700–2300	Bhaskaran, Frank, and Just (1979)[1]	(a)
$9.3 \cdot 10^{-11}$	296	Sworski, Hochanadel, and Ogren (1980)[2]	(b)
$k_3 = 1.5 \cdot 10^{-9}$ exp($-7800/T$)	1850–2500	Roth and Just (1984)[3]	(c)
Reviews and Evaluations			
$k_1 + k_2 = 9 \cdot 10^{-11}$	300–2500	Tsang and Hampson (1986)[4]	(d)

Comments

(a) Shock-tube decomposition of C_2H_6/O_2 mixtures with direct detection of H and O by atomic resonance absorption spectrometry. k_3 derived from a computer simulation of the experimental [H] and [O] profiles. It was suggested that channel (3) proceeds via the sequence OH + CH$_3$ → H + CH$_3$O and CH$_3$O → CH$_2$O + H, i.e. overall reaction OH + CH$_3$ → 2 H + CH$_2$O.

(b) Flash photolysis of H$_2$O in presence of CH$_4$ and N$_2$ or H$_2$. [CH$_3$] monitored by absorption at 216 nm. Rate coefficient obtained from a computer simulation of [CH$_3$] profiles, based on a mechanism of 11 elementary reactions.

(c) Similar study to that of Bhaskaran *et al.*[1] (see comment (a)) with CH$_4$/O$_2$ mixtures.

(d) The reaction channels (1), (2), and (3) were assumed and it was suggested that (2) would be more likely than (3) on thermochemical grounds. Hence $k_1 + k_2$ is an estimated high-pressure limiting value. RRKM calculations were carried out to obtain a pressure dependence of $k_1 + k_2$. Dean and Westmoreland[5] have recently made theoretical calculations of the energised complex, CH$_3$OH*, by unimolecular reaction rate theory, in which they consider six possible reaction channels.

Preferred Values

$k = 6 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1} over range 300–2000 K

Reliability

$\Delta\log k = \pm 0.7$ over range 300–2000 K

Comments on Preferred Values

The rate coefficients obtained by Bhaskaran *et al.*[1] and by Roth and Just[3] are in excellent agreement at 2000 K, i.e. $k_3 = 3.0 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1} and, within the experimental errors, equal to that of the low temperature study of Sworski *et al.*[2], $k = 9.3 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1}. Accordingly, we have selected a temperature independent overall rate coefficient of $k = 6 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

So far there has been no direct evidence concerning the product channels of this reaction. Channel (3) is the pathway suggested in the shock tube studies[1,3]. A recent report on the ^{1}CH$_2$ + H$_2$O reaction[6] has confirmed that the major products are CH$_3$ + OH and consequently channel (4) needs to be considered here. More experimental work is required on this aspect of the reaction together with direct measurements of k and any branching ratios as a function of temperature.

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OH + CH₄ → H₂O + CH₃

$$OH + CH_4 \rightarrow H_2O + CH_3$$
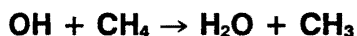
Thermodynamic Data

$\Delta H^\circ_{298} = -60.2 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} = 13.1 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p = 20.5 \ T^{-0.141} \exp(+7050/T)$

Rate Coefficient Data

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	Temperature [K]	Reference	Comments
Rate Coefficient Measurements			
$7.6 \cdot 10^{-15}$	296	Sworski *et al.* (1980)[1]	(a)
$1.32 \cdot 10^{-17} \ T^{1.32} \exp(-1355/T)$	298–1020	Tully and Ravishankara (1980)[2]	(b)
$7.7 \cdot 10^{-15}$	300	Husain *et al.* (1981)[3]	(c)
$5.6 \cdot 10^{-12} \exp(-1970/T)$	269–473	Jeong and Kaufman (1981)[4]	(d)
$1.28 \cdot 10^{-24} \ T^{4.32} \exp(-455/T)$	296–473	Jeong and Kaufman (1984)[5]	(d,e)
$1.5 \cdot 10^{-18} \ T^{2.3} \exp(-1370/T)$	300–2000	Cohen (1982)[6]	(f)
$1.3 \cdot 10^{-12}$	1030	Fairchild *et al.* (1982)[7]	(g)
$2.57 \cdot 10^{-17} \ T^{1.83} \exp(-1396/T)$	298–1512	Madronich and Felder (1984)[8]	(h)
$3.7 \cdot 10^{-11} \exp(-2550/T)$	340–1250	Jonah *et al.* (1984)[9]	(i)
$3.0 \cdot 10^{-12}$	1220	Cohen (1984)[10]	(j)
$(1.25, 2.25, 1.55) \cdot 10^{-12}$	(830, 870, 930)	Smith *et al.* (1985)[11]	(a)
$(2.1, 1.33, 3.6) \cdot 10^{-12}$	(975,1030,1120)		
$(1.7,2.35,3.3) \cdot 10^{-12}$	(1150,1176,1200)		
$(2.9,4.4,4.2) \cdot 10^{-12}$	(1240,1400,1412)		
Reviews and Evaluations			
$2.35 \cdot 10^{-12} \exp(-1710/T)$	240–373	Hampson (1980)[12]	(k)
$2.35 \cdot 10^{-12} \exp(-1710/T)$	200–300	CODATA (1982)[13]	(l)
$3.2 \cdot 10^{-19} \ T^{2.4} \exp(-1060/T)$	240–3000	Cohen and Westberg (1983)[14]	(m)
$2.65 \cdot 10^{-18} \ T^{2.1} \exp(-1240/T)$	300–2200	Warnatz (1984)[15]	(n)
$2.5 \cdot 10^{-18} \ T^{2.13} \exp(-1230/T)$	230–2000	Baulch *et al.* (1986)[16]	(o)
$3.2 \cdot 10^{-19} \ T^{2.4} \exp(-1060/T)$	240–2000	Tsang and Hampson (1986)[17]	(p)

Comments

(a) Flash photolysis of N₂/CH₄/H₂O mixtures. [CH₃] monitored by absorption at 216 nm.

(b) Flash photolysis of Ar/CH₄/H₂O mixtures. [OH] monitored by resonance fluorescence. Static system, first-order decay of [OH].

(c) Flash photolysis of He/CH₄/H₂O mixtures. [OH] monitored by resonance fluorescence. Flow system, first-order decay of [OH].

(d) Discharge flow system. [OH] monitored by resonance fluorescence. Pseudo-first-order conditions with [RH] > >[OH].

(e) Correction to fitting procedures applied, same kinetic data as for comment (d).

(f) Theoretical expression derived from transition state theory and calibrated using experimental data.

(g) Pulsed infrared CO₂ laser production of OH from H₂O₂; [OH] monitored by laser induced fluorescence.

(h) Flash photolysis of Ar/CH₄/H₂O mixtures; [OH] monitored by resonance fluorescence; first-order decay of [OH].

(i) Microwave discharge of He/CH₄/H₂O mixtures. Pseudo-first-order kinetics; [OH] monitored by resonance absorbance.

(j) Shock tube measurement, reported in comment on results of Ref. 8.

(k) Recommended value, based on low temperature data.

(l) Evaluation specifically for atmospheric modelling.

(m) Evaluation based on experimental data between 240 and 1600 K; favour the data of Tully and Ravishankara's[2] in making the recommendation.

(n) Recommends Tully and Ravishankara's expression without comment.

(o) Based on experimental data considered reliable, some weighting of data.

(p) Accept the recommendation given by Cohen and Westberg[14].

Preferred Values

$k = 2.57 \cdot 10^{-17} \ T^{1.83} \exp(-1396/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over range 240–2500 K

Reliability

$\Delta \log k = \pm 0.07$ between 240 and 1200 K rising to ± 0.15 at 2500 K

Comments on Preferred Values

The rate constant is now known with considerable reliability and precision between 240 and 1500 K with excellent agreement between a large number of techniques. The early data of Fenimore and Jones[18] has been re-interpreted using $k(\text{OH} + \text{CO})$ given by Baulch *et al.*[19]. The

preferred value of k is that obtained experimentally by Madronich and Felder[8] which predicts very precisely the data obtained between 240 and 2000 K. It is not clear why the data of Zellner and Steinert[20], and of Jonah, Mulac, and Zeglinski[9] lie consistently above the preferred values. Details of pre-1980 data are given in Ref. 16.

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OH + CH₄ → H₂O + CH₃

$$OH + CH_4 \rightarrow H_2O + CH_3$$

	EXPERIMENTAL DATA
☐	Sworski et al 1980
———	Tully and Ravishankara 1980
△	Husain et al 1981
— — — —	Jeong and Kaufman 1981
· · ·	Jeong et al 1984
●	Fairchild et al 1982
— · — · · —	Cohen 1982
— — · —	Madronich and Felder 1984
— · — · —	Jonah et al 1984
|	Cohen 1984
×	Smith et al 1985
◇	Baldwin et al 1970
◆	Greiner 1970
— · — · —	Baker et al 1971
▽	Simonaitis et al 1971
— · · — · —	Cardeiro 1973
▼	Davies et al 1973
◈	Peeters (and Manhen) 1974
◆	Davies et al 1974
◇	Margitan et al 1974
— — · — — ·	Benson 1975
◧	Gordon and Mulac 1975
◲	Hucknell et al 1975
▲	Overend et al 1975
— — · — · · —	Steinert and Zellner 1975
◆	Bradley et al 1976
◪	Cox et al (two works) 1976
◓	Howard and Evenson 1976
⊞	Zellner and Steinert 1976
◩	Ernst et al 1978
———	This Recommendation 1989

OH + CHO → CO + H₂O

Thermodynamic Data
$\Delta H^\circ_{298} = -435$ kJ mol^{-1}
$\Delta S^\circ_{298} = -21.9$ J K^{-1}mol^{-1}
$K_p = 1.29\ T^{-0.425}\ \exp(52200/T)$

Rate Coefficient Data

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$5.0 \cdot 10^{-11}$	1000–1700	Browne *et al*. (1969)[1]	(a)
$1.7 \cdot 10^{-10}$	1700–2500	Bowman (1970)[2]	(b)
$1.8 \cdot 10^{-10}$	296	Temps and Wagner (1984)[3]	(c)
Reviews and Evaluations			
$8.3 \cdot 10^{-11}$	1000–2500	Warnatz (1984)[4]	
$\approx 5.0 \cdot 10^{-11}$	300–2500	Tsang and Hampson (1986)[5]	

Comments

(a) Modelling study of rich and lean acetylene flames at low pressures. Species profiles by gas chromatography, [OH], [CH], and [C₂] by absorption measurements.

(b) Oxidation of methane and ethane in Ar behind incident or reflected shock waves; reaction monitored by infrared emission of CO₂, CO, and H₂O. Numerical modelling of 14 (11) reaction mechanism for CH₄ (C₂H₆) reaction. Results only slightly sensitive to variations in k.

(c) Discharge-flow reactor; [OH] and [CHO] from far infrared laser magnetic resonance spectroscopy. Total pressure $\approx$ 1.5 mbar He.

Preferred Values

$k = 1.7 \cdot 10^{-10}$ cm^3 molecule^{-1} s^{-1} over range 300–2500 K

Reliability
$\Delta\log k = \pm\ 0.3$ over range 300–2500 K

Comments on Preferred Values

The rate coefficient for this reaction is expected to have only a very small temperature coefficient. This is supported by the high values of k measured at 298 K and the few existing higher temperature measurements. The preferred values are based on all of the exisiting data[1,2,3].

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OH + HCHO → CHO + H$_2$O
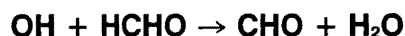
Thermodynamic Data

$\Delta H^\circ_{298} = -121$ kJ mol^{-1}

$\Delta S^\circ_{298} = 11.0$ J K^{-1}mol^{-1}

$K_p = 42.9\ T^{-0.318} \exp(+14400/T)$

Rate Coefficient Data

k [cm^3 molecule^{-1} s^{-1}]	T [K]	Reference	Comments
Rate Coefficient Measurements			
$3.8\cdot10^{-11}$	1600	Peeters and Mahnen (1973)[1]	(a)
$1.7\cdot10^{-11}$	485	Vandooren and	
$2.2\cdot10^{-11}$	570	Van Tiggelen (1977)[2]	(b)
$1.25\cdot10^{-11} \exp(-90/T)$	299–426	Atkinson and Pitts (1978)[3]	(c)
$1.25\cdot10^{-11} \exp(-84/T)$	1600–3000	Dean *et al.* (1980)[4]	(d)
$1.05\cdot10^{-11}$	228–363	Stief *et al.* (1980)[5]	(e)
$8.40\cdot10^{-12}$	299	Niki *et al.* (1984)[6]	(f)
$8.40\cdot10^{-12}$	299	Temps and Wagner (1984)[7]	(g)
$1.66\cdot10^{-11} \exp(-170/T)$	292–597	Zabarnick *et al.* (1988)[8]	(h)
Reviews and Evaluations			
$1.0\cdot10^{-11}$	200–425	Hampson (1980)[9]	(i)
$5.0\cdot10^{-11} \exp(-600/T)$	300–2500	Warnatz (1984)[10]	(j)
$1.1\cdot10^{-11}$	200–425	CODATA (1984)[11]	(k)
$1.0\cdot10^{-11}$	200–300	NASA (1985)[12]	(k)
$9.0\cdot10^{-12}$	228–426	Atkinson (1986)[13]	(l)
$5.7\cdot10^{-15}\ T^{1.18} \exp(+225/T)$	298–1600	Tsang and Hampson (1986)[14]	(m)

Comments

(a) CH$_4$/O$_2$ flames–mass spectrometric analysis.

(b) C$_2$H$_2$/O$_2$ flames–mass spectrometric analysis: k based on H$_2$O formation rate.

(c) Pulsed vacuum UV flash photolysis; OH detected by time resolved resonance fluorescence.

(d) HCHO oxidation studied using shock-tube–infrared emission spectroscopy. Computer fitting using 4 variable rate constants showed that k values from low temperature studies describe well the high temperature results. Not a true determination of k.

(e) Flash photolysis; resonance fluorescence detection of OH.

(f) FTIR study of products of photo-oxidation of RONO (R = CH$_3$ and C$_2$H$_5$) and ^{13}C labelled formaldehyde; k relative to
k(OH + C$_2$H$_4$) = $8.48\cdot10^{-12}$ cm^3 molecule^{-1} s^{-1}:
k(OH + HCHO)/k(OH + C$_2$H$_4$) = 0.99.

(g) Room temperature study using discharge flow; laser magnetic resonance detection of OH.

(h) Laser photolysis–laser induced fluorescence of OH. First order kinetics. Transition state theory used to extrapolate to combustion temperatures which gives
k = $1.2\cdot10^{-18}\ T^{2.46} \exp(+470/T)$ cm^3 molecule^{-1} s^{-1} over the range.

(i) Averages the results of Atkinson and Pitts[3] and Stief *et al.*[5].

(j) Uses high temperature data of Peeters and Mahnen[1], Vandooren and Van Tiggelen[2], together with the low temperature data cited in this data sheet, except that of Stief *et al.*[5].

(k) Based on results of Atkinson and Pitts[3] and Stief *et al.*[5].

(l) Based on Atkinson and Pitts[3], Stief *et al.*[5], Niki *et al.*[6], and Temps and Wagner[7].

(m) Uses data from Atkinson and Pitts[3], Stief *et al.*[5], and the high temperature data of Peeters[1] and Vandooren[2].

Preferred Values

$k = 5.7\cdot10^{-15}\ T^{1.18} \exp(+225/T)$ cm^3 molecule^{-1} s^{-1} over range 300–3000 K

Reliability

$\Delta\log k = \pm 0.7$ at 3000 K reducing to ± 0.1 at 300 K

Comments on Preferred Values

The low and intermediate temperature direct studies (200–600 K) are all in good agreement. The high temperature values of Dean *et al.*[4] and Peeters and Mahnen[1], and the intermediate temperature data of Vandooren and Van Tiggelen[2] and Hoare[15] are higher than expected by simple Arrhenius extrapolation. However, the earlier work is considered less reliable due to the complex systems used and the dependence of the derived k values on other rate constants in the models. We consider that the available data is best fitted by the expression of Tsang and Hampson[14], which we recommend here.

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OH + HCHO → CHO + H₂O

$$\text{OH} + \text{CN} \rightarrow \text{O} + \text{HCN} \quad (1)$$
$$\rightarrow \text{NCO} + \text{H} \quad (2)$$
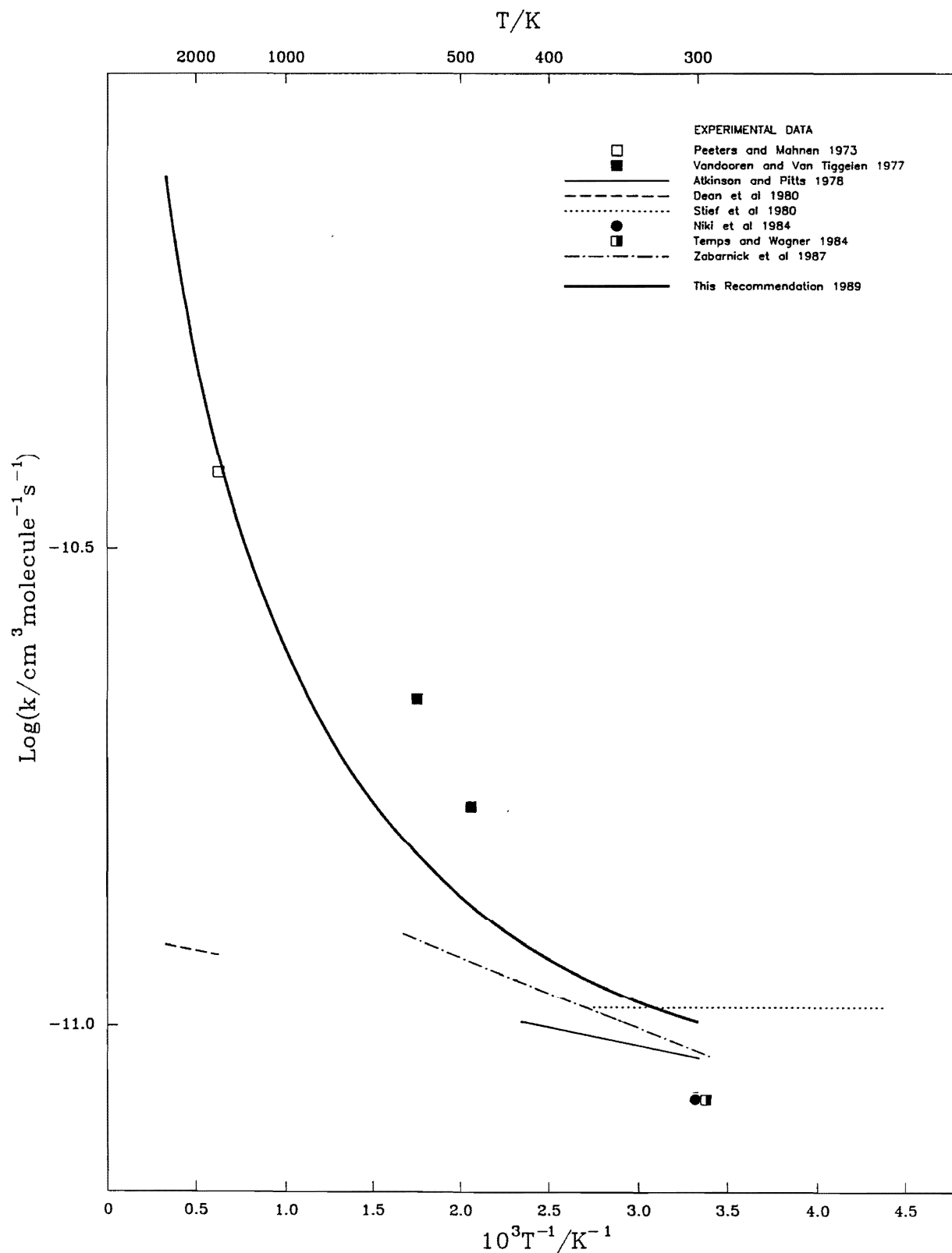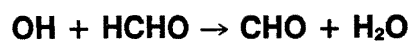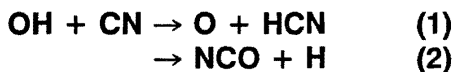
Thermodynamic Data

ΔH°_{298} (1) = -89.8 kJ mol^{-1}

ΔS°_{298} (1) = -23.5 J K^{-1}mol^{-1}

K_p(1) = $2.99 \cdot 10^{-4}$ $T^{0.744}$exp ($+11100/T$)

ΔH°_{298} (2) = -96.8 kJ mol^{-1}

ΔS°_{298} (2) = -39.4 J K^{-1}mol^{-1}

K_p(2) = $1.14 \cdot 10^{-6}$ $T^{1.29}$exp ($+12100/T$)

Rate Coefficient Data ($k = k_1 + k_2$)

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$1.0 \cdot 10^{-10}$	2300–2600	Morley (1976)[1]	(a)
$9.5 \cdot 10^{-11}$	1950–2380	Haynes (1977)[2]	(b)
$8.3 \cdot 10^{-12}$	1200–2600	Shaub and Bauer (1978)[3]	(c)
$< 1.85 \cdot 10^{-10}$	2460–2840	Szekely, Hanson, and Bowman (1984)[4]	(d)

Comments

(a) Hydrocarbon/O$_2$ flames with additions of CH$_3$CN and pyridine. Product profiles (HCN, NH$_3$, NO) determined by quadrupole mass spectrometry. k calculated from HCN profile. Equilibrium between CN and HCN assumed.

(b) Premixed hydrocarbon/O$_2$ flames with additions of NH$_3$, NO, or pyridine. Samples removed by water cooled silica probe for analysis by infrared spectrophotometry (NO), absorption in NaOH and determination of CN and NH species using ion-selective electrodes. [H] monitored by Li/LiOH technique.

(c) Single pulse shock tube study of Ar/O$_2$/hydrocarbon/NO mixtures. Products (CH$_4$, C$_2$H$_4$, C$_2$H$_2$, CO, CO$_2$, NO, N$_2$, Ar) determined by gas chromatography. Yields fitted using large reaction mechanism. Results only slightly sensitive to value of k.

(d) Shock tube study of C$_2$N$_2$/H$_2$O/Ar mixtures. [CN] monitored by broad band absorption at 388 nm, [OH] by laser absorption at 306.67 nm. Profiles fitted to reaction mechanism. Upper limit only to k obtained.

Preferred Values

$k = 1.0 \cdot 10^{-10}$ cm^3 molecule^{-1} s^{-1} over range 1500–3000 K

Reliability

Δlog $k = \pm 0.5$ over range 1500–3000 K

Comments on Preferred Values

All of the determinations of k involve computer modelling of substantial reaction mechanisms. The most direct determinations are those of Haynes[2] and Morley[1] which are the basis of our recommended values but with substantial error limits reflecting the lack of good quality direct measurements.

References

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$$OH + HCN \rightarrow H_2O + CN \qquad (1)$$
$$\rightarrow HOCN + H \qquad (2)$$
$$\rightarrow HNCO + H \qquad (3)$$
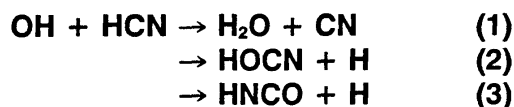
Thermodynamic Data

$\Delta H^\circ_{298} (1) = 19.2 \text{ kJ mol}^{-1}$
$\Delta S^\circ_{298} (1) = 5.91 \text{ J K}^{-1}\text{mol}^{-1}$
$K_p(1) = 2.09 \cdot 10^2 \, T^{-0.687} \exp(-2520/T)$

$\Delta H^\circ_{298} (2) = 34.3 \text{ kJ mol}^{-1}$
$\Delta S^\circ_{298} (2) = -22.9 \text{ J K}^{-1}\text{mol}^{-1}$
$K_p(2) = 1.04 \cdot 10^{-2} \, T^{0.254} \exp(-4010/T)$

$\Delta H^\circ_{298} (3) = -60.3 \text{ kJ mol}^{-1}$
$\Delta S^\circ_{298} (3) = -32.0 \text{ J K}^{-1}\text{mol}^{-1}$
$K_p(3) = 8.96 \cdot 10^{-5} \, T^{0.790} \exp(+7550/T)$

Rate Coefficient Data ($k = k_1 + k_2 + k_3$)

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	$T[\text{K}]$	Reference	Comments
Rate Coefficient Measurements			
$k_1 = 3.31 \cdot 10^{-11} \exp(-7554/T)$	1666–2300	Kanamura and Daito (1977)[1]	(a)
$k_3 = 3.32 \cdot 10^{-13}$	1950–2380	Haynes (1977)[2]	(b)
$k_1 = 1.60 \cdot 10^{-11} \, T^{-1} \exp(-1860/T)$	298–563	Phillips (1979)[3]	(c)
$k_1 = 1 \cdot 10^{-12}$	1800–2500	Roth, Löhr, and Hermanns (1980)[4]	(d)
$k_1 = 1.2 \cdot 10^{-12}$	≈ 2650	Szekely, Hanson, and Bowman (1984)[5]	(e)
$k_\infty = 1.16 \cdot 10^{-13} \exp(-400/T)$	298–500	Brasseur et al. (1985)[6,7]	(f)
$k_0 = 1.5 \cdot 10^{-31} \exp(-875/T)$ $\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$			
$k_1 = 1.3 \cdot 10^{-11} \exp(-4160/T)$	518–1027	Jacobs et al. (1988)[11]	(g)
Reviews and Evaluations			
$1.2 \cdot 10^{-13} \exp(-400/T)$ ($p = 1$ atm)	296–433	CODATA (1984)[12]	(h)

Comments

(a) Shock tube study, no experimental details.

(b) Flame study. Hydrocarbon/O_2 flames with small additions of NH_3, NO, or pyridine. Samples withdrawn via watercooled silica probe and analysed for NO (infrared absorption), HCN and NH species (by absorption in NaOH solution and use of ion-selective electrodes). [II] in post-flame gases determined by Li/LiOH technique.

(c) Discharge-flow study. OH generated by H + NO_2 reaction. [OH] monitored by resonance fluorescence at 306 nm. CN produced by channel (1) scavenged by added H_2. Results suggest pressure dependent k; quoted k measured at pressures exceeding 10 Torr.

(d) Shock tube study of Ar/HCN/N_2O mixtures. [H] and [O] monitored by resonance absorption at 121.6 nm and 130.5 nm respectively. Results fitted to 8 reaction mechanism but fit not very sensitive to assumed value of k.

(e) Shock tube study of $H_2O/C_2N_2/Ar$ mixtures. [CN] monitored by absorption at 288 nm and [OH] by absorption at 306 nm. Data fitted to 6 reaction mechanism to yield k_{-1}. k_1 calculated using $K(1) = 0.97$ at 2650 K gives $2.9 \cdot 10^{-12}$ cm^3 molecule^{-1} s^{-1}. Use of more recent thermodynamic data gives values of k tabulated.

(f) Flash photolysis study in flowing system. Decay of [OH] monitored by resonance absorption. Pressure dependent k found and fitted to Troe expression to give quoted k_0 and k_{infty}. Relatively long lived adduct HCNOH observed[10].

At temperatures above 500 K there is an increase in the activation energy interpreted as due to the onset of either channel (1) or (2).

(g) Derived from measurements of k_{-1} and thermodynamic data. Measurements of k_1 by laser photolysis with time resolved monitoring of [CN] and [OH] by laser induced fluorescence. Using our thermodynamic data we obtain $k_1 = 2.7 \cdot 10^{-9} \, T^{-0.687} \exp(-6770/T)$ cm^3 molecule^{-1} s^{-1}.

(h) Review of low temperature data. Accepts value of Fritz et al.[6].

Preferred Values

$k_1 = 1.5 \cdot 10^{-11} \exp(-5400/T)$ cm^3 molecule^{-1} s^{-1} over range 1500–2500 K

Reliability

$\Delta \log k_1 = \pm 0.5$ over range 1500–2500 K

Comments on Preferred Values

At high temperatures (1600–2500 K) the results of flame[2] and shock tube studies[4,5,11] are in reasonable agreement despite the fact that all of the techniques are indirect and values of k derived from computer fitting of substantial reaction mechanisms to the observed quanti

ties. At high temperatures it is most likely that channel (1) is dominant as discussed by Miller et al.[8] and as suggested by the work of Jacobs et al.[11] on the reaction of $CN + H_2O \rightarrow HCN + OH$.

At lower temperatures (< 500 K) the data of Phillips[3,9] and of Brasseur et al.[6,7] differ significantly. In both of these studies the rate constant was reported to be pressure dependent. No recommendation is made for this regime; further studies are required.

At high temperatures there are reliable data[11] for k_{-1}; our recommendation is derived from this and the thermodynamic data about which there is some uncertainty and hence large error limits must be assigned.

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OH + HCN → H₂O + CN

$$OH + HCN \rightarrow H_2O + CN$$
$$\rightarrow HOCN + H$$
$$\rightarrow HNCO + H$$

$$OH + CH_3OOH \rightarrow CH_2OOH + H_2O \qquad (1)$$
$$\rightarrow CH_3OO + H_2O \qquad (2)$$
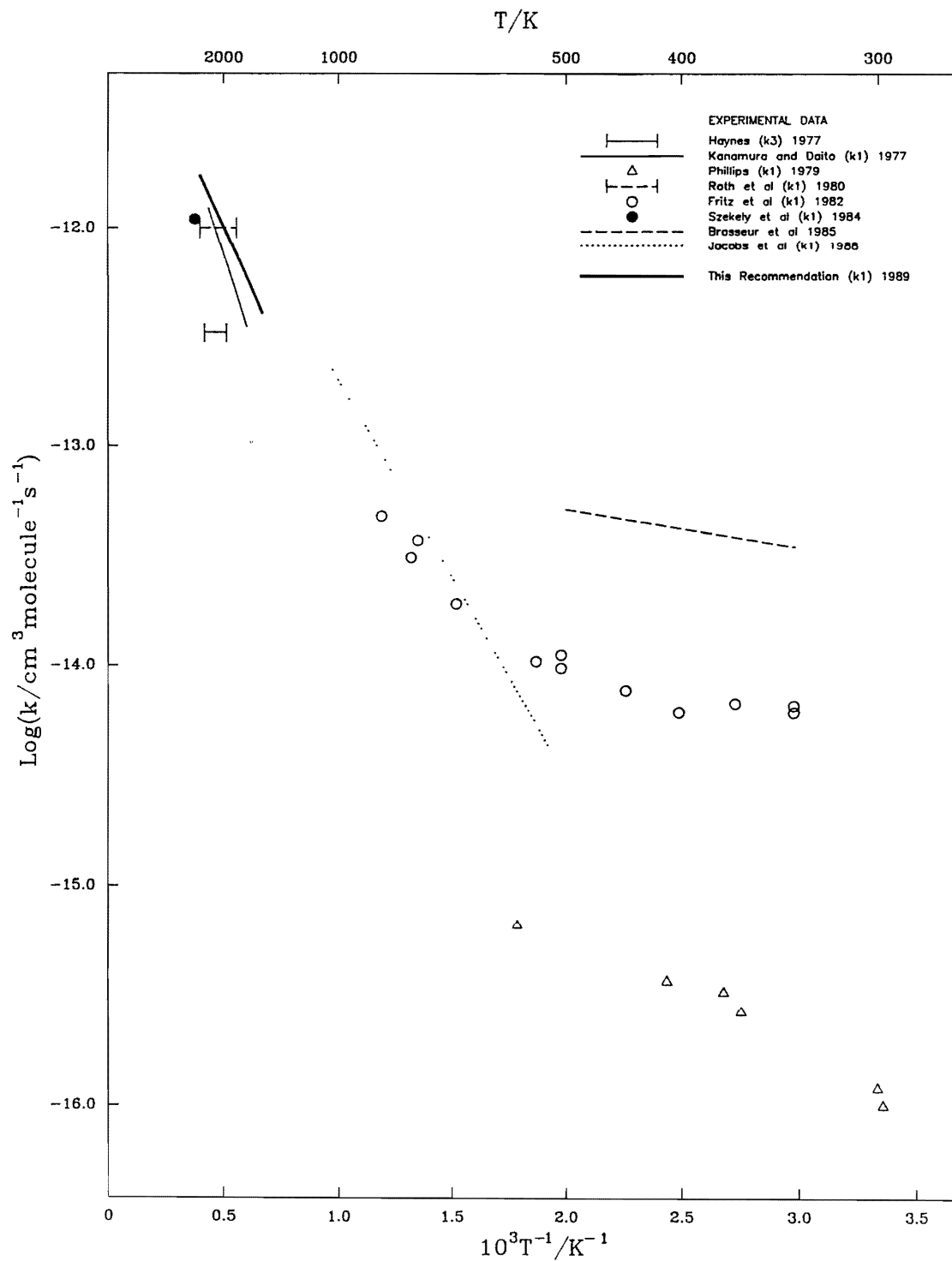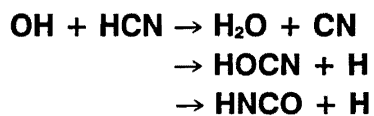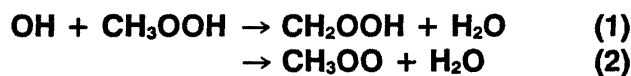
Thermodynamic Data

$\Delta H^{\circ}_{298} (1) = -132.0 \text{ kJ mol}^{-1}$

$\Delta H^{\circ}_{298} (2) = -85.8 \text{ kJ mol}^{-1}$

Rate Coefficient Data ($k = k_1 + k_2$)

$k [\text{cm}^3 \text{ molecule}^{-1}\text{s}^{-1}]$	T [K]	Reference	Comments
Rate Coefficient Measurements			
$1.0 \cdot 10^{-11}$	300	Niki *et al*. (1983)[1]	(a)
$2.93 \cdot 10^{-12}\exp(+190/T)$	203–423	Vaghjiani and	
$k_2 = 1.78 \cdot 10^{-12}\exp(+220/T)$		Ravishankara (1989)[2]	(b)

Comments

(a) FTIR spectroscopic study of photolysis of $C_2H_5ONO/$ CH_3OOH/air mixtures. k relative to rate constants for OH + C_2H_4 and OH + CH_3CHO: $k(CH_3OOH)/k(C_2H_4) = 1.2 \pm 0.09$; $k(CH_3OOH)/k(CH_3CHO) = 0.68 \pm 0.07$ at 1 atm pressure. Product yields were consistent with branching ratio $k_1/k_2 = 0.77 (\pm 20 \%)$.

(b) Pulsed photolysis – laser induced fluorescence detection of OH. First order decay of OH used to determine k_2. Because OH is regenerated rapidly from the CH_2OOH product in the first channel, the overall rate coefficient was determined from ^{18}OH loss and from OH production from the reaction of ^{18}OH or OD + CH_3OOH. A thorough investigation of the mechanism and error sources is given.

Preferred Values

$k_1 = 1.2 \cdot 10^{-12}\exp(+130/T) \text{ cm}^3 \text{ molecule}^{-1}\text{s}^{-1}$ over range 250–1000 K

$k_2 = 1.8 \cdot 10^{-12}\exp(+220/T) \text{ cm}^3 \text{ molecule}^{-1}\text{s}^{-1}$ over range 250–1000 K

Reliability

$\Delta\log k_1 = \pm 0.4$ at 1000 K reducing to ± 0.2 at 300 K

$\Delta\log k_2 = \pm 0.3$ at 1000 K reducing to ± 0.1 at 300 K

Comments on Preferred Values

The preferred values are based on the comprehensive and thorough study of Vaghjiani and Ravishankara[2]. Considering the uncertainties in the earlier study of Niki *et al*.[1], the agreement is satisfactory.

References

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$$OH + C_2H_2 \rightarrow C_2H + H_2O \quad (1)$$
$$\rightarrow H + CH_2CO \quad (2)$$
$$OH + C_2H_2 (+ M) \rightarrow C_2H_2OH (+ M) \quad (3)$$

Thermodynamic Data

$\Delta H^\circ_{298} (1) = 53.1 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (1) = 11.6 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(1) = 817 \ T^{-0.782} \exp(-6650/T)$

$\Delta H^\circ_{298} (2) = -99.6 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (2) = -28.1 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(2) = 5.64 \cdot 10^{-4} \ T^{0.572} \exp(+12240/T)$

No thermodynamic data available for channel (3). See text for estimate of $\Delta H^\circ(3)$.

Rate Coefficient Data ($k = k_1 + k_2$)

k [cm^3 molecule^{-1} s^{-1}]	T [K]	Reference	Comments
Rate Coefficient Measurements			
$3 \cdot 10^{-12}$	1700–2000	Fenimore and Jones (1964)[1]	(a)
$1.0 \cdot 10^{-11} \exp(-3500/T)$	1000–1700	Browne et al. (1969)[2]	(b)
$5.3 \cdot 10^{-13} \exp(-100/T)$	570–850	Vandooren and	
		Van Tiggelen (1977)[3]	(c)
$5.8 \cdot 10^{-12} \exp(-4500/T)$	~ 2650	Bar-Nun and Dove (1980)[4]	(d)
$3.0 \cdot 10^{-11} \exp(-3500/T)$	2000	Warnatz et al. (1982)[5]	(e)
$2.7 \cdot 10^{-13}$	1100	Smith, Fairchild, and	
$5.8 \cdot 10^{-13}$	1300	Crosley (1984)[6]	(f)
$4.5 \cdot 10^{-11} \exp(-5300/T)$	1100–1273	Liu, Mulac, and Jonah (1988)[7]	(g)
Reviews and Evaluations			
$1.0 \cdot 10^{-11} \exp(-3500/T)$	1000–2000	Warnatz (1984)[8]	(h)
$2.4 \cdot 10^{-20} \ T^{2.68} \exp(-6060/T)$		Tsang and Hampson (1986)[9]	(i)

Comments

(a) Acetylene/oxygen atmospheric flames, mass spectrometric sampling of the burned gas.

(b) Acetylene flame, concentration profiles by absorption and emission spectroscopy. Computer simulation.

(c) Acetylene/oxygen low pressure flame, molecular beam/mass spectrometric sampling. Suggest the reaction product is ketene.

(d) Shock tube study with mass spectrometric sampling.

(e) Burner stabilised laminar flat $C_2H_2/O_2/Ar$ flame. Sampling nozzle with mass spectrometric detection. Studied the formation of C_4H_2.

(f) CO_2 pulsed laser photolysis (SF_6, H_2O_2, N_2, C_2H_2), OH detected by laser induced fluorescence. At 900 K the reaction shows a pressure dependence, but this is lost at 1100 and 1300 K, suggesting that the low temperature addition channel no longer operates.

(g) Pulse radiolysis, resonance absorption spectroscopy. The rate constant shows a complex (p,T) dependence below 1100 K as the addition channel becomes important.

(h) Evaluation, based on the value of Browne et al.[2].

(i) Calculated BEBO value.

Preferred Values

$k_1 = 1.0 \cdot 10^{-10} \exp(-6500/T)$ cm^3 molecule^{-1} s^{-1} over range 1000–2000 K

Reliability

$\Delta \log k = \pm 1.0$

Comments on Preferred Values

In the absence of contrary evidence, an abstraction mechanism has been assumed at high temperatures. Even exothermic H abstractions have a small activation barrier and they show pronounced positive Arrhenius curvature. Accordingly, a large temperature dependence, compatible with the data of Smith et al.[6] and Fenimore and Jones[1] and with the endothermicity, has been chosen, together with a large A factor, by comparison with the OH + C_2H_4 reaction. This dependence is somewhat stronger than that obtained by Liu et al.[8] because their analysis does not make full allowance for the addition channel.

At temperatures below $\approx$ 1100 K and at atmospheric pressure, the addition channel (3) becomes important[7] and shows a strong pressure dependence[10–12]. More recent and more complete measurements have been made at 298 K[13,14], on the basis of which Atkinson[15] proposes the parameters $k_3^0 = 4 \cdot 10^{-30}$ cm^6 molecule^{-2} s^{-1}, $k_3^\infty = 8.7 \cdot 10^{-13}$ cm^3 molecule^{-1} s^{-1}, and $F_c = 0.6$ in air at room temperature, with a T dependence of the form $k_3^\infty = 1.9 \cdot 10^{-12} \exp(-230/T)$ cm^3 molecule^{-1} s^{-1}.

The following parameters give a reasonable representation of the high temperature data for k_3 and are also compatible with Atkinson's analysis at low temperatures:

$k_3^\infty = 2 \cdot 10^{-12} \exp(-230/T)$ cm^3 molecule^{-1} s^{-1}

$k_3^0 = 5 \cdot 10^{-35} \ T^{-2}$ cm^6 molecule^{-2} s^{-1}

$F_c = 0.6$

with $\Delta\log k_3 = \pm 1.0$. These parameters should be employed to assess the importance of the addition channel at temperatures below ≈ 1100 K. Smith *et al.*[6] estimated the dissociation energy, ΔE_0, for the adduct to be ≈ 140 kJ mol^{-1}.

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$$OH + C_2H_2 \rightarrow C_2H + H_2O$$
$$\rightarrow H + CH_2CO$$
$$\rightarrow C_2H_2OH$$

EXPERIMENTAL DATA

├────┤	Fenimore and Jones (k1) 1964
────────	Browne et al (k1) 1969
──── ────	Vandooren & Van Tiggelen (k1) 1977
▲	Bar—Nun and Dove (k1) 1980
○	Smith et al (k1) 1984
●	Liu et al 1988
◨	Warnatz et al (k1) 1982
▲	Breen and Glass (k3) 1970
◒	Wahner and Zetzsch (k3) 1985
+	Schmidt et al (k1) 1985
×	Schmidt et al (k3) 1985
◇	Hatakeyama et al (k3) 1986
◆	Atkinson et al (k3) 1984
▣	Perry et al (k3) 1982
▽	Michael et al (k3) 1980
▼	Perry et al (k3) 1977
────────	This Recommendation (k1) 1989

OH + C_2H_4 → H_2O + C_2H_3

Thermodynamic Data

$\Delta H^\circ_{298} = -47.4$ kJ mol^{-1}

$\Delta S^\circ_{298} = 17.5$ J K^{-1}mol^{-1}

$K_p = 526\ T^{-0.589}$ exp($+5413/T$)

Rate Coefficient Data

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$1.7 \cdot 10^{-11}$	1250–1400	Westenberg and Fristrom (1965)[1]	(a)
$1.8 \cdot 10^{-11}$	813	Baldwin, Simmons, and Walker (1966)[2]	(b)
$1.8 \cdot 10^{-11}$	1300	Bradley *et al.* (1976)[3]	(c)
$1.3 \cdot 10^{-12}$	591	Tully (1983)[4]	(d)
$5.7 \cdot 10^{-13}$	773	Baldwin *et al.* (1984)[5]	(e)
$2.4 \cdot 10^{-11}$ exp($-2104/T$)	748–1173	Liu, Mulac, and Jonah (1987)[6]	(f)
$2.5 \cdot 10^{-12}$	1220	Smith (1987)[7]	(g)
$3.4 \cdot 10^{-11}$ exp($-2992/T$)	651–901	Tully (1988)[8]	(h)
Reviews and Evaluations			
$5 \cdot 10^{-12}$	800–1500	Wilson (1972)[9]	(i)
$5 \cdot 10^{-11}$ exp($-1500/T$)	500–2000	Warnatz (1984)[10]	(j)

Comments

(a) Flame study of C_2H_4/O_2 flames, H and O profiles measured by e.s.r. and C_2H_4, CO, and CO_2 by mass spectrometry. Concentration profile of OH is calculated using k(CO + OH → CO_2 + H) $= 1.2 \cdot 10^{-11}$ exp($-3870/T$) cm^3 molecule^{-1} s^{-1} and [CO_2] and hence quoted value of k.

This is recalculated by Wilson[9] giving $k = 5.3 \cdot 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 1240 K, $k = 8.3 \cdot 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 1368 K, $k = 2.6 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 1447 K and $k = 1.0 \cdot 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 1491 K.

(b) Inhibition of H_2/O_2 reaction by addition of ethene. Ratio k/k(H_2 + OH) is obtained and use of k(H_2 + OH) $= 1.2 \cdot 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 813 K gives the quoted value.

This is recalculated by Wilson[9] giving $k = 1.0 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 813 K.

(c) Shock tube study, analysis by UV absorption for [OH]; quoted value of k obtained by computer modelling of a 28 reaction mechanism (proved to be sensitive to this reaction) and optimization.

(d) Flash photolysis of C_2H_4/He, N_2O/He, H_2O/He gas streams using an excimer laser. [OH] monitored by resonance fluorescence at $T > 500$ K. [OH] decay is not exponential.

(e) Addition of C_2H_4 to slowly reacting H_2/O_2 mixtures. Pressure change and product yields (C_2H_4O, HCHO, CH_4, C_2H_4, CO, CH_3CHO) in early stages of reaction measured. k sensitive to CO and HCHO yields. Difficult to distinguish between abstraction and OH + C_2H_4 → C_2H_4OH + O_2 → 2 HCHO + OH.

(f) Pulse radiolysis of H_2O/C_2H_4 mixtures in 1 atm Ar. [OH] monitored by resonance absorption. In temper-

ature range 343–563 K addition of OH to C_2H_4 is dominant; 563–748 K addition, adduct decomposition, and abstraction occur concurrently; above 748 K abstraction is dominant.

(g) Infrared laser pyrolysis of flowing mixtures of H_2O_2/ $CF_4/SF_6/C_2H_4$. [OH] monitored by laser induced fluorescence. Temperatures determined from population of OH rotational states.

(h) Laser photolysis of $N_2O/H_2O/C_2H_4$/He mixtures at 193 nm or H_2O/C_2H_4/Ar mixtures. [OH] monitored by laser induced fluorescence. Rate constant independent of nature or pressure of diluent gas.

(i) Review of results up to 1974, recalculation where necessary, separate incompatible values for k at high and at low temperatures recommended.

(j) Review of Refs. up to 1980. Expression for k at high temperatures which is compatible with low temperature results recommended.

Preferred Values

$k = 3.4 \cdot 10^{-11}$ exp($-2990/T$) cm^3 molecule^{-1} s^{-1} over range 650–1500 K

Reliability

$\Delta \log k = \pm 0.5$ over range 650–1500 K

Comments on Preferred Values

The experimental studies on this reaction show that the abstraction channel predominates over addition at temperatures above approximately 650 K. The measured values of k are in poor agreement at such temperatures. The most recent study of Tully[8] gives values much lower than those found in most other studies but compatible

with the work of Smith[7] and the most recent work of Baldwin et al.[5]. We accept Tully's expression as the one preferred.

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OH + C_2H_4 → C_2H_3 + H_2O

OH + C_2H_6 → H_2O + C_2H_5
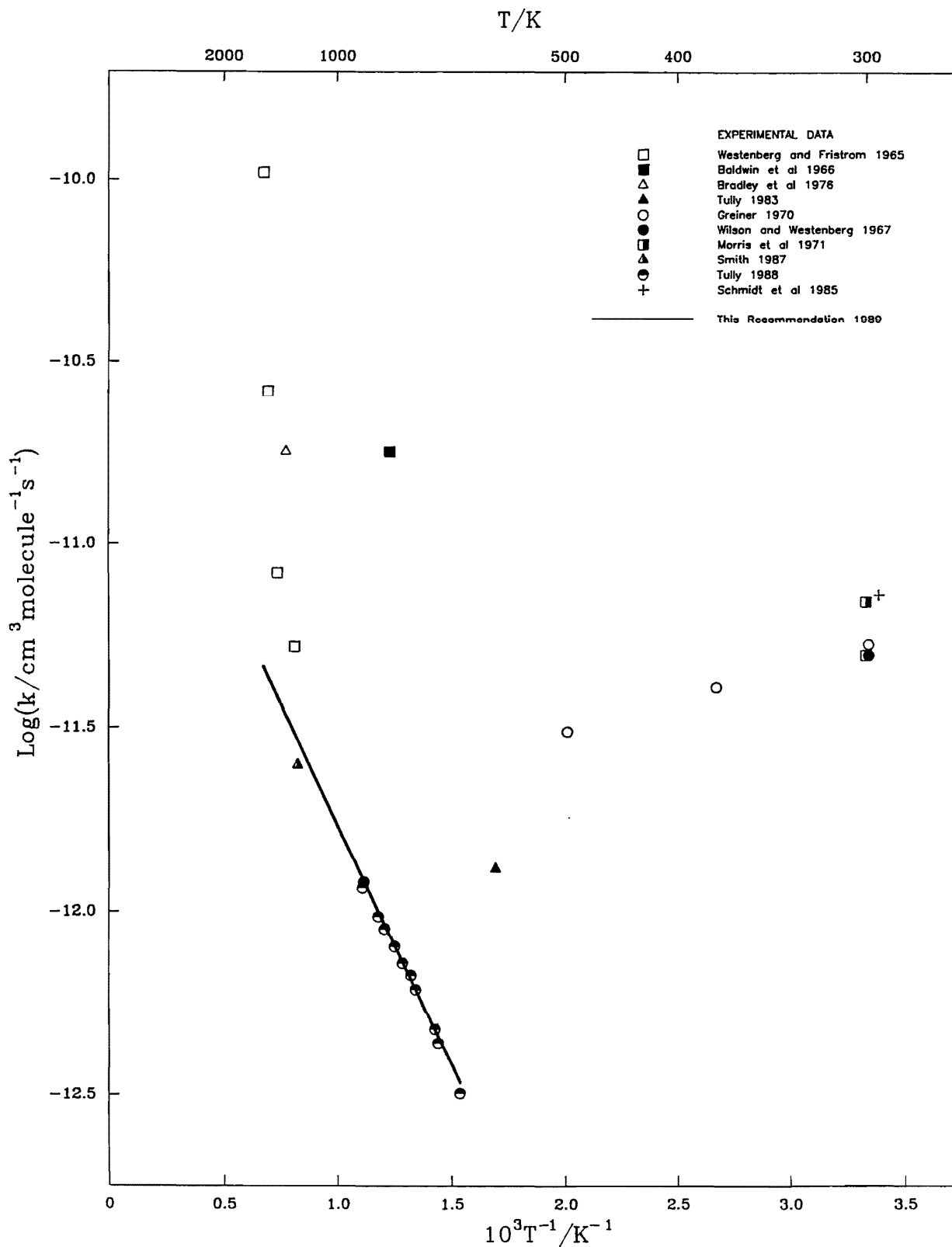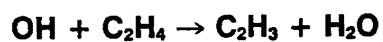
Thermodynamic Data

$\Delta H^{\circ}_{298} = -79.7$ kJ mol^{-1}

$\Delta S^{\circ}_{298} = 27.8$ J K^{-1}mol^{-1}

$K_p = 3.30 \cdot 10^3 \, T^{-0.692} \exp(+9340/T)$

Rate Coefficient Data
(for details of pre-1980 data, see Ref. 1)

k [cm^3 molecule^{-1} s^{-1}]	Temperature [K]	Reference	Comments
Rate Coefficient Measurements			
$2.32 \cdot 10^{-13}$	295	Lee and Tang (1982)[2]	(a)
$7.13 \cdot 10^{-14}$	238	Margitan and Watson (1982)[3]	(b)
(see Ref. 1)	403–683	Baulch et al. (1983)[4]	(c)
$1.43 \cdot 10^{-14} \, T^{1.05} \exp(-911/T)$	297–800	Tully et al. (1983)[5]	(d)
$3.9 \cdot 10^{-21} \, T^{3.09} \exp(+169/T)$	248–472	Kautman et al. (1984)[6]	(a)
$1.8 \cdot 10^{-11} \exp(-1240 /T)$	240–295	Molina et al. (1984)[7]	(e)
$2.68 \cdot 10^{-13}$	295	Baulch et al. (1985)[8]	(f)
$2.2 \cdot 10^{-13}$	295	Schmidt et al. (1985)[9]	(g)
$1.28 \cdot 10^{-13}$	248	Molina et al. (1986)[10]	(h)
$2.51 \cdot 10^{-13}$	297		
$2.98 \cdot 10^{-13}$	295	Nielsen et al. (1986)[11]	(i)
$8.51 \cdot 10^{-18} \, T^{2.06} \exp(-430/T)$	293–705	Tully et al. (1986)[12]	(k),(j)
$2.07 \cdot 10^{-11} \exp(-1299/T)$	205–364	Anderson and Stephens (1986)[13]	(a)
$2.74 \cdot 10^{-13}$	296	Bourmada, Lafage, and Devolder (1987)[14]	(a)
$8.4 \cdot 10^{-12} \exp(-1050 /T)$	234–438	Wallington, Neuman, and Kurylo (1987)[15]	(d)
Reviews and Evaluations			
$1.29 \cdot 10^{-17} \, T^{2.0} \exp(-430/T)$	300–2000	Cohen (1982)[16]	(k)
$3.6 \cdot 10^{-17} \, T^{1.9} \exp(-570/T)$	300–2000	Cohen and Westberg (1983)[17]	(l)
$1.05 \cdot 10^{-17} \, T^{2.0} \exp(-325/T)$	300–2000	Warnatz (1984)[18]	(m)
$1.47 \cdot 10^{-14} \, T^{1.04} \exp(-913/T)$	297–800	Tsang and Hampson (1986)[19]	(n)
$2.3 \cdot 10^{-11} \exp(-1340/T)$	250–1200	Baulch et al. (1986)[1]	(o)
$1.37 \cdot 10^{-17} \, T^{2.0} \exp(-444/T)$	240–900	Atkinson (1986)[20]	(p)

Comments

(a) Fast flow discharge, [OH] monitored by resonance fluorescence.

(b) Flash photolysis of $HNO_3/C_2H_6/He$ mixtures; [OH] monitored by resonance fluorescence.

(c) Static photolysis of $H_2O/CO/C_2H_6$ mixtures; competitive studies with GLC measurement of CO_2.

(d) Flash photolysis of $H_2O/C_2H_6/Ar$ mixtures in static vessel. $[C_2H_6]$ >> [OH] with [OH] monitored by resonance fluorescence.

(e) Flash photolysis of $HNO_3/C_2H_6/He$ mixtures; [OH] monitored by resonance fluorescence.

(f) Discharge flow, OH generated from H + NO_2 with [OH] monitored by resonance fluorescence.

(g) Laser photolysis of H_2O_2 or HNO_3; [OH] monitored by pulsed dye laser fluorescence.

(h) Laser flash photolysis of $HNO_3/C_2H_6/$inert gas mixtures; [OH] monitored by resonance fluorescence.

(i) Pulse radiolysis of $H_2O/C_2H_6/Ar$ mixtures; [OH] monitored by adsorption at about 309 nm.

(j) Flow laser photolysis; [OH] monitored by laser induced fluorescence.

(k) Calculated values based on transition state theory.

(l) Wide temperature evaluation of experimental data.

(m) Recommended without comment.

(n) Recommend expression given by Tully et al. (1983)[5].

(o) Recommend Arrhenius expression between 250 and 1200 K, based on comprehensive assessment of experimental data.

(p) Critical review of data between 240 and 900 K.

Preferred Values

$k = 1.20 \cdot 10^{-17} \, T^{2.0} \exp(-435/T)$ cm^3 molecule^{-1} s^{-1} over range 250–2000 K

Reliability

$\Delta \log k = \pm 0.07$ between 250 K and 1000 K rising to ± 0.15 at 2000 K

Comments on Preferred Values

The rate constant is now known with considerable reliability and precision between 250 and 2000 K, with excellent agreement between a large number of techniques. The early data of Fenimore and Jones[21] have been re-interpreted using k(OH + CO) given by Baulch et al.[22].

The preferred value of k is almost indistinguishable from the value obtained by Cohen[16] from transition state calculations carried out for temperatures between 300

and 2000 K. This agreement between theory and experiment may be coincidental, but suggests that extrapolations to at least 3000 K may be carried out reasonably reliably with $\Delta\log k = \pm 0.3$ at 3000 K.

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OH + C$_2$H$_6$ → H$_2$O + C$_2$H$_5$

$$OH + CH_2CO \rightarrow CH_2OH + CO \quad (1)$$
$$\rightarrow H_2CO + CHO \quad (2)$$
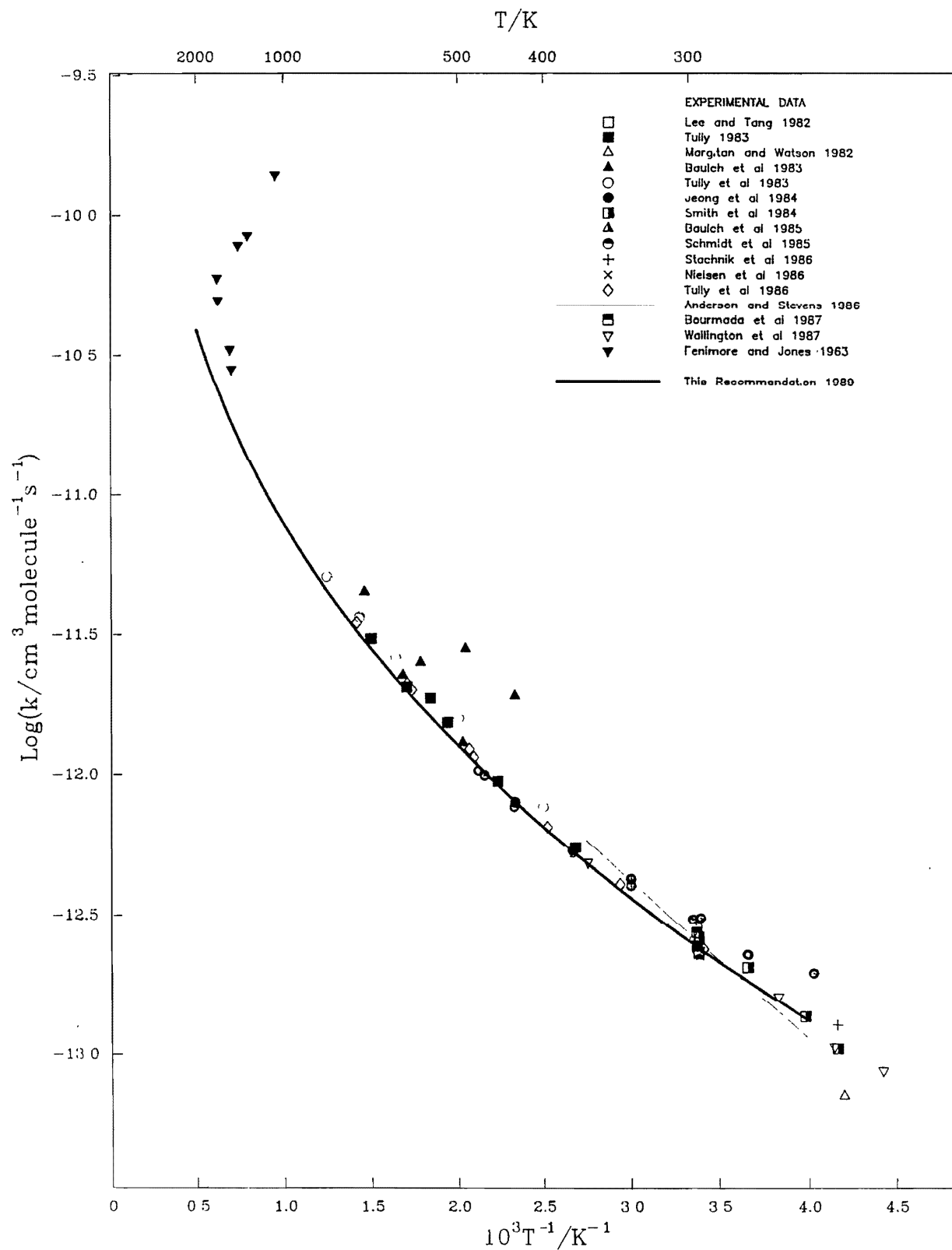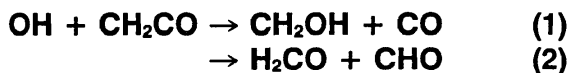
Thermodynamic Data

$\Delta H^\circ_{298} (1) = -115 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (1) = 18.5 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(1) = 210\ T^{-0.48} \exp(+13700/T)$

$\Delta H^\circ_{298} (2) = -59.5 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (2) = 17.7 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(2) = 969\ T^{-0.78} \exp(+7070/T)$

Rate Coefficient Data ($k = k_1 + k_2$)

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	$T[\text{K}]$	Reference	Comments
Rate Coefficient Measurements			
$4.65\cdot10^{-11}$	480–1000	Vandooren and Van Tiggelen (1977)[1]	(a)
$> 1.7\cdot10^{-12}$	295	Faubel, Wagner, and Witack (1977)[2]	(b)
$1.8\cdot10^{-11}$	299	Hatakeyama *et al.* (1985)[3]	(c)
Reviews and Evaluations			
$1.7\cdot10^{-11}$	300–1000	Warnatz (1984)[4]	

Comments

(a) Study of C_2H_2/O_2 flames. Analysis for CO_2, CO, C_2H_2, H_2, H_2O, Ar, H, O, and OH by molecular beam sampling mass spectrometry.

(b) Flow reactor, OH radicals produced by the reaction $H + NO_2 \rightarrow OH + NO$. Product analysis by mass spectrometry; C_2H, H_2CO, and CH_3OH found in products. Quoted lower limit for k obtained by comparison with the rate constant for the reaction $C_3O_2 + OH \rightarrow HC_2O + CO_2$ ($k(C_3O_2 + OH) = 1.2\cdot10^{-11} \exp(-620/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) also measured in this study.

(c) OH generated by photolysis of CH_3ONO in air at 1 atm. Analysis for CH_2CO by long path Fourier-transform infrared spectroscopy at 2164 cm^{-1}. Ratio $k/k(OH + c\text{-}C_6H_{12}) = 2.3$ obtained. $k(OH + c\text{-}C_6H_{12}) = 7.95\cdot10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ used[5] to obtain k. Main product observed was HCHO.

Preferred Values

$k = 1.7\cdot10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over range 300–2000 K

Reliability

$\Delta\log k = \pm 1.0$ over range 300–2000 K

Comments on Preferred Values

The measured values of k at low[3] and only slightly higher[1] temperatures differ by a factor of 10. The high value of k and comparison with the rate constants for O and H attack on CH_2CO both suggest a small activation energy ($< 6 \text{ kJ mol}^{-1}$) for the reaction. We follow Warnatz in recommending a temperature independent value of k and large error limits.

The detection of HCHO as a product[2,3] suggests that channel (2) plays a significant role but there is no other information about the branching ratios.

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$$OH + CH_3CHO \rightarrow H_2O + CH_3CO \qquad (1)$$
$$\rightarrow H_2O + CH_2CHO \qquad (2)$$
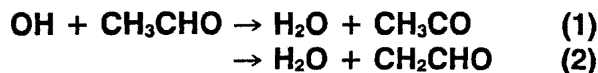
Thermodynamic Data

$\Delta H^\circ_{298} (1) = -138 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (1) = 8.0 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(1) = 136 \, T^{-0.557} \exp(+16400/T)$

$\Delta H^\circ_{298} (2) = -90.4 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (2) = 9.1 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(2) = 60 \, T^{0.398} \exp(+10650/T)$

Rate Coefficient Data

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	T [K]	Reference	Comments
Rate Coefficient Measurements			
$6.87 \cdot 10^{-12} \exp(+260/T)$	299–426	Atkinson and Pitts (1978)[1]	(a)
$5.52 \cdot 10^{-12} \exp(+307/T)$	244–528	Michael, Keil, and Klemm (1985)[2]	(b)
$7.1 \cdot 10^{-12} \exp(+165/T)$	253–424	Semmes *et al*. (1985)[3]	(c)
Reviews and Evaluations			
$6.9 \cdot 10^{-12} \exp(+260/T)$	298–450	CODATA (1984)[4]	(d)
$1.67 \cdot 10^{-11}$	300–2000	Warnatz (1984)[5]	(e)
$6.87 \cdot 10^{-12} \exp(+256/T)$	200–500	Atkinson (1986)[6]	(f)

Comments

(a) Pulsed VUV flash photolysis of H_2O; resonance fluorescence detection of OH.

(b) Discharge flow; resonance fluorescence detection of OH; CH_3CO shown to be most probable product up to 530 K.

(c) Flash photolysis of H_2O; resonance fluorescence detection of OH; some difficulty encountered in defining CH_3CHO concentration.

(d) Based on Ref. 1 and earlier room temperature data of Morris *et al*.[7], Cox *et al*.[8], Niki *et al*.[9], and Kerr and Sheppard[10].

(e) Recommendation based on mean of room temperature values and assumed independence of k on temperature over wide range.

(f) Based on Ref. 1. Data from Semmes *et al*. were not included because of reported difficulties in defining CH_3CHO concentration.

Preferred Values

$k = 3.89 \cdot 10^{-14} \, T^{0.73} \exp(+560/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

over range 250–1200 K

Reliability

$\Delta \log k = \pm 0.3$ at 1000 K reducing to ± 0.1 at 250 K

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$$OH + CH_3CHO \rightarrow H_2O + CH_3CO$$
$$\rightarrow H_2O + CH_2CHO$$

EXPERIMENTAL DATA
Atkinson and Pitts 1978
Michael, Keil and Klemm 1985
Semmes et al 1985
▲ Niki et al 1978
○ Avramenko and Lorentso 1949
● Morris et al 1971
▣ Cox et al 1976
△ Kerr and Sheppard 1981

This Recommendation 1989

$$OH + C_2H_5OOH \rightarrow H_2O + C_2H_5OO \qquad (1)$$
$$\rightarrow H_2O + C_2H_4OOH \qquad (2)$$

Thermodynamic Data

$\Delta H^0_{298} (1) = -131 \text{ kJ mol}^{-1}$

$\Delta H^0_{298} (2) = -91.2 \text{ kJ mol}^{-1}$

Comment

There are no experimental data for the reaction of OH with C_2H_5OOH. The overall rate expression $k = 3.0 \cdot 10^{-12} \exp(+190/T)$ cm^3 molecule^{-1} s^{-1} with channels (1) and (2) occurring at equal rates, is recommended by analogy with the reaction of OH with CH_3OOH. Temperature range 250–1000 K with $\Delta \log k = \pm 0.3$ at 250 K and ± 0.7 at 1000 K.

$$OH + C_6H_6 \rightarrow H_2O + C_6H_5 \qquad (1)$$
$$\rightarrow C_6H_5OH + H \qquad (2)$$
$$OH + C_6H_6 (+ M) \rightarrow C_6H_6OH (+ M) \qquad (3)$$
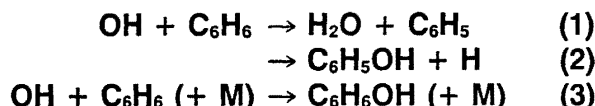
Thermodynamic Data

$\Delta H^0_{298} (1) = -35.3 \text{ kJ mol}^{-1}$
$\Delta S^0_{298} (1) = 24.2 \text{ J K}^{-1}\text{mol}^{-1}$
$K_p(1) = 8.1 \cdot 10^3 \, T^{-0.86} \exp(+3880/T)$

$\Delta H^0_{298} (2) = -0.3 \text{ kJ mol}^{-1}$
$\Delta S^0_{298} (2) = -23.5 \text{ J K}^{-1}\text{mol}^{-1}$
$K_p(2) = 4.7 \cdot 10^{-5} \, T^{1.11} \exp(+260/T)$

Rate Coefficient Data ($k = k_1 + k_2 + k_3$)

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$k_3 = 5.0 \cdot 10^{-12}\exp(-453/T)$	296–325	Perry, Atkinson and Pitts (1977)[1]	(a)
$k_1 = 4.0 \cdot 10^{-11} \exp(-2013/T)$	380–473		
$k_1 = 1.7 \cdot 10^{-11}\exp(-3019/T)$	1200–1900	Fujii and Asaba (1977)[2]	(b)
$3.1 \cdot 10^{-12} \exp(-270/T)$	250–298	Tully *et al.* (1981)[3]	(c)
$k_1 = 2.4 \cdot 10^{-11}\exp(-2260/T)$	450–1000		
$8.8 \cdot 10^{-13}$	295	Wahner and Zetzsch (1983)[4]	(d)
$k_3 = 6.3 \cdot 10^{-12} \exp(-500/T)$	244–330	Lorenz and Zellner (1983)[5]	(e)
$1.5 \cdot 10^{-12}$	298	Ohta and Ohyama (1985)[6]	(f)
$3.5 \cdot 10^{-11} \exp(-2300/T)$	790–1410	Felder and Madronich (1985)[7]	(g)
$1.3 \cdot 10^{-12}$	294		
$k_3 = 2.3 \cdot 10^{-12}\exp(-190/T)$	239–354	Witte, Urbanik, and Zetzsch (1986)[8]	(h)
$2.5 \cdot 10^{-11} \exp(-2050/T)$	790–1410	Madronich and Felder (1986)[9]	(i)
$1.3 \cdot 10^{-12}$	296	Edney *et al.* (1986)[10]	(j)
$2.0 \cdot 10^{-12}$	298	Atkinson (1987)[11]	(k)
$k_2 = 2.2 \cdot 10^{-11} \exp(-5330/T)$	1000–1150	He *et al.* (1988)[12]	(l)

Comments

(a) Flash photolysis–resonance fluorescence of OH at total pressures between 20 and 200 Torr.
(b) Rate expression for the addition channel was determined by a semi-empirical method. The pyrolysis and oxidation of benzene were studied by various methods using the shock tube technique. Experimental data on the formation of biphenyl and CO were modelled by computer simulation.
(c) Observed total rate coefficient is derived from the FP-RF technique for $20 < p < 200$ Torr. Discussion of the reaction mechanism is presented. A rate expression for the abstraction reaction (1) has been evaluated.

(d) VUV flash photolysis of water; detection of OH by resonance fluorescence at 309 nm.
(e) Laser photolysis–resonance fluorescence technique.
(f) Relative rate constant for the overall reaction. OH radicals were produced by photolyzing H_2O_2. Analysis of organic compounds was by GC. Reaction paths are discussed. Empirical relationships between structure and reactivity of aromatics towards OH radicals are derived.
(g) The high temperature photochemistry technique (HTPC) was applied. OH radicals were produced by standard flash photolysis. Time dependent resonance fluorescence detection of OH at 309 nm.
(h) Flash photolysis production of OH radicals. Monitoring of OH by resonance fluorescence at 309 nm.

(i) Same method as in (g). [']

(j) Observed total rate coefficient based on a procedure of "relative rate". OH radicals were produced by irradiation of methylnitrite. Decay rates of benzene and of the test compound were monitored by GC.

(k) Rate coefficient for OH consumption was calculated from structure-activity relationship (SAR) at atmospheric pressure.

(l) Results are from study of H and OH attack on phenol under single pulse shock tube conditions. The rate cofficient k_2 was calculated from the equilibrium constant and from the measured rate of the reverse of reaction (2).

Preferred Values

$k_1 = 2.7 \cdot 10^{-16} \ T^{1.42} \ \exp(-732/T) \ cm^3 \ molecule^{-1} \ s^{-1}$ over range 400–1495 K

$k_2 = 2.2 \cdot 10^{-11} \exp(-5530/T) \ cm^3 \ molecule^{-1} \ s^{-1}$ over range 1000–1150 K

$k_3 = 3.8 \cdot 10^{-12} \exp(-341/T) \ cm^3 \ molecule^{-1} \ s^{-1}$ over range 240–340 K

Reliability

$\Delta\log k_1 = \pm \ 0.3$ over range 400–1500 K
$\Delta\log k_2 = \pm \ 0.3$ over range 1000–1150 K
$\Delta\log k_3 = \pm \ 0.2$ over range 240–340 K

Comments on Preferred Values

The present studies indicate that the dominant reaction pathway at and below room temperature is the addition of the OH radical (channel (3)). Abstraction of ring hydrogen seems to be dominant at temperatures above 500 K (channel (1)). The displacement reaction (2) is not expected to be an elementary process but to proceed via the hydrocyclohexadienyl channel (3) at elevated temperatures.

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[12]Y. Z. He, W. G. Mallard, and W. Tsang, J. Phys. Chem. **92**, 2196 (1988).

OH + C$_6$H$_6$ → H$_2$O + C$_6$H$_5$
→ H + C$_6$H$_5$OH
→ C$_6$H$_6$OH

T/K

EXPERIMENTAL DATA

□ Wahner and Zetsch 1983
■ Witte et al (k3) 1986
— Fuji and Asaba (k1) 1977
▲ Tully et al (k1) 1981
○ Lorenz and Zellner (k3) 1983
● Ohta and Ohyama 1985
▣ Madronich and Felder 1985
– – – Felder and Madronich 1986
⊖ Edney et al 1986
+ Atkinson 1987
⋯⋯ He et al (k2) 1988
▤ Perry et al (k3) 1977
▽ Tully et al 1981
▼ Perry et al (k1) 1977

——— This Recommendation (k1) 1989

——— This Recommendation (k2) 1989

——— This Recommendation (k3) 1989

Log(k/cm^{3}molecule^{-1} s^{-1})

10^{3}T^{-1}/K^{-1}

(k3)

(k1)

(k2)

$$OH + C_6H_5OH \, (+ \, M) \rightarrow C_6H_5(OH)_2(+ \, M) \quad (1)$$
$$OH + C_6H_5OH \rightarrow C_6H_5O + H_2O \quad (2)$$
$$\rightarrow C_6H_4OH + H_2O \quad (3)$$

Thermodynamic Data

$\Delta H^\circ_{298} \, (2) = -136.7 \text{ kJ mol}^{-1}$
$\Delta S^\circ_{298} \, (2) = -1.9 \text{ J K}^{-1}\text{mol}^{-1}$
$K_p(2) = 1.6 \cdot 10^1 \, T^{-0.471} \exp(+16364/T)$

Rate Coefficient Data ($k = k_1 + k_2 + k_3$)

$k[\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}]$	$T[\text{K}]$	Reference	Comments
Rate Coefficient Measurements			
$k_1 = 2.8 \cdot 10^{-11}$	296	Rinke and Zetzsch (1984)[1]	(a)
$k_2 = 1.0 \cdot 10^{-11}$	1000–1150	He *et al.* (1988)[2]	(b)

Comments

(a) Direct measurement using flash photolysis with resonance fluorescence for OH. $p = 5$–733 mbar He. Low inital OH concentrations. Very good linearity of the decays.

(b) This is an extension of the phenol + H study of these authors (see data sheet: phenol + H). By using CO as an OH quencher, H atoms are formed and more benzene is produced. This process is in competition with phenol + OH. Thus rate data for phenol + OH may be deduced. However, very large amounts ($\approx$ 30%) of CO are needed. The kinetic system is not simple and a further uncertainty is introduced from the Ref. reaction CO + OH.

Preferred Values

$k_1 = 2.8 \cdot 10^{-11}\text{cm}^3 \text{ molecule}^{-1}\text{s}^{-1}\text{at 296 K and 733 mbar He}$

$k_2 + k_3 = 1.0 \cdot 10^{-11}\text{cm}^3 \text{ molecule}^{-1}\text{s}^{-1}\text{over range 1000–1150 K}$

Reliability

$\Delta \log k_1 = \pm 0.09 \text{ at 296 K}$
$\Delta \log (k_2 + k_3) = \pm 0.5$

Comments on Preferred Values

k_1 is the value reported by Rinke and Zetzsch[1].

For the abstraction channels (2) and (3) no information on the branching ratios exists. He, Mallard, and Tsang interpreted their results only in terms of channel (2).

References

[1]M. Rinke and C. Zetzsch, Ber. Bunsenges. Phys. Chem. **88**, 55 (1984).
[2]Y. Z. He, W. G. Mallard, and W. Tsang, J. Phys. Chem. **92**, 2196, (1988).

$$OH + C_6H_5CH_3 \rightarrow H_2O + C_6H_5CH_2 \, (+ \, M) \quad (1)$$
$$OH + C_6H_5CH_3 \, (+ \, M) \rightarrow C_6H_5CH_3OH \, (+ \, M) \quad (2)$$
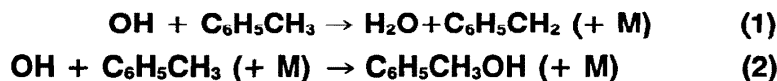
Thermodynamic Data

$\Delta H^\circ_{298} \, (1) = -130.8 \text{ kJ mol}^{-1}$
$\Delta S^\circ_{298} \, (1) = 1.4 \text{ J K}^{-1}\text{mol}^{-1}$
$K_p(1) = 3.2 \cdot 10^{-1} \, T^{0.23} \exp(+15730/T)$

Rate Coefficient Data ($k = k_1 + k_2$)

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	$T[\text{K}]$	Reference	Comments
Rate Coefficient Measurements			
$k_1 = 5.0 \cdot 10^{-12} \exp(-453/T)$	380–473	Perry, Atkinson, and Pitts (1977)[1]	(a)
$k_2 = 3.2 \cdot 10^{-13} \exp(+805/T)$	296–325		
$k_1 = 1.7 \cdot 10^{-11} \exp(-1510/T)$	1700–2800	McLain *et al.* (1979)[2]	(b)
$k_1 = 2.1 \cdot 10^{-11} \exp(-1300/T)$	500–1000	Tully *et al.* (1981)[3]	(c)
$k_2 = 3.8 \cdot 10^{-12} \exp(+180/T)$	213–298		
$k_2 = 6.4 \cdot 10^{-12}$	298	Ohta and Ohyama (1985)[4]	(d)
$k_2 = 5.4 \cdot 10^{-12}$	298	Edney *et al.* (1986)[5]	(e)
$k_2 = 6.2 \cdot 10^{-12}$	298	Atkinson (1987)[6]	(f)
$4.8 \cdot 10^{-12}$	773	Baldwin *et al.* (1987)[7]	(g)

Comments

(a) Flash photolysis–resonance fluorescence technique at total pressures around 10 Torr. Addition channel (2) is the dominant reaction pathway for temperatures below 325 K. The H abstraction reaction (channel (1)) was found to be the dominant reaction pathway for temperatures above 380 K.

(b) Incident shock wave investigation of the oxidation mechanism of $C_6H_6/O_2/Ar$ and $C_6H_5CH_3/O_2/Ar$ mixtures by monitoring UV and IR emission of CO, CO_2, and the product [O]·[CO]. Arrhenius expression for the products $C_6H_5CH_2 + H_2O$ (channel (1)) was estimated by comparison with data for benzene.

(c) Flash photolysis–resonance fluorescence technique. OH reactions with benzene, toluene, and selectively deuterated toluenes were studied in the temperature range 213 to 1150 K. The results indicate that the addition channel (2) is the dominant reaction pathway below 300 K and that side-chain hydrogen abstraction channels such as pathway (1) are the dominant reaction routes at higher temperatures. The rate expression for the side-chain hydrogen abstraction (channel (1)) has been estimated.

(d) Hexane was used as Ref. compound. Photolysis of H_2O_2 was the source of OH. Rate coefficient for OH consumption (channel (2)) was evaluated at atmospheric pressure.

(e) Rate constant value for reaction (2) derived by using a relative rate data procedure. Photolysis of methyl nitrite was the source of OH.

(f) Flash photolysis–resonance fluorescence. Measurement of rate coefficient for the addition reaction (2). An estimation of the rate coefficient for the addition reaction (2) by applying a structure activity relationship gave $5.5 \cdot 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

(g) Small amounts of toluene (0.05–0.5%) were added to slowly reaction mixtures of $H_2 + O_2$ at 773 K. Under the experimental conditions the hydrogen/oxygen system provides a reproducible source of radicals like H, O, and OH. The measurement of the relative consumption of additive and molecular hydrogen permits the evaluation of the rate constants for the reaction of H, O, and OH with toluene.

Preferred Values

$k_1 = 8.6 \cdot 10^{-15} \exp(-440/T)$ cm^3 $molecule^{-1}$ s^{-1} over range 400–1200 K

$k_2 = 3.8 \cdot 10^{-12} \exp(+180/T)$ cm^3 $molecule^{-1}$ s^{-1} over range 213–298 K

Reliability

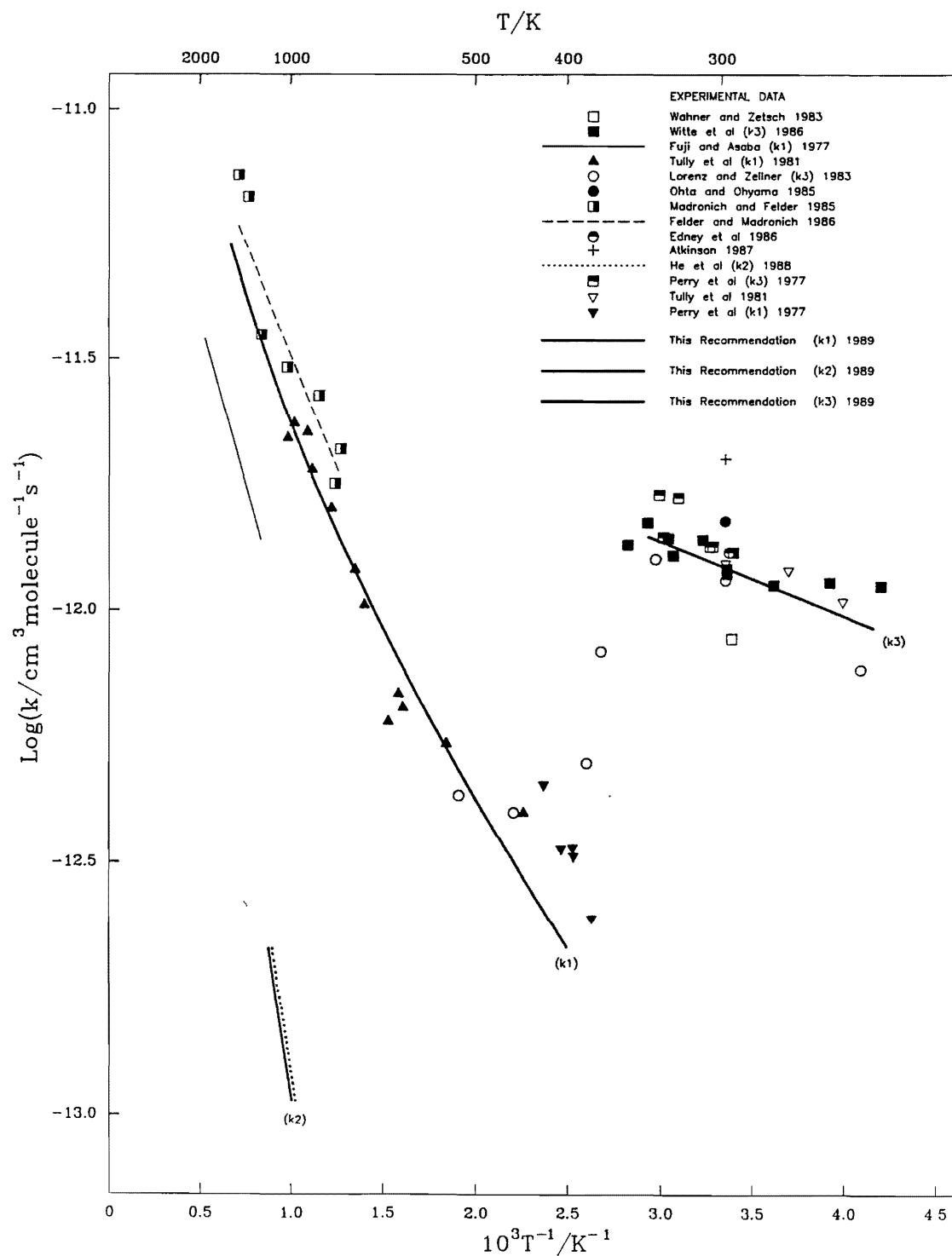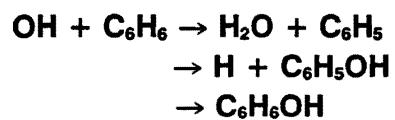$\Delta\log k_1 = \pm 0.5$ at 400 K reducing to ± 0.3 at 1200 K
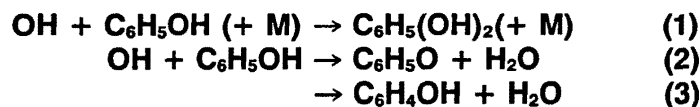$\Delta\log k_2 = \pm 0.4$ over the range 213–298 K

Comments on Preferred Values

The present studies indicate that the dominant reaction pathway at and below room temperature is the addition of the OH radical (channel (2)). Side-chain hydrogen abstraction reaction seems to be the reaction at higher temperatures (channel (1)). The present data are reliable, but owing to the pressure dependence of the reaction (2) only a rate expression can be recommended for temperatures below 300 K. For channel (1) the more indirect data of Ref. 2 have been not considered for the evaluation of the rate constant. The recommendation for channel (1) covers only an intermediate temperature range of about 800 degrees.

References

[1] R. A. Perry, R. Atkinson, and J. N. Pitts, Jr., J. Phys. Chem. **81**, 296 (1977).

[2] A. G. McLain, C. J. Jachimowski, and C. H. Wilson, NASA TP-1472 (1979).

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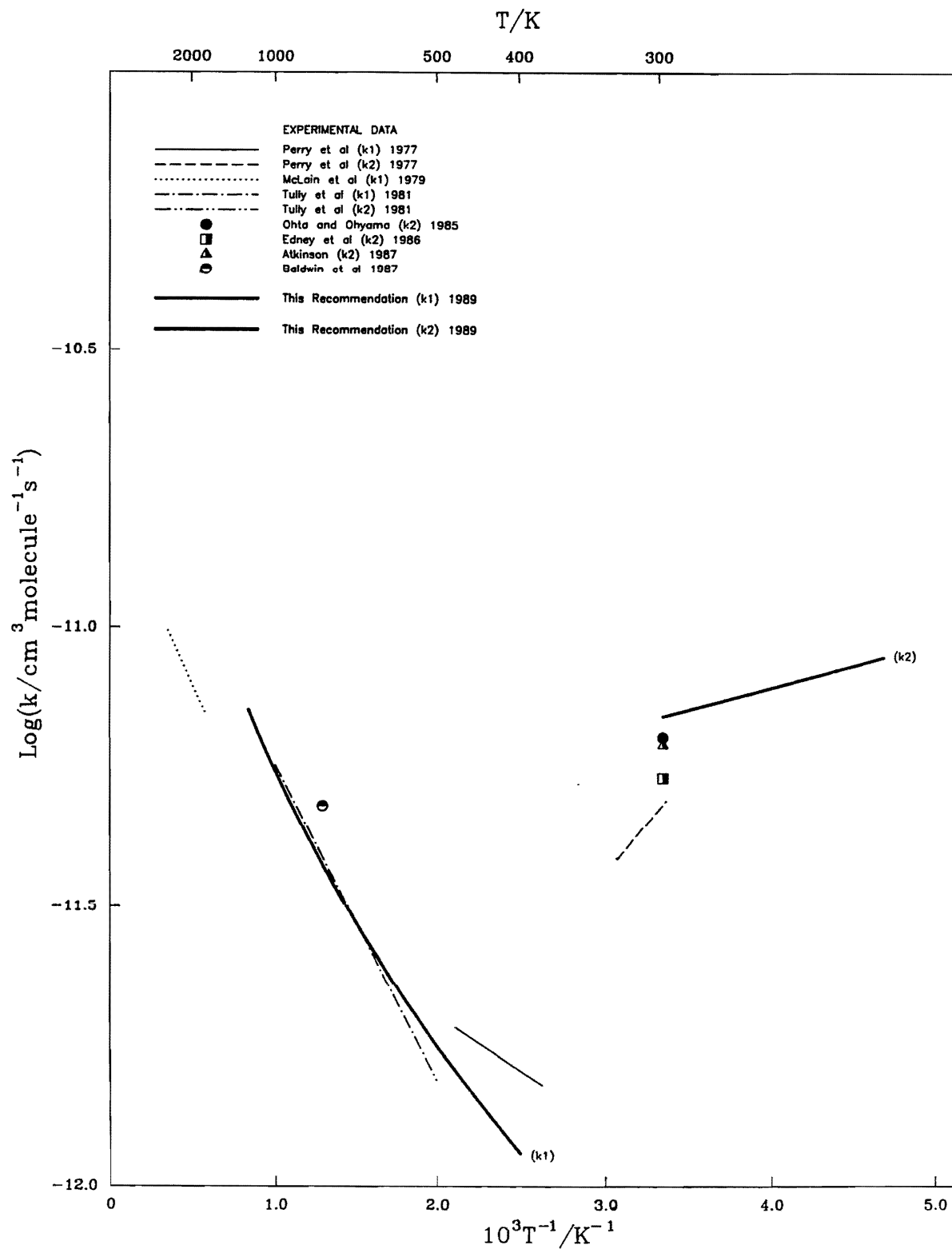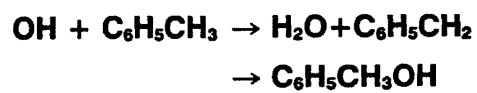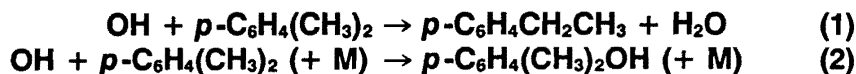
$$OH + C_6H_5CH_3 \rightarrow H_2O + C_6H_5CH_2$$
$$\rightarrow C_6H_5CH_3OH$$

T/K

$$OH + p\text{-}C_6H_4(CH_3)_2 \rightarrow p\text{-}C_6H_4CH_2CH_3 + H_2O \qquad (1)$$
$$OH + p\text{-}C_6H_4(CH_3)_2 \, (+ \, M) \rightarrow p\text{-}C_6H_4(CH_3)_2OH \, (+ \, M) \qquad (2)$$

Rate Coefficient Data ($k = k_1 + k_2$)

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	$T[\text{K}]$	Reference	Comments
Rate Coefficient Measurements			
$k_2 = 1.2 \cdot 10^{-11}$	298	Doyle *et al.* (1975)[1]	(a)
$k_2 = 1.2 \cdot 10^{-11}$	298	Hansen *et al.* (1975)[2]	(b)
$k_2 = 1.5 \cdot 10^{-11}$	298	Perry *et al.* (1977)[3]	(c)
$k_2 = 6.3 \cdot 10^{-12} \exp(+300/T)$	296–325		(d)
$k_1 = 6.3 \cdot 10^{-11} \exp(-1200/T)$	380–473		(e)
$k_2 = 8.8 \cdot 10^{-12}$	298	Ravishankara *et al.* (1978)[4]	(f)
$k_2 = 1.0 \cdot 10^{-11}$	298		(g)
$k_2 = 1.1 \cdot 10^{-11}$	298		(h)
$k_2 = 1.4 \cdot 10^{-11}$	298–320	Nicovich *et al.* (1981)[5]	(i)
$k_1 = 6.4 \cdot 10^{-11} \exp(-1440/T)$	500–960		(j)
$k_2 = 1.4 \cdot 10^{-11}$	298	Ohta and Ohyama (1985)[6]	(k)
$k_2 = 1.4 \cdot 10^{-11}$	296	Edney *et al.* (1986)[7]	(l)
$k_2 = 1.5 \cdot 10^{-11}$	298	Atkinson (1987)[8]	(m)

Comments

(a) Experimentally measured relative rate coefficient. $p \approx 1$ bar.

(b) to (e) Flash photolysis–resonance technique. OH radical concentrations monitored as a function of time. $p \approx 133$ mbar.

(f) Flash photolysis–resonance technique. $p \approx 4$ mbar Ar.

(g) Flash photolysis–resonance technique. $p \approx 27$ mbar He.

(h) Flash photolysis–resonance technique. $p \approx 270$ mbar He.

(i) Flash photolysis–resonance technique.

(j) Same method as in comment (i).

(k) Experimentally measured relative rate coefficient. $p \approx 1$ bar. Reference compound was hexane. H_2O_2 was the source of OH.

(l) Experimentally measured relative rate coefficient. $p \approx 1$ bar. Reference compound was cyclohexane. Methylnitrite was the source of OH.

(m) The source of the given experimental value is not cited. $p \approx 1$ bar.

Preferred Values

$k_1 = 6.4 \cdot 10^{-11} \exp(-1440/T)$ cm^3 molecule^{-1} s^{-1} over range 500–960 K

$k_2 = 1.4 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1} over range 298–320 K

Reliability

$\Delta \log k_1 = \pm 0.1$

$\Delta \log k_2 = \pm 0.1$

Comments on Preferred Values

The preferred value for k_1 is based on the data of Nicovich *et al.*[5]. The recommended k_2 is close to the high pressure limit.

References

[1] G. J. Doyle, A. C. Lloyd, K. R. Darnall, A. M. Winer, and J. N. Pitts, Jr., Environ. Sci. Technol. **9**, 237 (1975).

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$$\text{OH} + p\text{-C}_6\text{H}_4(\text{CH}_3)_2 \rightarrow p\text{-C}_6\text{H}_4\text{CH}_2\text{CH}_3 + \text{H}_2\text{O}$$
$$\rightarrow p\text{-C}_6\text{H}_4(\text{CH}_3)_2\text{OH}$$

EXPERIMENTAL DATA

☐   Doyle et al (k2) 1975
■   Hansen,Atkinson and Pitts (k2) 1975
△   Perry,Atkinson and Pitts (k2) 1977
▲   Perry,Atkinson and Pitts (k1) 1977
○   Ravishankara et al (k2)3Torr 1978
●   Ravishankara et al (k2)20Torr 1978
▣   Ravishankara et al (k2)200Torr 1978
⬭   Nicovich et al (k2) 1981
◓   Nicovich et al (k1) 1981
+   Ohta and Ohyama (k2) 1985
×   Edney et al (k2) 1986
◇   Atkinson (k2) 1987

————   This Recommendation (k1) 1989

————   This Recommendation (k2) 1989

$$OH + C_6H_5C_2H_5 \rightarrow C_6H_5C_2H_4 + H_2O \qquad (1)$$
$$\rightarrow C_6H_4C_2H_5 + H_2O \qquad (2)$$
$$OH + C_6H_5C_2H_5 (+ M) \rightarrow C_6H_5OHC_2H_5 (+ M) \qquad (3)$$

Thermodynamic Data
$\Delta H^\circ_{298} (1) = -157.4$ kJ mol^{-1}
$\Delta S^\circ_{298} (1) = 0.9$ J K^{-1}mol^{-1}
$K_p(1) = 3.4\ T^{-0.143} \exp(+18850/T)$

Rate Coefficient Data ($k = k_1 + k_2 + k_3$)

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$8.0 \cdot 10^{-12}$	305	Lloyd et al. (1976)[1]	(a)
$7.5 \cdot 10^{-12}$	298	Ravishankara et al. (1978)[2]	(b)
$7.1 \cdot 10^{-12}$	298		(c)
$8.0 \cdot 10^{-12}$	298		(d)
$6.8 \cdot 10^{-12}$	298	Ohta and Ohyama (1985)[3]	(e)

Comments

(a) Relative rates of disappearence of ethylbenzene in air. $p \approx 1$ bar. Analysis by GC.
(b) Flash photolysis–resonance fluorescence technique at pressure 4 mbar He.
(c) Same as comment (b); pressure 27 mbar He.
(d) Same as comment (b); pressure 270 mbar He.
(e) Photolysis at atmospheric pressure. Analysis by GC.

Preferred Values

$k = 7.5 \cdot 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K and $p \le 1$ bar

Reliability
$\Delta \log k = \pm 0.1$
$\Delta \log k_1 = \pm 0.1$

Comments on Preferred Values
The preferred value for k corresponds to the addition channel and is the average value of the cited data.

References

[1]A. C. Lloyd, K. R. Darnall, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **80**, 789 (1976).
[2]A. R. Ravishankara, S. Wagner, S. Fischer, G. Smith, R. Schiff, R. T. Watson, G. Tesi, and D. D. Davis, Int. J. Chem. Kin. **10**, 783 (1978).
[3]T. Ohta and T. Ohyama, Bull. Chem. Soc. Jpn. **58**, 3029 (1985).

$$H_2O (+ M) \rightarrow H + OH (+ M)$$

Thermodynamic Data
$\Delta H^\circ_{298} = 499$ kJ mol^{-1}
$\Delta S^\circ_{298} = 109$ J K^{-1}mol^{-1}
$K_p = 2.78 \cdot 10^2\ T^{1.2} \exp(-59800/T)$ atm

Rate Coefficient Data

k[cm^3 molecule^{-1} s^{-1}]	T[K]	M	Reference	Comments
Rate Coefficient Measurements				
Reviews and Evaluations				
$5.8 \cdot 10^{-9} \exp(-52920/T)$	2000–6000	N$_2$	Baulch et al. (1972)[1]	
$2.2 \cdot 10^{-8} \exp(-52920/T)$	2000–6000	Ar		
$3.7 \cdot 10^{-8} \exp(-52920/T)$	2000–6000	H$_2$O		
$5.8 \cdot 10^{-9} \exp(-52900/T)$	2000–6000	N$_2$	Tsang and Hampson (1986)[2]	

Preferred Values

$k = 5.8 \cdot 10^{-9} \exp(-52920/T)$ cm^3 molecule^{-1} s^{-1} over range 2000–6000 K for M = N$_2$

Reliability

$\Delta \log k = \pm 0.5$ for M = N$_2$

Comments on Preferred Values

The value preferred by Baulch *et al.*[1] is recommended because no new experimental data are available.

References

[1]D. L. Baulch, D. D. Drysdale, D. G. Horne, and A. C. Lloyd, "Evaluated Kinetic Data for High Temperature Reactions", Vol. 1: "Homogeneous Gas Phase Reactions of the H$_2$–O$_2$ System", London, Butterworths (1972).

[2]W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data **15**, 1987 (1986).

HO$_2$ + HO$_2$ → H$_2$O$_2$ + O$_2$
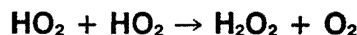
Thermodynamic Data

$\Delta H^{\circ}_{298} = -157$ kJ mol^{-1}

$\Delta S^{\circ}_{298} = -20.1$ J K^{-1}mol^{-1}

$K_p = 8.1 \cdot 10^{-3} \, T^{0.363} \exp(+19000/T)$

Rate Coefficient Data

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$(1.5–3.0) \cdot 10^{-12}$	1000–1250	Troe (1969)[1]	(a)
$1.14 \cdot 10^{-13} \exp(+1057/T)$	276–400	Lii *et al.* (1979)[2]	(b)
$3.8 \cdot 10^{-14} \exp(+1250/T)$	273–339	Cox and Burrows (1979)[3]	(c)
$4.1 \cdot 10^{-13} \exp(+630/T)$	298–510	Patrick and Pilling (1982)[4]	(d)
$2.3 \cdot 10^{-13} \exp(+600/T)$	230–420	Kircher and Sander (1984)[5]	(e)
$\quad + 8.4 \cdot 10^{-34} \exp(+1100/T)$ [Ar]			
$2.2 \cdot 10^{-13} \exp(+620/T)$			
$\quad + 1.9 \cdot 10^{-33} \exp(+980/T)$ [N$_2$]			
$(3.34 , 1.5 , 0.97) \cdot 10^{-12}$	298 , 418 , 577	Lightfoot *et al.* (1988)[6]	(f)
$(9.2 , 9.7 , 9.2) \cdot 10^{-13}$	623 , 677 , 723		
$1.14 \cdot 10^{-12}$	777		
Reviews and Evaluations			
$3.3 \cdot 10^{-12}$	300	Baulch *et al.* (1972)[7]	(g)
$2.3 \cdot 10^{-12}$	300	Baulch *et al.* (1980)[8]	(h)
$6.8 \cdot 10^{-14} \exp(+1155/T)$	300–400	Kaufman and Sherwell (1983)[9]	(i)
$3.3 \cdot 10^{-12}$	300–1200	Warnatz (1984)[10]	(j)
$3.0 \cdot 10^{-12}$	300–1200	Tsang and Hampson (1986)[11]	(k)
$5.0 \cdot 10^{-12} \exp(-698/T)$	570–770	Baldwin *et al.* (1986)[12]	(l)
$2.1 \cdot 10^{-10} \exp(-5050/T)$	300–1200	Lightfoot *et al.* (1988)[6]	(m)
$\quad + 1.8 \cdot 10^{-13} \exp(+885/T)$			
$5.7 \cdot 10^{-12} \exp(-2405/T)$			(n)
$\quad + 1.8 \cdot 10^{-13} \exp(+885/T)$			

Comments

(a) Thermal decomposition of H$_2$O$_2$ behind reflected shock waves in Ar carrier at total pressures between 0.6 and 12 atmospheres. Fitted k using complex mechanism. Value of k sensitive to k(OH + H$_2$O$_2$ → H$_2$O + HO$_2$) and consequently value of k may be slightly too high.

(b) Pulse radiolysis of mixtures containing 1200 Torr of H$_2$ and 5 Torr of O$_2$, to produce H atoms rapidly converted to HO$_2$. Decay of [HO$_2$] monitored by kinetic spectroscopy at 230 nm.

(c) Molecular modulation photolysis of Cl$_2$ in the presence of excess H$_2$ and O$_2$, or at lower pressures in the presence of HCHO and O$_2$. Total pressure varied between 3 and 760 Torr. [HO$_2$] measured by UV ab-

sorption at 230 nm. k found to be independent of pressure above 25 Torr.

(d) Flash photolysis of anhydrous Cl$_2$/CH$_3$OH/O$_2$ mixtures in N$_2$; total pressure of 700 Torr. [HO$_2$] measured by UV absorption at 227.5 nm.

(e) Flash photolysis of Cl$_2$/CH$_3$OH/O$_2$ mixtures. [HO$_2$] measured by UV absorption at 227.5 nm. Total pressure between 100 to 700 Torr with Ar and N$_2$. Authors observed both a zero-pressure bimolecular component and a termolecular component linearly dependent on pressure up to 700 Torr. Rate constants also determined when up to 10 Torr of H$_2$O added.

(f) Flash photolysis of Cl$_2$/CH$_3$OH/excess air mixtures at atmospheric pressure. [HO$_2$] measured by UV absorption between 200 and 227.5 nm. Allow for varia-

tion of extinction coefficient with temperature. No systematic dependence of k on experimental conditions other than temperature was observed, but pressure was not varied. Suggest a minimum value of k at about 700 K.

(g) Based on very limited data at room temperature.

(h) Recommend for atmospheric pressure only.

(i) Based on the results of Cox and Burrows[3] and of Lii et al.[2]. Values recommended refer to atmospheric pressure in the absence of H_2O and NH_3.

(j) Recommended without comment.

(k) Recommended as best value for a wide temperature range.

(l) A direct bimolecular abstraction reaction assumed at temperatures above 600 K. Troe's[1] value of k combined with a thermochemically-calculated A factor to give the activation energy quoted.

(m) Authors fitted a double Arrhenius expression to Troe's[1] single value of k at about 1150 K and their values at 760 Torr obtained between 298 and 777 K.

(n) An alternative fit to the above data based on the A factor recommended by Baldwin et al.[12]; Troe's value is effectively ignored.

Preferred Values

$k = 3.1 \cdot 10^{-12} \exp(-775/T) \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ between 550 and 1250 K

Reliability

$\Delta \log k = \pm 0.15$ between 550 and 800 K, rising to ± 0.3 at 1250 K

Comments on Preferred Values

The reaction is very important in combustion chemistry over the range 600–1200 K. Fortunately, a single, reliable recommendation may be made over this range. The graph shows data obtained above room temperature at pressures near to atmospheric (see comments). Troe's[1] single value of k was obtained from a study betweeen 0.6 and 12 atmospheres, and the Lii et al.[2] data were obtained at 1200 mmHg. Also shown is a theoretical estimate of k by Patrick, Golden, and Barker[13] over a wide range of temperatures for 700 mmHg of N_2. Below about 500 K, the rate constant varies with pressure and is particularly sen-

sitive to the presence of polar gases such as H_2O and NH_3. The existence of a negative temperature coefficient below 500 K is clearly established. Recommendation for the value of k below 500 K have been made by the IUPAC group[14]. Studies by Kircher and Sander[5], Lii et al.[2], Lightfoot, Veyret, and Lesclaux[6] all suggest that k becomes independent of pressure above about 500 K, and this is supported by the theoretical study[13]. Above 500 K, the recommendation is based on (i) Troe's shock-tube data point, which is sensitive to $k(OH + H_2O_2)$ required in a complex interpretation, (ii) the slight evidence obtained by Lightfoot, Veyret, and Lesclaux[6] for a minimum value for k at about 700 K, (iii) the theoretical study[13] which predicts a minimum at about 1000 K and then a steady increase in k up to 3000 K. Full details of the low-temperature data are given in the CODATA compilation[14].

To give a complete picture of the state of the data all of experimental results are included on the graph irrespective of whether the data are referenced in the text.

References

[1] J. Troe, Ber. Bunsenges. Phys. Chem. **73** 946 (1969).

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[5] C. C. Kircher and S. P. Sander, J. Phys. Chem. **88**, 2082 (1984).

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[7] D. L. Baulch, D. D. Drysdale, D. G. Horne and A. C. Lloyd, "Evaluated Kinetic Data for High Temperature Reactions", Vol. 1, Butterworths, London (1972).

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[9] M. Kaufman and J. Sherwell, Prog. Reactions Kinetics **12**, 1 (1983).

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[11] W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data **15**, 1087 (1986).

[12] R. R. Baldwin, C. E. Dean, M. R. Honeyman, and R. W. Walker, J. Chem. Soc., Faraday Trans. I, **82**, 89 (1986).

[13] R. Patrick, J. R. Barker and D. M. Golden, J. Phys. Chem. **88**, 128 (1984).

[14] R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, J. A. Kerr, and J. Troe, Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry, Supplement III, J. Phys. Chem. Ref. Data **18**, 881 (1989).

$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$

EXPERIMENTAL DATA

□ Troe 1969
■ Hochanadel et al 1972
△ Lii et al 1979
▲ Takacs and Howard 1986
○ Poukert and Johnston 1972
● Vardanyan et al 1974
◨ Hamilton and Lii 1977
▲ Graham et al 1979
— Cox and Burrows 1979
+ Burrows et al 1979
× Hochanadel et al 1980
◇ Thrush and Tyndall 1982
◆ Thrush and Tyndall 1982
▣ Patrick and Pilling 1982
▽ DeMore 1982
▼ Simonaitis and Heicklen 1982
▽ Sander et al 1982
◈ Sander 1984
◈ Rozenschtien et al 1985
◈ Tacaks and Howard 1984
◧ Catell and Cox 1986
▤ McAdam et al 1987
⊢—⊣ Baldwin et al 1984
▲ Andersson et al 1988
▼ Lightfoot et al 1988

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$$\text{HO}_2 + \text{NH}_2 \rightarrow \text{O}_2 + \text{NH}_3 \qquad (1)$$
$$\rightarrow \text{HNO} + \text{H}_2\text{O} \qquad (2)$$

Thermodynamic Data

$\Delta H^\circ_{298} (1) = -247 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (1) = -25.9 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(1) = 1.73 \cdot 10^{-2} \, T^{0.101} \exp(+29800/T)$

$\Delta H^\circ_{298} (2) = -343 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (2) = -14.3 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(2) = 0.472 \, T^{-0.138} \exp(+41200/T)$

Rate Coefficient Data ($k = k_1 + k_2$)

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	$T[\text{K}]$	Reference	Comments
Rate Coefficient Measurements			
$2.5 \cdot 10^{-11}$	298	Cheskis and Sarkisov (1979)[1]	(a)
$2.7 \cdot 10^{-11}$	349	Pagsberg, Eriksen, and Christensen (1979)[2]	(b)
Reviews and Evaluations			
$3.4 \cdot 10^{-11}$	298	CODATA (1984)[3]	(c)
–	–	Lesclaux (1984)[4]	(d)

Comments

(a) Flash photolysis of NH_3/O_2 mixtures. [NH_2] decay monitored by intracavity laser absorption spectroscopy at 598 nm. Reported value is based on ratio $k/k(\text{NH}_2 + \text{NH}_2) = 1.1$ at 570 Torr N_2 and $k(\text{NH}_2 + \text{NH}_2) = 2.5 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [6]. Measurements at 100 Torr N_2 give same value of k.

(b) Pulse radiolysis of NH_3/O_2 mixtures. [NH_2] decay monitored by absorption spectrometry at 598 nm. Absence of any effect of O_2 on the [NH_2] decay interpreted to imply that $k = k(\text{H} + \text{NH}_2)$. Value reported is value of $k(\text{H} + \text{NH}_2)$ determined in same study.

(c) Evaluation of room temperature data.

(d) Comprehensive review; no recommendation.

Preferred Values

$k = 2.6 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over range 300–400 K

Reliability

$\Delta \log k = \pm 0.4$ over the range 300–400 K

Comments on Preferred Values

There are no recent studies of this reaction; all previous Refs. have been reviewed[3,4]. There are two published studies[1,2] both giving rate constant ratios using different Ref. reactions but leading to values of k in excellent agreement. The recommended value is based on these. There is also some unpublished work of Kurasawa and Lesclaux[5] suggesting a value of k a factor of 2 higher. The recommended error limits encompass this value.

There are no measurements of branching ratios. Lesclaux, mainly on the basis of unpublished work, concludes that the most likely path is channel (2) but (1) probably occurs also.

References

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[3] CODATA Task Group on Chemical Kinetics, D. L. Baulch, R. A. Cox, R. F. Hampson, J. A. Kerr, J. Troe, and R. T. Watson, J. Phys. Chem. Ref. Data **11**, 385 (1982).

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[5] H. Kurasawa and R. Lesclaux, results presented at 14th Informal Conference on Photochemistry, Newport Beach, CA, March 1980.

[6] P. V. Khe, J. C. Soulignac, and R. Lesclaux, J. Phys. Chem. **81**, 210 (1977).

$$HO_2 + CH_3 \rightarrow OH + CH_3O \qquad (1)$$
$$\rightarrow O_2 + CH_4 \qquad (2)$$
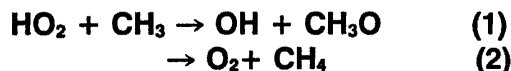
Thermodynamic Data

$\Delta H^\circ_{298} (1) = -101 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (1) = -11.0 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(1) = 9.33 \cdot 10^{-2} T^{1.00} \exp(+12300/T)$

$\Delta H^\circ_{298} (2) = -231 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (2) = -31.9 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(2) = 2.53 \cdot 10^{-2} T^{-1.05} \exp(+27900/T)$

Rate Coefficient Data

$k[\text{cm}^3 \text{ molecule}^{-1}\text{s}^{-1}]$	$T[\text{K}]$	Reference	Comments
Rate Coefficient Measurements			
$k_1 \simeq 3 \cdot 10^{-11}$	1030–1115	Colket, Naegeli, and Glassman (1977)[1]	(a)
Reviews and Evaluations			
$k_1 = 3.3 \cdot 10^{-11}$	300–2500	Tsang and Hampson (1986)[2]	(b)
$k_2 = 6.0 \cdot 10^{-12}$	300–2500		

Comments

(a) Study of the oxidation of CH_3CHO in a turbulent flow reactor at atmospheric pressure with end-product analysis by GC. Reaction (1) was proposed to account for the oxidation of CH_3 and a value of k was selected to obtain rate coefficients for other reactions in the mechanism consistent with literature data.

(b) k_1 taken from study of Colket *et al.*[1] and k_2 estimated from $k_2 = k_{-2}K_2$. It should be noted that the value of k_{-2} is very uncertain in this calculation.

Preferred Values

$k_1 = 3 \cdot 10^{-11} \text{cm}^3 \text{ molecule}^{-1}\text{s}^{-1}$ over range 600–1200 K

Reliability

$\Delta \log k_1 = \pm 1.0$ over range 600–1200 K

Comments on Preferred Values

We have recommended the value of k_1 determined indirectly by Colket *et al.*[1] but with wide error limits to indicate the large uncertainty. Direct measurements of the rate coefficient and its temperature dependence are needed.

References

[1]M. B. Colket, D. W. Naegeli, and I. Glassman, 16th Symp. (Int.) Combust., 1023 (1977).

[2]W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data 15,1087 (1986).

$$HO_2 + CH_4 \rightarrow H_2O_2 + CH_3$$

Thermodynamic Data

$\Delta H^\circ_{298} = 74.0 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} = 11.9 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p = 0.321 \, T^{0.468} \exp(-8950/T)$

Rate Coefficient Data

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	Temperature [K]	Reference	Comments
Rate Coefficient Measurements			
$4.2 \cdot 10^{-19}$	716	Baldwin, Jones and Walker (1988)[1]	(a)
Reviews and Evaluations			
$3.0 \cdot 10^{-13} \exp(-9350/T)$	no range quoted	Tsang and Hampson (1986)[2]	(b)
$1.5 \cdot 10^{-11} \exp(-12440 /T)$	625–1275	Baldwin, Jones, and Walker (1988)[1]	(c)

Comments

(a) Decomposition of tetramethylbutane in presence of O_2 as source of HO_2 with GLC analysis for products. Competitive study giving $k/k_1^{1/2}$; $k_1 = 3.1 \cdot 10^{-12}$

$\exp(-775/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ (see present recommended value).

(b) Estimate based on relation given by Walker[3] for HO_2 attack on alkane.

(c) Assumed A factor (per C—H bond) in Arrhenius expression is the same for HO_2 + CH_4 and HO_2 + C_2H_6, activation energy calculated from single temperature point.

Preferred Values

k = $1.5 \cdot 10^{-11}$ exp($-12440/T$) cm^3 molecule^{-1} s^{-1} over range 600–1000 K

Reliability

$\Delta \log k$ = ± 0.1 at 700 K rising to ± 0.2 at 600 K and ± 0.3 at 1000 K

Comments on Preferred Values

The value at 716 K is the only experimental determina-

tion of k. The value of $k/k_1^{1/2}$ is reliable and any error in k_1 is reduced by 50% in calculating k. The preferred value of k is based on the single determination and thermochemical considerations involving the reliable values of the rate constant for HO_2 + C_2H_6. The constants in the preferred value of k are reasonable for the reaction but if k is of the form $A\,T^n$ exp(E/RT) with n likely to be between 2 and 3, then extrapolation will lead to low values of k above 1000 K.

References

[1] R. R. Baldwin, P. N. Jones, and R. W. Walker, J. Chem. Soc., Faraday Trans. 2, **84**, 199 (1988).

[2] W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data **15**, 1087 (1986).

[3] R. W. Walker, in "Gas Kinetics and Energy Transfer", Specialist Periodical Report, Chemical Society, London, Vol. 2, 296 (1977).

HO_2 + HCHO → H_2O_2 + CHO
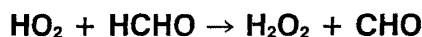
Thermodynamic Data

ΔH°_{298} = 12.9 kJ mol^{-1}

ΔS°_{298} = 9.8 J K^{-1}mol^{-1}

K_p = 0.673 $T^{0.292}$ exp($+9840/T$)

Rate Coefficient Data

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
k/k(HO_2 + CO) = 340	798	Blundell et al. (1965)[1]	(a)
k/k(HO_2 + CO) = 280	798	Hoare et al. (1967)[2]	(b)
$k/k^{0.5}$ (HO_2 + HO_2) = $9.2 \cdot 10^{-10}$	773	Baldwin et al. (1972)[3]	(c)
$1.9 \cdot 10^{-11}$ exp($-5230/T$)	773–973	Vardanyan et al. (1971)[4]	(d)
Reviews and Evaluations			
$1.7 \cdot 10^{-12}$ exp($-4030/T$)		Lloyd (1974)[5]	(e)
$3.3 \cdot 10^{-12}$ exp($-5870/T$)		Walker (1975)[6]	(f)
$3.3 \cdot 10^{-12}$exp($-5870/T$)		Tsang and Hampson (1986)[7]	(g)

Comments

(a) Study of the combustion of CH_4 in HF washed vessel. Attack of HO_2 on intermediate HCHO and CO compared by measuring O_2, CH_4, CO, CO_2, HCHO, and H_2O_2.

→ k = $2.8 \cdot 10^{-14}$ cm^3 molecule^{-1} s^{-1} if Tsang and Hampson's k(HO_2 + CO) is used.

(b) Same as (a) with boric acid coated vessel.

→ k = $2.3 \cdot 10^{-14}$ cm^3 molecule^{-1} s^{-1} if Tsang and Hampson's k(HO_2 + CO) is used.

(c) Measurement of the effect of HCHO in reducing the induction times of $H_2/O_2/N_2$ mixtures.

> k = $1.6 \cdot 10^{-15}$ cm^3 molecule^{-1} s^{-1} if Tsang and Hampson's k(HO_2 + HO_2) is used.

(d) ESR detection of HO_2 during oxidation of HCHO. H_2O_2 and HCHO trapped to measure H_2O_2 accumulation and HCHO decay. k calculated assuming H_2O_2 concentrations governed only by the HO_2/HCHO reaction, i.e. HO_2 + HO_2 → H_2O_2 and H_2O_2 + M →

2 OH are assumed to have a negligible effect on measured H_2O_2.

(e) Arrhenius factor A estimated. Combination with reported values leads to temperature dependence. Absolute values from relative rate studies are different however from above because of different Ref. rate constants.

(f) Based on the result of Baldwin et al. Assumed A leads to temperature dependence. A factor assumption based on a value of $1.7 \cdot 10^{-12}$ cm^3 molecule^{-1} s^{-1} per C—H bond.

(g) Recommend Walker's expression.

Preferred Values

k = $5.0 \cdot 10^{-12}$ exp($-6580/T$) cm^3 molecule^{-1} s^{-1} over range 600–1000 K

Reliability

$\Delta \log k$ = ± 0.5 over range 600–1000 K

Comments on Preferred Values

The preferred value is based on the determination of Baldwin *et al*.[3] at 773 K together with an assumed A factor of $5.0 \cdot 10^{-12}$ cm^3 molecule^{-1} s^{-1}. The only temperature dependence study gives a value for k at 773 K which is a factor of 20 higher and is considered unreliable.

References

[1]R. V. Blundell, W. G. A. Cook, D. E. Hoare, and G. C. Milne, 10th Symp. (Int.) Combust., 445 (1965).

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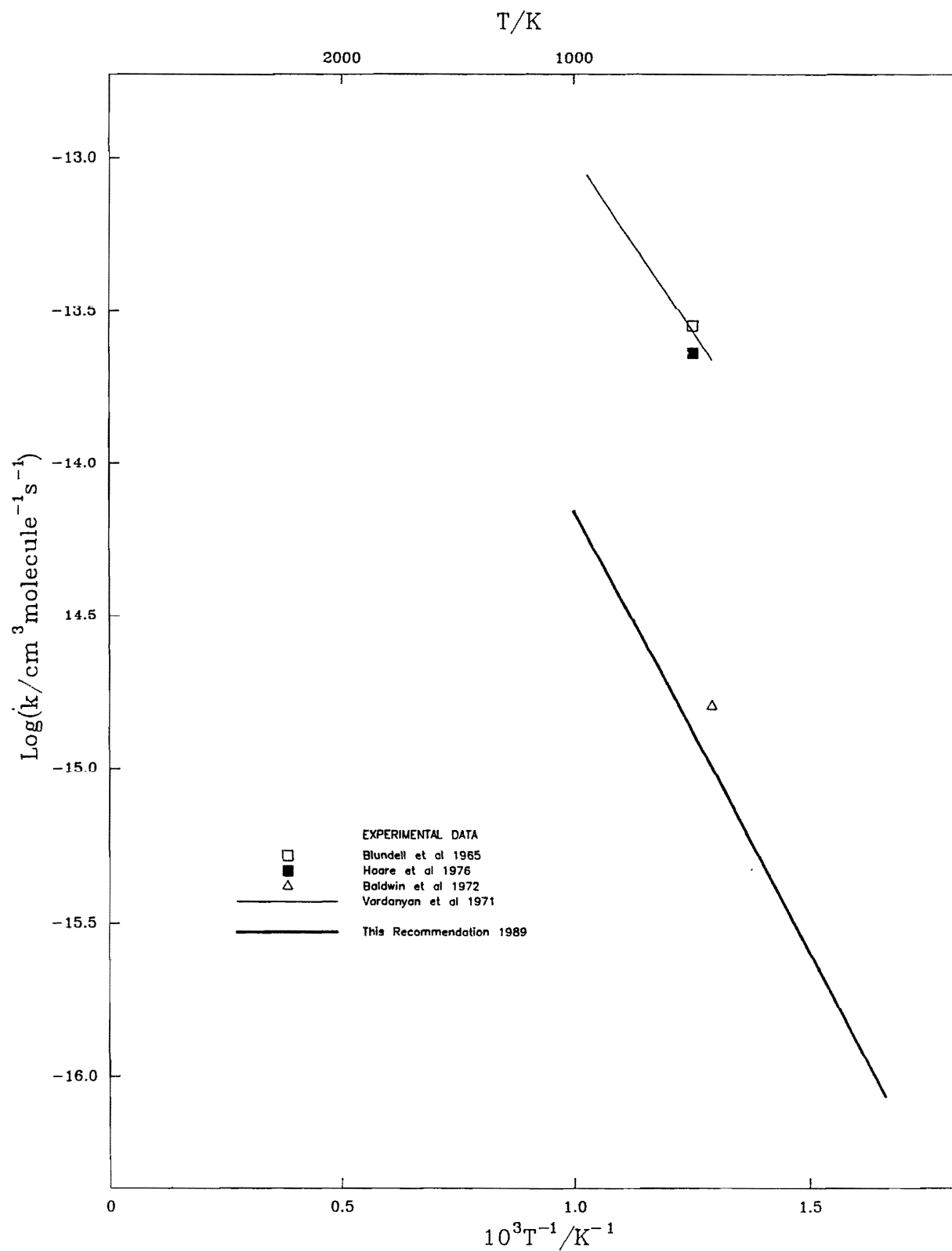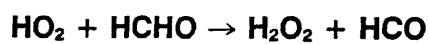
$$HO_2 + HCHO \rightarrow H_2O_2 + HCO$$

T/K

EXPERIMENTAL DATA

□ Blundell et al 1965
■ Hoare et al 1976
△ Baldwin et al 1972
─ Vardanyan et al 1971

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$HO_2 + C_2H_4 \rightarrow C_2H_4O + OH$

Rate Coefficient Data

$k[cm^3 \, molecule^{-1} \, s^{-1}]$	Temperature [K]	Reference	Comments
Rate Coefficient Measurements			
$1.6 \cdot 10^{-17}$	773	Walker (1973)[1]	(a)
$4.8 \cdot 10^{-17}$	773	Baldwin and Walker (1981)[2]	(b)
$1.05 \cdot 10^{-11} \exp(-9590/T)$	673–773	Baldwin *et al.* (1984)[3]	(c)
$3.7 \cdot 10^{-12} \exp(-8650/T)$	653–773	Baldwin *et al.* (1986)[4]	(d)
Reviews and Evaluations			
No reliable reviews			

Comments

(a) Thermal oxidation of HCHO used as source of HO_2. Measurement of relative yields of CO and oxirane gave $k/k(HO_2 + HCHO) = 0.016$ at 773 K. Use[5] of $k(HO_2 + HCHO) = 9.8 \cdot 10^{-16}$ cm^3 molecule^{-1} s^{-1} (based on $k(HO_2 + HO_2) = 3.1 \cdot 10^{-12} \exp(-775/T)$ cm^3 molecule^{-1} s^{-1} [6]) gives the absolute value of k.

(b) Addition of C_2H_4 to slowly reacting mixtures of $H_2 + O_2$, and measurement of yield of oxirane. Computer interpretation to determine $[HO_2]$.

(c) Decomposition of tetramethylbutane in presence of O_2 in KCl-coated vessels as source of HO_2 radicals, with GLC analysis of products. Competitive studies give $k/k_1^{0.5}$.
$k_1 = 3.1 \cdot 10^{-12} \exp(-775/T)$ cm^3 molecule^{-1} s^{-1} for reaction $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$. Later[4] shown that values of k are slightly too high above 723 K.

(d) Similar study to that referred to in comment (c), but aged-boric-acid-coated vessels used. Lack of surface effects makes results more reliable.

Preferred Values

$k = 3.7 \cdot 10^{-12} \exp(-8650/T)$ cm^3 molecule^{-1} s^{-1} over range 600–900 K

Reliability
$\Delta \log k = \pm 0.15$ between 600 and 750 K, rising to ± 0.25 at 900 K

Comments on Preferred Values

No absolute determinations of k have been made, and all are based on measurements of oxirane. The values of $k/k_1^{0.5}$ in the Baldwin, Dean, and Walker study[4] are reliable, and any error in k_1 is reduced by 50% in calculating k. The preferred values for k form part of a consistent set of data for HO_2 addition to a number of alkenes[7]. On the basis of this it has been argued that the rate parameters do refer to the addition steps $HO_2 + C_2H_4 \rightarrow CH_2-CH_2OOH$[3,7]. This reaction is unlikely to be important in combustion chemistry above 900 K.

The recommended values are preferred to those of a previous study[3] which was carried out in KCl-coated vessels as it is possible that $[HO_2]$ may be affected by a small amount of radical generation at the surface above 720 K.

References

[1] R. W. Walker, 14th Symp. (Int.) Combust., 265 (1973).

[2] R. R. Baldwin and R. W. Walker, 18th Symp. (Int.) Combust., 819 (1981).

[3] R. R. Baldwin, D. E. Hopkins, D. G. Malcolm, and R. W. Walker, Oxid. Comm. 6, 231 (1984).

[4] R. R. Baldwin, C. E. Dean, and R. W. Walker, J. Chem. Soc., Faraday Trans. I, 82, 1445 (1986).

[5] R. R. Baldwin, A. R. Fuller, D. Longthorn, and R. W. Walker, J. Chem. Soc., Faraday Trans. I, 68, 1362 (1972).

[6] See recommendation for $k(HO_2 + HO_2 \rightarrow H_2O_2 + O_2)$.

[7] S. K. Gulati, S. Mather, and R. W. Walker, J. Chem. Soc., Faraday Trans. II, 83, 2171 (1987).

$HO_2 + C_2H_4 \rightarrow C_2H_4O + OH$

T/K

EXPERIMENTAL DATA
□   Walker 1973
■   Baldwin and Walker 1981
── Baldwin et al 1984
▲   Baldwin et al 1986

─── This Recommendation 1989

$10^3 T^{-1}/K^{-1}$

HO₂ + C₂H₆ → H₂O₂ + C₂H₅
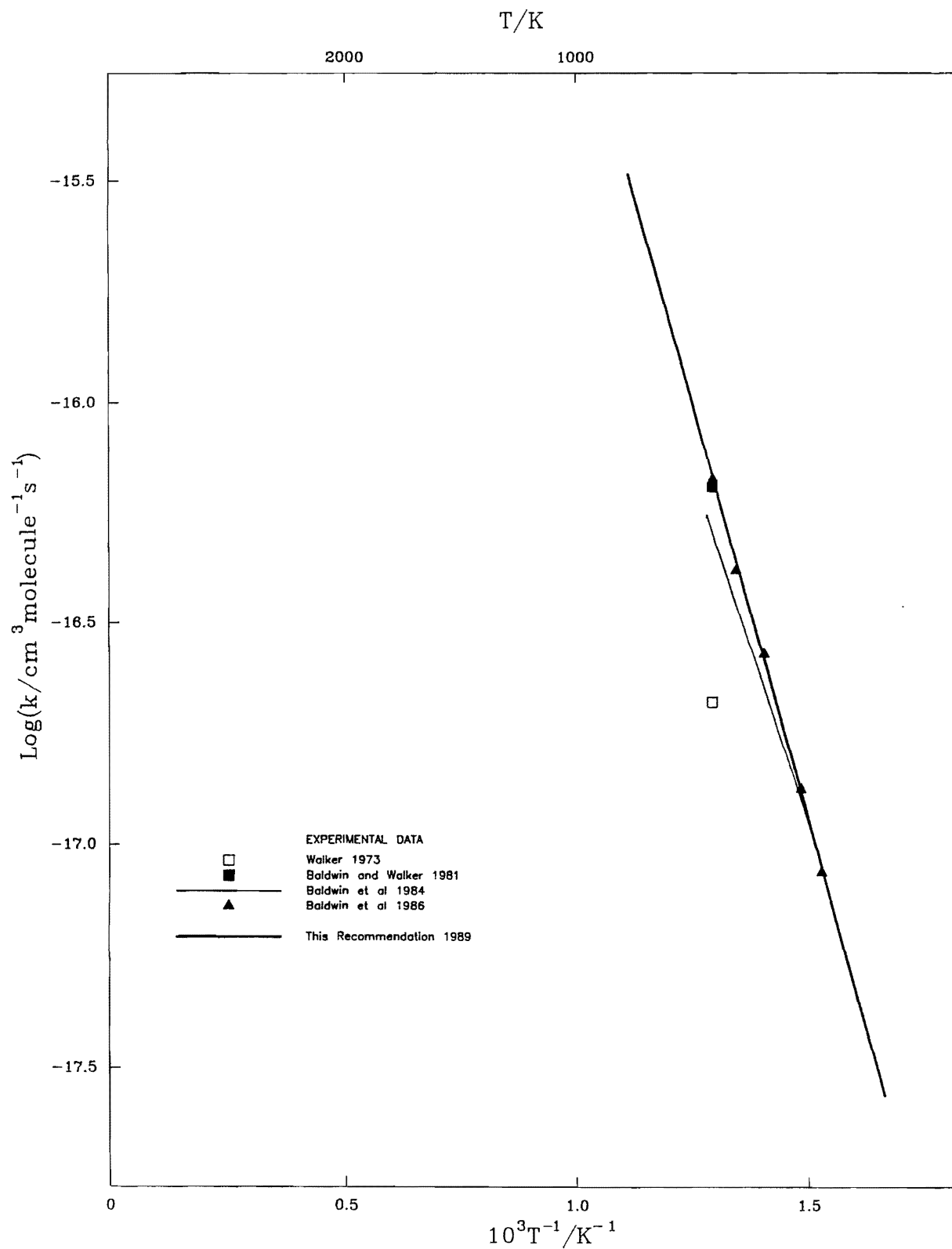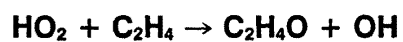
Thermodynamic Data
ΔH°_{298} = 54.5 kJ mol⁻¹
ΔS°_{298} = 26.5 J K⁻¹mol⁻¹
K_p = 51.8 $T^{-0.082}$ exp(−6650/T)

Rate Coefficient Data

k [cm³ molecule⁻¹ s⁻¹]	Temperature [K]	Reference	Comments
Rate Coefficient Measurements			
9.5·10⁻¹⁸	734	Hoare and Patel (1969)[1]	(a)
2.0·10⁻¹⁶	773		
2.22·10⁻¹¹ exp(−10335 /T)	673–773	Baldwin *et al*. (1986)[2]	(b)
Reviews and Evaluations			
1.7·10⁻¹² exp(−7050/T)	–	Lloyd (1974)[3]	(c)
4.9·10⁻¹³ exp(−7520/T)	300–800	Walker (1977)[4]	(d)
1.0·10⁻¹¹ exp(−9770/T)	300–1000	Warnatz (1984)[5]	(e)

Comments

(a) Oxidation of CH₄/C₂H₆ mixtures. Obtained k/k(HO₂ + CO) = 3.8 ± 0.7 and 0.4 at 773 K and 734 K, respectively. Authors consider values unreliable. Values of k obtained from k(HO₂ + CO) = 2.5·10⁻¹⁰ exp(−11870/T) cm³ molecule⁻¹ s⁻¹ given by Baulch *et al*.[6].

(b) Decomposition of tetramethylbutane in presence of O₂ as source of HO₂ radicals, with GLC analysis of products. Competitive studies giving $k/k_1^{1/2}$;
k_1 = 3.1·10⁻¹² exp(−775/T) cm³ molecule⁻¹ s⁻¹ for HO₂ + HO₂ → H₂O₂ + O₂ (see present recommended value).

(c) An upper limit for k, based on early H₂ + O₂ addition studies by Baldwin *et al*.[3].

(d) Estimate based on rate constant for HO₂ attack on *i*-butane and 2,3-dimethylbutane.

(e) Recommended without comment, but based on an estimate by Baldwin and Walker[7].

Preferred Values

k = 2.22·10⁻¹¹ exp(−10335/T) cm³ molecule⁻¹ s⁻¹ over range 500–1000 K

Reliability
Δlog k = ± 0.1 between 670 K and 770 K rising to ± 0.2 at 500 K and ± 0.3 at 1000 K

Comments on Preferred Values
The only reliable experimental results are those of Baldwin *et al*. The values of $k/k_1^{1/2}$ are reliable and any error in k_1 is reduced by 50% in calculating k. The constants in the preferred expression are reasonable, but if k is of the form A T^n exp(E/RT) with n likely to be between 2 and 3, then extrapolation will lead to low values of k above 1000 K.

References

[1]D. E. Hoare and M. Patel, Trans. Faraday Soc. **65**, 1325 (1969).
[2]R. R. Baldwin, C. E. Dean, M. R. Honeyman, and R. W. Walker, J. Chem. Soc., Faraday Trans. 1, **82**, 89 (1986).
[3]A. C. Lloyd, Int. J. Chem. Kin. **6**, 169 (1974).
[4]R. W. Walker, in "Gas Kinetics and Energy Transfer", Specialist Periodical Review, Chemical Society, London, Vol 2, 297 (1977).
[5]J. Warnatz, in "Combustion Chemistry", ed. W. C. Gardiner, Springer-Verlag, New York (1984).
[6]D. L. Baulch, D. D. Drysdale, J. Duxbury, and S. Grant, Evaluated Kinetic Data for High Temperature Reactions, Vol. 3, 263, Butterworths, London (1976).
[7]R. R. Baldwin, J. P. Bennett, and R. W. Walker, 16th Symp. (Int.) Combust., 1041 (1977).

HO₂ + CH₃CHO → CH₃CO + H₂O₂

Thermodynamic Data
ΔH°_{298} = −3.85 kJ mol⁻¹
ΔS°_{298} = 6.78 J K⁻¹ mol⁻¹
K_p = 2.13 $T^{0.0524}$ exp(+385/T)

Rate Coefficient Data

k [cm³ molecule⁻¹ s⁻¹]	T[K]	Reference	Comments
Rate Coefficient Measurements			
2.8·10⁻¹² exp(−5350/T)	1030–1115	Colket *et al*. (1975)[1]	(a)

Comments

(a) High temperature oxidation of CH_3CHO (1030–1115 K). Turbulent flow – stable species determined by GC. The time dependence of $[CH_3CHO]$, $[H_2]$, $[CO]$, $[CH_4]$, $[C_2H_6]$, $[CO_2]$, $[C_2H_4]$, and $[HCHO]$ results modelled by a 25 reaction chemical scheme. Rate constants were derived for 4 reactions.

Preferred Values

$k = 5.0 \cdot 10^{-12} \exp(-6000/T)$ cm^3 molecule^{-1} s^{-1} over range 900–1200 K

Reliability
$\Delta \log k = \pm 0.7$ over range 900–1200 K

Comments on Preferred Values

The experimental value of Colket *et al.* is compatible with the current knowledge of HO_2 abstraction reactions although the determination was very indirect. The preferred expression is based on a value of $1.7 \cdot 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 1050 K from this study and an assumed A factor of $5.0 \cdot 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

References

[1]M. B. Colket, D. W. Naegeli, and I. Glassman, 16th Symp. (Int.) Combust., 1023 (1976).

H_2O_2 (+ M) → OH + OH (+ M)

Thermodynamic Data
$\Delta H^\circ_{298} = 214$ kJ mol^{-1}
$\Delta S^\circ_{298} = 134$ J K^{-1}mol^{-1}
$K_p = 4.42 \cdot 10^7 \, T^{-0.091} \exp(-26000/T)$ atm

Rate Coefficient Data

$k[s^{-1}]$	$T[K]$	[M] [molecule cm^{-3}]	Reference	Comments
Rate Coefficient Measurements				
Low Pressure Range				
[Ar] $3.0 \cdot 10^{-8} \exp(-21600/T)$	450–1450	$(0.5-5) \cdot 10^{19}$	Kijewski and Troe (1972)[1]	(a)
Intermediate Fall-off Range				
$2.0 \cdot 10^{12} \exp(-21600/T)$	1100–1300	$1.2 \cdot 10^{20}$ (Ar)	Meyer *et al.* (1969)[2]	(b)
Reviews and Evaluations				
$k_0 = [N_2] \, 2.0 \cdot 10^{-7} \exp(-22900/T)$	700–1500		Baulch *et al.* (1972)[3]	(c)
$k_0 = [N_2] \, 3.6 \cdot 10^{-15} \, T^{-4.86} \exp(-26795/T)$	500–1500		Tsang and Hampson (1986)[4]	(d)
$k_0 = [Ar] \, 10^{-7.5} \exp(-21640/T)$	1000–1400		Brouwer *et al.* (1987)[5]	(e)
$k_\infty = 10^{14.47} \exp(-24374/T)$	1000–1500			
$F_c(Ar) = 0.5$	500–1500			

Comments

(a) Shock wave experiments of H_2O_2 decomposition monitoring UV absorption from H_2O_2 and HO_2. Minor correction of earlier results from Refs. 2 and 6 taking into account water content of the shock-heated H_2O_2/Ar mixtures.

(b) As comment (a).

(c) Comprehensive review of static reactor, flow system, and shock wave results including Refs. 2 and 6.

(d) Based on Ref. 3. RRKM calculations of the forward and reverse reaction are given.

(e) Theoretical evaluation of low pressure, high pressure, and fall-off data for dissociation and recombination in comparison to energy-resolved dissociation lifetime measurements after laser excitation.

Preferred Values

$k_0 = [Ar] \, 3.0 \cdot 10^{-8} \exp(-21600/T)$ s^{-1} over range 1000–1500 K

$k_0 = [N_2] \, 2.0 \cdot 10^{-7} \exp(-22900/T)$ s^{-1} over range 700–1500 K

$k_\infty = 3.0 \cdot 10^{14} \exp(-24400/T)$ s^{-1} over range 1000–1500 K

$F_c = 0.5$ for M = Ar over range 700–1500 K

Reliability
$\Delta \log k_0 = \pm 0.2$ over range 700–1500 K
$\Delta \log k_\infty = \pm 0.5$ over range 700–1500 K
$\Delta F_c = \pm 0.1$ over range 700–1500 K

Comments on Preferred Values

The preferred values represent the experimental results in satisfactory comparison with theoretical modelling.

The high pressure data are from a single experiment only and, therefore, require independent confirmation. However, they are consistent with non-thermal dissociation results.

References

[1]H. Kijewski and J. Troe, Helv. Chim. Acta 55, 205 (1972).
[2]E. Meyer, H. A. Olschewski, J. Troe, and H. Gg. Wagner, 12th Symp. (Int.) Combust., 345 (1969).

[3]D. L. Baulch, D. D. Drysdale, D. G. Horne, and A. C. Lloyd, "Evaluated Kinetic Data for High Temperature Reactions", Vol. 1: "Homogeneous Gas Phase Reactions of the H_2–O_2 System", London, Butterworths (1972).
[4]W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data 15, 1087 (1986).
[5]L. Brouwer, C. J. Cobos, J. Troe, H. R. Dübal, and F. F. Crim, J. Chem. Phys. 86, 6171 (1987).
[6]J. Troe, Ber. Bunsenges. Phys. Chem. 73, 946 (1969).

N + CN → N₂ + C
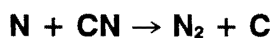
Thermodynamic Data
$\Delta H^\circ_{298} = -191 \text{ kJ·mol}^{-1}$
$\Delta S^\circ_{298} = -6.22 \text{ J·K}^{-1}\text{mol}^{-1}$
$K_p = 0.937 \ T^{-0.095} \exp(+22900/T)$

Rate Coefficient Data

$k[\text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	$T[\text{ K }]$	Reference	Comments
Rate Coefficient Measurements			
$1.0 \cdot 10^{-10}$	300	Whyte and Phillips (1983)[1]	(a)
Reviews and Evaluations			
–	–	Baulch *et al*. (1981)[2]	(b)

Comments

(a) Fast flow system, CN generated by pulsed laser photolysis of C_2N_2 at 193 nm. N generated by electrical discharge in N_2 and [N] measured by titration with NO. [CN] decay in excess N monitored by laser induced fluorescence. Total pressures 1.5–3.5 Torr.

(b) Survey of all data to 1980; no recommendation.

Preferred Values

$k = 3 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over range 300–2500 K

Reliability
$\Delta \log k = \pm 1.0$ over range 300–2500 K

Comments on Preferred Values

Results up to 1980 have been reviewed[2]. Only more recent results are tabulated.

The mechanism of the reaction of CN radicals with N atoms is not well understood. It is not clear whether N_2 molecules are formed directly by the reaction CN + N →

C + N_2 or by the sequence N + CN → CN_2 + M, N + CN_2 → CN + N_2. The only data at high temperatures comes from Slack and Fishburne[3]. These data have been re-evaluated by Slack[4,5]. Confirmatory studies are required before they can be recommended.

At low temperatures the measurements scatter over four orders of magnitude. The most recent study gives a value of k at 300 K comparable with the only high temperature data.

The recommended value together with the substantial error limits encompass the high temperature and recent low temperature data.

References

[1]A. R. Whyte and L. F. Phillips, Bull. Soc. Chim. Belg. 92, 635 (1983).
[2]D. L. Baulch, J. Duxbury, S. J. Grant, and D. C. Montague, "Evaluated Kinetic Data for High Temperature Reactions", Vol. 4, Homogeneous Gas Phase Reactions of Halogen- and Cyanide-containing Species. J. Phys. Chem. Ref. Data 10, Suppl. 1 (1981).
[3]M. W. Slack and E. S. Fishburne, J. Chem. Phys. 52, 5830 (1970).
[4]M. W. Slack, Proc. 10th Int. Shock Tube Symp., 544 (1975).
[5]M. W. Slack, J. Chem. Phys. 64, 228 (1983).

$$\text{N + NCO} \rightarrow \text{NO + CN} \qquad (1)$$
$$\rightarrow \text{N}_2 + \text{CO} \qquad (2)$$
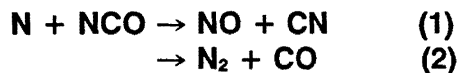
Thermodynamic Data

$\Delta H^\circ_{298} (1) = -107 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (1) = -2.79 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(1) = 2.68 \cdot 10^4 \, T^{-0.995} \exp(+12500/T)$

$\Delta H^\circ_{298} (2) = -743 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (2) = -3.73 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(2) = 5.20 \cdot 10^3 \, T^{-1.18} \exp(+88900/T)$

Rate Coefficient Data ($k = k_1 + k_2$)

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	$T[\text{K}]$	Reference	Comments
Rate Coefficient Measurements			
$k_1 = 1.7 \cdot 10^{-12}$	1700	Lifshitz and Frenklach (1980)[1]	(a)
$k_2 = 3.3 \cdot 10^{-11}$	1700		

Comments

(a) Measurement of the induction time for ignition behind reflected shocks in $C_2N_2/O_2/Ar$ mixtures. Values of k obtained by computer fitting to assumed reaction mechanism. Fitting reasonably sensitive to value of k_2 but not to k_1.

Preferred Values

$k_2 = 3.3 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 1700 K

Reliability

$\Delta \log k_2 = \pm 0.5$ at 1700 K

Comments on Preferred Values

There have been no direct measurements of the rate coefficients of this reaction. The two channels have been assumed to be of similar importance[1] but there is no experimental confirmation.

Louge and Hanson[2,3] have calculated values of k_1 from the equilibrium constant and the only measured values of k_{-1} by Colket[4]. They obtain

$k_1 = 7.6 \cdot 10^{-10} \exp(-5580/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the range 2150–2400 K. Using Colket's expression for k_{-1} and more recent thermodynamic data, we obtain

$k_1 = 4.6 \cdot 10^{-6} \, T^{-0.995} \exp(-8690/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the same temperature range. This gives a value close to that assigned to k_1 at 1700 K by Lifshitz and Frenklach[1] confirming the predominance of channel (2).

We accept the only experimental data available for k_2 as our recommended value but with large error limits.

References

[1] A. Lifshitz and M. Frenklach, Int. J. Chem. Kin. 12, 159 (1980).

[2] M. Y. Louge and R. K. Hanson, Int. J. Chem. Kin. 16, 213 (1984).

[3] M. Y. Louge and R. K. Hanson, Comb. Flame 58, 291 (1984).

[4] M. B. Colket, Am. Chem. Soc. 183rd Meeting, Abstr. of Papers, Phys. 7 (1982).

$$\text{NH + O}_2 \rightarrow \text{NO + OH} \qquad (1)$$
$$\rightarrow \text{NO}_2 + \text{H} \qquad (2)$$
$$\rightarrow \text{HNO + O} \qquad (3)$$
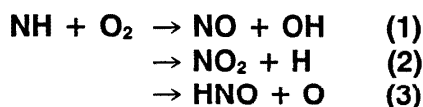
Thermodynamic Data (See Comments on Preferred Values)

$\Delta H^\circ_{298} (1) = -227 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (1) = 8.05 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(1) = 8.27 \, T^{-0.154} \exp(+27200/T)$

$\Delta H^\circ_{298} (2) = -105 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (2) = -31.7 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(2) = 2.22 \cdot 10^{-4} \, T^{0.655} \exp(+12900/T)$

$\Delta H^\circ_{298} (3) = -7.73 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (3) = 4.65 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(3) = 9.64 \cdot 10^{-2} \, T^{0.237} \exp(+1060/T)$

Rate Coefficient Data ($k = k_1 + k_2 + k_3$)

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	$T[\text{K}]$	Reference	Comments
Rate Coefficient Measurements			
$8.5 \cdot 10^{-15}$	296	Zetzsch and Hansen (1978)[1]	(a)
$< 3.32 \cdot 10^{-14}$	300	Pagsberg *et al.* (1979)[2]	(b)
$1.26 \cdot 10^{-13} \exp(-770/T)$	268–543	Hack, Kurzke, and Wagner (1985)[3]	(c)
Reviews and Evaluations			
–		Hanson and Salimian (1984)[4]	(d)

Comments

(a) Flash photolysis study. NH generated by photolysis of $NH_3/O_2/He$ mixtures. [NH] monitored by resonance fluorescence. No effect of changes in total pressure observed.

(b) Pulse radiolysis of NH_3/O_2 mixtures. [NH] monitored by absorption spectroscopy. Decay of [NH] fitted by computer modelling of reaction mechanism.

(c) Discharge flow system. NH produced by the sequence $F + NH_3 \rightarrow NH_2 + HF$, $NH_2 + F \rightarrow NH + HF$. [O] and [H] monitored by resonance fluorescence and [NH] and [OH] by laser induced fluorescence. Reaction $NH + O_2(^1\Delta_g) \rightarrow$ products also studied; $k \leqslant (1 \pm 2) \cdot 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1} obtained for it.

(d) Review of all data to 1984; theoretical expression due to Miller *et al*.[5] suggested but no expression recommended.

Preferred Values

$k = 1.26 \cdot 10^{-13}$ $\exp(-770/T)$ cm^3 $molecule^{-1}$ s^{-1} over range 270–550 K

Reliability

$\Delta\log k = \pm 0.2$ at 270 K rising to ± 0.5 at 550 K

Comments on Preferred Values

The preferred rate expression is that of Hack *et al*.[3] with which the k value of Zetzsch and Hansen[1] at 296 K is in close agreement, but wide error limits are assigned reflecting the lack of confirmatory data over the temper-

ature range. There is only one experimental measurement of the temperature coefficient of k and, in view of the low values of the pre-exponential factor and E/R, there may be appreciable upward curvature of the Arrhenius plot. Extrapolation to higher temperature is thus very uncertain.

Hansen and Salimian[4] quote an expression derived by Miller *et al*.[5] $(k = 1.66 \cdot 10^{-11}$ $\exp(-6000/T))$ but this gives values much lower than the sparse experimental data available.

The only experimental information on the branching ratios comes from the work of Hack *et al*.[3] who observed no H atom production in their study at 268–543 K. They favour channel (1) as the predominant channel.

Theoretical calculations by Melius and Binkley[6] favour channels (1) and (2) as the most likely low temperature paths with channel (3) becoming dominant at higher temperatures.

The thermodynamic data should be used with caution. There are significant uncertainties associated with the data on NH.

References

[1]C. Zetzsch and I. Hansen, Ber. Bunsenges. Phys. Chem. **82**, 830 (1978).

[2]P. B. Pagsberg, J. Eriksen, and H. C. Christensen, J. Phys. Chem. **83**, 582 (1979).

[3]W. Hack, H. Kurzke, and H. Gg. Wagner, J. Chem. Soc., Faraday Trans. II, **81**, 949 (1985).

[4]R. K. Hanson and S. Salimian, in "Combustion Chemistry", ed. W. C. Gardiner, Springer-Verlag, New York (1984).

[5]J. A. Miller, M. D. Smooke, R. M. Green, and R. J. Kee, Fall Meeting Western Sec. Comb. Inst. (1982).

[6]C. F. Melius and J. S. Binkley, in "The Chemistry of Combustion Processes", ed. T. M. Sloane, A. C. S. Symp. Series **249**, 103 (1984).

$$NH + NO \rightarrow H + N_2O \qquad (1)$$
$$\rightarrow HN_2 + O \qquad (2)$$
$$\rightarrow N_2 + OH \qquad (3)$$
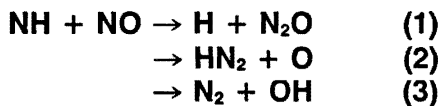
Thermodynamic Data (See Comments on Preferred Values)

$\Delta H^\circ_{298} (1) = -147$ kJ mol^{-1}

$\Delta S^\circ_{298} (1) = -57.3$ J $K^{-1}mol^{-1}$

$K_p(1) = 4.64 \cdot 10^{-7}$ $T^{1.10}\exp(+18100/T)$

$\Delta H^\circ_{298} (2) = 47.5$ kJ mol^{-1}

$\Delta S^\circ_{298} (2) = -6.48$ J $K^{-1}mol^{-1}$

$K_p(2) = 3.58 \cdot 10^{-2}$ $T^{0.346}\exp(-5530/T)$

$\Delta H^\circ_{298} (3) = -408$ kJ mol^{-1}

$\Delta S^\circ_{298} (3) = -16.7$ J $K^{-1}mol^{-1}$

$K_p(3) = 0.484$ $T^{-0.180}$ $\exp(+49000/T)$

Rate Coefficient Data ($k = k_1 + k_2 + k_3$)

$k[cm^3$ $molecule^{-1}$ $s^{-1}]$	$T[K]$	Reference	Comments
Rate Coefficient Measurements			
$4.8 \cdot 10^{-11}$	300	Cox, Nelson, and McDonald (1985)[1]	(a)
$5.78 \cdot 10^{-11}$	269–373	Harrison, Whyte, and Phillips (1986)[2]	(b)
Reviews and Evaluations			
	—	Hanson and Salimian (1985)[3]	(c)

Comments

(a) Pulsed laser photolysis of N_2H_4/He/NO mixtures at 266 nm in flowing system. [NH] decay monitored by laser induced fluorescence at 304.85 nm.

(b) Pulsed laser photolysis of N_2H_4/Ar/NO mixtures at 248 nm in flowing system. [NH] decay monitored by laser induced fluorescence at 336 nm. He, N_2, and N_2O also used as carrier gases give same results.

(c) Review of data to 1985; no recommendation.

Preferred Values

$k = 5.0 \cdot 10^{-11}$ over range 269–373 K

Reliability
$\Delta \log k = \pm 0.2$ over range 269–373 K

Comments on Preferred Values

Studies up to 1985 have been reviewed[3]. Only more recent measurements are tabulated here.

At low temperatures there is excellent agreement between all of the available studies. Our recommendation is based on all of them[1,2,4,5].

At higher temperatures there are three studies[6,7,8] covering the range 670–2850 K. They are extremely divergent both in absolute values of k and their temperature coefficients of k. All are nearly an order of magnitude or more lower than the values measured at temperatures close to 300 K. Further high temperature studies are required be-fore any recommendation can be made for this temperature regime.

There are no experimental data on the relative importance of the various channels. Calculations[9] suggest that, of the bimolecular routes, channel (1) is likely to predominate since channel (2) is highly endothermic and channel (3), although exothermic, is likely to have a substantial activation energy as a result of the 1–3 hydrogen shift required to produce N_2 and OH from the initially formed HNNO.

The thermodynamic data should be used with caution. There are significant uncertainties associated with the data on NH.

References

[1] J. W. Cox, H. H. Nelson, and J. R. McDonald, Chem. Phys. **96**, 175 (1985).

[2] J. A. Harrison, A. R. Whyte, and L. F. Phillips, Chem. Phys. Lett. **129**, 346 (1986).

[3] R. K. Hanson and S. Salimian, in "Combustion Chemistry", ed. W. C. Gardiner, Springer-Verlag, New York (1984).

[4] S. Gordon, W. Mulac, and P. Nangia, J. Phys. Chem. **75**, 2087 (1971).

[5] I. Hansen, K. Höinghaus, C. Zetzsch, and F. Stuhl, Chem. Phys. Lett. **42**, 370 (1976).

[6] W. S. Nip, Ph. D. Thesis, University of Toronto (1974), reported in Ref. 3.

[7] T. R. Roose, R. K. Hanson, and C. H. Kruger, 18th Symp. (Int.) Combust., 853 (1981).

[8] R. C. Petersen, Ph. D. Thesis, Purdue University (1981), reported in Ref. 3.

[9] C. F. Melius and J. S. Binkley, 20th Symp. (Int.) Combust., 575 (1984).

NH + NO → H + N$_2$O
→ HN$_2$ + O
→ N$_2$ + OH

$$NH_2 + O_2 \rightarrow NO + H_2O \qquad (1)$$
$$\rightarrow NO_2 + H_2 \qquad (2)$$
$$\rightarrow HNO + OH \qquad (3)$$
$$\rightarrow HNO_2 + H \qquad (4)$$
$$\rightarrow H_2NO + O \qquad (5)$$
$$NH_2 + O_2 + M \rightarrow NH_2O_2 + M \qquad (6)$$
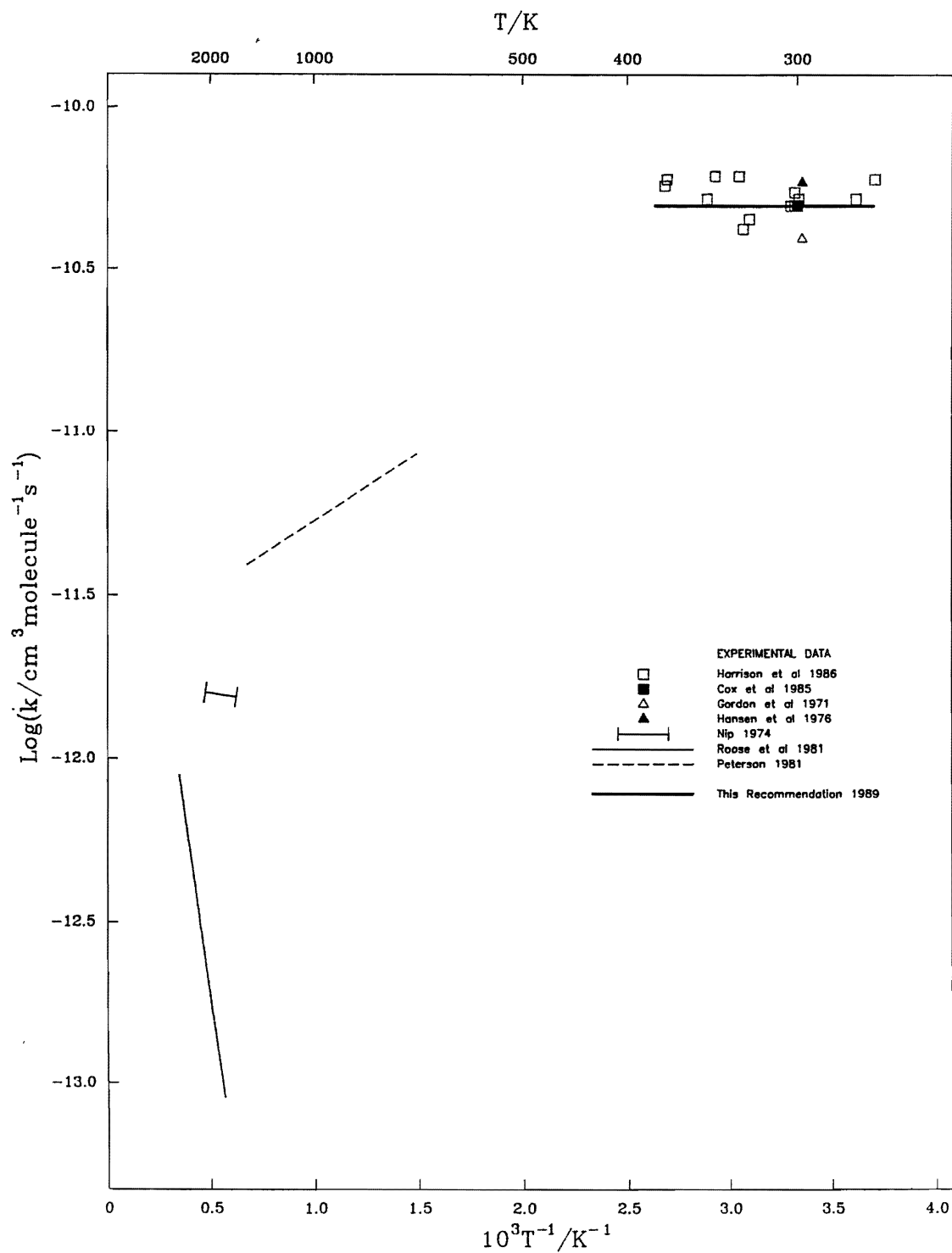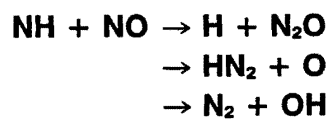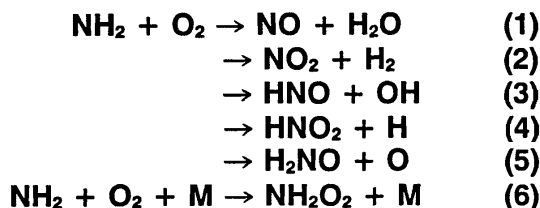
Thermodynamic Data

$\Delta H^o_{298} (1) = -342$ kJ mol^{-1}

$\Delta S^o_{298} (1) = 0.281$ J K^{-1}mol^{-1}

$K_p(1) = 4.89 \; T^{-0.266}\exp(+41000/T)$

$\Delta H^o_{298} (2) = -157$ kJ mol^{-1}

$\Delta S^o_{298} (2) = -29.1$ J K^{-1}mol^{-1}

$K_p(2) = 1.16 \cdot 10^{-3} \; T^{0.499} \exp(+19000/T)$

$\Delta H^o_{298} (3) = -51.8$ kJ mol^{-1}

$\Delta S^o_{298} (3) = 4.56$ J K^{-1}mol^{-1}

$K_p(3) = 0.914 \; T^{0.109} \exp(+6240/T)$

$\Delta H^o_{298} (4) = -49.1$ kJ mol^{-1}

$\Delta S^o_{298} (4) = -35.7$ J K^{-1}mol^{-1}

$K_p(4) = 1.43 \cdot 10^{-6} \; T^{1.34} \exp(+6370/T)$

There are no thermodynamic data available for channels (5) and (6).

Rate coefficient data ($k = k_1 + k_2 + k_3 + k_4 + k_5 + k_6$)

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$<4.6 \cdot 10^{-17}$	1245	Michael *et al*. (1985)[1]	(a)
$<7.7 \cdot 10^{-18}$	298		
$<5.6 \cdot 10^{-18}$	459		
$<3 \cdot 10^{-18}$	298	Losovsky, Ioffe, and Sarkisov (1984)[2]	(b)
Reviews and Evaluations			
$< 3 \cdot 10^{-18}$	298	CODATA (1984)[3]	(c)
	–	Lesclaux (1984)[4]	(d)
	–	Hanson and Salimian (1985)[5]	(e)

Comments

(a) Flash photolysis of NH$_3$/O$_2$/He mixtures. [NH$_2$] monitored by laser induced fluorescence at 578 nm. Total pressure 25 Torr He. Flash energy varied 1.5 – 15.8 J. No effect of O$_2$ at low flash energies.

(b) Flash photolysis of NH$_3$/O$_2$/N$_2$ mixtures at total pressures < 30 Torr. [NH$_2$] monitored by intracavity laser absorption spectroscopy at 598 nm. Decay rate of NH$_2$ observed to be independent of O$_2$ pressure above 1 Torr. Observed decay attributed to NH$_2$ + HO$_2$ reaction.

(c) Evaluation of low temperature data only.

(d) Comprehensive review, no recommendation.

(e) Comprehensive review, no recommendation.

Preferred Values

k < $3 \cdot 10^{-18}$ cm^3 molecule^{-1} s^{-1} at 298 K

Comments on Preferred Values

Studies up to 1984 have been tabulated and reviewed. elsewhere[3,4,5].

There has been considerable interest in this reaction because of its likely importance in ammonia oxidation but at low temperatures it is so slow that it is difficult to study by the usual fast reaction techniques. Furthermore, the measurements are very sensitive to the presence of H atoms which initiate NH$_2$ oxidation by HO$_2$ formation in NH$_3$/O$_2$ systems which have been used frequently in these studies. At low temperatures only upper limits to k are available, mostly determined by flash photolysis. Our preferred value for k is that of Lesclaux and Demissy[8]. The only discharge-flow study[12] suggests a pressure dependent rate coefficient, interpreted as due to the formation of NH$_2$O$_2$ as a relatively stable intermediate, but this is not supported by the flash photolysis studies and theoretical calculations[15,17].

At high temperatures the only available data are from a shock tube study[13] and one in which NH$_3$/O$_2$ mixtures were passed through a hot tubular reactor[14]. Interpretation of the results required computer fitting using large reaction schemes and values obtained differ substantially. We do not consider these results to be certain enough to make a recommendation without further studies.

There is no conclusive experimental evidence on the relative importance of the various possible reaction channels. Recent theoretical calculations[15] suggest the NH$_2$O$_2$ is stable only to the extent of $\approx$ 20 kJ mol^{-1} and hence is very short-lived, even at 300 K. As suggested by Benson[17], these calculations favour channel (5) as the preferred route despite its estimated endothermicity of $\approx$125 kJ mol^{-1}. The exothermic channels proceed via NH$_2$O$_2$ which must surmount a large energy barrier to

before going on to form products [channels (1), (2), (3), (4)]. Channel (3) has been widely accepted in many modelling studies and despite the theoretical evidence against it, the possibility of it making a contribution at high temperatures should not be ruled out.

In contrast to the reaction of ground state O_2, the rate of reaction between NH_2 and $\dot{O}_2$ ($^1\Delta_g$) has been measured by discharge flow methods. A value of $1.0 \cdot 10^{-14}$ cm^3 molecule^{-1} s^{-1} over the range 295–353 K was obtained[19].

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$$NH_2 + NO \rightarrow N_2 + H_2O \quad (1)$$
$$\rightarrow N_2 + H + OH \quad (2)$$
$$\rightarrow NH + HNO \quad (3)$$
$$\rightarrow NH_2NO \quad (4)$$
$$\rightarrow N_2H + OH \quad (5)$$
$$\rightarrow N_2O + H_2 \quad (6)$$
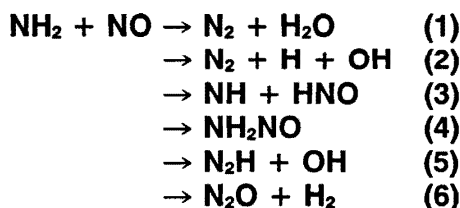
Thermodynamic Data

$\Delta H^\circ_{298} (1) = -523$ kJ mol^{-1}
$\Delta S^\circ_{298} (1) = -25.0$ J K^{-1}mol^{-1}
$K_p(1) = 0.286\ T^{0.252} \exp(+62700/T)$

$\Delta H^\circ_{298} (2) = -23.7$ kJ mol^{-1}
$\Delta S^\circ_{298} (2) = 84.5$ J K^{-1}mol^{-1}
$K_p(2) = 79.6\ T^{0.945} \exp(+2960/T)$

$\Delta H^\circ_{298} (3) = 175$ kJ mol^{-1}
$\Delta S^\circ_{298} (3) = -3.49$ J K^{-1}mol^{-1}
$K_p(3) = 0.110\ T^{0.363} \exp(-2100/T)$

$\Delta H^\circ_{298} (5) = 3.37$ kJ mol^{-1}
$\Delta S^\circ_{298} (5) = 2.73$ J K^{-1}mol^{-1}
$K_p(5) = 0.339\ T^{0.218} \exp(-357/T)$

$\Delta H^\circ_{298} (6) = -199$ kJ mol^{-1}
$\Delta S^\circ_{298} (6) = -54.8$ J K^{-1}mol^{-1}
$K_p(6) = 2.43 \cdot 10^{-6}\ T^{0.946} \exp(+24200/T)$

Rate Coefficient Data ($k = k_1 + k_2 + k_3 + k_4 + k_5 + k_6$)

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$1.4 \cdot 10^{-11}$	298	Gericke *et al.* (1984)[1]	(a)
$2.17 \cdot 10^{-11}$	297	Stephens *et al.* (1984)[2]	(b)
$k_2 = 5 \cdot 10^{-12}$			
$1.7 \cdot 10^{-11}$	298	Dreier and Wolfrum (1985)[3]	(c)
$1.3 \cdot 10^{-11}$	298		
$1.6 \cdot 10^{-11}$	298	Hall *et al.* (1986)[4]	(d)
$k_1 = 1.06 \cdot 10^{-11}$			
$k_2 = 1.36 \cdot 10^{-11}$			
$k_3 = 2.98 \cdot 10^{-12}$			
$k_1 \leqslant 1.73 \cdot 10^{-11}$	300	Dobson (1986)[5]	(e)
$k_5 \geqslant 2.6 \cdot 10^{-12}$			
$k_5/(k_1 + k_5) = 0.12$	298	Silver and Kolbe (1987)[6]	(f)
$k_5 = 7.9 \cdot 10^{15}\ T^{-1.17}$	294–1027	Atakan *et al.* (1989)[7]	(g)
Reviews and Evaluations			
$1.8 \cdot 10^{-11}\ (T/298)^{-1.5}$	200–1000	Lesclaux (1984)[8]	(h)
$1.6 \cdot 10^{-11}\ (T/298)^{-1.5}$	210–500	CODATA (1989)[9]	(i)

Comments

(a) NH_2 generated by multiphoton dissociation of N_2H_4 or CH_3NH_2. [NH_2] monitored by laser induced fluorescence.

(b) Discharge flow study of $OH + NH_3$ reaction. [OH] monitored by resonance fluorescence. Secondary chemistry modelled to give quoted k value.

(c) Flow reactor. Laser flash photolysis of NH_3 at 193 nm. NH_2 radicals and product N_2 monitored by CARS. Independent value of k obtained by monitoring vibrationally excited H_2O by time resolved infrared fluorescence.

(d) Infrared kinetic spectroscopy detection of products in range 2.3–3.2 μm following NH_2 production by laser photolysis of NH_3. Detection of vibrationally excited H_2O as product.

(e) Fast-flow tube reactor with modulated beam mass spectrometry detection. [OH] / [H_2O] product ratio measured.

(f) Re-evaluation of branching ratio from data reported in earlier paper.

(g) Laser photolysis of NH_3. Laser induced fluorescence monitoring of [NH_2] and [OH]. It is concluded that OH is a direct product of the reaction. [OH]/[NH_2]$_0$ = 0.1 at 300 K rising to 0.19 at 1000 K.

(h) Comprehensive review of all studies up to 1984.

(i) Based mainly on sparse low temperature data.

Preferred Values

$k = 1.8 \cdot 10^{-12} \exp(+650/T)$ cm^3 molecule^{-1} s^{-1} over range 220–2000 K

$(k_2 + k_5)/k = 0.12$ at 298 K

Reliability
$\Delta \log k = \pm 0.5$ over range 220–2000 K

Comments on Preferred Values

The major studies prior to 1984 have been reviewed and are not tabulated here.

The data close to room temperature range over a factor of 3 there being a significant discrepancy between those from flash photolysis studies ($\approx 20 \cdot 10^{-12}$ cm^3 molecule^{-1} s^{-1}) and those from discharge flow measurements ($\approx 9 \cdot 10^{-12}$ cm^3 molecule^{-1} s^{-1}). We take a mean value of $1.6 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1} based on Refs. 3, 10–19.

It is clear that the rate coefficient has a significant negative temperature dependence. Our recommendations

are based on all of these studies[7,10,12,17,18] on the temperature dependence which are in reasonable agreement.

The relative importance of the various reaction channels has been the subject of considerable experimental work and theoretical calculations. The negative temperature dependence suggests formation and subsequent rearrangement and dissociation of the addition product NH_2NO.

At high temperatures little information about the branching ratios is available. Channels (1), (2) and (5) are likely to be important but N_2O production has also been observed at high temperatures[19]. The energetics of the reaction pathways have been the subject of several theoretical studies[20,21,22,23,24].

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$$NH_2 + NO \rightarrow N_2 + H_2O$$
$$\rightarrow N_2 + H + OH$$
$$\rightarrow N_2H + OH$$
$$\rightarrow N_2O + H_2$$

EXPERIMENTAL DATA

□	Gordon et al 1971
■	Gehring et al 1973
△	Kaskan and Hughes 1973
▲	Duxbury and Pratt 1974
——	Lesclaux et al 1975
●	Hancock et al 1975
⊢——⊣	Fenimore 1976
▲	Sarkisov et al 1978
⊖	Kurosawa 1979
+	Boettner 1979
– – –	Hack et al 1979
◇	Kurosawa and Lesclaux 1979
◆	Morley 1981
············	Roose et al 1981
▽	Stief et al 1982
▼	Silver and Kolbe 1982
▽	Andresen et al 1982
◈	Whyte and Phillips 1983
◉	Duncanson et al 1983
◆	Dreier and Wolfrum 1985
◪	Gericke et al 1984
▣	Stephens (k2) 1984
⊟	Hall et al 1986
▲	Stephens 1984
∨	Hall et al (k1) 1986
◆	Hall et al (k2) 1986
◪	Hall et al (k3) 1986
⊖	Dobson (k1) 1986
⊞	Dobson (k5) 1986
–··–··–	Atakan et al 1989
———	This Recommendation 1989

Reactions of C$_2$ Species

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
	$C_2(X^1\Sigma_g^+)$ + O$_2$ → Products		
$2.8 \cdot 10^{-12}$	298	Pasternack and McDonald (1979)[4]	(a)
$3.0 \cdot 10^{-12}$	300	Reisler et al. (1980)[5]	(b)
	C$_2$ $(X^1\Sigma_g^+)$ + H$_2$ → Products		
$1.4 \cdot 10^{-12}$	298	Pasternack and McDonald (1979)[4]	(a)
$1.4 \cdot 10^{-12}$	300	Reisler et al. (1980)[6]	(c)
$1.8 \cdot 10^{-12}$ exp($-1470/T$)	300–600	Pitts et al. (1982)[10]	(d)
	$C_2(X^1\Sigma_g^+)$ + CO$_2$ → Products		
no apparent reaction	298	Pasternack and McDonald (1979)[4]	(a)
< $3 \cdot 10^{-14}$	300	Reisler et al. (1980)[6]	(c)
	$C_2(X^1\Sigma_g^+)$ + CH$_4$ → Products		
$1.9 \cdot 10^{-11}$	298	Pasternack and McDonald (1979)[4]	(a)
$1.7 \cdot 10^{-11}$	300	Reisler et al. (1980)[6]	(c)
$5.0 \cdot 10^{-11}$ exp($-297/T$)	300–600	Pitts et al. (1982)[10]	(d)
	$C_2(X^1\Sigma_g^+)$ + C$_2$H$_6$ → Products		
$1.6 \cdot 10^{-10}$	298	Pasternack and McDonald (1979)[4]	(a)
	$C_2(X^1\Sigma_g^+)$ + C$_3$H$_8$ → Products		
$3.3 \cdot 10^{-10}$	300	Reisler et al. (1980)[6]	(c)
	$C_2(X^1\Sigma_g^+)$ + C$_2$H$_4$ → Products		
$3.3 \cdot 10^{-10}$	298	Pasternack and McDonald (1979)[4]	(a)
	$C_2(X^1\Sigma_g^+)$ + C$_2$H$_2$ → Products		
$4.3 \cdot 10^{-10}$	300	Reisler et al. (1980)[6]	(c)
	$C_2(X^1\Sigma_g^+)$ + H$_2$O → Products		
< $3 \cdot 10^{-14}$	300	Reisler et al. (1980)[6]	(c)
	$C_2(a^3\Pi_u)$ + CH$_4$ → Products		
$1.7 \cdot 10^{-11}$ exp($-2805/T$)	337 605	Pasternack et al. (1980)[8]	(e)
< $3 \cdot 10^{-14}$	300	Reisler et al. (1980)[6]	(c)
< $1 \cdot 10^{-16}$	298	Donnelly and Pasternack (1981)[1]	(f)
	$C_2(a^3\Pi_u)$ + C$_2$H$_6$ → Products		
$1.3 \cdot 10^{-12}$	298	Donnelly and Pasternack (1979)[1]	(f)
$2.4 \cdot 10^{-11}$ exp($-920/T$)	300–600	Pasternack et al. (1981)[9]	(g)
	$C_2(a^3\Pi_u)$ + C$_3$H$_8$ → Products		
$1.7 \cdot 10^{-10}$	300	Reisler et al. (1980)[6]	(c)
$1.8 \cdot 10^{-11}$ exp($-97/T$)	300–600	Pasternack et al. (1981)[9]	(g)
	$C_2(a^3\Pi_u)$ + n-C$_4$H$_{10}$ → Products		
$4.9 \cdot 10^{-11}$ exp($-71/T$)	300–600	Pasternack et al. (1981)[9]	(g)

Reactions of C_2 Species — Continued

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
$C_2(a\,^3\Pi_u)$ + $C_2H_4 \rightarrow$ Products			
$1.7 \cdot 10^{-10}$	300	Reisler *et al*. (1979)[2]	(h)
$1.4 \cdot 10^{-10}$	298	Donnelly and Pasternack (1979)[1]	(f)
$1.2 \cdot 10^{-10}$ exp($+5/T$)	300–600	Pasternack *et al*. (1981)[9]	(g)
$C_2(a\,^3\Pi_u)$ + $C_2H_2 \rightarrow$ Products			
$9.6 \cdot 10^{-11}$	298	Donnelly and Pasternack (1979)[1]	(f)
$C_2(a\,^3\Pi_u)$ + $H_2O \rightarrow$ Products			
$< 3 \cdot 10^{-14}$	300	Reisler *et al*. (1980)[6]	(c)
$C_2(a\,^3\Pi_u)$ + $O_2 \rightarrow$ Products			
$3.4 \cdot 10^{-12}$	300	Filseth *et al*. (1979)[3]	(i)
$3.0 \cdot 10^{-12}$	298	Donnelly and Pasternack (1979)[1]	(f)
$3.0 \cdot 10^{-12}$	300	Reisler *et al*. (1980)[5]	(b)
$C_2(a\,^3\Pi_u)$ + $O_2(X^3\Sigma_g^-) \rightarrow C_2(X^1\Sigma_g^+)$ + $O_2(X^3\Sigma_g^-)$			
$2.7 \cdot 10^{-11}$	300	Mangir *et al*. (1980)[7]	(j)
$C_2(a\,^3\Pi_u)$ + Ar $\rightarrow$ Products			
$< 2 \cdot 10^{-15}$	300	Filseth *et al*. (1979)[3]	(i)
$< 3 \cdot 10^{-14}$	300	Reisler *et al*. (1980)[6]	(c)
$C_2(a\,^3\Pi_u)$ + Kr $\rightarrow C_2(X^1\Sigma_g^+)$ + Kr			
$2.0 \cdot 10^{-13}$	300	Reisler *et al*. (1980)[6]	(c)
$C_2(a\,^3\Pi_u)$ + Xe $\rightarrow C_2(X^1\Sigma_g^+)$ + Xe			
$4.5 \cdot 10^{-12}$	300	Reisler *et al*. (1980)[6]	(c)
$5.5 \cdot 10^{-12}$ exp($+24/T$)	300–500	Pasternack *et al*. (1981)[9]	(g)
$C_2(X^1\Sigma_g^+/a\,^3\Pi_u)_{eq}$ + $O_2 \rightarrow$ Products			
$1.1 \cdot 10^{-11}$ exp($-337/T$)	300–600	Pitts *et al*. (1982)[10]	(d)

Comments

(a) $C_2(X^1\Sigma_g^+)$ produced by multiphoton UV excimer laser photodissociation of hexafluorobutyne-2; monitored by laser induced fluorescence at 691 nm. The authors explain the faster reaction rates of $C_2(X^1\Sigma_g^+)$ with H_2 and hydrocarbons by a hydrogen atom exchange reaction to form ground state C_2H which is forbidden for $C_2(a\,^3\Pi_u)$.

(b) IR multiple photon dissociation of C_2H_3CN. Radical depletion monitored by laser induced fluorescence, CO formation by chemiluminescence. Total pressures 1–4 Torr Ar. The authors conclude that CO in highly excited triplet states is the primary product.

(c) IR multiple photon dissociation of C_2H_3CN or C_2HCl_3. C_2 monitored by laser induced fluorescence. Total pressures 1–4 Torr Ar or He. Measurements of intersystem crossing rates with C_2Cl_4 as scavenger.

Considerable intersystem crossing with heavy collision partners or with non-singlet partners.

(d) Production of $C_2(X^1\Sigma_g^+)$ by photolysis of hexafluorobutyne-2 in 10 Torr He. C_2 monitored by time resolved laser induced fluorescence, in the cases of O_2 as reactant only at low temperatures (at high temperature [$^1C_2$] from chemiluminescence of excited CO from C_2 + O_2 reaction). Propose insertion mechanism for reaction of $C_2(X^1\Sigma_g^+)$ with H–H and C–H bonds. Very fast equilibration between $C_2(X^1\Sigma_g^+)$ and $C_2(a\,^3\Pi_u)$ in the presence of O_2. Different sets of Arrhenius parameters for C_2 + O_2 under the assumptions that (1) $k(^1C_2 + O_2) \approx k(^3C_2 + O_2)$, and (2) $k(^1C_2 + O_2) >> k(^3C_2 + O_2)$.

(e) C_2 produced by 193 nm excimer laser photolysis of hexafluorobutyne-2 and monitored by laser induced fluorescence. Total pressure 10–170 Torr CH_4.

(f) $C_2(a^3\Pi_u)$ formed by multiphoton UV photolysis of C_2H_2 or C_2H_4 at 193 nm; monitored by laser induced fluorescence. Total pressures 0–300 Torr.

(g) $C_2(a^3\Pi_u)$ produced by multiphoton UV excimer laser photodissociation of hexafluorobutyne-2 or benzene. C_2 depletion measured by laser induced fluorescence. Authors suggest that the reactions of $^3C_2$ with H_2 and saturated hydrocarbons proceed via H atom abstraction (supported by BEBO techniques, linear free energy correlations, and Evans-Polanyi plots) whereas with unsaturated hydrocarbons faster insertion reactions take place.

(h) $C_2(a^3\Pi_u)$ by IR multiple photon dissociation of either vinylcyanide or ethylene in the presence of NO or Ar. Decay of $C_2(a^3\Pi_u)$ monitored by laser induced fluorescence; slow flow conditions. CN formation observed by chemiluminescence.

(i) IR multiple photon dissociation of acrylonitrile C_2H_3CN, laser induced fluorescence of $C_2(a^3\Pi_u)$; total pressures up to 50 Torr. A VUV chemiluminescence signal was observed when O_2 was present in the mixture; electronically excited $CO(A^1\Pi)$ proposed.

(j) IR-MPD of vinylcyanide or trichloroethylene. $C_2(a^3\Pi_u)$ and $C_2(X^1\Sigma_g^+)$ observed by laser induced fluorescence. The intersystem crossing rates were obtained by increasing the concentration of O_2 in the sample and comparing the removal rates of $^1C_2$ and $^3C_2$. At 300 K the intersystem crossing is much faster than chemical reactions; therefore it is impossible to measure distinct reaction rates of $^1C_2$ and $^3C_2$, only the rate of equilibrated $^1C_2/^3C_2$ mixtures.

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[5]H. Reisler, M. Mangir, C. Wittig, Chem. Phys. **47**, 49 (1980).

[6]H. Reisler, M. S. Mangir, C. Wittig, J. Chem. Phys. **73**, 2280 (1980).

[7]M. S. Mangir, H. Reisler, C. Wittig, J. Chem. Phys. **73**, 829 (1980).

[8]L. Pasternack, A. P. Baronavski, J. R. McDonald, J. Chem. Phys. **73**, 3508 (1980).

[9]L. Pasternack, W. M. Pitts, J. R. McDonald, Chem. Phys. **57**, 19 (1981).

[10]W. M. Pitts, L. Pasternack, J. R. McDonald, Chem. Phys. **68**, 417 (1982).

$$CH + O_2 \rightarrow CHO + O \quad (1)$$
$$\rightarrow CO + OH \quad (2)$$
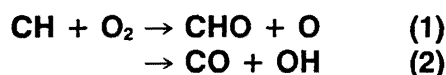
Thermodynamic Data

$\Delta H^\circ_{298} (1) = -301 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (1) = -2.5 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(1) = 0.487 \; T^{0.0499} \exp(+36300/T)$

$\Delta H^\circ_{298} (2) = -666 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (2) = -6.82 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(2) = 10.1 \; T^{-0.432} \exp(+79900/T)$

Rate Coefficient Data ($k = k_1 + k_2$)

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$< 4{\cdot}10^{-11}$	298	Bosnali and Perner (1971)[1]	(a)
$1.7{\cdot}10^{-11}$	1815–2365	Jachimowski (1977)[2]	(b)
$3.3{\cdot}10^{-11}$	298	Messing, Sadowsky, and Filseth (1979)[3]	(c)
$5.9{\cdot}10^{-11}$	298	Butler *et al.* (1980,1981)[4,5]	(d)
$5.4{\cdot}10^{-11}$	297–676	Berman *et al.* (1982)[6]	(e)
$2.1{\cdot}10^{-12}$	298	Duncanson and Guillory (1983)[7]	(f)
$k_2 = 8{\cdot}10^{-11}$	298	Lichtin, Berman, and Lin (1984)[8]	(g)
$2.3{\cdot}10^{-11}$	290	Anderson, Freedman, and Kolb (1987)[9]	(h)

Comments

(a) Pulse radiolysis of 15 Torr CH_4 with various amounts of O_2 added; [CH] by absorption spectroscopy at 314.4 nm.

(b) Oxidation of C_2H_2 and C_2H_4 behind incident shock waves. Emission monitored at 370 nm (CO + O → CO_2 + hν), at 5.0 μm (CO), and at 4.3 μm (CO_2). Total pressure 1.1–1.7 atm Ar. Numerical modelling of 38 reaction mechanism. k(CH + O_2) arbitrarily set.

(c) Multiphoton dissociation of methylamine at 1047 cm^{-1}; [CH] by laser induced fluorescence at 431.4

nm, [OH($A^2\Sigma^+$)] by chemiluminescence. Total pressure 10–30 Torr Ar. No pressure dependence reported.

(d) Multiphoton dissociation of $CHBr_3$ at 193 nm; [CH] by laser induced fluorescence near 430 nm. Total pressure 100 Torr Ar.

(e) Multiphoton dissociation of $CHBr_3$ at 266 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 100 Torr Ar. No significant temperature dependence.

(f) IR-multiphoton dissociation of CH_3OH; [CH($X^2\Pi$), $v = 0$ and $v = 1$)] by laser induced fluorescence at 430.0 nm and 487.3 nm. Total pressure 10 Torr Ar.

Given value of k for $v = 0$. $k_{(v = 1)} = 4.3 \cdot 10^{-12}$ cm^3 molecule^{-1} s^{-1} including vibrational relaxation.

(g) Multiphoton dissociation of CHBr$_3$ at 266 nm; [OH $(A^2\Sigma^+)$] by chemiluminescence. Total pressure 21 Torr, mainly Ar.

(h) Fast flow reactor; CH formation by sequential Br atom abstraction from CHBr$_3$ with excess alkalimetal atoms (Na or K); [CH] and [OH] by laser induced fluorescence. Total pressure 2 Torr He/Ar mixture.

Preferred Values

$k = 5.5 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1} over range 300–2000 K

Reliability
$\Delta \log k = \pm 0.3$ at 300 K rising to ± 0.5 at 2000 K

Comments on Preferred Values

The recommendation is based on the study of Berman *et al.*[6] because it covers a large temperature range and is in reasonable agreement with other recent studies.

References

[1]M. W. Bosnali and D. Perner, Z. Naturforsch. A26, 1768 (1971).
[2]C. J. Jachimowski, Comb. Flame 29, 55 (1977).
[3]I. Messing, C. M. Sadowsky, and S. V. Filseth, Chem. Phys. Lett. 66, 95 (1979).
[4]J. E. Butler, J. W. Fleming, L. P. Goss, and M. C. Lin, ACS Symp. Ser. (Laser Probes Combust. Chem.), 134, 397 (1980).
[5]J. E. Butler, J. W. Fleming, L. P. Goss, and M. C. Lin, Chem. Phys. 56, 355 (1981).
[6]M. R. Berman, J. W. Fleming, A. B. Harvey, and M. C. Lin, 19th Symp. (Int.) Combust., 73 (1982).
[7]J. A. Duncanson, Jr., and W. A. Guillory, J. Chem. Phys. 78, 4958 (1983).
[8]D. A. Lichtin, M. R. Berman, and M. C. Lin, Chem. Phys. Lett. 104, 18 (1984).
[9]S. M. Anderson, A. Freedman, and C. E. Kolb, J. Phys. Chem. 91, 6272 (1987).

$$CH + O_2 \rightarrow CHO + O$$
$$\rightarrow CO + OH$$

T/K

EXPERIMENTAL DATA

Bosnali and Perner 1971
Jachimowski 1977
Messing et al 1979
Butler et al 1980
Berman et al 1982
Duncanson and Guillory 1983
Anderson et al 1987
Lichtin et al (2 works) (k2) 1984

This Recommendation 1989

$$CH + H_2 \rightarrow H + CH_2 \qquad (1)$$
$$\rightarrow CH_3 \qquad (2)$$
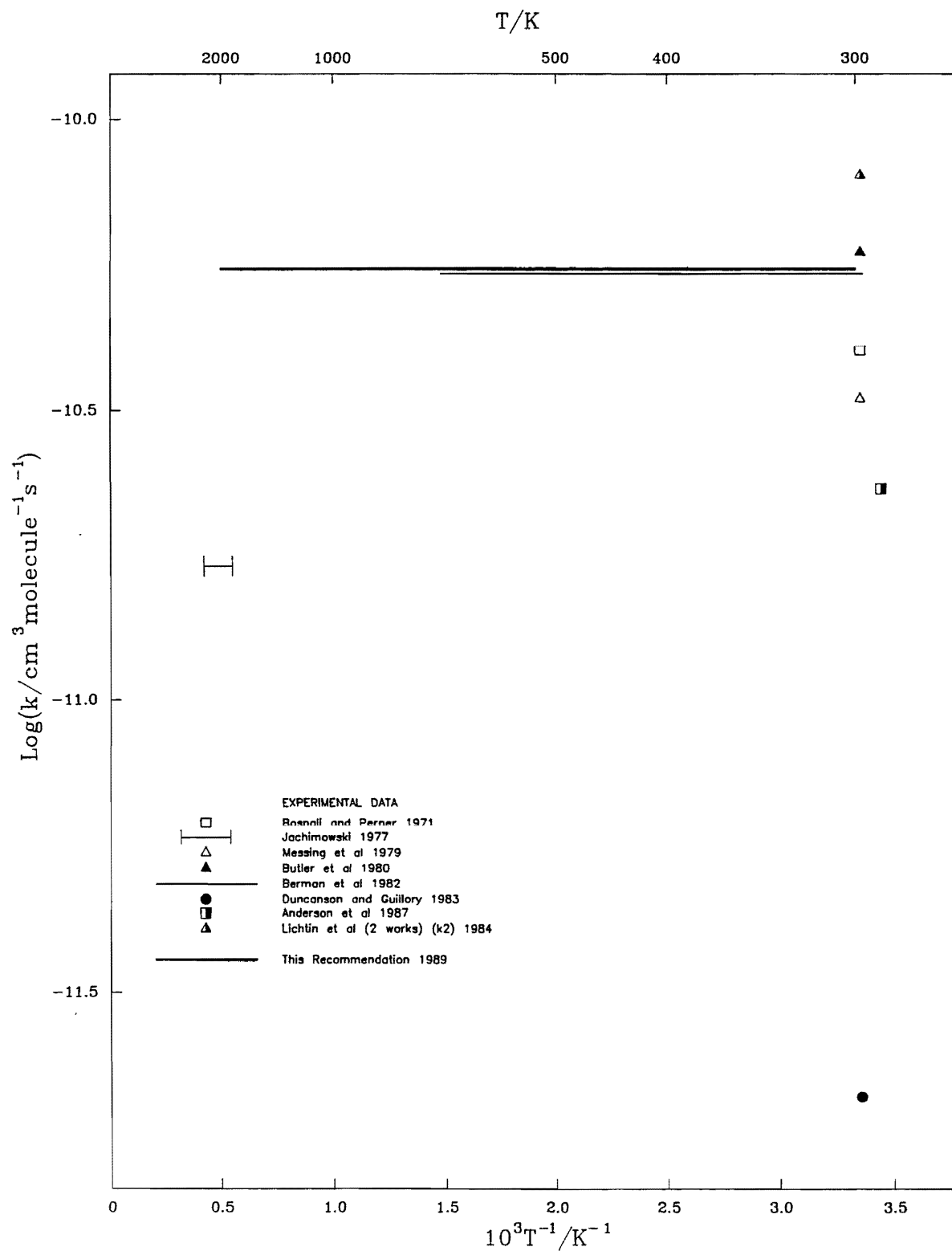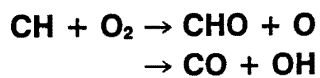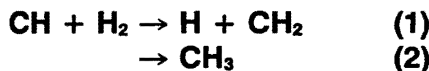
Thermodynamic Data

$\Delta H^\circ_{298} (1) = 10.8 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (1) = -3.44 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(1) = 0.275 \, T^{0.109} \exp(-1220/T)$

$\Delta H^\circ_{298} (2) = -448 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (2) = -119 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(2) = 1.71 \cdot 10^{-5} \, T^{-0.623} \exp(+54000/T) \text{ atm}^{-1}$

Rate Coefficient Data ($k = k_1 + k_2$)

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	$T[\text{K}]$	Reference	Comments
Rate Coefficient Measurements			
$1.0 \cdot 10^{-12}$	298	Braun *et al.* (1967)[1]	(a)
$1.7 \cdot 10^{-11}$	298	Bosnali and Perner (1971)[2]	(b)
$2.3 \cdot 10^{-11}$	298	Butler *et al.* (1979,80)[3,4]	(c)
$k_2 = 2.4 \cdot 10^{-12} \exp(+520/T)$	159–300	Berman and Lin (1984)[5]	(d)
$k_1 = 3.6 \cdot 10^{-10} \exp(-1960/T)$	400–660		
$k_1 = 2.4 \cdot 10^{-10} \exp(-1760/T)$	372–675	Zabarnick, Fleming,	
$k_1 = 1.5 \cdot 10^{-13} \, T^{1.022} \exp(-1260/T)$	300–2500	and Lin (1986)[6]	(e)
$1.4 \cdot 10^{-11}$	297		

Comments

(a) VUV flash photolysis of CH_4 with added H_2; [CH] by absorption spectroscopy at 314.3 nm. Total pressures 1–10 Torr.

(b) Pulse radiolysis of 15 Torr CH_4 with added H_2; [CH] by absorption spectroscopy at 314.3 nm.

(c) Multiphoton dissociation of $CHBr_3$ at 193 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressures 30–100 Torr Ar.

(d) Multiphoton dissociation of $CHBr_3$ at 266 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 100 Torr Ar. Pressure dependence of k studied at 297 K over range 25–600 Torr; k increasing from $7.9 \cdot 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 25 Torr to $4.5 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 600 Torr. Temperature and pressure dependence of k, isotopic effects and a transition-state model support an addition mechanism.

(e) Multiphoton dissociation of $CHBr_3$ at 266 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 100 Torr Ar. k_1 determined by measuring total rate at higher temperatures and subtracting k_2 from Ref. 5. Rate coefficient over range 300–2500 K from transition-state theory.

Preferred Values

$k_1 = 2.4 \cdot 10^{-10} \exp(-1760/T)$ cm^3 molecule^{-1} s^{-1} over range 300–1000 K

Reliability

$\Delta \log k = \pm 0.3$ over range 300–1000 K

Comments on Preferred Values

The most recent value of Lin and coworkers has been taken as the recommendation which is in reasonable agreement with the other data at higher temperatures. At lower temperatures there is evidence for channel (2) becoming significant.

References

[1] W. Braun, J. R. McNesby, and A. M. Bass, J. Chem. Phys. 46, 2071 (1967).

[2] M. W. Bosnali and D. Perner, Z. Naturforsch. A26, 1768 (1971).

[3] J. E. Butler, L. P. Goss, M. C. Lin, and J. W. Hudgens, Chem. Phys. Lett. 63, 104 (1979).

[4] J. W. Butler, J. W. Fleming, L. P. Goss, and M. C. Lin, ACS Symp. Ser. (Laser Probes Combust. Chem.) 134, 397 (1980).

[5] M. R. Berman and M. C. Lin, J. Chem. Phys. 81, 5743 (1984).

[6] S. Zabarnick, J. W. Fleming, and M. C. Lin, J. Chem. Phys. 85, 4373 (1986).

CH + H₂ → CH₂ + H
→ CH₃

EXPERIMENTAL DATA

☐   Berman and Lin (k1) 1984
■   Zabarnick et al (k1) 1986
△   Braun et al 1967
▲   Bosnali and Perner 1971
○   Butler et al (2 works) 1980
☐   Zabarnick et al (k2) 1986
▲   Berman and Lin (k2) 1984

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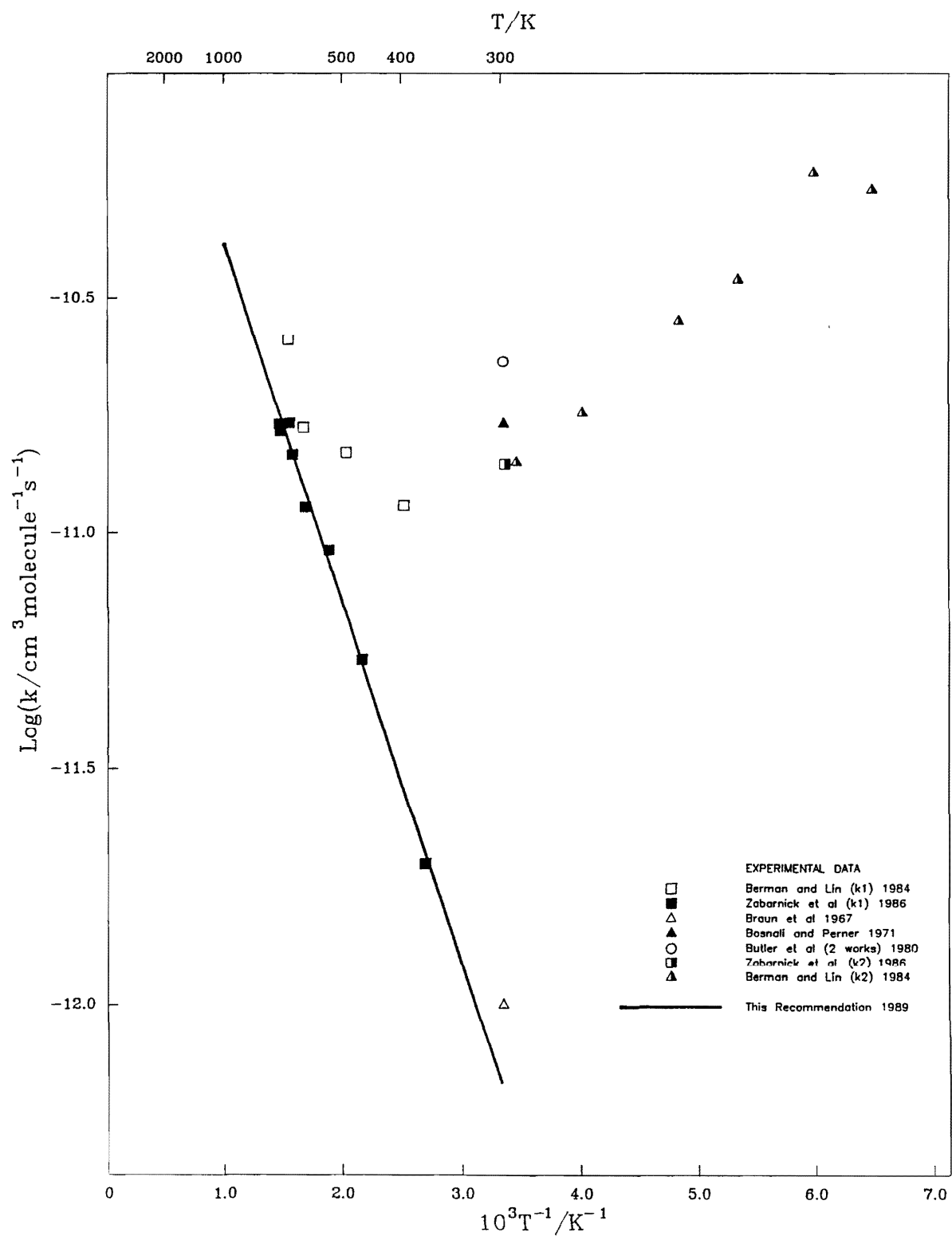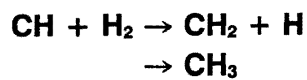
CH + H₂O → Products

Rate Coefficient Data

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	$T[\text{K}]$	Reference	Comments
Rate Coefficient Measurements			
$4.5 \cdot 10^{-11}$	298	Bosnali and Perner (1971)[1]	(a)
$9.5 \cdot 10^{-12} \exp(+380/T)$	298–669	Zabarnick, Fleming, and Lin (1988)[2]	(b)

Comments

(a) Pulse radiolysis of 15 Torr CH₄; [OH] by absorption at 314.4 nm.

(b) Multiphoton dissociation of CHBr₃ at 266 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 100 Torr Ar. k independent of pressure over range 20–300 Torr at room temperature.

Preferred Values

$k = 9.5 \cdot 10^{-12} \exp(+380/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over range 300–1000 K

Reliability

$\Delta \log k = \pm 1.0$ over range 300–1000 K

Comments on Preferred Values

The rate coefficient given by Zabarnick, Fleming, and Lin[2] is recommended but with wide error limits.

References

[1]M. W. Bosnali and D. Perner, Z. Naturforsch. A26, 1768 (1971).

[2]S. Zabarnick, J. W. Fleming, and M. C. Lin, 21st Symp. (Int.) Combust., 713 (1988).

CH + CO → Products

Rate Coefficient Data

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	$T[\text{K}]$	Reference	Comments
Rate Coefficient Measurements			
$4.8 \cdot 10^{-12}$	298	Bosnali and Perner (1971)[1]	(a)
$2.1 \cdot 10^{-11}$	298	Butler *et al.* (1980,1981)[2,3]	(b)
$4.6 \cdot 10^{-13} \exp(+861/T)$	297–676	Berman *et al.* (1982)[4]	(c)

Comments

(a) Pulse radiolysis of 15 Torr CH₄; [OH] by absorption at 314.4 nm.

(b) Multiphoton dissociation of CHBr₃ at 193 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 100 Torr Ar. k probably pressure dependent; suggest an addition mechanism similar to the CH + N₂ reaction.

(c) Multiphoton dissociation of CHBr₃ at 266 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 100 Torr Ar. k(CH + CO) increases by a factor of 3 over range 50–640 Torr Ar. Possible products of CH + CO₂ either CHO + CO or H + 2 CO.

Preferred Values

$k = 4.6 \cdot 10^{-13} \exp(+861/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over range 300–1000 K

Reliability

$\Delta \log k = \pm 1.0$ over range 300–1000 K

Comments on Preferred Values

The rate coefficient of Berman *et al.*[4] (which is consistent with the room temperature value of Butler *et al.*[2,3]) is taken as the recommendation but with wide error limits.

References

[1]M. W. Bosnali and D. Perner, Z. Naturforsch. A26, 1768 (1971).

[2]J. E. Butler, J. W. Fleming, L. P. Goss, and M. C. Lin, ACS Symp. Ser. (Laser Probes Combust. Chem.), 134, 397 (1980).

[3]J. E. Butler, J. W. Fleming, L. P. Goss, and M. C. Lin, Chem. Phys. 56, 355 (1981).

[4]M. R. Berman, J. W. Fleming, and M. C. Lin, 19th Symp. (Int.) Combust., 73 (1982).

CH + CO$_2$ → Products

Rate Coefficient Data

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$1.9 \cdot 10^{-12}$	298	Butler *et al.* (1980,81)[1,2]	(a)
$5.7 \cdot 10^{-12}$ exp($-345/T$)	297–676	Berman *et al.* (1982)[3]	(b)

Comments

(a) Multiphoton dissociation of CHBr$_3$ at 193 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 100 Torr Ar. k probably pressure dependent; suggest an addition mechanism similar to the CH + N$_2$ reaction.

(b) Multiphoton dissociation of CHBr$_3$ at 266 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 100 Torr Ar. k(CH + CO) increases by a factor of 3 over range 50–640 Torr Ar. Possible products of CH + CO$_2$ either HCO + CO or H + 2 CO.

Preferred Values

$k = 5.7 \cdot 10^{-12}$ exp($-345/T$) cm^3 molecule^{-1} s^{-1} over range 300–1000 K

Reliability

Δlog k = ± 1.0 over range 300–1000 K

Comments on Preferred Values

The value of Berman *et al.*[3] is recommended but with wide error limits.

References

[1] J. E. Butler, J. W. Fleming, L. P. Goss, and M. C. Lin, ACS Symp. Ser. (Laser Probes Combust. Chem.), **134**, 397 (1980).

[2] J. E. Butler, J. W. Fleming, L. P. Goss, and M. C. Lin, Chem. Phys. **56**, 355 (1981).

[3] M. R. Berman, J. W. Fleming, and M. C. Lin, 19th Symp. (Int.) Combust., 73 (1982).

CH + CH₄ → Products

Rate Coefficient Data

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	$T[\text{K}]$	Reference	Comments
Rate Coefficient Measurements			
$2.5 \cdot 10^{-12}$	298	Braun, McNesby, and Bass (1967) [1]	(a)
$3.3 \cdot 10^{-11}$	298	Bosnali and Perner (1971)[2]	(b)
$3.0 \cdot 10^{-10}$	298	Butler *et al.* (1979)[3]	(c)
$1.0 \cdot 10^{-10}$	298	Butler *et al.* (1981)[4]	(d)
$5.0 \cdot 10^{-11} \exp(+200/T)$	167–652	Berman and Lin (1983) [5]	(e)
$5.4 \cdot 10^{-11}$	290	Anderson, Freedman, and Kolb (1987)[6]	(f)

Comments

(a) VUV flash photolysis of pure CH₄; [CH] by absorption measurement at 314.3 nm. Addition of a diluent gas (Ar) resulted in decreasing [CH] to a limiting value of 0.6 times [CH](pure CH₄) at 10 Torr of Ar and a rate coefficient of $3.3 \cdot 10^{-12}$ cm³ molecule⁻¹ s⁻¹; this effect is also influenced by the flash intensity and probably due to quenching of an excited species otherwise leading to CH.

(b) Pulse radiolysis of 15 Torr CH₄; [OH] by absorption at 314.4 nm.

(c) Multiphoton dissociation of CHBr₃ at 193 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 30–100 Torr Ar.

(d) Multiphoton dissociation of CHBr₃ at 193 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 100 Torr Ar.

(e) Multiphoton dissociation of CHBr₃ at 266 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 100 Torr Ar. k(CH + C₃H₈) estimated, based on the observed linear dependence of k on the number of C−H bonds. k(CH + CH₄) pressure-independent between 25 Torr and 200 Torr. Formation of an excited insertion intermediate C₂H₆‡ leading to C₂H₄ + H confirmed by transition-state and RRKM theory.

(f) Fast flow reactor. CH formation by sequential Br atom abstraction from CHBr₃ with excess alkali-metal atoms (Na or K); [CH] by laser induced fluorescence. Total pressure 2 Torr He/Ar mixture.

Preferred Values

$k = 5.0 \cdot 10^{-11} \exp(+200/T)$ cm³ molecule⁻¹ s⁻¹ over range 200–700 K

Reliability

$\Delta \log k = \pm 1$ over range 200–700 K

Comments on Preferred Values

The available data shows considerable scatter. The preferred values are those of Berman *et al.*[5] but wide error limits are suggested.

References

[1] W. Braun, J. P. McNesby, and A. M. Bass, J. Chem. Phys. **46**, 2071 (1967).
[2] M. W. Bosnali and D. Perner, Z. Naturforsch. **A26**, 1768 (1971).
[3] J. E. Butler, L. P. Goss, M. C. Lin, and J. W. Hudgens, Chem. Phys. Lett. **63**, 104 (1979).
[4] J. E. Butler, J. W. Fleming, L. P. Goss, and M. C. Lin, Chem. Phys. **56**, 355 (1981).
[5] M. R. Berman and M. C. Lin, Chem. Phys. **82**, 435 (1983).
[6] S. M. Anderson, A. Freedman, and C. E. Kolb, J. Phys. Chem. **91**, 6272 (1987).

CH + C₂H₂ → Products

Rate Coefficient Data

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	$T[\text{K}]$	Reference	Comments
Rate Coefficient Measurements			
$8.1 \cdot 10^{-11}$	298	Bosnali and Perner (1971)[1]	(a)
$2.2 \cdot 10^{-10}$	298	Butler *et al.* (1981)[2]	(b)
$3.5 \cdot 10^{-10} \exp(+61/T)$	171–657	Berman *et al.* (1982)[3]	(c)

Comments

(a) Pulse radiolysis of 15 Torr CH₄; [OH] by absorption at 314.4 nm.

(b) Multiphoton dissociation of CHBr₃ at 193 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 100 Torr Ar.

(c) Multiphoton dissociation of CHBr₃ at 266 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 100 Torr Ar. Discrepancies with Butler's results[4] probably due to photolysis of reactants (C₂H₄, C₂H₂) at 193 nm. Suggest an addition mechanism of CH to the C−C double or triple bond leading to a three-membered ring followed by rapid ring opening.

Preferred Values

$k = 3.5 \cdot 10^{-10} \exp(+61/T)$ cm^3 molecule^{-1} s^{-1} over range 200–700 K

Reliability

$\Delta \log k = \pm 0.7$ over range 200–700 K

Comments on Preferred Values

The most recent study[3] is in reasonable agreement with the similar earlier study by Butler et al.[2] and is adopted as our recommendation but with wide error limits.

References

[1]M. W. Bosnali and D. Perner, Z. Naturforsch. A26, 1768 (1971).
[2]J. E. Butler, J. W. Fleming, L. P. Goss, and M. C. Lin, Chem. Phys. 56, 355 (1981).
[3]M. R. Berman, J. W. Fleming, A. B. Harvey, and M. C. Lin, Chem. Phys. 73, 27 (1982).

CH + C$_2$H$_4$ → Products

Rate Coefficient Data

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$1.2 \cdot 10^{-10}$	298	Bosnali and Perner (1971)[1]	(a)
$2.1 \cdot 10^{-10}$	298	Butler et al. (1981)[2]	(b)
$2.2 \cdot 10^{-10} \exp(+173/T)$	160–652	Berman et al. (1982)[3]	(c)

Comments

(a) Pulse radiolysis of 15 Torr CH$_4$; [OH] by absorption at 314.4 nm.

(b) Multiphoton dissociation of CHBr$_3$ at 193 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 100 Torr Ar.

(c) Multiphoton dissociation of CHBr$_3$ at 266 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 100 Torr Ar. Discrepancies with Butler's results[4] probably due to photolysis of reactants (C$_2$H$_4$, C$_2$H$_2$) at 193 nm. Suggest an addition mechanism of CH to the C—C double or triple bond leading to a three-membered ring followed by rapid ring opening.

Preferred Values

$k = 2.2 \cdot 10^{-10} \exp(+173/T)$ cm^3 molecule^{-1} s^{-1} over range 200–700 K

Reliability

$\Delta \log k = \pm 0.7$ over range 200–700 K

Comments on Preferred Values

The preferred values are based on the two most recent studies[2,3] which are in reasonable agreement but wide error limits are suggested.

References

[1]M. W. Bosnali and D. Perner, Z. Naturforsch. A26, 1768 (1971).
[2]J. E. Butler, J. W. Fleming, L. P. Goss, and M. C. Lin, Chem. Phys. 56, 355 (1981).
[3]M. R. Berman, J. W. Fleming, A. B. Harvey, and M. C. Lin, Chem. Phys. 73, 27 (1982).

CH + C₂H₆ → Products

Rate Coefficient Data

k[cm³ molecule⁻¹ s⁻¹]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$4.0 \cdot 10^{-10}$	298	Butler *et al.* (1981)[1]	(a)
$1.8 \cdot 10^{-10} \exp(+132/T)$	162–650	Berman and Lin (1983)[2]	(b)

Comments

(a) Multiphoton dissociation of CHBr₃ at 193 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 100 Torr Ar.

(b) Multiphoton dissociation of CHBr₃ at 266 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 100 Torr Ar. k(CH + C₃H₈) estimated, based on the observed linear dependence of k on the number of C—H bonds.

Preferred Values

k = $1.8 \cdot 10^{-10} \exp(+132/T)$ cm³ molecule⁻¹ s⁻¹ over range 200–700 K

Reliability

$\Delta \log k$ = ± 1 over range 200–700 K

Comments on Preferred Values

The available data are in reasonable agreement but until they are confirmed wide error limits are suggested.

References

[1] J. E. Butler, J. W. Fleming, L. P. Goss, and M. C. Lin, Chem. Phys. **56**, 355 (1981).

[2] M. R. Berman and M. C. Lin, Chem. Phys. **82**, 435 (1983).

CH + C₃H₈ → Products

Rate Coefficient Data

k[cm³ molecule⁻¹ s⁻¹]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$1.4 \cdot 10^{-10}$	298	Bosnali and Perner (1971)[1]	(a)
$3.7 \cdot 10^{-10}$	298	Berman and Lin (1983)[2]	(b)
$1.9 \cdot 10^{-10} \exp(+240/T)$	298–689	Zabarnick, Fleming, and Lin (1987)[3]	(c)

Comments

(a) Pulse radiolysis of 15 Torr CH₄; [OH] by absorption at 314.4 nm.

(b) Multiphoton dissociation of CHBr₃ at 266 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 100 Torr Ar. k(CH + C₃H₈) estimated, based on the observed linear dependence of k on the number of C—H bonds.

(c) Multiphoton dissociation of CHBr₃ at 266 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 20–300 Torr Ar. Rates independent of total pressure.

Preferred Values

k = $1.9 \cdot 10^{-10} \exp(+240/T)$ cm³ molecule⁻¹ s⁻¹ over range 300–700 K

Reliability

$\Delta \log k$ = ± 0.7 over range 300–700 K

Comments on Preferred Values

The preferred values are based on the two most recent studies[2,3] which are in good agreement but wide error limits are suggested.

References

[1] M. W. Bosnali and D. Perner, Z. Naturforsch. **A26**, 1768 (1971).

[2] M. R. Berman and M. C. Lin, Chem. Phys. **82**, 435 (1983).

[3] S. Zabarnick, J. W. Fleming, and M. C. Lin, Chem. Phys. **112**, 409 (1987).

CH + n-C$_4$H$_{10}$ → Products

Rate Coefficient Data

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$1.3 \cdot 10^{-10}$	298	Bosnali and Perner (1971)[1]	(a)
$5.8 \cdot 10^{-10}$	298	Butler et al. (1981)[2]	(b)
$4.4 \cdot 10^{-10}$ exp($+28/T$)	257–653	Berman and Lin (1983)[3]	(c)

Comments

(a) Pulse radiolysis of 15 Torr CH$_4$; [OH] by absorption at 314.4 nm.

(b) Multiphoton dissociation of CHBr$_3$ at 193 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 100 Torr Ar.

(c) Multiphoton dissociation of CHBr$_3$ at 266 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 100 Torr Ar. k(CH + C$_3$H$_8$) estimated, based on the observed linear dependence of k on the number of C−H bonds.

Preferred Values

$k = 4.4 \cdot 10^{-10}$ exp($+28/T$) cm^3 molecule^{-1} s^{-1} over range 250–700 K

Reliability
Δlog k = ± 0.7 over range 250–700 K

Comments on Preferred Values

The preferred values are based on the two most recent studies[2,3] which are in reasonable agreement but wide error limits are suggested.

References

[1] M. W. Bosnali and D. Perner, Z. Naturforsch. **A26**, 1768 (1971).
[2] J. E. Butler, J. W. Fleming, L. P. Goss, and M. C. Lin, Chem. Phys. **56**, 355 (1981).
[3] M. R. Berman and M. C. Lin, Chem. Phys. **82**, 435 (1983).

CH + i-C$_4$H$_{10}$ → Products

Rate Coefficient Data

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$2.0 \cdot 10^{-10}$ exp($+240/T$)	298–689	Zabarnick, Fleming, and Lin (1988)[1]	(a)

Comments

(a) Multiphoton dissociation of CHBr$_3$ at 266 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 20–300 Torr Ar. Rates independent of total pressure.

Preferred Values

$k = 2.0 \cdot 10^{-10}$ exp($+240/T$) cm^3 molecule^{-1} s^{-1} over range 300–700 K

Reliability
Δlog k = ± 1 over range 300–700 K

Comments on Preferred Values

The only available experimental measurement is adopted but with wide error limits.

Reference

[1] S. Zabarnick, J. W. Fleming, and M. C. Lin, Chem.Phys. **112**, 409 (1987).

CH + neo-C₅H₁₂ → Products

Rate Coefficient Data

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$1.6 \cdot 10^{-10}$ exp($+340/T$)	298–689	Zabarnick, Fleming, and Lin (1988) [1]	(a)

Comments

(a) Multiphoton dissociation of CHBr₃ at 266 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 20–300 Torr Ar. Rates independent of total pressure.

Preferred Values

$k = 1.6 \cdot 10^{-10}$ exp($+340/T$) cm^3 molecule^{-1} s^{-1} over range 300–700 K

Reliability
$\Delta \log k = \pm 1$ over range 300–700 K

Comments on Preferred Values
The only available experimental measurement is adopted but with wide error limits.

References

[1] S. Zabarnick, J. W. Fleming, and M. C. Lin, Chem. Phys. **112**, 409 (1987).

CH + CH₃C₂H → Products

Rate Coefficient Data

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$4.6 \cdot 10^{-10}$	298	Butler *et al.* (1981)[1]	(a)

Comments

(a) Multiphoton dissociation of CHBr₃ at 193 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 100 Torr Ar.

Preferred Values

No recommendation.

References

[1] J. E. Butler, J. W. Fleming, L. P. Goss, and M. C. Lin, Chem. Phys. **56**, 355 (1981).

CH + CH$_2$O → Products

Rate Coefficient Data

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$1.6 \cdot 10^{-10}$ exp($+260/T$)	297–670	Zabarnick, Fleming, and Lin (1988) [1]	(a)

Comments

(a) Multiphoton dissociation of CHBr$_3$ at 266 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 20–300 Torr Ar. Rates independent of total pressure.

Preferred Values

$k = 1.6 \cdot 10^{-10}$ exp($+260/T$) cm^3 molecule^{-1} s^{-1} over range 300–700 K

Reliability

$\Delta \log k = \pm 1$ over range 300–700 K

Comments on Preferred Values

The only available experimental measurement is adopted but with wide error limits.

References

[1]S. Zabarnick, J. W. Fleming, and M. C. Lin, 21st Symp. (Int.) Combust., 713 (1988).

$$^3CH_2 + O_2 \rightarrow H + CO + OH \quad (1)$$
$$\rightarrow H_2 + CO_2 \quad (2)$$
$$\rightarrow CO + H_2O \quad (3)$$
$$\rightarrow CH_2O + O \quad (4)$$
$$\rightarrow CO_2 + 2 H \quad (5)$$
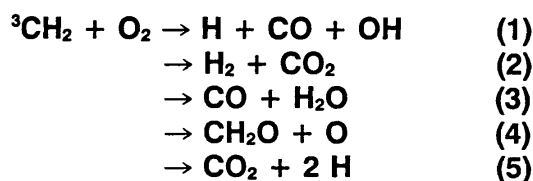
Thermodynamic Data

$\Delta H^\circ_{298} (1) = -241$ kJ mol^{-1}
$\Delta S^\circ_{298} (1) = 95.2$ J K^{-1}mol^{-1}
$K_p(1) = 1.15 \cdot 10^3 \, T^{0.74}$ exp($+29000/T$)atm

$\Delta H^\circ_{298} (3) = -739$ kJ mol^{-1}
$\Delta S^\circ_{298} (3) = -14.3$ J K^{-1}mol^{-1}
$K_p(3) = 4.14 \, T^{-0.456}$ exp($+88800/T$)

$\Delta H^\circ_{298} (5) = -345$ kJ mol^{-1}
$\Delta S^\circ_{298} (5) = 42.4$ J K^{-1}mol^{-1}
$K_p(5) = 4.87 \cdot 10^{-4} \, T^{1.92}$ exp($+42000/T$)atm

$\Delta H^\circ_{298} (2) = -781$ kJ mol^{-1}
$\Delta S^\circ_{298} (2) = -56.2$ J K^{-1}mol^{-1}
$K_p(2) = 1.55 \cdot 10^{-5} \, T^{0.637}$ exp($+94100/T$)

$\Delta H^\circ_{298} (4) = -254$ kJ mol^{-1}
$\Delta S^\circ_{298} (4) = -21.0$ J K^{-1}mol^{-1}
$K_p(4) = 4.66 \cdot 10^{-3} \, T^{0.34}$ exp($+30800/T$)

Rate Coefficient Data ($k = k_1 + k_2 + k_3 + k_4 + k_5$)

k[cm^3 molecule^{-1} s^{-1}]	T [K]	Reference	Comments
Rate Coefficient Measurements			
$1.5 \cdot 10^{-12}$	298	Laufer and Bass (1974)[1]	(a)
$1.2 \cdot 10^{-12}$	298	Pilling and Robertson (1977)[2]	(a)
$1.7 \cdot 10^{-12}$	298	Vinckier and Debruyn (1978)[3]	(b)
$2.2 \cdot 10^{-11}$ exp($-750/T$)	290–600	Vinckier and Debruyn (1979)[4]	(b)
$k_5 = 6.7 \cdot 10^{-11}$ exp($-1100/T$)	1100–1300	Warnatz (1981)[5]	(c)
$3.3 \cdot 10^{-12}$	298	Böhland *et al*. (1984)[6]	(d)
Reviews and Evaluations			
$1.4 \cdot 10^{-12}$	298	Tsang and Hampson (1986)[7]	(e)

Comments

(a) Flash photolysis of ketene in helium[1] and argon[2]. Products analysed by GC and simulated by numerical integration. Rate coefficient determined primarily relative to that for $^3CH_2$ + $^3CH_2$ which was taken as $5.3 \cdot 10^{-11}$ cm³ molecule⁻¹ s⁻¹.

(b) Discharge flow study of O + C_2H_2 with molecular beam sampling and mass spectrometric analysis. Rate coefficient obtained from the effect of $[O_2]$ on the steady-state $[CH_2]$ signal.

(c) Modelling acetylene/O_2 laminar flames. Channel and rate coefficient correctly predict the mole fractions and temperature profiles in lean flames.

(d) Discharge flow with LMR detection of $^3CH_2$; the methylene was generated either from discharging ketene or from O + CH_2CO.

(e) Based on an earlier evaluation by Laufer[8] which relied on the data from Refs. 1 and 2.

Preferred Values

$k = 4.1 \cdot 10^{-11} \exp(-750/T)$ cm³ molecule⁻¹ s⁻¹ over range 300–1000 K

Reliability

$\Delta \log k = \pm 0.5$ at 1000 K reducing to ± 0.3 at 300 K

Comments on Preferred Values

The more directly determined rate coefficient of Böhland *et al.*[6] has been adopted, together with the temperature dependence of Vinckier and Debruyn[4]. Tsang and Hampson[7] give $k_1/k_3 = 2.5$, based on the measurement by Shaub *et al.*[9] of the vibrational distribution in the product CO, following flash photolysis of CH_2I_2 + O_2. Rowland *et al.*[10], in a tracer (^{14}C) study of the steady-state photolysis and the photosensitized decomposition of ketene, showed that the relative yields of CO and CO_2 are about the same at 298 K, i.e. $(k_2 + k_5)/(k_1 + k_3) \simeq 1.0$. Evidence for channels (1) and/or (5) was provided by the formation of hot T atoms in studies of ^3CHT.

References

[1] A. H. Laufer and A. M. Bass, J. Phys. Chem. **78**, 1344 (1974).
[2] M. J. Pilling and J. A. Robertson, J. Chem. Soc. Faraday Trans. 1, **73**, 968 (1977).
[3] C. Vinckier and W. Debruyn, 17th Symp. (Int.) Combust., 623 (1978).
[4] C. Vinckier and W. Debruyn, J. Phys. Chem. **83**, 2057 (1979).
[5] J. Warnatz, 18th Symp. (Int.) Combust., 369 (1981).
[6] T. Böhland, F. Temps, and H. Gg. Wagner, Ber. Bunsenges. Phys. Chem. **88**, 1222 (1984).
[7] W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data, **15**, 1087 (1986).
[8] A. H. Laufer, Rev. Chem. Intermed. **4**, 225 (1981).
[9] W. M. Shaub, D. S. Y. Hsu, T. L. Birks, and M. C. Lin, 18th Symp. (Int.) Combust., 811 (1981).
[10] F. S. Rowland, P. S. -T. Lee, D. C. Montague, and R. L. Russell, Faraday Disc. Chem. Soc. **53**, 111 (1972).

$$^3CH_2 + {}^3CH_2 \rightarrow C_2H_2 + H_2 \quad (1)$$
$$\rightarrow C_2H_2 + 2H \quad (2)$$
$$\rightarrow C_2H_3 + H \quad (3)$$
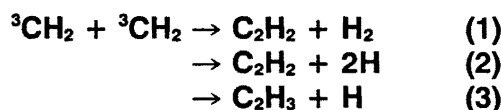
Thermodynamic Data

$\Delta H^\circ_{298}(1) = -547.2$ kJ mol⁻¹
$\Delta S^\circ_{298}(1) = -59.5$ J K⁻¹mol⁻¹
$K_p(1) = 1.66 \cdot 10^{-7} T^{1.24}\exp(+66240/T)$

$\Delta H^\circ_{298}(3) = -269.7$ kJ mol⁻¹
$\Delta S^\circ_{298}(3) = -44.8$ J K⁻¹mol⁻¹
$K_p(3) = 2.15 \cdot 10^{-6} T^{1.02}\exp(+33010/T)$

$\Delta H^\circ_{298}(2) = -111.3$ kJ mol⁻¹
$\Delta S^\circ_{298}(2) = 39.2$ J K⁻¹mol⁻¹
$K_p(2) = 5.22 \cdot 10^{-6} T^{2.52}\exp(+14130/T)$atm

Rate Coefficient Data

k[cm³ molecule⁻¹ s⁻¹]	T [K]	Reference	Comments
Rate Coefficient Measurements			
$5.3 \cdot 10^{-11}$	298	Braun *et al.* (1970)[1]	(a)
$k_2/k \geq 0.9$	298	Becerra *et al.* (1987)[2]	(b)
$k_2 = 1.7 \cdot 10^{-10}$	2000–2800	Frank, Bhaskaran, and Just (1987)[3]	(c)
Reviews and Evaluations			
$5.3 \cdot 10^{-11}$	298	Laufer (1981)[4]	(d)

Comments

(a) VUV flash photolysis of ketene, time-dependence of $^3CH_2$ and of C_2H_2 monitored by absorption spectroscopy.

(b) Reanalysis of earlier work based on excimer laser flash photolysis of ketene (308 nm). Source of molecular hydrogen now identified as $^3CH_2$ + H, leaving atomic products as the more likely for $^3CH_2$ + $^3CH_2$. Their analysis allowed up to 10% of the reaction to occur via channel (1).

(c) Absorption spectroscopy study of H and CO in thermal decomposition of dilute ketene mixtures in argon behind reflected shock waves.

(d) Evaluation based on Ref. 1.

Preferred Values

$k = 2.0 \cdot 10^{-10} \exp(-400/T)$ cm^3 molecule^{-1} s^{-1} over range 300–3000 K

$k_2/k = 0.9$ over range 300–3000 K

Reliability

$\Delta \log k = \pm 0.5$

$\Delta k_2/k = \pm 0.1$

Comments on Preferred Values

After a period of uncertainty, it now seems clear that channel (2) predominates. The reaction probably proceeds via $C_2H_5^*$ + H, with, Becerra *et al.* argue, $C_2H_5^*$ decomposing too quickly for collisional stabilization at normal pressures.

References

[1] W. Braun, A. M. Bass, and M. J. Pilling, J. Chem. Phys. **52**, 5131 (1970).

[2] R. Becerra, C. E. Canosa-Mas, H. M. Frey, and R. Walsh, J. Chem. Soc. Faraday Trans. 2, **83**, 435 (1987).

[3] P. Frank, K. A. Bhaskaran, and Th. Just, J. Phys. Chem. **90**, 2226 (1986).

[4] A. H. Laufer, Rev. Chem. Intermed. **4**, 225 (1981).

$^3CH_2$ + CH_3 → C_2H_4 + H
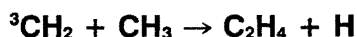
Thermodynamic Data

$\Delta H_{298}^\circ = -262$ kJ mol^{-1}

$\Delta S_{298}^\circ = -55.7$ J K^{-1}mol^{-1}

$K_p = 2.36 \cdot 10^{-7} T^{1.14} \exp(+32200/T)$

Rate Coefficient Data

k[cm^3 molecule^{-1} s^{-1}]	T [K]	Reference	Comments
Rate Coefficient Measurements			
$5 \cdot 10^{-11}$	298	Pilling and Robertson (1975)[1]	(a)
$1.0 \cdot 10^{-10}$	298	Laufer and Bass (1975)[2]	(b)
$3 \cdot 10^{-11}$	1800–2700	Olson and Gardiner (1978)[3]	(c)
$3 \cdot 10^{-11}$	1700–2200	Bhaskaran, Frank, and Just (1979)[4]	(d)
$(7–10) \cdot 10^{-11}$	1320–2300	Frank and Braun-Unkhoff (1987)[5]	(e)
Reviews and Evaluations			
$7 \cdot 10^{-11}$	298	Laufer (1981)[6]	(f)
$7 \cdot 10^{-11}$	300–2500	Warnatz (1984)[7]	(g)

Comments

(a) Flash photolysis of mixtures of ketene and azomethane, end product analysis by GC. Products simulated by numerical integration. Rate coefficient sensitive to value chosen for CH_3 + CH_3 ($4.2 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1}).

(b) Flash photolysis of mixtures of ketene and azomethane, end product analysis by GC. Products simulated by numerical integration. Rate coefficient sensitive to value chosen for CH_3 + CH_3 ($9.5 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1}).

(c) IR absorption study of fuel rich $CH_4/O_2/Ar$ mixtures behind incident shock waves. Product yields by numerical integration.

(d) Atomic resonance absorption study of H in reflected shock waves.

(e) Atomic resonance absorption study of H in reflected shock waves using a range of CH_3 precursors ($CH_3N_2CH_3$, CH_3I, C_2H_6) to obtain data over a wide range of temperatures.

(f) Evaluation based on a reanalysis of Refs. 1 and 2.

(g) Evaluation based on both low and high temperature data (Refs. 1–4).

Preferred Values

$k = 7.0 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1} over range 300–3000 K

Reliability

$\Delta\log k = \pm 0.3$ at 300 K rising to ± 0.5 at 3000 K

## Comments on Preferred Values

The rate data of Refs. 1 and 2 need correction for the methyl recombination rate coefficients used in the simulations. Taking $k(CH_3 + CH_3) = 6 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1} (Ref. 8) at 298 K at the pressures employed, increases the rate coefficient in Ref. 1 to $6 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1} and decreases that in Ref. 2 to $8 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

The reaction presumably proceeds via an ethyl radical adduct. A significant temperature dependence is not, therefore, expected and is confirmed by the results of Refs. 3–5.

References

[1] M. J. Pilling and J. A. Robertson, Chem. Phys. Lett. 33, 336 (1975).
[2] A. H. Laufer and A. M. Bass, J. Phys. Chem. 79, 1635 (1975).
[3] D. B. Olson and W. C. Gardiner, Comb. Flame 32, 151 (1978).
[4] K. A. Bhaskaran, P. Frank, and Th. Just, 12th Shock Tube Symposium, Jerusalem (1979).
[5] P. Frank and M. Braun-Unkhoff, 16th Symposium on Shock Waves, Aachen (1987).
[6] A. H. Laufer, Rev. Chem. Intermed. 4, 225 (1981).
[7] J. Warnatz, in "Combustion Chemistry", ed. W. C. Gardiner, Springer-Verlag, New York (1984).
[8] I. R. Slagle, D. Gutman, J. W. Davies, and M. J. Pilling, J. Phys. Chem. 92, 2455 (1988).

$$^3CH_2 + C_2H_2 \rightarrow CH_2CCH_2 \quad (1)$$
$$\rightarrow CH_3CCH \quad (2)$$
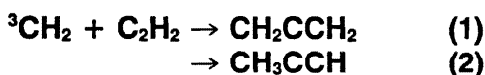
Thermodynamic Data

$\Delta H^\circ_{298}(1) = -424$ kJ mol^{-1}

$\Delta S^\circ_{298}(1) = -167$ J K^{-1}mol^{-1}

$K_p(1) = 9.37 \cdot 10^{-11} \, T^{0.285} \exp(+51500/T)$ atm^{-1}

$\Delta H^\circ_{298}(2) = -430$ kJ mol^{-1}

$\Delta S^\circ_{298}(2) = -189$ J K^{-1}mol^{-1}

$K_p(2) = 1.27 \cdot 10^{-11} \, T^{0.189} \exp(+52080/T)$ atm^{-1}

Rate Coefficient Data ($k = k_1 + k_2$)

k[cm^3 molecule^{-1} s^{-1}]	T [K]	Reference	Comments
Rate Coefficient Measurements			
$7.5 \cdot 10^{-12}$	298	Laufer and Bass (1974)[1]	(a)
$4.0 \cdot 10^{-12}$	298	Pilling and Robertson (1977)[2]	(a)
$1.3 \cdot 10^{-12}$	295	Vinckier and Debruyn (1979)[3]	(b)
$3.1 \cdot 10^{-12}$	298	Homann and Schweinfurth (1981)[4]	(c)
$<10^{-15}$	298	Canosa-Mas, Frey, and Walsh (1984)[5]	(d)
$<2.6 \cdot 10^{-15}$	298	Canosa-Mas, Frey, and Walsh (1985)[6]	(d)
$2.0 \cdot 10^{-11}\exp(-3330/T)$	296–700	Böhland, Temps, and Wagner (1986)[7]	(e)

Comments

(a) Flash photolysis of ketene, end product analysis by GC. Rate related to production of allene and propyne in presence of inert gas.

(b) Fast flow reactor study of O + C$_2$H$_2$. Products and intermediates detected by molecular beam sampling and mass spectrometry. Reaction attributed to production of C$_3$H$_3$ + H.

(c) Discharge flow study of O + C$_2$H$_2$. C$_3$H$_4$ detected by mass spectrometry. Reaction attributed to formation of C$_3$H$_3$ + H and C$_3$H$_2$ + H$_2$. Pressure = 1–6 Torr.

(d) Laser flash photolysis of ketene (308 nm) in presence of Ar and C$_2$H$_2$. Products detected by GC. High rate coefficients in Refs. 1 and 2 attributed to failure to account properly for reactions of $^1CH_2$. Suggest rate is probably less than $2.6 \cdot 10^{-16}$ cm^3 molecule^{-1} s^{-1}.

e) Flow tube study, $^3CH_2$ generated fron discharge or laser flash photolysis of CH$_2$CO (308 nm). $^3CH_2$ detected by LMR.

Preferred Values

$k = 2.0 \cdot 10^{-11} \exp(-3330/T)$ cm^3 molecule^{-1} s^{-1} over range 300–1000 K

Reliability

$\Delta\log k = \pm 0.3$

Comments on Preferred Values

The recent careful work of Canosa-Mas *et al.*[5,6] has revealed the deficiencies in the mechanistic interpretations of Refs. 1–4. Canosa-Mas *et al.* employed a full reaction scheme using predominantly available literature data. The observed yields of C$_3$H$_4$ were fully explained by the reactions of $^1CH_2$ with C$_2$H$_2$. Their conclusions have recently been fully endorsed by the direct measurements of Böhland *et al.*[7].

References

[1]A. H. Laufer and A. M. Bass, J. Phys. Chem. **78**, 1344 (1974).
[2]M. J. Pilling and J. A. Robertson, J. Chem. Soc. Faraday Trans. 1, **73**, 968 (1977).
[3]C. Vinckier and W. Debruyn, 17th Symp. (Int.) Combust., 623 (1979).
[4]K. H. Homann and H. Schweinfurth, Ber. Bunsenges. Phys. Chem. **85**, 569 (1981).

[5]C. E. Canosa-Mas, H. M. Frey, and R. Walsh, J. Chem. Soc. Faraday Trans. 2, **80**, 561 (1984).
[6]C. E. Canosa-Mas, H. M. Frey, and R. Walsh, J. Chem. Soc. Faraday Trans. 2, **81**, 283 (1985).
[7]T. Böhland, F. Temps, and H. Gg. Wagner, 21st Symp. (Int.) Combust., 841 (1986).

$$^3CH_2 + C_2H_4 \rightarrow C_3H_6 \qquad (1)$$
$$\rightarrow c\text{-}C_3H_6 \qquad (2)$$
$$\rightarrow C_3H_5 + H \qquad (3)$$

Thermodynamic Data

$\Delta H^\circ_{298} (1) = -419 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (1) = -157 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(1) = 5.68 \cdot 10^{-11} T^{0.562} \exp(+50900/T) \text{ atm}^{-1}$

$\Delta H^\circ_{298} (3) = -87.3 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (3) = -42.9 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(3) = 3.03 \cdot 10^{-9} T^{2.08} \exp(+11300/T)$

Rate Coefficient Data ($k = k_1 + k_2 + k_3$)

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	T [K]	Reference	Comments
Rate Coefficient Measurements			
$\leq 3 \cdot 10^{-14}$	298	Laufer and Bass (1975)[1]	(a)
$< 5 \cdot 10^{-16}$	298	Canosa-Mas, Frey, and Walsh (1985)[2]	(b)
$5.3 \cdot 10^{-12} \exp(-2660/T)$	296–728	Böhland, Temps, and Wagner (1986)[3]	(c)

Comments

(a) Flash photolysis of ketene + C_2H_4 + 700 Torr He. End product analysis by GC. Rate measured relative to $^3CH_2 + {}^3CH_2$.

(b) Excimer laser flash photolysis (308 nm) of ketene + C_2H_4 + 400 Torr Ar. End product analysis by GC. Product yields simulated by numerical integration.

(c) Discharge flow, $^3CH_2$ monitored by LMR and generated from O + CH_2CO and by laser flash photolysis (308 nm) of CH_2CO. Correction made for reaction proceeding via activation to singlet.

Preferred Values

$k = 5.3 \cdot 10^{-12} \exp(-2660/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over range 300–1000 K

Reliability

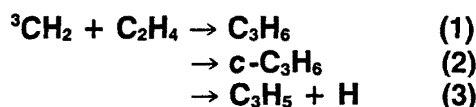$\Delta \log k = \pm 0.3$ at 1000 K reducing to ± 0.2 at 300–700 K

Comments on Preferred Values

The rate coefficients were measured over the pressure range 0.4–5.7 Torr and were found to be independent of pressure[3]. RRKM calculations demonstrate that the most likely fate of the energised triplet adduct, under these conditions, is decomposition to generate H + C_3H_5. At higher pressures propene is formed and cyclopropane is the major product in the high pressure limit. Propene is the major product for reaction in excess C_2H_4 in the range 10–175 Torr and cyclopropane predominates at higher pressures[4], although the yields of propene and cyclopropane will decrease with increasing temperature.

References

[1]A. H. Laufer and A. M. Bass, J. Phys. Chem. **79**, 1635 (1975).
[2]C. E. Canosa-Mas, H. M. Frey, and R. Walsh, J. Chem. Soc. Faraday Trans. 2, **81**, 283 (1985).
[3]T. Böhland, F. Temps, and H. Gg. Wagner, Ber. Bunsenges. Phys. Chem. **90**, 468 (1986).
[4]F. S. Rowland, P. S. -T. Lee, D. C. Montague, and R. L. Russell, Disc. Faraday Soc. **53**, 111 (1972).

$^1CH_2 + M \rightarrow {}^3CH_2 + M$
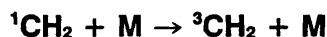
Thermodynamic Data

$\Delta H_{298}^\circ = -37.7$ kJ mol^{-1} (see comment (a)[1])

$\Delta S_{298}^\circ = 6.8$ J K^{-1}mol^{-1}

$K_p = 2.17\ T^{0.016}\ \exp(+4520/T)$

Rate Coefficient Data (Preferred Values)

[M]	k[cm^{3}molecule^{-1} s^{-1}]	T[K]	Comments
Ar	$6.0 \cdot 10^{-12}$	298	(b)[2], (c)[3]
N$_2$	$1.0 \cdot 10^{-11}$	298	(b)[2], (c)[3]
CH$_4$	$1.2 \cdot 10^{-11}$	298	(b)[2], (c)[3], (d)[4]
C$_2$H$_2$	$8.0 \cdot 10^{-11}$	298	(e)[5]
C$_2$H$_4$	$2.3 \cdot 10^{-11}$	298	(c)[3], (d)[4]
C$_2$H$_6$	$3.6 \cdot 10^{-11}$	298	(c)[3], (d)[4]

Comments

(a) Based on an analysis of spectroscopic data from a variety of sources [including LMR and diode laser spectroscopy of CH$_2(\tilde{X}^3B_1)$], and photoelectron spectroscopy of CH$_2^-$ ($\tilde{X}^2B_1$). The value for ΔH_{298}° is calculated from the quoted value for ΔH_0° given in Ref. 1, using recent spectroscopic and theoretical data to calculate $\Delta C_p(T)$.

(b) Room temperature laser pump and probe experiments, using IRMPD of acetic anhydride to generate $^1CH_2$ and LIF to detect it. Total removal rate (reaction + deactivation) measured.

(c) Room temperature excimer laser flash photolysis of ketene (308 nm) and time-resolved cw dye laser absorption spectroscopy of $^1CH_2$. Total removal rate (reaction + deactivation) measured.

(d) Room temperature LMR measurements of the fractional yield of $^3CH_2$ following photolysis of ketene at 308 nm. The quantum yield, ϕ, for the production of $^3CH_2$ in the photolysis was assumed zero. The absolute deactivation rate coefficients were calculated from the fractional yield and the rate coefficients for total removal from refs. 2 and 3. Since ϕ was assumed zero, these rate coefficients represent upper limits.

(e) Room temperature laser flash photolysis of ketene at 308 nm. $^1CH_2$ detected by LIF. Production of $^3CH_2$ detected by LMR.

Reliability

$\Delta \log k = \pm 0.3$ for Ar and N$_2$ over range 300–2000 K

$\Delta \log k = \pm 0.4$ for hydrocarbons over range 300–2000 K

Comments on Preferred Values

There is excellent agreement between the overall removal rate coefficients reported in Refs. 2 and 3. For Ar and N$_2$ at room temperatures, these represent exclusively the deactivation channel, although reactive channels probably become available for N$_2$ at higher temperatures and association at higher pressures. The deactivation channel efficiencies, required to determine k for the hydrocarbons, are less precisely known. The rate coefficients may be assumed temperature independent, although a slight decrease with increasing temperatures may occur.

References

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[3] A. O. Langford, H. Petek, and C. B. Moore, J. Chem. Phys. 78, 6650 (1983).

[4] T. Böhland, F. Temps, and H. Gg. Wagner, Ber. Bunsenges. Phys. Chem. 89, 1013 (1985).

[5] W. Hack, M. Koch, and H. Gg. Wagner, Ber. Bunsenges. Phys. Chem. 92, 674 (1988).

$$^1CH_2 + O_2 \rightarrow H + CO + OH \qquad (1)$$
$$\rightarrow H_2 + CO_2 \qquad (2)$$
$$\rightarrow CO + H_2O \qquad (3)$$
$$\rightarrow {}^3CH_2 + O_2 \qquad (4)$$
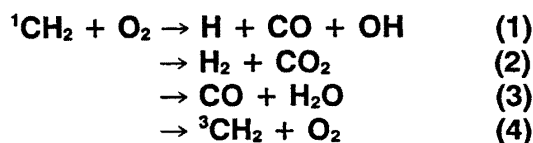
Thermodynamic Data

ΔH°_{298} (1) = -278 kJ mol^{-1}

ΔS°_{298} (1) = 102 J K^{-1}mol^{-1}

$K_p(1)$ = 2.49·10^3 $T^{0.757}$ exp($+33500/T$)atm

ΔH°_{298} (3) = -777 kJ mol^{-1}

ΔS°_{298} (3) = -7.49 J K^{-1}mol^{-1}

$K_p(3)$ = 8.96 $T^{-0.44}$ exp($+93300/T$)

ΔH°_{298} (2) = -818 kJ mol^{-1}

ΔS°_{298} (2) = -49.4 J K^{-1}mol^{-1}

$K_p(2)$ = 3.37·10^{-5} $T^{0.653}$ exp($+98600/T$)

ΔH°_{298} (4) = -37.7 kJ mol^{-1}

ΔS°_{298} (4) = 6.8 J K^{-1}mol^{-1}

$K_p(4)$ = 2.17 $T^{0.016}$ exp($+4520/T$)

Rate Coefficient Data ($k = k_1 + k_2 + k_3 + k_4$)

k [cm^3 molecule^{-1} s^{-1}]	T [K]	Reference	Comments
Rate Coefficient Measurements			
3.0·10^{-11}	298	Ashfold et al. (1981)[1]	(a)
7.4·10^{-11}	298	Langford, Petek, and Moore (1983)[2]	(b)
Reviews and Evaluations			
<3.0·10^{-10}	298	Laufer (1981)[3]	(c)
5.2·10^{-11}	298	Tsang and Hampson (1986)[4]	(d)

Comments

(a) Pump and probe experiments, with $^1CH_2$ produced by IRMPD of acetic anhydride and detected by LIF. Measured total rate of removal of $^1CH_2$.

(b) Excimer laser flash photolysis of ketene at 308 nm and time-resolved dye laser absorption spectroscopy of $^1CH_2$. Measured total rate of removal of $^1CH_2$.

(c) Based on flash photolysis – gas chromatography study of ketene[5]. Rate coefficient determined relative to a value of 3.4·10^{-13} cm^3 molecule^{-1} s^{-1} for deactivation of $^1CH_2$ by He. More recent measurements give the latter as 3.3·10^{-12} cm^3 molecule^{-1} s^{-1}[1,2], requiring a tenfold increase in the upper estimate for $^1CH_2$ + O_2 to ≤ 3·10^{-10} cm^3 molecule^{-1} s^{-1} .

(d) Based on Refs. 1 and 2.

Preferred Values

k = 5.2·10^{-11} cm^3 molecule^{-1} s^{-1} over range 300–1000 K

Reliability

Δlog k = ± 0.5 at 1000 K reducing to ± 0.3 at 300 K

Comments on Preferred Values

The agreement between the measured values of rate coefficients in Refs. 1 and 2 was significantly worse for this reaction than for any others. It was suggested that there may be a precursor dependence, which might be connected with a vibrational energy dependence of the reaction and incomplete vibrational relaxation before reaction. The rate coefficient refers to total removal, but Ashfold et al.[1] argue that k is three times greater than the value expected for deactivation and that a chemical mechanism predominates. In $^{14}CH_2CO$ tracer studies, Rowland et al.[6] found similar relative product yields for both $^1CH_2$ and $^3CH_2$ + O_2. They suggested that this might indicate that the main mechanism of reaction of $^1CH_2$ with O_2 is deactivation to $^3CH_3$, in contrast with the conclusions of Ashfold et al.[1].

References

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[3] A. H. Laufer, Rev. Chem. Intermed. **4**, 225 (1981).

[4] W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data **15**, 1087 (1986).

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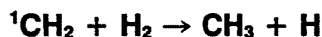# $^1CH_2 + H_2 \rightarrow CH_3 + H$

Thermodynamic Data

$\Delta H^\circ_{298} = -61.0 \text{ kJ mol}^{-1}$
$\Delta S^\circ_{298} = -10.7 \text{ J K}^{-1}\text{mol}^{-1}$
$K_p = 4.22 \cdot 10^{-2} \, T^{0.57} \exp(+7640/T)$

Rate Coefficient Data

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	T [K]	Reference	Comments
Rate Coefficient Measurements			
$1.3 \cdot 10^{-10}$	298	Ashfold *et al.* (1981)[1]	(a)
$1.05 \cdot 10^{-10}$	298	Langford, Petek, and Moore (1983)[2]	(b)
Reviews and Evaluations			
$1.2 \cdot 10^{-10}$	298	Tsang and Hampson (1986)[3]	(c)

Comments

(a) Pump and probe experiments, with $^1CH_2$ produced by IRMPD of acetic anhydride and detected by LIF. Measure total rate of removal of $^1CH_2$.

(b) Excimer laser flash photolysis of ketene at 308 nm and time-resolved dye laser absorption spectroscopy of $^1CH_2$. Measure total rate of removal of $^1CH_2$.

(c) Based on Refs. 1 and 2.

Preferred Values

$k = 1.2 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over range 300–1000 K

Reliability

$\Delta \log k = \pm 0.3$ at 1000 K reducing to ± 0.1 at 300 K

Comments on Preferred Values

Both measurements refer to the total rate of removal of $^1CH_2$ and could include a contribution from the deacti-

vation to $^3CH_2$. Ashfold *et al.*[1] argue against such a contribution from a comparison of the magnitude of the rate coefficient with those for deactivation of $^1CH_2$ to $^3CH_2$ by inert gases. In addition, Braun *et al.*[4] detected the CH_3 product and demonstrated that more than 80% of the overall $^1CH_2$ removal led to methyl radical production.

References

[1] M. N. R. Ashfold, M. A. Fullerton, G. Hancock, and G. W. Ketley, Chem. Phys. **55**, 245 (1981).
[2] A. O. Langford, H. Petek, and C. B. Moore, J. Chem. Phys. **78**, 6650 (1983).
[3] W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data **15**, 1087 (1986).
[4] W. Braun, A. M. Bass, and M. J. Pilling, J. Chem. Phys. **52**, 5131 (1970).

$^1CH_2 + C_2H_2 \rightarrow CH_2CCH_2$ (1)
$\rightarrow CH_3CCH$ (2)
$\rightarrow C_3H_3 + H$ (3)
$\rightarrow \, ^3CH_2 + C_2H_2$ (4)
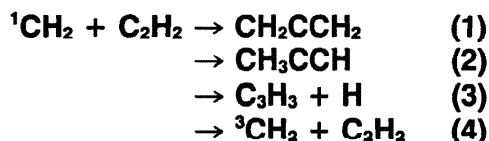
Thermodynamic Data

$\Delta H^\circ_{298} (1) = -462 \text{ kJ mol}^{-1}$
$\Delta S^\circ_{298} (1) = -160 \text{ J K}^{-1}\text{mol}^{-1}$
$K_p(1) = 2.03 \cdot 10^{-10} \, T^{0.3} \exp(+56020/T) \text{ atm}^{-1}$

$\Delta H^\circ_{298} (3) = -113 \text{ kJ mol}^{-1}$
$\Delta S^\circ_{298} (3) = -24.4 \text{ J K}^{-1}\text{mol}^{-1}$
$K_p(3) = 4.76 \cdot 10^{-5} \, T^{1.01} \exp(+14020/T)$

$\Delta H^\circ_{298} (2) = -467 \text{ kJ mol}^{-1}$
$\Delta S^\circ_{298} (2) = -183 \text{ J K}^{-1}\text{mol}^{-1}$
$K_p(2) = 2.75 \cdot 10^{-11} \, T^{0.21} \exp(+56600/T) \text{ atm}^{-1}$

$\Delta H^\circ_{298} (4) = -37.7 \text{ kJ mol}^{-1}$
$\Delta S^\circ_{298} (4) = 6.8 \text{ J K}^{-1}\text{mol}^{-1}$
$K_p(4) = 2.17 \, T^{0.016} \exp(+4520/T)$

Rate Coefficient Data ($k = k_1 + k_2 + k_3 + k_4$)

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	T [K]	Reference	Comments
Rate Coefficient Measurements			
$2.1 \cdot 10^{-10}$	295	Canosa-Mas, Frey, and Walsh (1983)[1,2]	(a)
$3.7 \cdot 10^{-10}$	298	Hack *et al.* (1988)[3]	(b)
$k_4/k = 0.22$			

Comments

(a) Excimer laser flash photolysis of ketene (308 nm) in the presence of Ar and C_2H_2. Products detected by GC. Pressure = 400 Torr. Product distribution simulated by numerical integration. Partial decomposition of the adduct occurred at the pressure employed. An RRKM calculation[2] gives a decomposition rate for $C_3H_4^*$ of $4.5 \cdot 10^8$ s^{-1}, and an effective stabilization rate constant in argon of $2.1 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1}. The complexity of the system suggests a greater uncertainty than the ± 25% proposed by the authors. The relative rates of reactions (1) and (2) are given as 1:1.6.

(b) Laser flash photolysis of ketene (308 nm), $^1CH_2$ detected by LIF. Production of $^3CH_2$ (channel (4)) detected by LMR.

Preferred Values

$k = 3.7 \cdot 10^{-10}$ cm^3 molecule^{-1} s^{-1} over range 300–1000 K
$k_4/k = 0.22$

Reliability

$\Delta \log k = \pm 0.7$ at 1000 K reducing to ± 0.3 at 300 K
$\Delta k_4 / k = \pm 0.1$

Comments on Preferred Values

The direct measurement of Hack et al.[3] has been preferred, the complexity of the system employed by Canosa-Mas et al.[1,2] makes their value less reliable, although their measurements help to confirm the overall rate coefficient, which is unlikely to show a strong temperature dependence. A general discussion of the $^1CH_2 \rightarrow {}^3CH_2$ deactivation may be found on p644. k_2 may decrease slightly with temperature.

References

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$$^1CH_2 + C_2H_4 \rightarrow C_3H_6 \qquad (1)$$
$$\rightarrow {}^3CH_2 + C_2H_4 \qquad (2)$$
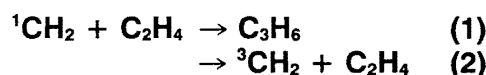
Thermodynamic Data

$\Delta H^\circ_{298} (1) = -457$ kJ mol^{-1}
$\Delta S^\circ_{298} (1) = -150$ J K^{-1}mol^{-1}
$K_p(1) = 25.7\ T^{0.578} \exp(+55400/T)$ atm^{-1}

$\Delta H^\circ_{298} (2) = -37.7$ kJ mol^{-1}
$\Delta S^\circ_{298} (2) = 6.8$ J K^{-1}mol^{-1}
$K_p(2) = 2.17\ T^{0.016} \exp(+4520/T)$

Rate Coefficient Data ($k = k_1 + k_2$)

k[cm^3 molecule^{-1} s^{-1}]	T [K]	Reference	Comments
Rate Coefficient Measurements			
$1.5 \cdot 10^{-10}$	295	Langford, Petek, and Moore (1983)[1]	(a)
$k_1 = 2.1 \cdot 10^{-10}$	295	Canosa-Mas, Frey, and Walsh (1985)[2]	(b)
$k_2/k_1 = 0.15$	295	Bohland, Temps, and Wagner (1985)[3]	(c)

Comments

(a) Excimer laser flash photolysis of ketene (308 nm) followed by time-resolved detection of $^1CH_2$ by cw dye laser absorption.

(b) Excimer laser flash photolysis of ketene (308 nm) in the presence of Ar and C_2H_4. Products detected by GC. Pressure approximately 400 Torr. Product distribution simulated by numerical integration. Assumed same rate coefficient for $^1CH_2 + C_2H_4$ and $^1CH_2 + CH_2CO$.

(c) Excimer laser flash photolysis of ketene (308 nm), LMR detection of $^3CH_2$. Assumed triplet quantum yield at 308 nm = 0.0. The k_2/k_1 value represents an upper limit.

Preferred Values

$k = 1.5 \cdot 10^{-10}$ cm^3 molecule^{-1} s^{-1} over range 300–1000 K
$k_2/k_1 = 0.15$ over range 300–1000 K

Reliability

$\Delta \log k = \pm 0.5$ at 1000 K, reducing to ± 0.2 at 300 K
$\Delta(k_2/k_1) = \pm 0.1$

Comments on Preferred Values

The more direct measurement of Langford et al.[1] is preferred, because of the assumptions made by Canosa-Mas et al.[2] and the complexity of their system; their value provides confirmation of the direct value. The temperature dependence is unlikely to be pronounced for such a large rate coefficient. Even at 295 K, in the presence of 400 Torr of Ar, Canosa-Mas et al.[2] failed to detect signif-

icant yields of cyclopropane and, especially at higher temperatures, the product can be taken as propene. A general discussion of $^1CH_2 \rightarrow {}^3CH_2$ deactivation may be found on p644. k_2 may decrease slightly with temperature.

References

[1] A. O. Langford, H. Petek, and C. B. Moore, J. Chem. Phys. **78**, 6650 (1983).

[2] C. E. Canosa-Mas, H. M. Frey, and R. Walsh, J. Chem. Soc. Faraday Trans. 2, **81**, 283 (1985).

[3] T. Böhland, F. Temps, and H. Gg. Wagner, Ber. Bunsenges. Phys. Chem. **89**, 1013 (1985).

$CH_3 + M \rightarrow CH_2 + H + M$

Thermodynamic Data

$\Delta H^{\circ}_{298} = 459 \text{ kJ mol}^{-1}$

$\Delta S^{\circ}_{298} = 116 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p = 1.61 \cdot 10^4 \ T^{0.731} \exp(-55200/T) \text{ atm}$

Rate Coefficient Data

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	$T[\text{K}]$	Reference	Comments
Rate Coefficient Measurements			
$1.0 \cdot 10^{-8} \exp(-44900/T)$	1700–2300	Bhaskaran, Frank, and Just (1979)[1]	(a)
$3.23 \cdot 10^{-8} \exp(-46100/T)$	2150–2850	Roth, Barner, and Löhr (1979)[2]	(b)
Reviews and Evaluations			
$1.7 \cdot 10^{-8} \exp(-45600/T)$	1500–3000	Warnatz (1984)[3]	(c)

Comments

(a) Shock-tube decomposition of C_2H_6/O_2 mixtures with direct detection of H and O by atomic resonance absorption spectrometry.

(b) Shock-tube study of the decomposition of C_2H_6 in Ar with direct measurement of time dependent [H].

(c) Based on data of Bhaskaran *et al.*[1] and Roth *et al.*[2].

Preferred Values

$k = 1.7 \cdot 10^{-8} \exp(-45600/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over range 1500–3000 K

Reliability

$\Delta \log k = \pm 0.5$ over range 1500–3000 K

Comments on Preferred Values

We have adopted the recommendation of Warnatz[3] which is based on the experimental data of Bhaskaran *et al.*[1] and of Roth *et al.*[2].

References

[1] K. A. Bhaskaran, P. Frank, and Th. Just, "High Temperature Methyl Radical Reaktions with Atomic and Molecular Oxygen", Proc. 12th Symp. on Shock Tubes And Waves (The Magnes Press, Jerusalem) 503 (1979).

[2] P. Roth, U. Barner, and R. Löhr, Ber. Bunsenges. Phys. Chem. **83**, 929 (1979).

[3] J. Warnatz, in "Combustion Chemistry", ed. W. C. Gardiner, Springer-Verlag, New York (1984).

$$CH_3 + O_2 \rightarrow CH_3O + O \quad (1)$$
$$\rightarrow CH_2O + OH \quad (2)$$
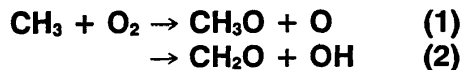
Thermodynamic Data

$\Delta H^\circ_{298} (1) = 120 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (1) = -96.6 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(1) = 1.13 \cdot 10^{-2} T^{0.404} \exp(-14100/T)$

$\Delta H^\circ_{298} (2) = -223 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (2) = 3.1 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(2) = 4.32 \ T^{-0.179} \exp(+26800/T)$

Rate Coefficient Data

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	$T[\text{K}]$	Reference	Comments
Rate Coefficient Measurements			
$< 5 \cdot 10^{-17}$	1000–1220	Baldwin and Golden (1978)[1]	(a)
$k_1 = 1.2 \cdot 10^{-11} \exp(-12900/T)$	1700–2300	Bhaskaran, Frank,	(b)
$k_2 = 8.6 \cdot 10^{-11} \exp(-17400/T)$	1700–2300	and Just (1979)[2]	
$k_1 = 1.67 \cdot 10^{-10} \exp(-15500/T)$	1150–1560	Hsu et al. (1983)[3]	(c)
$k_1 = 3.7 \cdot 10^{-10} \exp(-17000/T)$	1430–2150	Saito et al. (1986)[4]	(d)
$k_2 = 5.3 \cdot 10^{-13} \exp(-4500/T)$	1430–2150		
$k_2 = 5.6 \cdot 10^{-13} \exp(-4500/T)$	1100–1600	Fraak and Zellner[5]	(e)
Reviews and Evaluations			
$k_1 = 2.5 \cdot 10^{-11} \exp(-14400/T)$	1000–2300	Warnatz (1984)[7]	(f)
$k_1 = 3.3 \cdot 10^{-6} T^{-1.57} \exp(-14710/T)$	300–2500	Tsang and Hampson (1986)[8]	(g)

Comments

(a) Very low pressure pyrolysis of $(CH_3)_2N_2$ in the presence of O_2, with mass spectrometric detection of CH_3. With $[O_2]$ in excess of $(CH_3)_2N_2$ by a factor of 100, no detectable change in CH_3 mass peak was observed. Upper limit rate coefficient deduced from estimated limit of detection of change in CH_3 peak.

(b) Shock-tube decomposition of C_2H_6/O_2 mixtures with direct detection of H and O by atomic resonance absorption spectrometry. Rate coefficients derived from a computer simulation of the [H] and [O] profiles.

(c) Shock-tube study of the decomposition of dilute mixtures of $(CH_3N)_2$ in O_2 with detection of time-resolved profiles of CO product formation. Rate data derived from kinetic modelling of CO formation.

(d) Shock-tube study of the decomposition of mixtures of $C_2H_6/O_2/Ar$ and $CH_3I/O_2/Ar$ with time-resolved monitoring of O, H, and OH. Rate coefficients derived from kinetic modelling of experimental profiles based on a mechanism of 18 elementary reactions.

(e) Shock-tube study of the decomposition of $(CH_3N)_2$ in presence of O_2 and Ar with time-resolved measurements of $[CH_3]$ and $[OH]$ at 216 and 308 nm respectively. Derived rate coefficients are comparable with above tabulated Arrhenius equation obtained from an RRKM calculation[6] for k_2.

(f) Based on data of Brabbs and Brokaw[9] and of Bhaskaran et al.[1].

(g) Based on data of Bhaskaran et al.[1] and of Hsu et al.[2] and assuming that the reaction proceeds via $CH_3O_2^*$.

Preferred Values

$k_1 = 2.2 \cdot 10^{-10} \exp(-15800/T)$ over range 300–2500 K

$k_2 = 5.5 \cdot 10^{-13} \exp(-4500/T)$ over range 1000–2500 K

Reliability

$\Delta \log k_1 = \pm 0.5$

$\Delta \log k_2 = \pm 0.5$

Comments on Preferred Values

The rate coefficients reported for channel (1) fall into two groups, i.e. the data of (i) Brabbs and Brokaw[9] and of Bhaskaran et al.[2] and the data of (ii) Hsu et al.[3] and of Saito et al.[4]. At 1669 K these two sets of results yield values of k, which differ by about a factor of 2.5. We have derived the preferred rate expression from an analysis of the data of Hsu et al.[3] and of Saito et al.[4] mainly on the grounds that they involved more comprehensive experimental data than the other two studies. Reitelboim et al.[10], Dean and Westmoreland[11], and Zellner and Ewig[6] have calculated values of k_1 from RRKM theory involving a $CH_3O_2^*$ intermediate. In all cases the calculated rate coefficients are lower than the above recommended value of k_1. The recent studies of Saito et al.[4] and of Fraak and Zellner[5] have confirmed that channel (2) is the favoured route in the reaction between CH_3 and O_2. The above recommended value of k_2 is a mean of the sets of results[4,5], which are in excellent agreement. In this case the calculated rate coefficients (k_2) based on RRKM theory are totally consistent with the experimental data.

References

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[2]K. A. Bhaskaran, P. Frank, and Th. Just, "High Temperature Methyl Radical Reactions with Atomic and Molecular Oxygen", Proc. 12th Symp. on Shock Tubes and Waves (The Magnes Press, Jerusalem) 503 (1979).

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[10]M. A. Reitelboim, L. B. Romanovich, and B. I. Vedeneev, Kinet. Katal. **19**, 399 (1978).

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$CH_3 + O_2 (+ M) \rightarrow CH_3O_2 (+ M)$
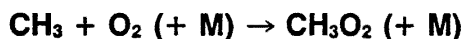
Thermodynamic Data

$\Delta H^\circ_{298} = -135 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} = -126 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p = 9.45 \cdot 10^{-5} \, T^{-0.857} \exp(+15930/T) \text{ atm}^{-1}$

Rate Coefficient Data

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	$T[\text{K}]$	$[\text{M}] [\text{molecule cm}^{-3}]$	Reference	Comments
Rate Coefficient Measurements				
Low Pressure Range				
$3.4 \cdot 10^{-31}$ [He]	295	$(0.2–2.2) \cdot 10^{17}$ (He)	Plumb and Ryan (1982)[1]	(a)
$8.0 \cdot 10^{-32} \exp(+560/T)$ [Ar]	230–568	$(6–30) \cdot 10^{16}$ (Ar)	Pratt and Wood (1984)[2]	(b)
$4.8 \cdot 10^{-31}$ [Ar]	298	$(1.7–19) \cdot 10^{16}$ (Ar)	Selzer and Bayes (1983)[3]	(c)
$4.8 \cdot 10^{-31}$ [Ar]	298	$(1.0–15) \cdot 10^{18}$ (Ar)	Pilling and Smith (1985)[4]	(d)
$7.0 \cdot 10^{-31}$ [Ar] $8.0 \cdot 10^{-31}$ [N$_2$]	298	$(6.0–3600) \cdot 10^{18}$ (Ar) } (N$_2$)	Cobos *et al.* (1985)[5]	(e)
$1.5 \cdot 10^{-22} \, T^{-3.3}$ [Ar]	334–582	$(0.5–15) \cdot 10^{18}$ (Ar)	Keiffer, Pilling, and Smith (1987)[6]	(f)
High Pressure Range				
$1.1 \cdot 10^{-12}$	298	$(1.0–15) \cdot 10^{18}$ (Ar)	Pilling and Smith (1985)[4]	(d)
$2.2 \cdot 10^{-12}$	298	$(6.0–3600) \cdot 10^{18}$ (N$_2$,Ar)	Cobos *et al.* (1985)[5]	(e)
$1.3 \cdot 10^{-15} \, T^{1.2}$	334–582	$(0.5–15) \cdot 10^{18}$ (Ar)	Keiffer, Pilling, and Smith (1987)[6]	(f)
$1.2 \cdot 10^{-12}$	298	$(3.3–450) \cdot 10^{17}$ (He)	Caldwell, Parent, and Nelson (1989)[7]	(g)
Reviews and Evaluations				
$k_0 = 7.0 \cdot 10^{-24} \, T^{-3.0}$ [N$_2$] $k_\infty = 2.0 \cdot 10^{-12}$ $F_c(N_2) = \exp(-T/360) + \exp(-1440/T)$	260–300 260–400		Baulch *et al.* (1982)[8]	(h)
$k_0 = 4.1 \cdot 10^{-26} \, T^{-2.0}$ [N$_2$] $k_\infty = 2.9 \cdot 10^{-8} \, T^{-1.7}$ $F_c = 0.6$	200–300		DeMore *et al.* (1987)[9]	(i)

Comments

(a) Discharge flow, mass spectrometry. CH$_3$ generated from F + CH$_4$. k_0 obtained by extrapolation using $k_\infty = 2 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $F_c = 0.51$.

(b) Discharge flow, analysis by gas chromatography. CH$_3$ generated by H + C$_2$H$_4$. k_0 obtained by fits using same parameters as Plumb and Ryan[1].

(c) Laser flash photolysis, photoionisation mass spectrometry. CH$_3$ generated by 193 nm photolysis of nitromethane. Relative collisional efficiencies Ar : N$_2$: O$_2$: He determined as 1.0 : 1.1 : 1.1 : 1.9.

(d) Laser flash photolysis, absorption spectroscopy. CH$_3$ generated by 193 nm photolysis of azomethane. Demonstrated that earlier flash photolysis/absorption spectroscopy experiments were in error because of neglect of CH$_3$ + CH$_3$O$_2$. Technique devised to eliminate contributions from this reaction.

(e) Laser flash photolysis, absorption spectroscopy in high pressure cell. CH$_3$ generated by 193 nm photolysis of azomethane.

(f) Laser flash photolysis, absorption spectroscopy. CH$_3$ from 193 nm photolysis of acetone.

(g) Laser flash photolysis, resonance enhanced multiphoton ionisation detection of CH_3. CH_3 generated from 266 nm photolysis of CH_3I.

(h) Based mainly on earlier flash photolysis studies at high radical densities, where radical–radical reactions play a significant role.

(i) Based on Ref. 5 (k_∞) and on the low pressure results of Refs. 1 and 3.

Preferred Values

$k_0 = 1.5 \cdot 10^{-22} \, T^{-3.3}$ [Ar] cm^3 molecule^{-1} s^{-1} over range 300–800 K

$k_0 = 1.6 \cdot 10^{-22} \, T^{-3.3}$ [N_2] cm^3 molecule^{-1} s^{-1} over range 300–800 K

$k_\infty = 1.3 \cdot 10^{-15} \, T^{1.2} \, cm^3$ molecule^{-1} s^{-1} over range 300–800 K

$F_c = 0.466 - 1.30 \cdot 10^{-4} \, T$

Reliability

$\Delta \log k = \pm 0.3$ over the temperature range 300–800 K and the pressure range 0.5–1500 Torr

Comments on Preferred Values

The rate parameters are determined from the data of Refs. 3, 4, and 6 but they are in good agreement with the data of Refs. 2 and 7. The fits do not reproduce the high pressure data of Cobos *et al.* suggesting that this representation is unsatisfactory at higher pressures.

References

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$$CH_3 + O_2 \rightarrow CH_3O + O$$
$$\rightarrow HCHO + OH$$
$$\rightarrow CH_3O_2$$

CH₃ + H₂ → CH₄ + H
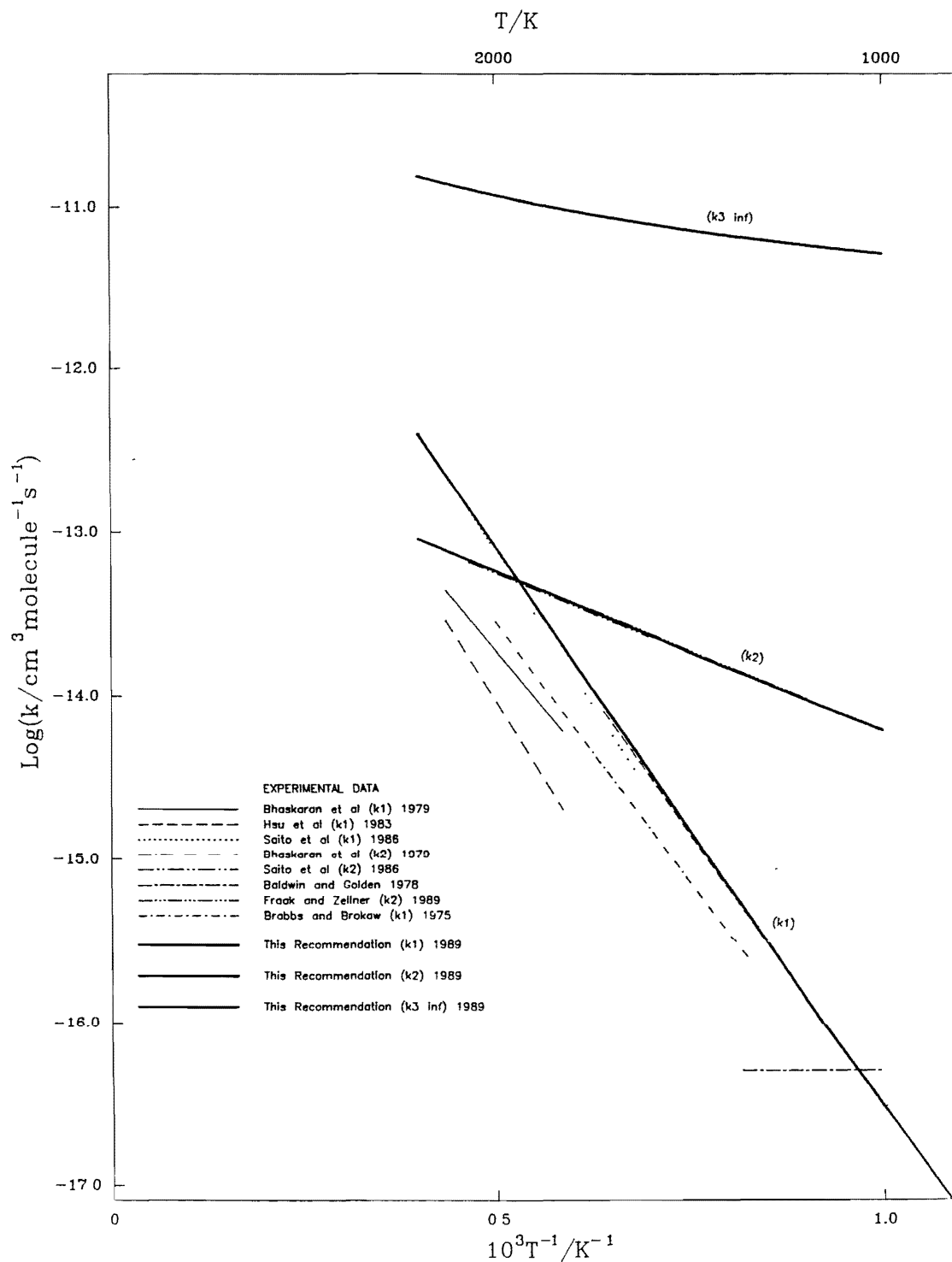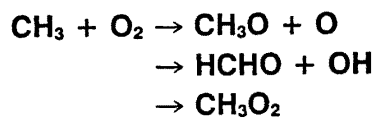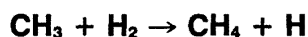
Thermodynamic Data

$\Delta H^\circ_{298} = -2.6$ kJ mol^{-1}

$\Delta S^\circ_{298} = -24.0$ J K^{-1}mol^{-1}

$K_p = 5.51 \cdot 10^{-3} T^{0.225} \exp(+638/T)$

Rate Coefficient Data

k[cm³ molecule⁻¹ s⁻¹]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$1.32 \cdot 10^{-18} T^2 \exp(-4810/T)$	372–1370	Kobrinsky and Pacey (1974)[1]	(a)
$8.3 \cdot 10^{-13} \exp(-5290/T)$	584–671	Marshall and Shahkar (1981)[2]	(b)
$3.3 \cdot 10^{-11} \exp(-7200/T)$	1066–2166	Möller, Mozzhukhin, and Wagner (1986)[3]	(c)
Reviews and Evaluations			
$2.57 \cdot 10^{-11} \exp(-7801/T)$	1200–2000	Clark and Dove (1973)[4]	(d)
$1.4 \cdot 10^{-12} \exp(-5490/T)$	370–700	Kerr and Parsonage (1976)[5]	(e)
$1.1 \cdot 10^{-21} T^{3.0} \exp(-3900/T)$	300–2500	Warnatz (1984)[6]	(f)
$4.8 \cdot 10^{-22} T^{3.12} \exp(-4384/T)$	300–2500	Tsang and Hampson (1986)[7]	(g)

Comments

(a) Pyrolysis of neo-C₅H₁₂ in the presence of H₂ in a flow system over the temperature range 826–968 K. End-product analysis for CH₄ and C₂H₆. Rate equation for temperature range 372–1370 K includes earlier data.

(b) Pyrolysis of (CH₃N)₂ in the presence of H₂ in a flow system. End-product analysis for CH₄ and C₂H₆. Kinetic treatment of data gives k(CH₃ + H₂) directly without involving k(CH₃ + CH₃).

(c) Shock-tube study with time resolved measurement of [CH₃] by absorption at 216.5 nm. CH₃ produced from decomposition of (CH₃)₄Sn, (CH₃)₂N₂ or (CH₃)₂Hg.

(d) Shock-tube study of the pyrolysis of (CH₃N)₂ in the presence of H₂ over the temperature range 1272–1370 K. Rate coefficient at 1340 K derived from a computer simulation of the experimental concentration-time profiles of CH₄ and C₂H₆. Rate equation for temperature range 1200–2000 K includes earlier literature data.

(e) Linear least-mean squares fit of literature experimental rate coefficients.

(f) Fit of three parameter rate equation to data analysed in comment (d).

(g) Rate equation obtained from re-analysis of available experimental data.

Preferred Values

$k = 1.14 \cdot 10^{-20} T^{2.74} \exp(-4740/T)$ cm³ molecule⁻¹ s⁻¹ over range 300–2500 K

Reliability

$\Delta \log k = \pm 0.15$ over range 300–700 K

$= \pm 0.3$ over range 700–2500 K

Comments on Preferred Values

The above recommendation is from a re-analysis of the data base used by Tsang and Hampson[7] together with the more recent high temperature measurements of Möller *et al.*[3]. This latter study, which involved direct monitoring of [CH₃], provides a firmer base concerning the curvature of the Arrhenius plot and the reliability of the rate coefficients at higher temperatures.

It has already been pointed out[5,7] that there is a discrepancy between the ratio of rate coefficients for this reaction and the reverse reaction and the equilibrium constant calculated from thermochemical data.

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$$CH_3 + H_2 \rightarrow CH_4 + H$$

T/K

EXPERIMENTAL DATA
□ Gowenlock et al 1953
—— Gesser and Steacie 1956
△ Benson and Jain 1959
— — — Shapiro and Weston 1972
○ Clark and Dove 1973
● Kobrinsky and Pacey 1974
◨ Marshall and Shahkar 1981
·········· Moller et al 1986

—— This Recommendation 1989

$10^3 T^{-1}/K^{-1}$

$Log(k/cm^3 molecule^{-1} s^{-1})$

$$CH_3 + CH_3 \rightarrow H + C_2H_5 \qquad (1)$$
$$\rightarrow H_2 + C_2H_4 \qquad (2)$$
$$CH_3 + CH_3 (+ M) \rightarrow C_2H_6 (+ M) \qquad (3)$$
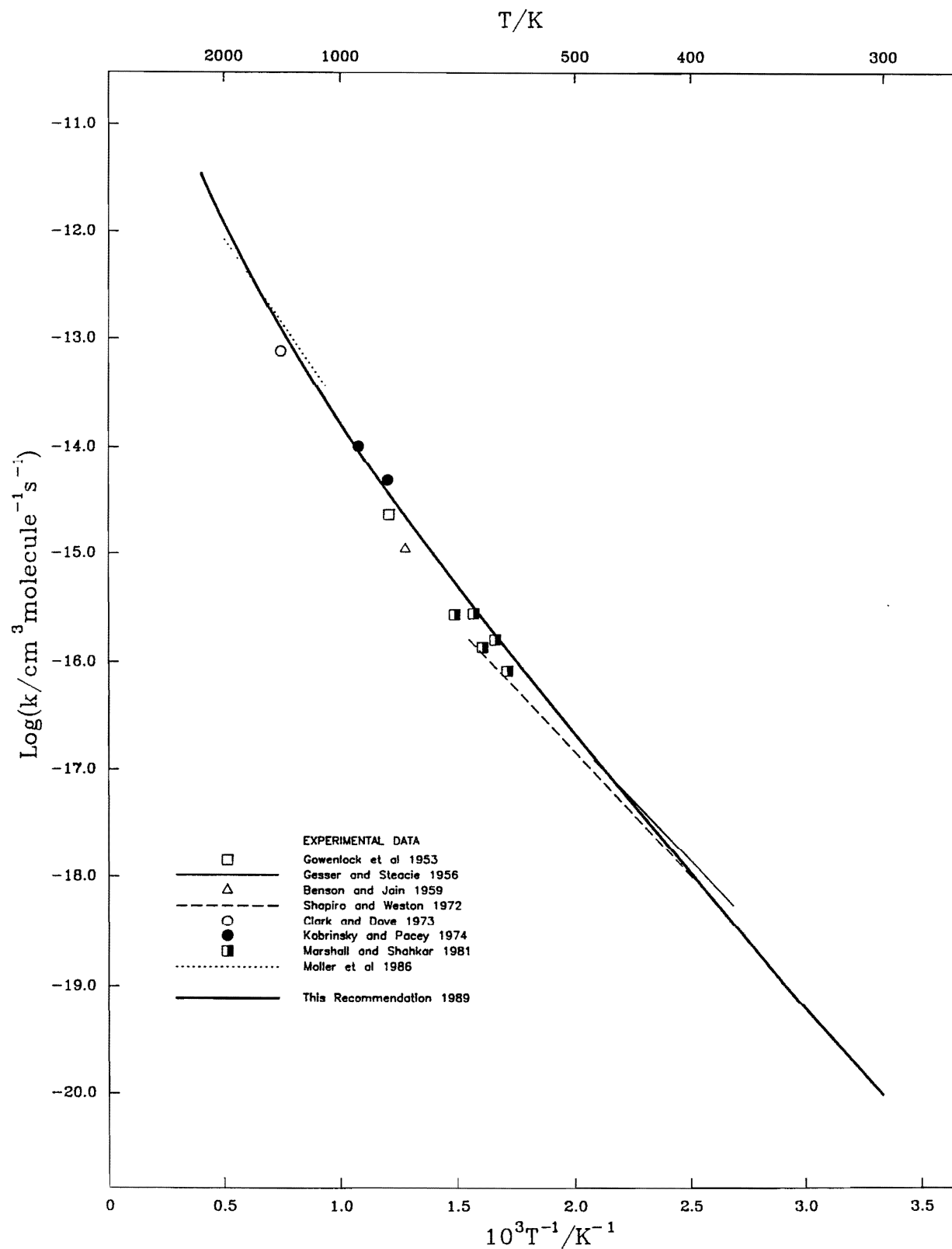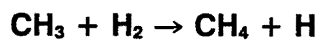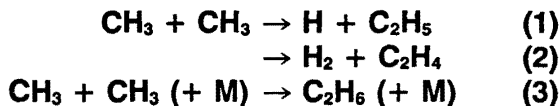
Thermodynamic Data

$\Delta H^\circ_{298} (1) = 43.8 \text{ kJ mol}^{-1}$
$\Delta S^\circ_{298} (1) = -21.9 \text{ J K}^{-1}\text{mol}^{-1}$
$K_p(1) = 2.21 \cdot 10^{-4} \, T^{0.741} \exp(-4790/T)$

$\Delta H^\circ_{298} (2) = -239 \text{ kJ mol}^{-1}$
$\Delta S^\circ_{298} (2) = -38.3 \text{ J K}^{-1}\text{mol}^{-1}$
$K_p(2) = 1.21 \cdot 10^{-4} \, T^{0.59} \exp(+29050/T)$

$\Delta H^\circ_{298} (3) = -375 \text{ kJ mol}^{-1}$
$\Delta S^\circ_{298} (3) = -159 \text{ J K}^{-1}\text{mol}^{-1}$
$K_p(3) = 2.41 \cdot 10^{-10} \, T^{0.236} \exp(+45700/T) \text{ atm}^{-1}$

Rate Coefficient Data ($k = k_1 + k_2 + k_3$)

k [cm^3 molecule^{-1} s^{-1}]	T [K]	Reference	Comments
Rate Coefficient Measurements			
$k_2 = 1 \cdot 10^{-7} \exp(-21600/T)$	2000–2700	Gardiner *et al.* (1975)[1]	(a)
$k = 1.6 \cdot 10^{-8} \exp(-15400/T)$	1700–2000	Tsuboi (1978)[2]	(b)
$k_1/k_2 = 1.0$			
$k_1 = 1.3 \cdot 10^{-9} \exp(-13400/T)$	1650–2100	Roth and Just (1979)[3]	(c)
$k_2 = 1.7 \cdot 10^{-8} \exp(-16100/T)$			
$k_1 = 2.5 \cdot 10^{-13}$	1700	Chiang and Skinner (1981)[4]	(d)
$k_1 = 1.3 \cdot 10^{-12} \exp(-6562/T)$	1600–2500	Kiefer and Budach (1984)[5]	(e)
$k_1 = 4.7 \cdot 10^{-11} \exp(-6840/T)$	1320–2300	Frank and Braun-Unkhoff (1987)[6]	(f)
Reviews and Evaluations			
$k_1 = 1.3 \cdot 10^{-9} \exp(-13400/T)$	1500–3000	Warnatz (1984)[7]	(g)
$k_2 = 1.7 \cdot 10^{-8} \exp(-16100/T)$	1500–2500		
$k_1 = 3 \cdot 10^{-12} \exp(-5248/T)$		Tsang and Hampson (1986)[8]	(h)

Comments

(a) Methane pyrolysis in shock wave; time of flight mass spectrometry. IR laser absorption and laser schlieren. Numerical integration of complex scheme.

(b) Shock tube study of C_2H_6, C_2H_6/O_2. Monitored CH_3 by absorption, decay second order in methyl, suggested contribution from ($k_1 + k_2$).

(c) Reflected shock wave study of dilute C_2H_6 in Ar; H detected by atomic resonance absorption spectroscopy.

(d) Study of shock heated C_2H_6, C_2D_6 mixtures by atomic resonance absorption spectroscopy of H. Need additional source of H at higher temperatures when H + $C_2H_6 \rightarrow C_2H_5 \rightarrow C_2H_4$ + H becomes unimportant on the monitoring time scale.

(e) Argue that previous estimates are too high. Shock wave study of C_2H_6/Kr mixtures by laser schlieren.

(f) Shock tube/atomic resonance absorption study of H with a variety of CH_3 precursors ($CH_3N_2CH_3$, CH_3I, C_2H_6, all in Ar) to cover a wide range of temperatures. Numerical integration.

(g) Evaluation. Adopted the values of Roth and Just[3].

(h) Based on k_{-1} and K_p.

Preferred Values

$k_1 = 5 \cdot 10^{-11} \exp(-6800/T)$ cm^3 molecule^{-1} s^{-1} over range 1300–2500 K

k_2 no recommendation

Reliability
$\Delta \log k_1 = \pm 0.6$

Comments on Preferred Values

Considering the indirect nature of most of the experiments, they give remarkably consistent results, although Kiefer and Budach's[5] values seem too low. The preferred value is based on the recent, more direct data of Frank and Braun-Unkhoff[6]. It should be noted, however, that extrapolation of values based on the low temperature k_{-1} values and the equilibrium constant gives $k_1 = 7 \cdot 10^{-12} \exp(-6300/T)$ cm^3 molecule^{-1} s^{-1} over the range 1300–2500 K.

There are insufficient data to make a recommendation on k_2.

References

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[8] W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data 15, 1087 (1986).

$CH_3 + CH_3(+M) \rightarrow C_2H_6(+M)$

Thermodynamic Data

$\Delta H^\circ_{298} = -375$ kJ mol^{-1}

$\Delta S^\circ_{298} = -159$ J K^{-1}mol^{-1}

$K_p = 2.41 \cdot 10^{-10}\ T^{0.236} \exp(+45700/T)$ atm^{-1}

Rate Coefficient Data

k[cm^3 molecule^{-1} s^{-1}]	T[K]	[M] [molecule cm^{-3}]	Reference	Comments
Rate Coefficient Measurements				
Intermediate Fall-off Range				
$4.0 \cdot 10^{-11}$	250–450	$(3.2–29.4) \cdot 10^{18}$ (N$_2$)	Parkes *et al.* (1976)[1]	(a)
$5.5 \cdot 10^{11}$	295	$1.6 \cdot 10^{18}$ (N$_2$)	Callear and Metcalfe (1976)[2]	(b)
$2.0 \cdot 10^{-11}$	450	$6.4 \cdot 10^{16}$ (He)	Van den Berg (1976)[3]	(c)
$4.0 \cdot 10^{-11}$		$6.4 \cdot 10^{17}$		
$3.2 \cdot 10^{-12}$	1350	$1.2 \cdot 10^{18}$ (Ar)	Glänzer *et al.* (1976)[4]	(d)
$1.3 \cdot 10^{-11}$		$1.5 \cdot 10^{19}$		
$1.8 \cdot 10^{-11}$		$6.0 \cdot 10^{19}$		
$1.6 \cdot 10^{-11}$		$1.2 \cdot 10^{20}$		
$5.2 \cdot 10^{-11}$	295	$2.5 \cdot 10^{19}$ (N$_2$)	Hochanadel *et al.* (1977)[5]	(e)
$7.0 \cdot 10^{-12}$	640–818	$1.0 \cdot 10^{17}$ (Ar)	Sepehrad *et al.* (1979)[6]	(f)
$8.0 \cdot 10^{-12}$		$1.9 \cdot 10^{17}$		
$2.4 \cdot 10^{-12}$	1700–1800	$1.4 \cdot 10^{18}$ (Ar)	Zaslonko and Smirnov (1979)[7]	(g)
$5.3 \cdot 10^{-11}$	295	$1.6 \cdot 10^{18}$ (*n*-pentane)	Adachi *et al.* (1980)[8]	(h)
$1.1 \cdot 10^{-11}$	823	$4.7 \cdot 10^{16}$ (*n*-pentane)	Pacey and Wimalasena (1980)[9]	(i)
$2.6 \cdot 10^{-11}$		$5.4 \cdot 10^{17}$		
$6.0 \cdot 10^{-11}$		$3.9 \cdot 10^{18}$		
$5.5 \cdot 10^{-11}$	296	$2.5 \cdot 10^{19}$ (Ar)	Hippler *et al.* (1984)[10]	(j)
$6.3 \cdot 10^{-11}$		$2.5 \cdot 10^{20}$		
$5.0 \cdot 10^{-11}$		$5.2 \cdot 10^{21}$		
$5.0 \cdot 10^{-11}$		$2.8 \cdot 10^{19}$ (N$_2$)		
$4.6 \cdot 10^{-11}$		$2.5 \cdot 10^{20}$		
$2.6 \cdot 10^{-11}$		$2.5 \cdot 10^{21}$		
$1.8 \cdot 10^{-11}$		$5.0 \cdot 10^{21}$		
$5.2 \cdot 10^{-11}$	296	$1.6 \cdot 10^{17}$ (Ar)	Macpherson *et al.* (1985)[11]	(k)
$5.7 \cdot 10^{-11}$		$1.3 \cdot 10^{18}$		
$6.0 \cdot 10^{-11}$		$1.6 \cdot 10^{19}$		
$1.9 \cdot 10^{-11}$	577	$8.4 \cdot 10^{16}$ (Ar)		
$3.5 \cdot 10^{-11}$		$1.1 \cdot 10^{18}$		
$4.1 \cdot 10^{-11}$		$6.6 \cdot 10^{18}$		
$3.8 \cdot 10^{-11}$	302	$1.3 \cdot 10^{17}$ (N$_2$)	Arthur (1986)[12]	(l)
$4.0 \cdot 10^{-11}$		$2.7 \cdot 10^{18}$		
$4.0 \cdot 10^{-11}$		$1.8 \cdot 10^{19}$		
$4.7 \cdot 10^{-11}$	373–463	$6.3 \cdot 10^{17}$ (N$_2$)	Arthur and Biordi (1986)[13]	(m)
$4.4 \cdot 10^{-11}$	296	$3.8 \cdot 10^{16}$ (Ar)	Slagle *et al.* (1988)[14]	(n)
$5.2 \cdot 10^{-11}$		$3.4 \cdot 10^{17}$		
$3.4 \cdot 10^{-12}$	906	$4.0 \cdot 10^{16}$ (Ar)		
$1.5 \cdot 10^{-12}$		$7.9 \cdot 10^{17}$		
$2.9 \cdot 10^{-11}$		$6.4 \cdot 10^{18}$		
High Pressure Range				
$5.8 \cdot 10^{-11}$	296	$(2.5–523) \cdot 10^{19}$ (Ar)	Hippler *et al.* (1984)[10]	(j)
Reviews and Evaluations				
$k_\infty = 5.1 \cdot 10^{-11}$	300		Quack and Troe (1977)[15]	(o)
$k_\infty = 4.8 \cdot 10^{-11}$	1300			
$k_\infty = 4 \cdot 10^{-11}$	250–420		Baulch and Duxbury (1980)[17]	(p)
$k_\infty = 4 \cdot 10^{-10}\ T^{-0.4}$	300–1200		Warnatz (1984)[18]	(q)
$k_\infty = 1.7 \cdot 10^{-9}\ T^{-0.64}$	250–1400		Tsang and Hampson (1986)[19]	(r)
$k_\infty = 1.5 \cdot 10^{-7}\ T^{-1.18} \exp(-329/T)$	300–2000		Wagner and Wardlaw (1988)[20]	(s)
$k_0 = $ [Ar] $8.8 \cdot 10^{-7}\ T^{-7} \exp(-1390/T)$				
$F_c = 0.38 \exp(-T/73) + 0.62 \exp(-T/1180)$				
$k_\infty = 6 \cdot 10^{-11}$	300–1400		Troe (1989)[21]	(t)
$k_\infty = 1.7 \cdot 10^{-?}\ T^{-0.04}$	250–1400		Tsang (1989)[22]	(u)

Comments

(a) Molecular modulation spectroscopy, CH_3 detection at 216 nm.

(b) Flash photolysis of $HgMe_2$, $k = 4.9 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1} for $2\,CD_3 + M \rightarrow C_2D_6 + M$; CH_3 detection at 216 nm.

(c) Flash photolysis of $HgMe_2$, CH_3 detection at 216 nm, pressure dependence between 3 and 30 Torr.

(d) Shock wave pyrolysis study of azomethane at 1200–1500 K, CH_3 detection at 216 nm, fall-off curve between 170 and 17000 Torr, rate coefficients for $2\,CD_3 + Ar \rightarrow C_2D_6 + Ar$ identical to those for methyl recombination.

(e) Flash photolysis of azomethane, CH_3 detection at 216 nm.

(f) Discharge-flow study of the reaction $H + CH_4$, modelling of the mechanism.

(g) Shock wave pyrolysis study of tetramethyl tin, CH_3 detection at 216 nm.

(h) Flash photolysis of azomethane, CH_3 detection at 216 nm.

(i) Flow pyrolysis of neo-pentane, study of the induction period.

(j) Excimer laser flash photolysis of azomethane at 193 nm, CH_3 detection at 216 nm, onset of diffusion control seen in high pressure N_2. Results for Ar shown in Fig. 1.

(k) Excimer laser flash photolysis of azomethane at 193 nm, CH_3 detection at 216 nm, temperature dependence between 296 and 577 K.

(l) Molecular modulation spectroscopy, CH_3 detection at 216 nm.

(m) Rotating sector measurements based on acetone photolysis.

(n) Excimer laser flash photolysis of acetone at 193 nm, analysis by photoionization mass spectrometry at low pressures and by absorption spectroscopy at higher pressures. Results shown in Fig. 1. Experiments also with M = He from 296 to 810 K. Fall-off curves with M = Ar for many temperatures between 296 and 906 K.

(o) Statistical adiabatic channel modelling. Value for 300 K fitted to the experiments, value for 1300 K calculated on the basis of this fit. Evaluation of earlier work in Ref. 16.

(p) Systematic evaluation of earlier work.

(q) Data evaluation and simplified fall-off construction.

(r) Construction of fall-off curves over the range 300–2500 K.

(s) Modelling with variational transition state theory, RRKM theory, and including weak collision effects. Based on experimental data from refs. 4, 10, 11, and 14.

(t) Modelling of experimental data form refs. 4, 10, 11, and 14 with constant $k_{rec,\infty}$ such as suggested by statistical adiabatic channel model from Ref. 15.

(u) See comment (r).

Preferred Values

$k_\infty = 6.0 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1} over range 300–2000 K

$k_0 = [Ar]\,3.5 \cdot 10^{-7}\, T^{-7} \exp(-1390/T)$ cm^3 molecule^{-1} s^{-1} over range 300–2000 K

$F_c = 0.38 \exp(-T/73) + 0.62 \exp(-T/1180)\}$ over range 300–2000 K

Reliability

$\Delta \log k_\infty = \pm\ 0.05$ at 300 K

$\Delta \log k_\infty = \pm\ 0.3$ at 2000 K

$\Delta \log k_0 = \pm\ 0.3$ over range 300–2000 K

$\Delta F_c = \pm\ 0.1$ over range 300–2000 K

Comments on Preferred Values

The recent work from Refs. 4, 10, 11, and 14 has provided extensive data on the pressure and temperature dependence of this reaction for temperatures below 1000 K. At $T > 1000$ K, data are still scarce and reliable extrapolations to the limiting rate coefficients are difficult to make. Fig. 1 summarizes these experimental results. Theoretical modelling helps to extend the range of conditions. The modelling of k_∞ from Ref. 15 here is preferred, since it appears to give a better fit to the high temperature data[21] and is in better accord with weak temperature coefficients found for a series of bimolecular capture rate constants. The expressions for k_0 and F_c are based on the modelling of Ref. 20, however, the values for k_0 had to be scaled by a temperature-independent factor in order to accomodate the chosen k_∞ value.

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$$CH_3 + CH_3 \rightarrow H + C_2H_2$$
$$\rightarrow H_2 + C_2H_4$$
$$\rightarrow C_2H_6$$

T/K

EXPERIMENTAL DATA

——————————	Gordiner et al (k2) 1975
– – – – – –	Tsuboi 1978
· · · · · · · · · · · ·	Roth and Just (k1) 1979
▲	Chiang and Skinner (k1) 1981
–·––·––·	Klefer and Budoch (k1) 1984
–·—·—·—	Frank and Braun-Unkhoff (k1) 1987
–·—·—·—·	Roth and Just (k2) 1979
–··—··—··	Parkes et al (k3) (N2) 1976
⊖	Callear and Metcalf (k3) (N2) 1976
+	Hochanadel et al (k3) (N2) 1977
×	Adachi et al (k3) (n-pentane) 1980
◇	Hippler et al (k3) (Ar) 1984
◆	Hippler et al (k3) (N2) 1984
▣	Macpherson et al (k3) (Ar) 1985
▽	Arthur et al (k3) (N2) 1986
–·—··—·—	Slagle et al (k3) (Ar) 1988
——————————	This Recommendation (k1) 1989
——————————	This Recommendation k3 (inf) 1989

CH_3 + HCHO → CH_4 + CHO

Thermodynamic Data
$\Delta H^\circ_{298} = -61.2$ kJ mol^{-1}

$\Delta S^\circ_{298} = -20.7$ J K^{-1}mol^{-1}

$K_p = 2.1\ T^{-0.176}$ exp($+7360/T$)

Rate Coefficient Data

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$5.33 \cdot 10^{-14}$	1005	Held *et al*. (1977)[1]	(a)
$2.1 \cdot 10^{-11}$ exp($-5415/T$)	788–935	Manthorne and Pacey (1978)[2]	(b)
$1.66 \cdot 10^{-12}$ exp($-3887/T$)	399–434	Selby (1978)[3]	(c)
$1.4 \cdot 10^{-12}$ exp($-3502/T$)	500–603	Anastasi (1983)[4]	(d)
Reviews and Evaluations			
$1.75 \cdot 10^{-13}$ exp($-3080/T$)	300–500	Kerr and Parsonage (1976)[5]	(e)
$1.75 \cdot 10^{-13}$ exp($-3080/T$)	300–500	Warnatz (1984)[6]	(f)
$9.2 \cdot 10^{-21}\ T^{2.81}$ exp($-2950/T$)	300–2500	Tsang and Hampson (1986)[7]	(g)

Comments

(a) Flow pyrolysis of dimethyl ether to generate CH_3 and HCHO. [CH_3] measured by UV absorption, CO, CH_4, and C_2H_6 by gas chromatography. Independent values of k and k(CH_3 + CH_3) reported.

(b) Flow pyrolysis of dimethyl ether; CO, CH_4, and C_2H_6 measured by gas chromatography. k relative to k(CH_3 + CH_3) = $4.03 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

(c) Pyrolysis of di-*t*-butylperoxide; product analysis by gas chromatography.

(d) Molecular modulation–UV absorption detection of CH_3 at 216 nm in presence of excess HCHO; CH_3 produced by photolysis of acetone; first order rate constants corrected for contribution (up to 30%) due to CH_3 + CH_3COCH_3 reaction. Contribution due to radical + radical reactions estimated from measurements of CH_4 and other products by gas chromatography.

(e) Based on data of Blake and Kutske[8] and Toby and Kutske[9] obtained from pyrolysis of di-*t*-butylperoxide and photolysis of of CH_3NNCH_3 respectively.

(f) Accepts the recommendation of Kerr and Parsonage[5].

(g) Based on data in Refs. 1, 2, and 4 and the low temperature data evaluation of Kerr and Parsonage[5].

Preferred Values

$k = 6.8 \cdot 10^{-12}$ exp($-4450/T$) cm^3 molecule^{-1} s^{-1} over range 300–1000 K

Reliability
Δlog $k = \pm 0.3$ over range 300–1000 K

Comments on Preferred Values

The only direct study of this reaction is that of Anastasi, the other values being relative to methyl radical recombination. The direct measurements which cover an intermediate temperature range are higher than predicted from the expression given by Manthorne *et al*.from non-linear least squares analysis of the high (800–1000 K) and low (350–420 K) temperature data. The evidence for non-Arrhenius behaviour is less clear cut than in the case of CH_3 + CH_3CHO, in the absence of reliable data at $T > 1000$ K. The preferred Arrhenius expression is based on a best fit to the data of Selby[3], Anastasi[4], and Manthorne *et al*.[2].

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CH$_3$ + HCHO → CH$_4$ + HCO

$$\text{CH}_3 + \text{C}_2\text{H}_2 \rightarrow \text{CH}_3\text{CH}=\text{CH} \qquad (1)$$
$$\rightarrow \text{CH}_4 + \text{C}_2\text{H} \qquad (2)$$
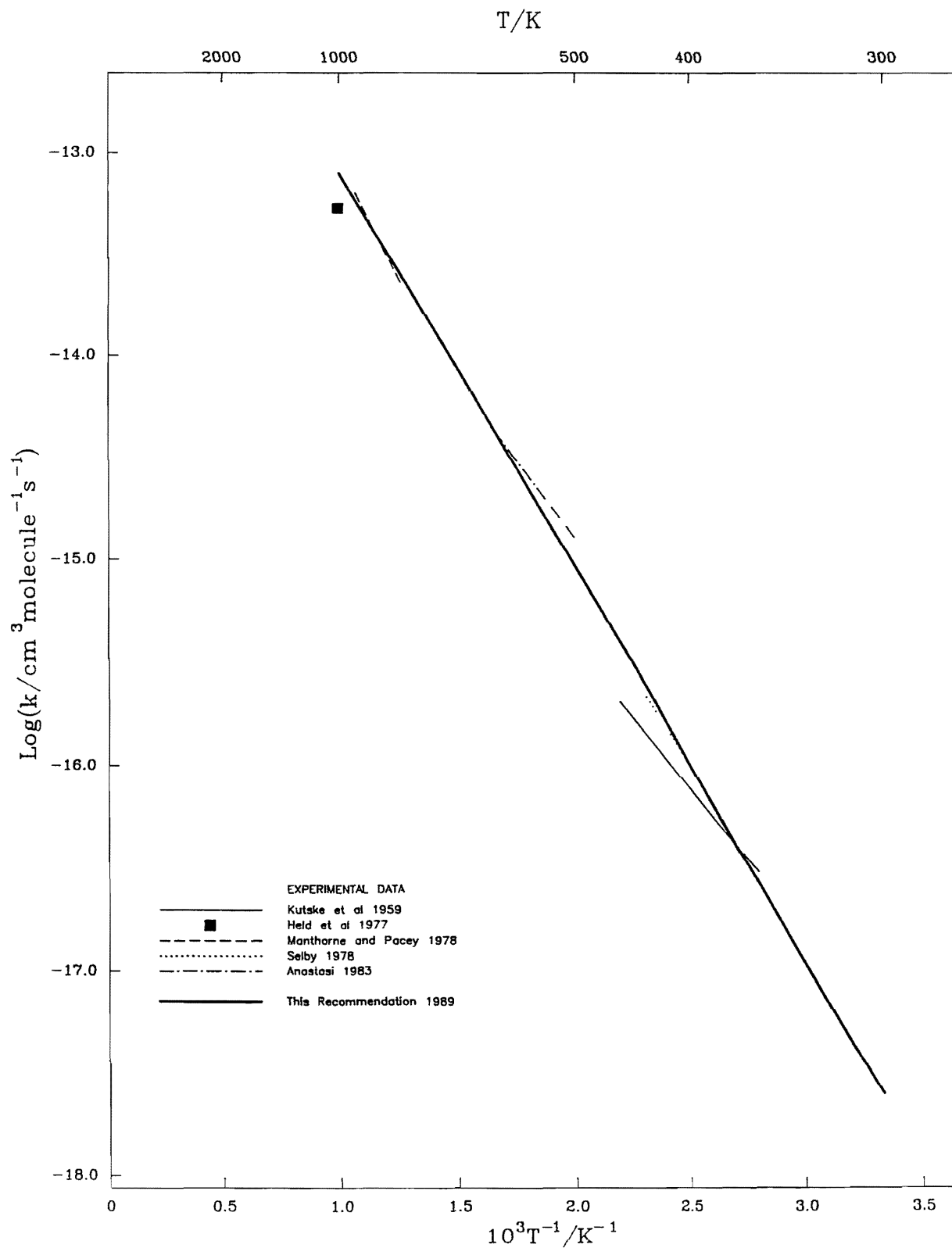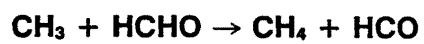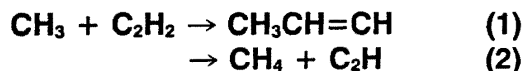
Thermodynamic Data

$\Delta H^\circ_{298}(1) = -238 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298}(1) = -138 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(1) = 1.37 \cdot 10^{-10} T^{-0.705} \exp(+29300/T)$

$\Delta H^\circ_{298}(2) = 113 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298}(2) = -1.5 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(2) = 39.9 T^{0.64} \exp(-13700/T)$

Rate Coefficient Data

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	$T[\text{K}]$	Reference	Comments
Rate Coefficient Measurements			
$k_1 = 1.3 \cdot 10^{-13} \exp(-2760/T)$	417–514	Mandelcorn and Steacie (1954)[1]	(a)
$k_1 = 4.2 \cdot 10^{-13} \exp(-3900/T)$	371–479	Garcia-Dominguez and	
		Trotman-Dickenson (1962)[2]	(b)
$k_1 = 1.0 \cdot 10^{-12} \exp(-3900/T)$	379–487	Holt and Kerr (1977)[3]	(c)
Reviews and Evaluations			
$k_1 = 4.2 \cdot 10^{-13} \exp(-3900/T)$	371–514	Kerr and Parsonage (1972)[4]	(d)

Comments

(a) Steady-state photolysis of CH_3COCH_3 in presence of C_2H_2. End-product analysis for CH_4, C_2H_6 and CO. k derived from a kinetic analysis based on a mass balance, and a calculated relative to $k(\text{CH}_3 + \text{CH}_3) = 3.6 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

(b) Steady-state photolysis of CH_3CHO in presence of C_2H_2 with end-product analysis for adduct products and radical dimer. k derived from rate of formation of adduct produced and calculated relative to $k(\text{CH}_3 + \text{CH}_3) = 3.6 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

(c). Steady-state photolysis of $(\text{CH}_3\text{CO})_2$ in the presence of C_2H_2 and $i\text{-C}_4\text{H}_{10}$ with end-product analysis for CH_4 and CO. k derived from a kinetic analysis based on a mass balance and calculated relative to $k(\text{CH}_3 \ i\text{-C}_4\text{H}_{10}) = 1.38 \cdot 10^{-13}\exp(-4030/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

(d) Based on data of Garcia-Dominguez and Trotman-Dickenson[2].

Preferred Values

$k_1 = 1 \cdot 10^{-12} \exp(-3900/T)$ over range 300–600 K

Reliability

$\Delta \log k = \pm 0.5$ over range 300–600 K

Comments on Preferred Values

As pointed out by Holt and Kerr[3] the agreement between the three determinations of the rate coefficient k_1 is poor. The largest discrepancy is between the values of k_1 reported by Mandelcom and Steacie[1] and by Garcia-Dominguez and Trotman-Dickenson[2]. Here we have recommended the rate expression determined by Holt and Kerr[3] which represents a median position, but this has been assigned larger error limits. What is required in this case is a direct study of the rate of this reaction. Use of the preferred rate equation at temperatures above 600 K should involve error limits of $\Delta \log k \pm 1.0$. There appears to be no published data[5] on the rate coefficient k_2, but in view of its endothermic nature this must be a considerably slower reaction than reaction (1). We estimate a rate coefficient of $k_2 < 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 600 K, based on the enthalpy change $\Delta H^\circ = 113 \text{ kJ mol}^{-1}$ and an assumed value of $A_2 < 1 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

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$$CH_3 + C_2H_2 \rightarrow C_3H_5$$
$$\rightarrow CH_4 + C_2H$$

T/K

EXPERIMENTAL DATA

——————— Mandelcorn and Steacie (k1) 1954
— — — — Garcia—Dominguez et al (k1) 1962
············· Holt and Kerr (k1) 1977

—————— This Recommendation (k1) 1989

$$CH_3 + C_2H_4 \rightarrow n\text{-}C_3H_7 \quad (1)$$
$$\rightarrow CH_4 + C_2H_3 \quad (2)$$
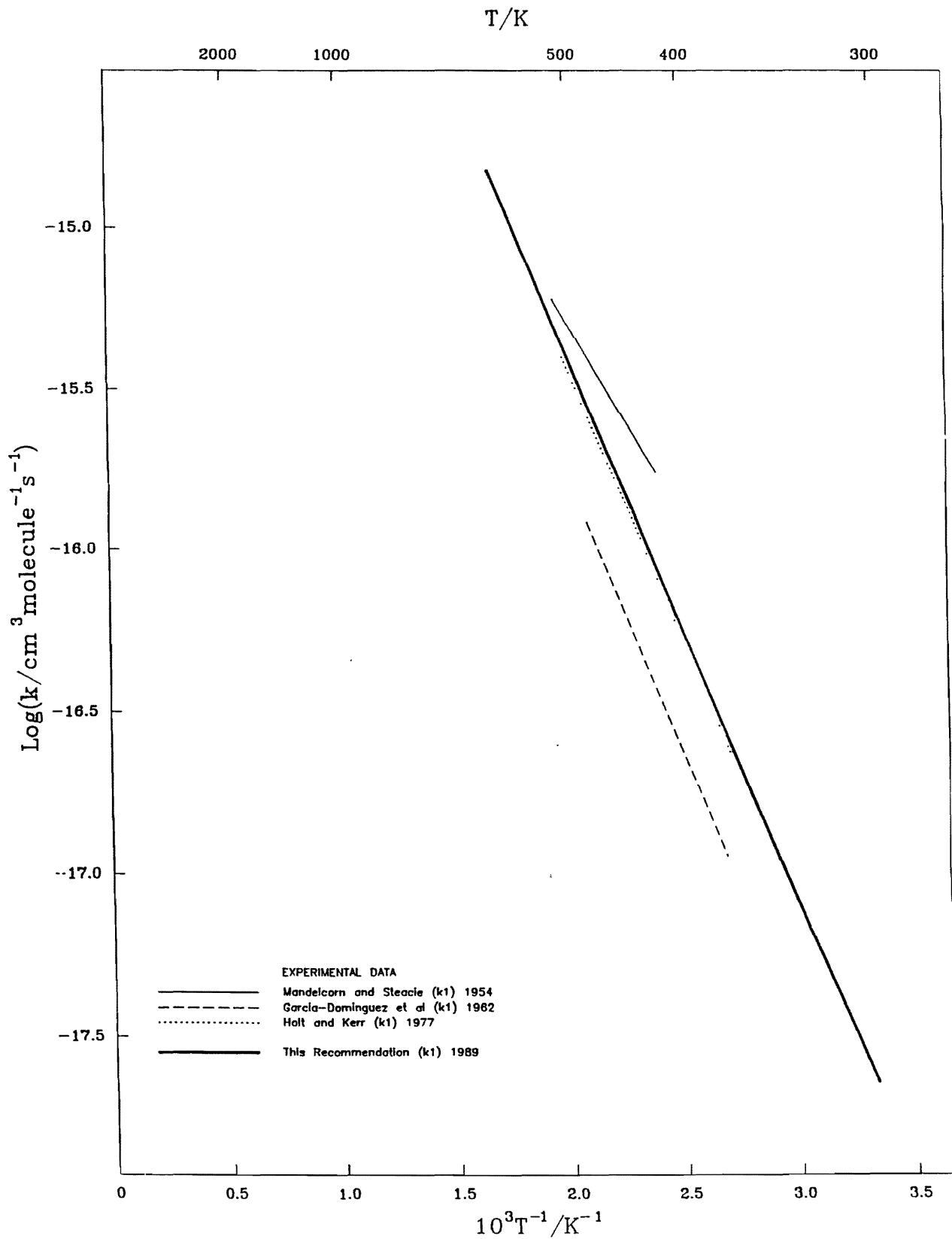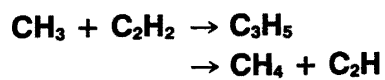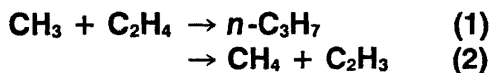
Thermodynamic Data

$\Delta H^{\circ}_{298} (1) = -104 \text{ kJ mol}^{-1}$

$\Delta S^{\circ}_{298} (1) = -145 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(1) = 1.38\cdot10^{-10} T^{-0.708} \exp(+12800/T)$

$\Delta H^{\circ}_{298} (2) = 13.2 \text{ kJ mol}^{-1}$

$\Delta S^{\circ}_{298} (2) = 4.4 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(2) = 25.7 T^{0.447} \exp(-1630 /T)$

Rate Coefficient Data

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	$T[\text{K}]$	Reference	Comments
Rate Coefficient Measurements			
$k_2 = 1.7\cdot10^{-15}$	1038	Chen, Back, and Back (1976)[1]	(a)
$k_1 = 3.5\cdot10^{-13} \exp(-3700/T)$	305–503	Holt and Kerr (1977)[2]	(b)
$k_2 = 8.3\cdot10^{-12} \exp(-6540/T)$	1950–2770	Tabayashi and Bauer(1979)[3]	(c)
Reviews and Evaluations			
$k_1 = 5.5\cdot10^{-13} \exp(-3700/T)$	305–503	Kerr and Parsonage (1972)[4]	(d)
$k_2 = 6.9\cdot10^{-12} \exp(-5590/T)$	460–650	Kerr and Parsonage (1976)[5]	(e)

Comments

(a) Pyrolysis of CH_4 in a static reaction vessel with end-product analysis by GC. Value of k_2 derived from measured ratio k_3K_4/k_2 (obtained from yields of propene and acetylene) where k_3 refers to the reaction $n\text{-}C_3H_7 \rightarrow C_3H_6 + M$ (3) and K_4 to the equilibrium $CH_3 + C_2H_4 \rightleftharpoons n\text{-}C_3H_7$ (4).

(b) Steady-state photolysis of $(CH_3CO)_2$ in the presence of C_2H_4 and $i\text{-}C_4H_{10}$ with end-product analysis for CH_4 and CO. k derived from a kinetic analysis based on a mass balance and calculated relative to $k(CH_3 + i\text{-}C_4H_{10} = 1.38\cdot10^{-13} \exp(-4030/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Data incorporated into an updated evaluation of previous data considered by Kerr and Parsonage[2].

(c) Shock-tube study of the early stages of the pyrolysis of CH_4. Rate expression derived from a computer analysis to fit predicted to observed profiles of density gradients. Mechanism of twelve elementary reactions considered.

(d) Evaluation based on data of Brinton[6], Hogg and Kebarle[7], Endrenyi and Le Roy[8], and Cvetanovic and Irwin[9].

(e) Evaluation based on data of Trotman-Dickenson and Steacie[10].

Preferred Values

$k_1 = 3.5\cdot10^{-13} \exp(-3700/T)$ over range 300–600 K

$k_2 = 6.9\cdot10^{-12} \exp(-5600/T)$ over range 400–3000 K

Reliability

$\Delta \log k_1 = \pm 0.3$ over range 300–500 K

$\Delta \log k_2 = \pm 1.0$ over range 400–3000 K

Comments on Preferred Values

There is reasonable agreement among the steady-state photolysis measurements of k_1 over the temperature range 300–500 K. Here we have selected the updated evaluation of Holt and Kerr[2] which includes several earlier studies[6-9]. The use of this rate expression at temperatures above 500 K should certainly involve larger error limits and we suggest $\Delta \log k_1 = \pm 0.5$ up to 2500 K. The preferred rate expression for k_2 is from the evaluation of Kerr and Parsonage[5] which is derived from the low-temperature steady-state experiments of Trotman-Dickenson and Steacie[10]. This expression is in good agreement with the indirect rate coefficients reported by Tabayashi and Bauer[3] from high-temperature shock-tube measurements but not in such good agreement with the rate coefficient reported by Chen et al.[1] at 1038 K. More definitive measurements are required at the higher end of the temperature range. The existing results indicate no curvature in the Arrhenius plot for k_2 and it has been suggested[1] that this could be due to a mechanism involving an addition complex rather than a simple H-transfer process.

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$$CH_3 + C_2H_4 \rightarrow n\text{-}C_3H_7$$
$$\rightarrow CH_4 + C_2H_3$$

$$CH_3 + C_2H_5 \rightarrow C_3H_8 \qquad (1)$$
$$\rightarrow CH_4 + C_2H_4 \qquad (2)$$
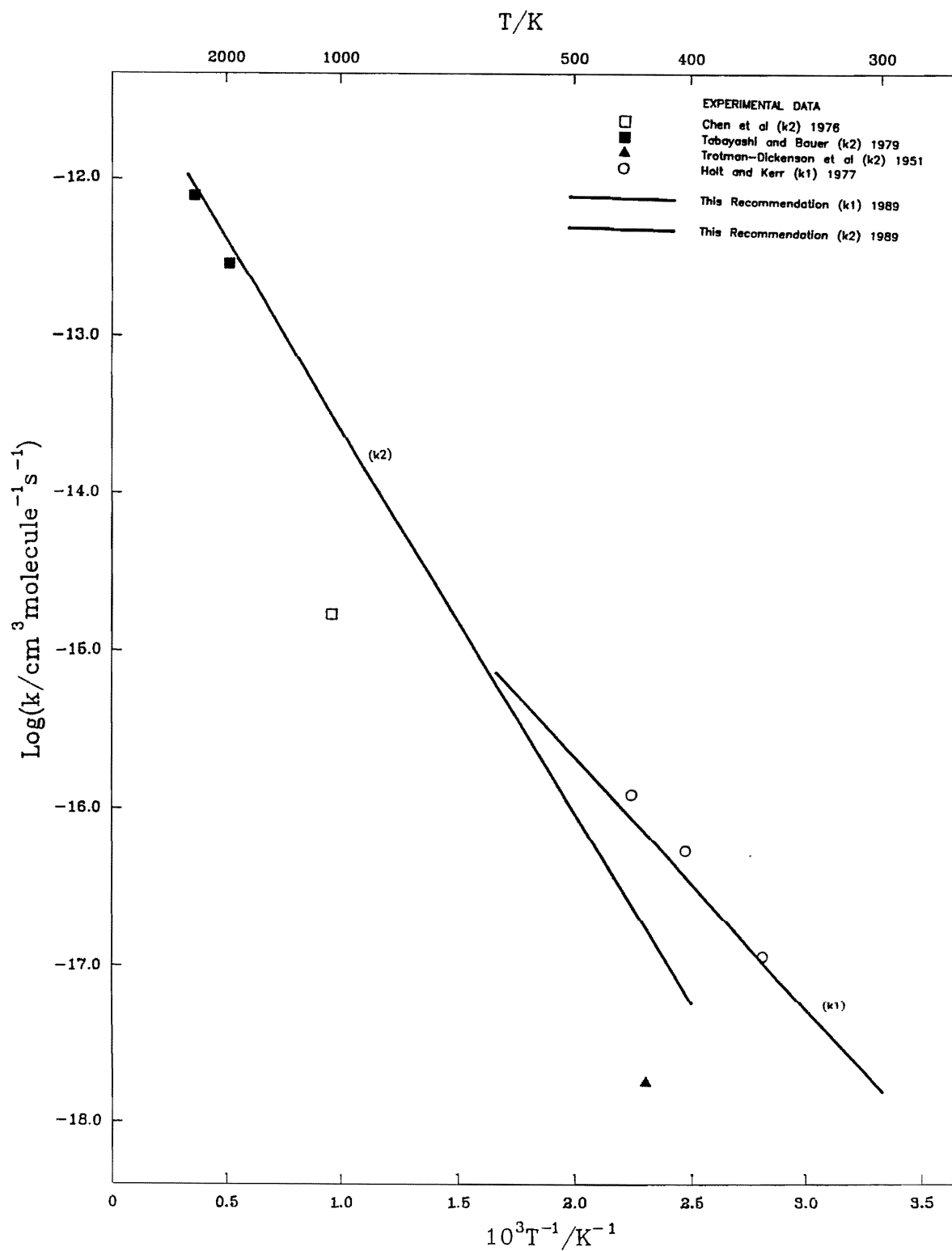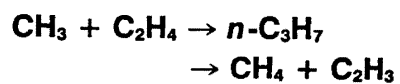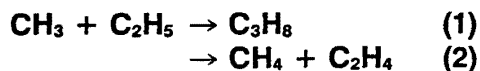
Thermodynamic Data

$\Delta H^{\circ}_{298} (1) = -367 \text{ kJ mol}^{-1}$

$\Delta S^{\circ}_{298} (1) = -175 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(1) = 4.40 \cdot 10^{-12} \, T^{0.962} \exp(+44700/T)$

$\Delta H^{\circ}_{298} (2) = -285 \text{ kJ mol}^{-1}$

$\Delta S^{\circ}_{298} (2) = -40.5 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(2) = 3.01 \cdot 10^{-3} \, T^{0.078} \exp(+34500/T)$

Rate Coefficient Data

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	$T[\text{K}]$	Reference	Comments
Rate Coefficient Measurements			
$k_1 = 4.2 \cdot 10^{-12}$	1050–1700	Lifshitz and Frenklach (1975)[1]	(a)
$k_1 = 1.2 \cdot 10^{-11}$	1300–1700	Koike and Gardiner (1980)[2]	(b)
$k_1 = 1.3 \cdot 10^{-13} \exp(+5700/T)$	1300–1700	Simmie, Gardiner, and	
		Eubank (1982)[3]	(c)
$k_1 = 1.5 \cdot 10^{-16} \exp(+14700/T)$	1500–1650		(d)
$k_1 = 4.5 \cdot 10^{-11}$	308	Arthur and Anastasi (1983)[4]	(e)
$k_1 = 1.48 \cdot 10^{-11} \exp(+856/T)$	773–793	Kanan, Purnell, and Smith (1983)[5]	(f)
$k_1 = 4.73 \cdot 10^{-11}$	308	Anastasi and Arthur (1987)[6]	(e)
$k_2/k_1 = 0.036$	308		
Reviews and Evaluations			
$k_1 = 1.2 \cdot 10^{-11}$	300–2000	Warnatz (1984)[7]	(g)
$k_1^{\infty} = 4.7 \cdot 10^{-11} \, (300/T)^{0.5}$	300–2500	Tsang and Hampson (1986)[8]	(h)
$k_2/k_1 = 0.04$	300–2500		

Comments

(a) Estimated from $k_1 = k_{-1}K$.

(b) Pyrolysis of C_3H_8 in Ar behind reflected shock waves at pressures near 760 Torr, with IR laser absorption kinetic spectroscopy. k derived from a computer fit of the absorption profiles based on a mechanism of 44 elementary reactions.

(c) Re-analysis of data of Koike and Gardiner[2] for experiments with 4.3% C_3H_8 in Ar.

(d) Same experimental procedure as in (b) but at pressures of $\sim$ 1400 Torr and with a mixture of 5% C_3H_8 in Ar.

(e) Molecular modulation spectroscopy. CH_3 and C_2H_5 produced from photolysis of azo compounds at 350 nm. [CH_3] and [C_2H_5] monitored by UV absorption. k obtained from computer simulation of concentration profiles.

(f) Study of the pyrolysis of C_3H_8 in a static reaction vessel in the presence of C_2H_4. k_1 calculated from $k_{-1}K$.

(g) Based on results of Koike and Gardiner[2].

(h) Calculated from $k(CH_3 + CH_3)$ and $k(C_2H_5 + C_2H_5)$ and and combination/cross-combination ratio. Tabulated data also presented to allow for presure dependence.

Preferred Values

$k_1^{\infty} = 4.7 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over range 300–800 K

$k_2 / k = 0.04$

Reliability

$\Delta \log k_1 = \pm 0.3$ over range 300–800 K

$\Delta k_2/k = \pm 0.005$

Comments on Preferred Values

The preferred value of k_1 is from the work of Anastasi and Arthur[6] at 308 K, which is the most direct study so far reported. This recommendation is in excellent agreement with the value of k_1 derived from a study[5] of the pyrolysis of C_3H_8 at temperatures near 800 K, and based on a calculated equilibrium constant for the reaction. From these two determinations the temperature coefficient of k_1 would appear to be negligible. At the same time the preferred value of k_1 is in reasonable agreement with the value of k_1 derived by Tsang and Hampson[8] on the basis of the values of $k(CH_3 + CH_3)$ and $k(C_2H_5 + C_2H_5)$ and the cross-combination/combination ratio of rate coefficients. The preferred value of k_2/k is from the recommended value of the ratio $k_2/k_1 = 0.04$ which has been established from low temperature studies[9]. In keeping with other disproportionation/combination ratios of rate coefficients, this value of k_2/k_1 would not be expected to show any marked temperature dependence.

Tsang and Hampson[8] have made calculations of the dependence of the value of k_1 upon concentration and temperature. These become important at temperatures above 1000 K.

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$$CH_3 + C_2H_5 \rightarrow CH_4 + C_2H_4$$
$$\rightarrow C_3H_8$$

T/K

EXPERIMENTAL DATA

———————	Lifshitz and Frenklach (k2) 1975
⊢———⊣	Koike and Gardiner (k2) 1980
– – – – –	Simmie et al (k2) 1980
▲	Arthur and Anastasi (k2) 1983
⊢– – –⊣	Kanan et al (k2) 1983
●	Anastasi and Arthur (k2) 1987
▣	Anastasi and Arthur (k1) 1987
··················	Simmie et al (k1) 1980
———————	This Recommendation (k1) 1989
———————	This Recommendation (k2) 1989

Log(k/cm ^{3} molecule $^{-1}$ s $^{-1}$)

$10^3 T^{-1}/K^{-1}$

$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5$
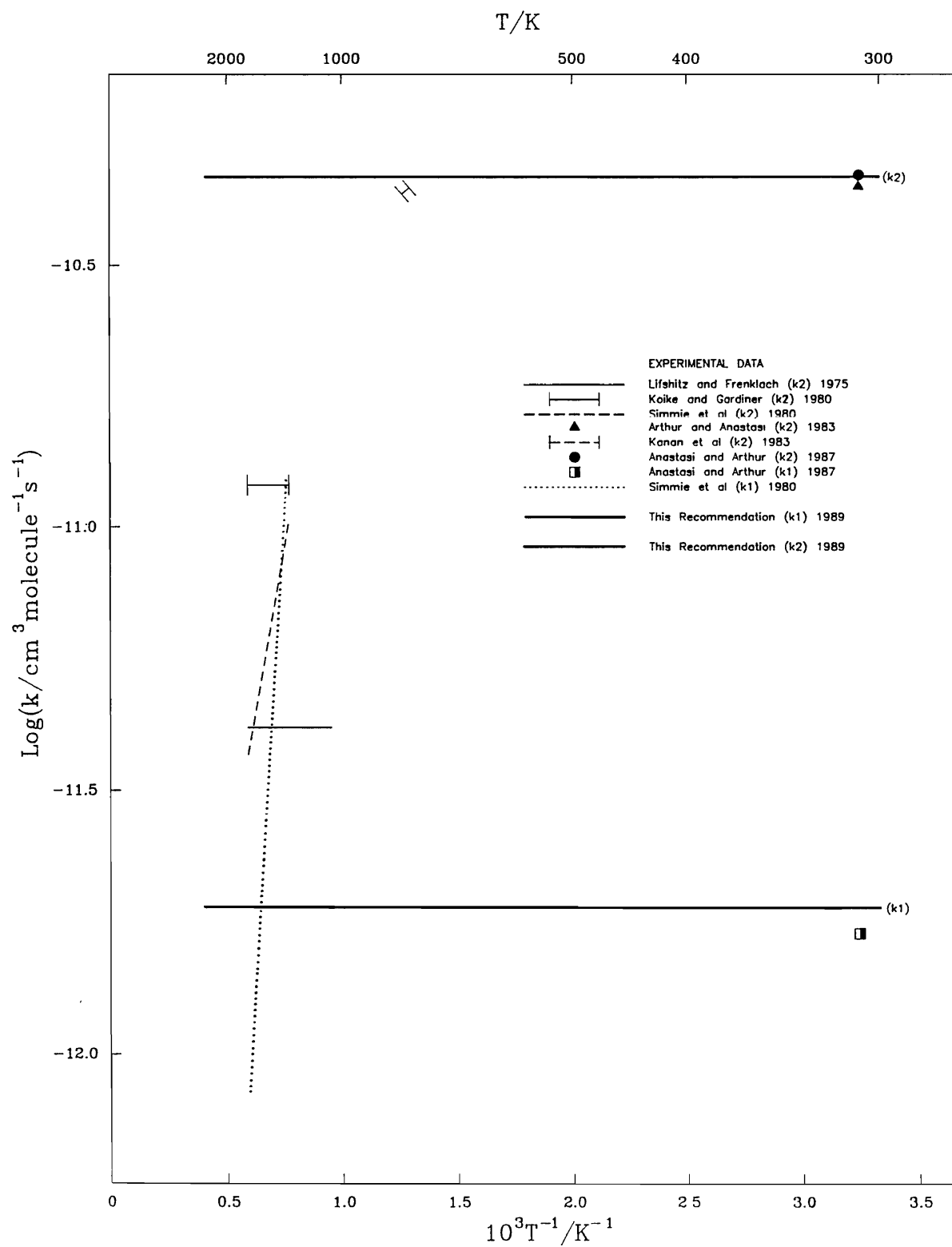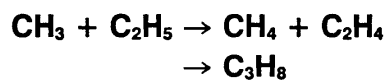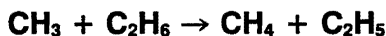
Thermodynamic Data
$\Delta H^\circ_{298} = -19.5 \text{ kJ mol}^{-1}$
$\Delta S^\circ_{298} = 14.7 \text{ J K}^{-1}\text{mol}^{-1}$
$K_p = 1.61 \cdot 10^2 \, T^{-0.55} \exp(+2300/T)$

Rate Coefficient Data

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	Temperature [K]	Reference	Comments
Rate Coefficient Measurements			
$3.3 \cdot 10^{-13} \exp(-5250/T)$	389–567	Trotman-Dickenson *et al.* (1951)[1]	(a)
$7.1 \cdot 10^{-13} \exp(-5710/T)$	435–614	Wijnen (1955)[2]	(b)
$1.32 \cdot 10^{-12} \exp(-5810/T)$	519–797	McNesby and Gordon (1955)[3]	(c)
$5.9 \cdot 10^{-13}$	1350	Clark *et al.* (1971)[4]	(d)
$8.3 \cdot 10^{-10} \exp(-10800/T)$	1055–1325	Pacey and Purnell (1972)[5]	(e)
$7.4 \cdot 10^{-11} \exp(-8770/T)$	980–1130	Yampolskii and Rybin (1974)[6]	(f)
$5.4 \cdot 10^{-11} \exp(-9060/T)$	1055–1325	Bradley and West (1976)[7]	(g)
$6.0 \cdot 10^{-15}$	880	Chen, Back, and Back (1976)[8]	(h)
$7.8 \cdot 10^{-15}$	995		
$17.1 \cdot 10^{-15}$	1038		
$19.8 \cdot 10^{-15}$	1068		
$1.1 \cdot 10^{-13}$	1206	Lee and Yeh (1979)[9]	(i)
$6.8 \cdot 10^{-15}$	902	Pacey and Wimalasena (1984)[10]	(j)
$3.3 \cdot 10^{-11} \exp(-6800/T)$	1100–1400	Möller *et al.* (1987)[18]	(p)
Reviews and Evaluations			
$1.17 \cdot 10^{-9} \exp(-12030/T)$			
$\quad + 4.2 \cdot 10^{-14} \exp(-4580/T)$	300–1350	Pacey and Purnell (1972)[5]	(k)
$9.15 \cdot 10^{-25} \, T^4 \exp(-4167/T)$	300–1800	Clark and Dove (1973)[11]	(l)
$9.3 \cdot 10^{-13} \exp(-5840/T)$	300–700	Kerr and Parsonage (1976)[12]	(m)
$9.15 \cdot 10^{-25} \, T^4 \exp(-4167/T)$	300–2000	Warnatz (1984)[13]	(n)
$9.15 \cdot 10^{-25} \, T^4 \exp(-4167/T)$	400–2000	Tsang and Hampson (1986)[14]	(o)

Comments

(a) Competitive photolysis of acetone-d_6. k for CD_3 reaction, relative to $k(CD_3 + CD_3) = 4.15 \cdot 10^{-11}$ cm³ molecule⁻¹ s⁻¹.

(b) Competitive photolysis of acetone-d_6. k for CD_3 reaction, relative to $k(CD_3 + CD_3COCD_3) = 8.0 \cdot 10^{-13} \exp(-5760/T)$ cm³ molecule⁻¹ s⁻¹ [15].

(c) Competitive photolysis of acetone-d_6. k for CD_3 reaction, relative to $k(CD_3 + CD_3COCD_3)$ (k_1) as in (b). Values of k_1 extrapolated from low T data. If log k_1-$1/T$ plot shows upward curvature, values of k may be too low (see graph).

(d) Shock tube, time-of-flight mass spectrometry, complex system.

(e) Pyrolysis, computer fit of products. Complex system, k values quoted with considerable error limits, log A = -9.1 ± 1.0, E = 90 ± 20 kJ mol⁻¹.

(f) Pyrolysis of $C_2H_6 + D_2$ mixture; competitive technique. Obtained $k/k(CH_3 + D_2)$. Original values corrected by use of high temperature value of $k(CH_3 + D_2) = 2.3 \cdot 10^{-11} \exp(-8120/T)$ cm³ molecule⁻¹ s⁻¹ based[16] on Tsang and Hampson's[14] recommended value for $k(CH_3 + H_2)$.

(g) Shock tube, computer simulation of reaction products. Value of k dependent on a number of rate constants.

(h) Thermal decomposition of C_2H_6, product analysis, complex system. Value of k dependent on a number of rate constants.

(i) Ethane pyrolysis, computer simulation of products, complex system. Value of k dependent on a number of rate constants.

(j) Pyrolysis in flow system giving $k/k^{1/2}(CH_3 + CH_3)$. k calculated from $k(CH_3 + CH_3) = 4.15 \cdot 10^{-11}$ cm³ molecule⁻¹ s⁻¹.

(k) Fit to experimental points between 300 and 1350 K.

(l) Simplified BEBO calculation of k values.

(m) Detailed review of low temperature data.

(n) Recommended without comment.

(o) Recommend the Clark and Dove BEBO calculations in order to relate the high and low temperature data.

(p) Shock-tube determination with UV detection of CH_3.

Preferred Values

$k = 2.45 \cdot 10^{-31} \, T^6 \exp(-3043/T)$ cm³ molecule⁻¹ s⁻¹ over range 300–1500 K

Reliability

$\Delta \log k = \pm 0.1$ at 300 K rising to ± 0.15 at 1000 K and to ± 0.2 at 1500 K
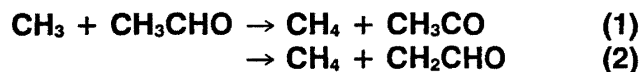
Comments on Preferred Values

A sharply curved non-Arrhenius dependence is required to account for the low and high temperature results. The Clark and Dove expression lies above the experimental k values at low temperatures, but does give a good fit above 800 K. The preferred value of k fits at high and low temperature, but lies above the McNesby and Gordon values between 650 and 800 K. However, as pointed out in comment (c), these values of k may have been seriously underestimated. A T^6 term is required to explain the curvature observed, although Furue and Pacey[17] suggest a $T^{2.5}$ expression gives a good fit if tunnelling is considered. For high temperature values (1500–2500 K) Clark and Dove's expression is recommended $(9.15 \cdot 10^{-25} \ T^4 \ \exp(-4167/T) \ \text{cm}^3 \ \text{molecule}^{-1} \ \text{s}^{-1})$. Non-allowance for fall-off in $k(\text{CH}_3 + \text{CH}_3)$ may be responsible for higher than expected values of k at high temperatures.

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$$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5$$

T/K

EXPERIMENTAL DATA

□   Yampolskii and Rybin 1974
■   Clark et al 1971
──   Trotman—Dickenson et al 1951
─ ─   Wijnen 1955
····· McNesby and Gordon 1955
●   Pacey and Purnell 1972
─·─   Bradley and West 1976
△   Chen et al 1976
⊖   Lee and Yeh 1979
+   Pacey and Wimalasena 1984
×   Moller et al 1987

━━━   This Recommendation 1989

$$CH_3 + CH_3CHO \rightarrow CH_4 + CH_3CO \quad \text{(1)}$$
$$\rightarrow CH_4 + CH_2CHO \quad \text{(2)}$$
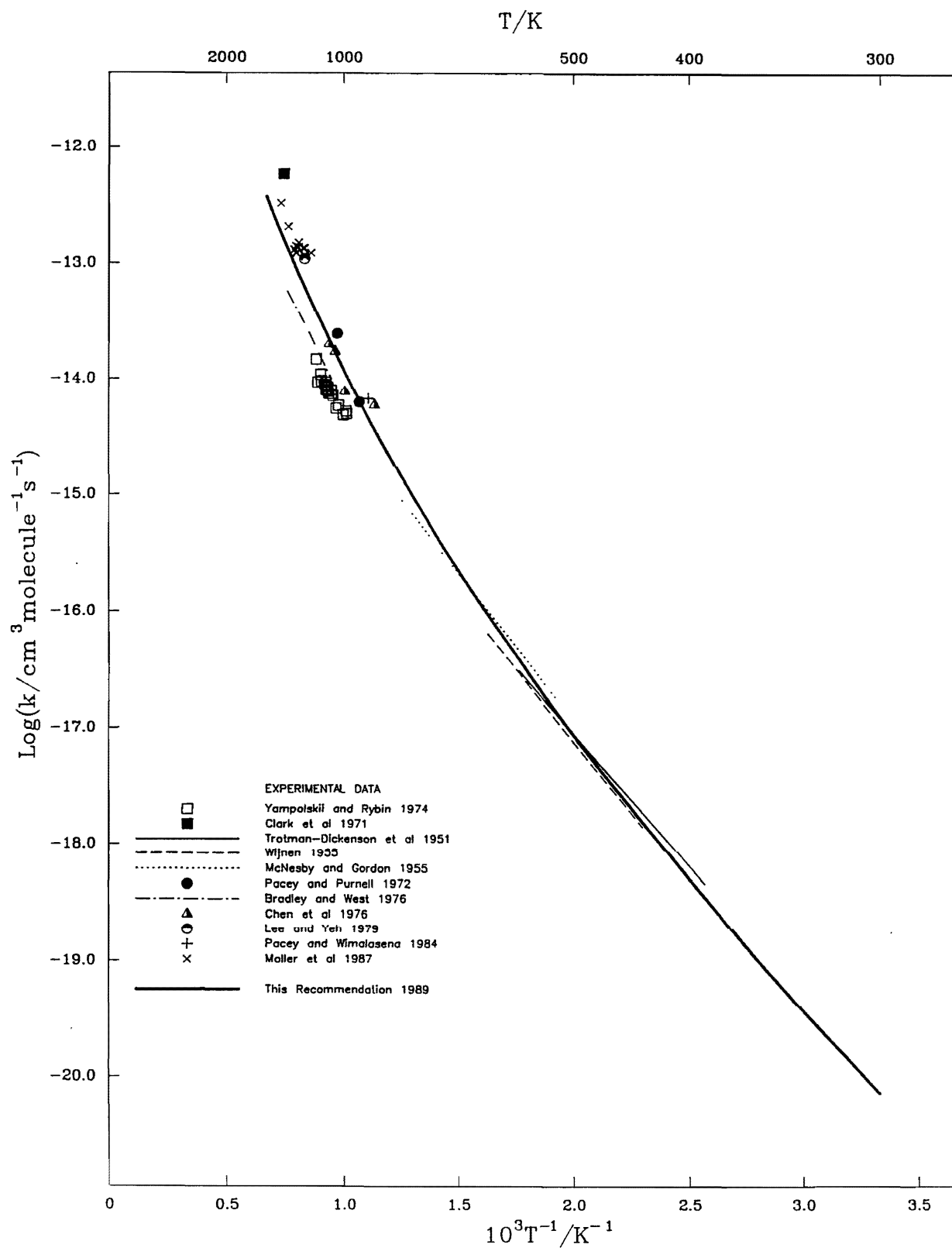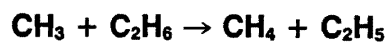
Thermodynamic Data

$\Delta H^{\circ}_{298} (1) = -77.9 \text{ kJ mol}^{-1}$

$\Delta S^{\circ}_{298} (1) = -5.09 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(1) = 66.5 \ T^{-0.416} \exp(+9330/T)$

$\Delta H^{\circ}_{298} (2) = -30.2 \text{ kJ mol}^{-1}$

$\Delta S^{\circ}_{298} (2) = -4.0 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(2) = 2.93 \ T^{-0.257} \exp(+3600/T)$

Rate Coefficient Data

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	$T [\text{K}]$	Reference	Comments
Rate Coefficient Measurements			
$2.64 \cdot 10^{-12} \exp(-4240/T)$	753–813	Liu and Laidler (1968)[1]	(a)
$3.3 \cdot 10^{-31} \ T^{5.9} \exp(-860/T)$	1051–1225	Colket et al. (1975)[2]	(b)
Reviews and Evaluations			
$6.2 \cdot 10^{-12} \exp(-3020/T)$	300–525	Kerr and Parsonage (1976)[3]	(c)
$6.2 \cdot 10^{-12} \exp(-3020/T)$	300–525	Warnatz (1984)[4]	(d)

Comments

(a) Pyrolysis of CH_3CHO; k relative to $k(CH_3 + CH_3 \rightarrow C_2H_6) = 3.67 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

(b) Pyrolysis of CH_3CHO in 1 atm N_2; k relative to $k(CH_3 + CH_3) \rightarrow C_2H_6$. Above expression obtained using $k(CH_3 + CH_3) = 4.0 \cdot 10^{-10} \ T^{-0.4}$ from Ref. 4 and the expression for $k/k^{0.5}(CH_3 + CH_3)$ derived by Colket et al. from their data together with earlier lower temperature data.

(c) Based on low temperature relative rate data of Kerr and Calvert[5], Brinton and Volman[6], Dodd[7], Calvert et al.[8], Buchanan and McRae[9], and Birrel and Trotman-Dickenson[10].

(d) Accepts recommendation of Kerr and Parsonage.

Preferred Values

$k = 3.3 \cdot 10^{-30} \ T^{5.64} \exp(-1240/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over range 300–1250 K

Reliability

$\Delta \log k = \pm 0.3$ over range 300–1250 K

Comments on Preferred Values

There are no direct studies of the kinetics of this reaction and all of the k values are relative to methyl recombination. The results of Colket et al. at $T > 1000$ K show a significantly greater activation energy than the data from lower temperature and taken with the intermediate temperature data of Liu and Laidler, the rate coefficient clearly shows non-Arrhenius temperature dependence. The large amount of low temperature data is broadly self consistent, although there is a spread of approximately a factor of 2 in the values near 400 K. The preferred values are based on a line constructed through the mean of the low temperature data and the data of Liu and Laidler[1] and Colket et al.[2], both of which appear to be reliable relative rate studies. There is no experimental data on the contribution of the second channel. Assuming $k_2 = 1/2 \ k(CH_3 + C_2H_6)$, this channel contributes 1% and 7.8% of the total rate at 500 K and 1000 K respectively.

References

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$CH_3 + CH_3CHO \rightarrow CH_4 + CH_3CO$

$CH_4(+M) \rightarrow CH_3 + H(+M)$
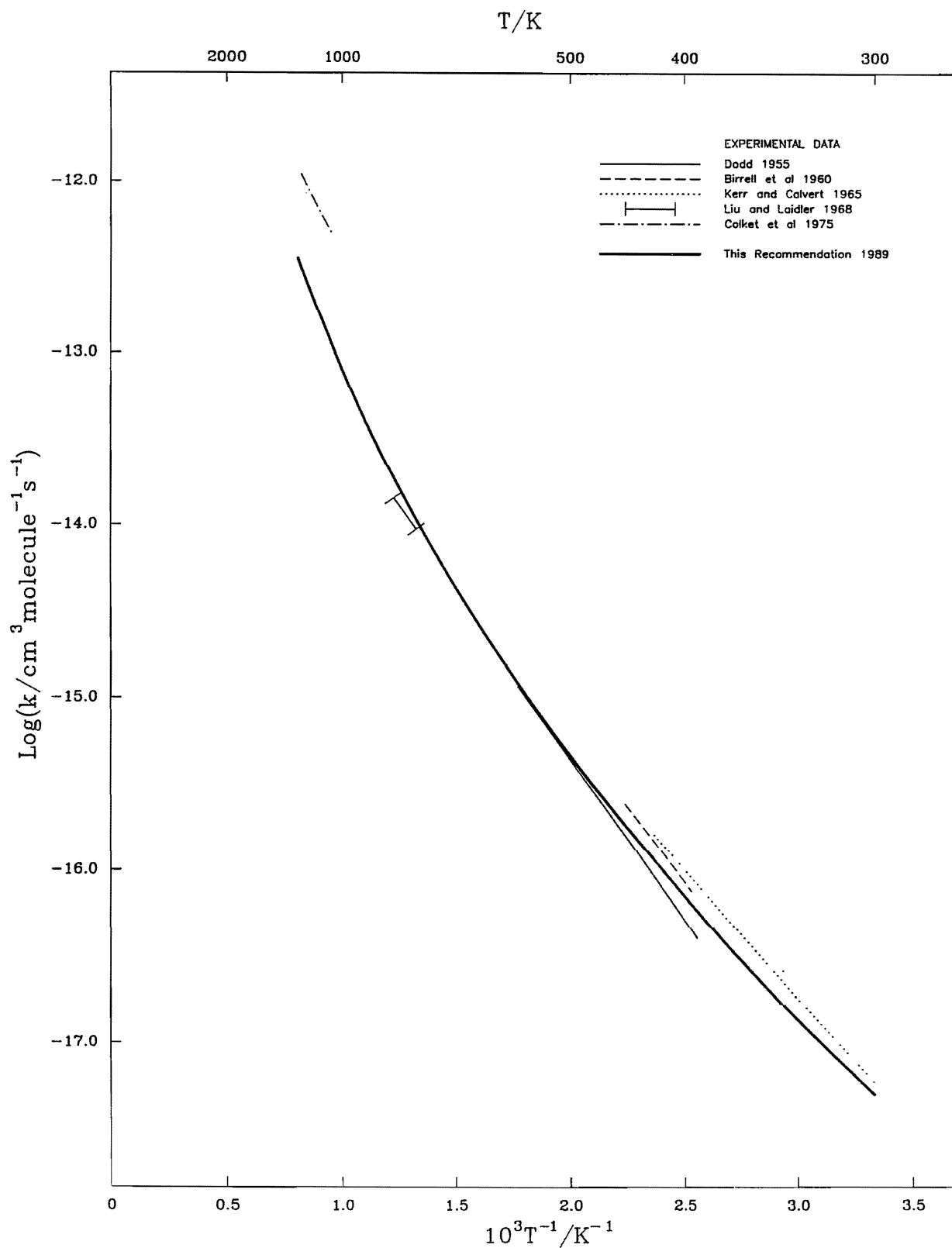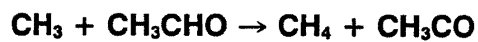
Thermodynamic Data
$\Delta H^\circ_{298} = 439 \text{ kJ mol}^{-1}$
$\Delta S^\circ_{298} = 123 \text{ J K}^{-1}\text{mol}^{-1}$
$K_p = 5.68 \cdot 10^3 \, T^{1.06} \exp(-52700/T)$ atm

Rate Coefficient Data

$k[s^{-1}]$	$T[K]$	$[M]$ [molecule cm^{-3}]	Reference	Comments
Rate Coefficient Measurements				
Low Pressure Range				
[Ar] $3.3 \cdot 10^{-7} \exp(-44800/T)$	1850–2500	$(3.3–90.0) \cdot 10^{19}$ (Ar)	Hartig *et al.* (1971)[1]	(a)
Intermediate Fall-off Range				
$2.5 \cdot 10^{13} \exp(-48300/T)$	1850–2500	$3.3 \cdot 10^{19}$ (Ar)	Hartig *et al.* (1971)[1]	(a)
$4.0 \cdot 10^{14} \exp(-50800/T)$		$9.0 \cdot 10^{20}$ (Ar)		
$1.4 \cdot 10^{12} \exp(-51800/T)$	1750–2575	$5.0 \cdot 10^{17}$ (Ar)	Dean and Kistiakowsky (1971)[2]	(b)
$3.8 \cdot 10^{13} \exp(-47100/T)$	1750–2700	$4.0 \cdot 10^{19}$ (Ar)	Napier and Subrahmanyan (1972)[3]	(c)
$4.0 \cdot 10^9 \exp(-31700/T)$	2000–2700	$2.4 \cdot 10^{18}$ (Ne)	Vompe (1973)[4]	(d)
$4.7 \cdot 10^{12} \exp(-46900/T)$	1700–2300	$6.0 \cdot 10^{18}$ (Ar)	Roth and Just (1975)[5]	(e)
$2.3 \cdot 10^8 \exp(-32500/T)$	2000–2700	$6.0 \cdot 10^{17}$ (Ar)	Gardiner *et al.* (1975)[6]	(f)
$2.3 \cdot 10^9 \exp(-32500/T)$		$6.0 \cdot 10^{18}$ (Ar)		
$0.74 \cdot 10^{-8}$	995	$0.5 \cdot 10^{18}$ (CH$_4$)	Chen *et al.* (1975)[7]	(g)
$1.32 \cdot 10^{-8}$		$3.2 \cdot 10^{18}$		
$2.82 \cdot 10^{-8}$		$7.2 \cdot 10^{18}$		
$0.39 \cdot 10^{-7}$	1038	$0.3 \cdot 10^{17}$		
$1.38 \cdot 10^{-7}$		$3.1 \cdot 10^{18}$		
$2.57 \cdot 10^{-7}$		$6.9 \cdot 10^{18}$		
$0.98 \cdot 10^{-7}$	1068	$0.23 \cdot 10^{18}$		
$4.9 \cdot 10^{-7}$		$2.1 \cdot 10^{18}$		
$8.71 \cdot 10^{-7}$		$6.7 \cdot 10^{18}$		
$0.69 \cdot 10^{-6}$	1103	$0.43 \cdot 10^{18}$		
$2.06 \cdot 10^{-6}$		$2.0 \cdot 10^{18}$		
$3.86 \cdot 10^{-6}$		$6.5 \cdot 10^{18}$		
$2.8 \cdot 10^{12} \exp(-44500/T)$	1875–2240	$1.2 \cdot 10^{19}$ (Ar)	Bowman (1975)[8]	(h)
$2.2 \cdot 10^{12} \exp(-45400/T)$	2000–2700	$6.0 \cdot 10^{18}$ (Ar)	Heffington *et al.* (1977)[9]	(i)
$6.3 \cdot 10^{12} \exp(-45400/T)$		$17 \cdot 10^{18}$		
$2.3 \cdot 10^{11} \exp(-43200/T)$	1950–2770	$1.4 \cdot 10^{18}$ (Ar)	Tabayashi and Bauer (1979)[10]	(j)
$9.1 \cdot 10^{11} \exp(-43200/T)$		$5.4 \cdot 10^{18}$		
$1.13 \cdot 10^{-5}$	1098	$2.0 \cdot 10^{20}$ (He)	Barnes, Pratt, and Wood (1989)[11]	(k)
$1.37 \cdot 10^{-5}$		$3.3 \cdot 10^{20}$		
$2.52 \cdot 10^{-5}$	1123	$6.5 \cdot 10^{19}$		
$3.17 \cdot 10^{-5}$		$1.9 \cdot 10^{20}$		
$4.12 \cdot 10^{-5}$		$3.2 \cdot 10^{20}$		
$5.30 \cdot 10^{-5}$	1148	$3.2 \cdot 10^{19}$		
$8.30 \cdot 10^{-5}$		$1.9 \cdot 10^{20}$		
$10.1 \cdot 10^{-5}$		$3.2 \cdot 10^{20}$		
$4.44 \cdot 10^{-6}$	1073	$2.0 \cdot 10^{20}$ (Ar)		
$5.28 \cdot 10^{-6}$		$3.4 \cdot 10^{20}$		
$9.80 \cdot 10^{-6}$	1098	$6.6 \cdot 10^{19}$		
$1.20 \cdot 10^{-5}$		$2.0 \cdot 10^{20}$		
$1.46 \cdot 10^{-5}$		$3.3 \cdot 10^{20}$		
$1.87 \cdot 10^{-5}$	1123	$3.2 \cdot 10^{19}$		
$2.31 \cdot 10^{-5}$		$6.5 \cdot 10^{19}$		
$3.19 \cdot 10^{-5}$		$1.9 \cdot 10^{20}$		
$4.32 \cdot 10^{-5}$	1148	$3.2 \cdot 10^{19}$		
$5.39 \cdot 10^{-5}$		$6.3 \cdot 10^{19}$		
$3.04 \cdot 10^{-6}$	1073	$3.4 \cdot 10^{19}$ (CH$_4$)		
$5.11 \cdot 10^{-6}$		$1.4 \cdot 10^{20}$		
$4.93 \cdot 10^{-6}$		$3.4 \cdot 10^{20}$		
$8.25 \cdot 10^{-6}$	1098	$3.3 \cdot 10^{19}$		
$1.52 \cdot 10^{-5}$		$1.3 \cdot 10^{20}$		
$1.55 \cdot 10^{-5}$		$3.3 \cdot 10^{20}$		
$2.27 \cdot 10^{-5}$	1123	$3.2 \cdot 10^{19}$		
$3.63 \cdot 10^{-5}$		$1.3 \cdot 10^{20}$		
$4.20 \cdot 10^{-5}$		$3.2 \cdot 10^{20}$		
$6.03 \cdot 10^{-5}$	1148	$3.2 \cdot 10^{19}$		
$8.50 \cdot 10^{-5}$		$1.3 \cdot 10^{20}$		
$1.20 \cdot 10^{-4}$		$3.2 \cdot 10^{20}$		

CH$_4$(+M) $\rightarrow$ CH$_3$ + H(+M)   —   Continued

Rate Coefficient Data

$k[\mathrm{s^{-1}}]$	$T[\mathrm{K}]$	[M] [molecule cm^{-3}]	Reference	Comments
Rate Coefficient Measurements				
High Pressure Range				
$1.3{\cdot}10^{15}\,\exp(-52300/T)$	1850–2500	$(3.3–90.0){\cdot}10^{19}$ (Ar)	Hartig *et al*. (1971)[1]	(a)
$2.8{\cdot}10^{16}\,\exp(-54100/T)$	995–1103	$(0.43–7.2){\cdot}10^{18}$ (CH$_4$)	Chen *et al*. (1975)[7]	(g)
$1.75{\cdot}10^{16}\,\exp(-53000/T)$	1073–1148	$(3.2–33.4){\cdot}10^{19}$ (CH$_4$)	Barnes, Pratt, and Wood (1989)[11]	(k)
Reviews and Evaluations				
$k_\infty = 2.0{\cdot}10^{15}\,\exp(-52300/T)$	–		Benson and Orq Neal (1970)[12]	(l)
$k_0 = [\mathrm{Ar}]\,3.3{\cdot}10^{-7}\,\exp(-44500/T)$	1500–3000		Warnatz (1984)[13]	(m)
$k_\infty = 1.0{\cdot}10^{15}\,\exp(-50500/T)$	1000–3000			
$k_\infty = 3.7{\cdot}10^{15}\,\exp(-52200/T)$	300–2500		Tsang and Hampson (1986)[14]	(n)
$k_\infty = 3.7{\cdot}10^{17}\,T^{-0.558}\,\exp(-52782/T)$	300–2500		Stewart *et al*. (1989)[15]	(o)
$k_0 = [\mathrm{Ar}]\,1.2{\cdot}10^{16}\,\exp(-47000/T)$	1000–3000		Cobos and Troe (1990)[16]	(p)
$k_\infty = 2.4{\cdot}10^{16}\,\exp(-52800/T)$	1000–3000			
$F_c(\mathrm{Ar}) = \exp(-0.45–T/3231)$	1000–3000			

Comments

(a) Shock wave study of CH$_4$/Ar mixtures. The reaction was followed by infrared emission of CH$_4$ and by infrared emission and ultraviolet absorption of the formed species.

(b) Shock wave study of CH$_4$/O$_2$/CO/Ar mixtures. The reaction was followed by measuring infrared emissions from CO and O$_2$.

(c) The CH$_4$ pyrolysis was investigated by a shock waves technique.

(d) Shock wave study of CH$_4$/Ne mixtures. The reaction was analysed by time-of-flight mass spectrometry.

(e) Direct measurements of the time dependent H atom concentration during the pyrolysis of CH$_4$/Ar mixtures using shock waves technique.

(f) Pyrolysis of CH$_4$ in shock waves. The reaction was followed by time-of-flight mass spectrometry, infrared laser absorption, and laser schlieren technique.

(g) Pyrolysis of CH$_4$ in a static system. Initial rates based on analysis of H$_2$, C$_2$H$_6$, and C$_2$H$_4$. k_∞ values extrapolated with RRKM theory.

(h) Shock waves study of CH$_4$/O$_2$/Ar mixtures. Reaction followed by absorption measurements of OH and by emission from the chemiluminescent reaction O + CO.

(i) Shock waves study of CH$_4$ pyrolysis. The reaction was followed monitoring the CH$_4$ emission and absorption at 3.392 μm.

(j) Shock waves measurements of CH$_4$/Ar mixtures. Modelling of 12 reactions.

(k) Pyrolysis of CH$_4$ at very early stages (0.003–0.05% reaction) in a quartz-lived flow reactor. Reactant and products (ethyne, ethylene, acetylene, and propylene) detected by gas chromatography.

(l) Review of literature previous to 1966.

(m) Review of literature previous to 1980.

(n) The k_∞ recommended is based on the Hartig *et al*.[1] results scaled up by a factor 3.

(o) Single-channel hindered Gorin model RRKM calculations of the CH$_4$ decomposition with a fit to experimental results.

(p) The experiments by Hartig *et al*.[1] have been re-evaluated taking into account the increasing amount of IR emissions from species other than CH$_4$ such as documented in Ref. 1. These corrections become most pronounced in the high pressure experiments. The theoretical calculations were done using the k_0 formalism from Ref. 16, fall-off expression from Ref. 17, and SACM-modified PST calculations from Ref. 18 which lead to a nearly temperature independent value of k_∞ for the reverse recombination H + CH$_3$ $\rightarrow$ CH$_4$ of $3.5{\cdot}10^{-10}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

$k_0 = [\mathrm{Ar}]\,1.2{\cdot}10^{-6}\,\exp(-47000/T)$ s^{-1} over range 1000–3000 K

$k_0 = [\mathrm{CH_4}]$ $1.4{\cdot}10^{-5}$ $\exp(-48100/T)$ s^{-1} over range 1000–2000 K

$k_\infty = 2.4{\cdot}10^{16}\,\exp(-52800/T)$ s^{-1} over range 1000–3000 K

$F_c = \exp(-0.45 – T/3231)$ for M = Ar

$F_c = \exp(-0.37 – T/2210)$ for M = CH$_4$

Reliability

$\Delta\log k_0 = \pm 0.3$ over range 1000–3000 K

$\Delta\log k_\infty = \pm 0.5$ over range 1000–3000 K
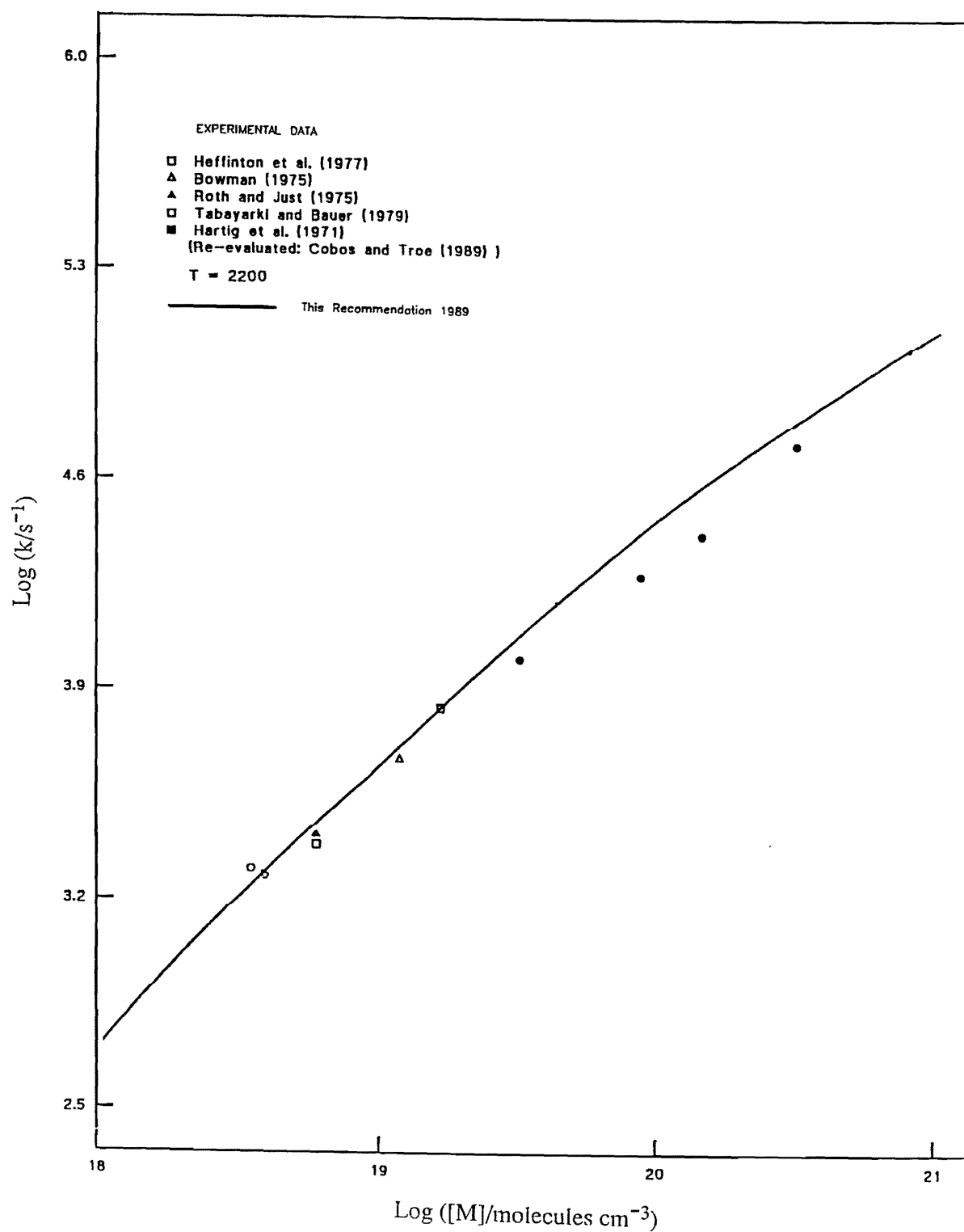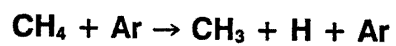
$\Delta F_c = \pm 0.1$ over range 1000–3000 K
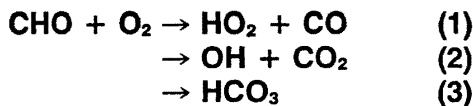
Comments on Preferred Values

The preferred values for k_0 are taken from the comparison of the experimental data from Refs. 1, 5, 7, 8–10 with the theoretical modelling from Ref. 16. This is based on the assumption of nearly temperature independent

$\beta_c = 0.11$ for $M = CH_4$ and $\beta_c = 0.03$ for $M = Ar$ which was rationalized by very inefficient energy transfer and a positive temperature coefficient of $<\Delta E>$ at low temperatures. The preferred values of k_∞ are consistent with a nearly temperature independent k_∞ of $3.5 \cdot 10^{-10}$ cm^3 molecule^{-1} s^{-1} for the reverse recombination $H + CH_3 \rightarrow CH_4$. Since the evaluation of the high pressure data from Ref. 1 there appears to be no experimental evidence for a stronger negative temperature coefficient of k_∞ for the recombination such as was suggested in Ref. 15. Recent theoretical models based on realistic potential energy surfaces have all predicted temperature coefficients consistent with the presently preferred values (see e.g. Cobos[20]).

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$$CH_4 + Ar \rightarrow CH_3 + H + Ar$$

EXPERIMENTAL DATA

□ Heffinton et al. (1977)
△ Bowman (1975)
▲ Roth and Just (1975)
▢ Tabayarki and Bauer (1979)
■ Hartig et al. (1971)
  (Re—evaluated: Cobos and Troe (1989))

T = 2200

———————— This Recommendation 1989

$$CHO + O_2 \rightarrow HO_2 + CO \qquad (1)$$
$$\rightarrow OH + CO_2 \qquad (2)$$
$$\rightarrow HCO_3 \qquad (3)$$

Thermodynamic Data

ΔH°_{298} (1) = -144 kJ mol^{-1}

ΔS°_{298} (1) = -3.03 J K^{-1}mol^{-1}

K_p(1) = $2.5\ T^{-0.178} \exp(+17200/T)$

ΔH°_{298} (2) = -398 kJ mol^{-1}

ΔS°_{298} (2) = -32.2 JK^{-1} mol^{-1}

K_p (2) = $2.65\ 10^{11}\ T^{-0.678} \exp(+47960/T)$

Rate Coefficient Data ($k = k_1 + k_2 + k_3$)

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$\approx 5 \cdot 10^{-11}$	1400–1800	Peeters and Mahnen (1973)[1]	(a)
$5.7 \cdot 10^{-12}$	297	Washida, Martinez, and Bayes (1974)[2]	(b)
$1.3 \cdot 10^{-11}$	≈ 2000	Tsuboi (1976)[3]	(c)
$k_3/k_1 = 5$	266–298	Osif and Heicklen (1976) [4]	(d)
$k_2/k_1 \leqslant 0.19$			
$5.6 \cdot 10^{-12}$	298	Shibuya *et al.* (1977)[5]	(e)
$5.5 \cdot 10^{-12} \exp(-3522/T)$	1000–1350	Westbrook *et al.* (1977) [6]	(f)
$4.0 \cdot 10^{-12}$	298	Reilly *et al.* (1978)[7,8]	(g)
$k_3 = 1.2 \cdot 10^{-30}$ [M]	298	Horowitz, Su, and Calvert (1978)[9]	(h)
$4.0 \cdot 10^{-12}$	298	Nadtochenko *et al.* (1979)[10]	(i)
$5.5 \cdot 10^{-11}\ T^{-0.4}$	298–503	Veyret and Lesclaux (1981)[11]	(j)
$5.8 \cdot 10^{-12}$	≈ 1100	Cherian *et al.* (1981)[12]	(k)
$5.2 \cdot 10^{-12}$	296	Temps and Wagner (1984)[13]	(l)
$k_2/k_{ges} < 4 \cdot 10^{-3}$			
$k_3/k_{ges} < 0.07$			
$4.7 \cdot 10^{-12}$	295	Langford and Moore (1984)[14]	(m)
$3.0 \cdot 10^{-11}$	1450–1550	Vandooren *et al.* (1986) [15]	(n)
$4.5 \cdot 10^{-11} \exp(-600/T)$	300–1600		
$1.3 \cdot 10^{-11} \exp(-205/T)$	295–713	Timonen *et al.* (1988)[16]	(o)
Reviews and Evaluations			
$5.1 \cdot 10^{-12}$	298	Baulch *et al.* (1980)[17]	
$5 \cdot 10^{-12}$	300–2000	Warnatz (1984)[18]	
$8.5 \cdot 10^{-11} \exp(-854/T)$	300–2500	Tsang and Hampson (1986) [19]	

Comments

(a) Investigation of lean and stoichiometric CH$_4$/O$_2$/Ar flames burning at 40 Torr; concentration measurements by molecular beam sampling – mass spectrometry. O$_2$ considered as the only reaction partner of CHO.

(b) Discharge-flow system; total pressure near 4 Torr. [CHO] measured during the reaction of C$_2$H$_4$ with O atoms by photoionization mass spectrometry. Addition of O$_2$ resulted in a decrease of the steady-state concentration of CHO.

k(CHO + O$_2$)/k(CHO + O) = $2.7 \cdot 10^{-2}$. Given value of k based on k(CHO + O) = $2.1 \cdot 10^{-10}$ cm^3 molecule^{-1} s^{-1}.

(c) Computer simulation of a 39 reaction mechanism and comparison with experimental induction periods and concentration profiles.

(d) Photolysis of Cl$_2$/CH$_2$O/O$_2$ mixtures. [CO] and [CO$_2$] by gas chromatography, [HCOOH] by IR spectroscopy. Total pressures 62–704 Torr (298 K) and 344–688 Torr (266 K). Reaction (3) was found to be

in the second-order region. No indication of a total pressure effect in [HCOOH].

(e) Flash photolysis of acetaldehyde in He with small amounts of O$_2$ (λ > 200 nm). [CHO] monitored by absorption around 613.8 nm. Total pressures in the range 10–530 Torr; no pressure dependence of k within the experimental limits.

(f) Computer modelling of 56 reaction mechanism for the reaction of dilute moist CO in air and of dilute CH$_4$ in air at atmospheric pressure. Comparison with experimental concentration profiles of stable species obtained by gas chromatography of quenched samples.

(g) Near-UV laser photolysis of CH$_2$/O$_2$ mixtures; intracavity laser spectroscopy of CHO absorbance near 614 nm. Total pressure near 10 Torr.

(h) Photolysis of CH$_2$O at 313 nm in the presence of O$_2$. Gas chromatographic analysis of products. Total pressure 7–8 Torr CH$_2$O. Computer simulation of a 20 reaction mechanism.

(i) Photolysis of CH$_2$O or CH$_3$CHO in the presence of O$_2$. Intracavity laser spectroscopy of CHO ab-

sorbance. No pressure dependence observed between 13 and 100 Torr.

(j) Flash photolysis of CH_2O or CH_3CHO; total pressures 45 and 500 Torr. [CHO] by resonance absorption at 614.5 nm.

(k) Computer modelling of 27 reaction mechanism and comparison of burning velocities of premixed CH_4/air flames.

(l) Discharge-flow reactor; [CHO], [HO₂], and [OH] monitored by laser magnetic resonance. Total pressures 1.3–4.1 mbar. Channel (1) was found to be predominant.

(m) Laser photolysis of formaldehyde or glyoxal; total pressures up to 1000 Torr N_2. [CHO] by resonance absorption. No pressure dependence observed. *k* increased for reaction of DCO indicating that the reaction occurs via formation of a $HCOO_2$ adduct and not by simple hydrogen abstraction.

(n) Study of lean CH_2O / O_2 flames burning at 22.5 Torr by molecular beam sampling coupled with mass spectrometric analysis. Combination of their experimental results with the low temperature value k (300 K) $= 5.8 \cdot 10^{-12} \, cm^3 \, molecule^{-1} \, s^{-1}$ gave the temperature dependent rate parameters.

(o) Flash photolysis of CH_3CHO, photoionisation mass spectrometry.

Preferred Values

$k = 5.0 \cdot 10^{-12} \, cm^3 \, molecule^{-1} \, s^{-1}$ over range 300–2500 K

Reliability
$\Delta \log k = \pm 0.3$ over range 300–2500 K

Comments on Preferred Values

A temperature independent recommendation is given because the temperature dependent measurements give no or only a very weak dependence[11,16].

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$$CHO + O_2 \rightarrow HO_2 + CO$$
$$\rightarrow OH + CO_2$$
$$\rightarrow HCO_3$$

CHO + CHO → CH₂O + CO
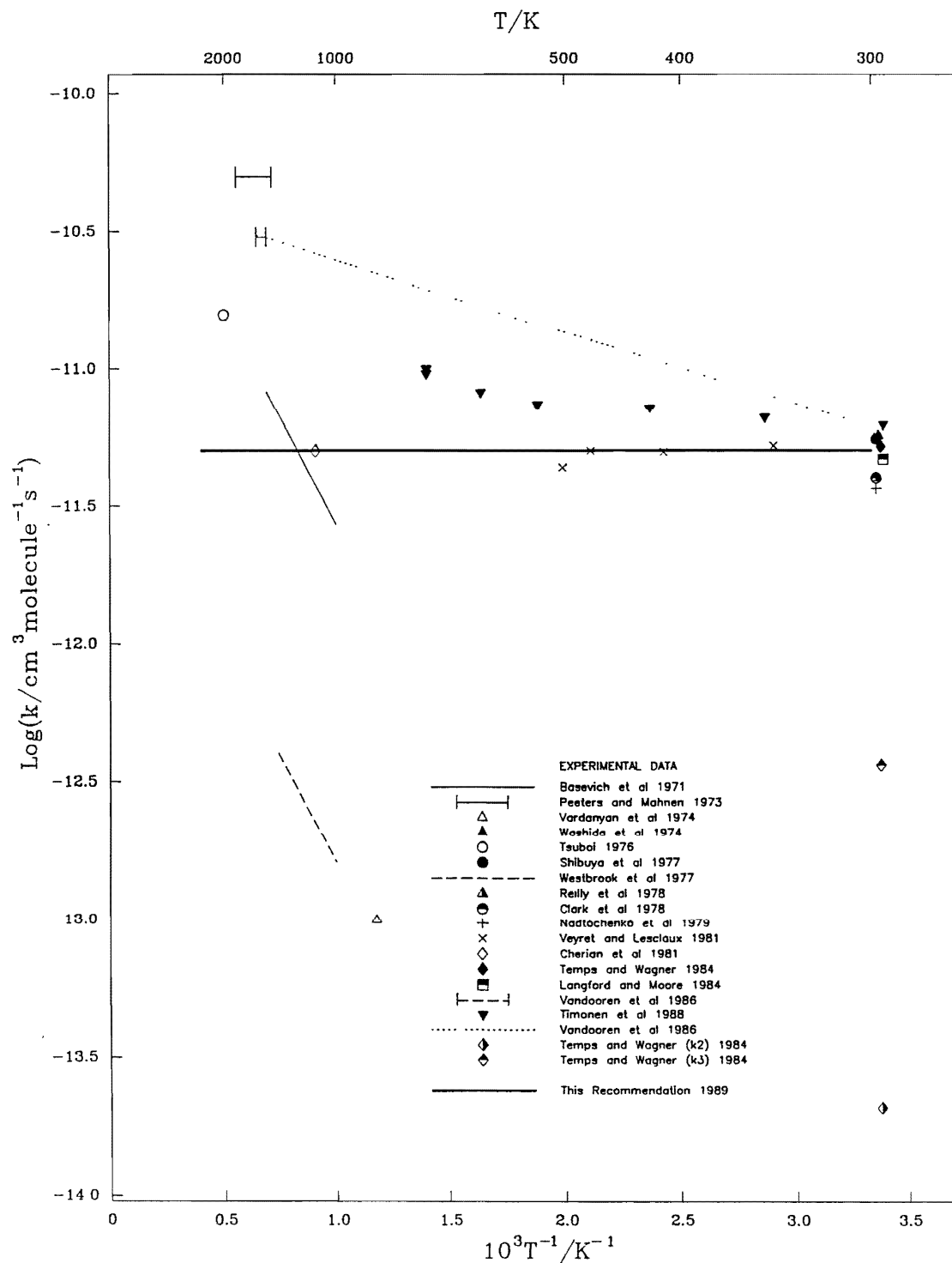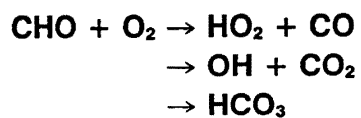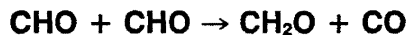
Thermodynamic Data

ΔH°_{298} (1) = −329 kJ mol⁻¹

ΔS°_{298} (1) = −32.9 J K⁻¹mol⁻¹

K_p(1) = 2.98·10⁻² $T^{-0.167}$ exp(+37773/T)

Rate Coefficient Data

k[cm³ molecule⁻¹ s⁻¹]	T[K]	Reference	Comments
Rate Coefficient Measurements			
(3–10)·10⁻¹¹	298	Reilly *et al*. (1978)[1]	(a)
3.0·10⁻¹¹	298	Nadtochenko, Sarkisov, and Vedeneev (1979)[2]	(b)
2.3·10⁻¹¹	298	Hochanadel, Sworsky, and Ogren (1980)[3]	(c)
3.4·10⁻¹¹	298–475	Veyret, Lesclaux, and Roussel (1984)[4]	(d)
4.5·10⁻¹¹	296	Temps and Wagner (1984)[5]	(e)
7.5·10⁻¹¹	295	Baggott *et al*. (1986)[6]	(f)

Comments

(a) Near-UV pulsed photolysis of formaldehyde; intra-cavity dye laser spectroscopy of CHO absorption at 613.8 nm or 614.5 nm. Total pressure 10 Torr pure formaldehyde. Fitting of a kinetic scheme. Large error limits due to non-uniform distribution of CHO in the reaction cell.

(b) Pulse photolysis of acetaldehyde in Ar; total pressures 10–200 Torr. Intracavity dye laser spectroscopy of CHO.

(c) Flash photolysis of H₂O in the presence of CO; total pressures 1–3 atm CO. [CHO] and [CH₃] monitored by UV absorption. Modelling of a 17 reaction mechanism.

(d) Flash photolysis of CH₂O; [CHO] monitored by resonance absorption at 614.5 nm. Total pressures 10–20 Torr. No temperature dependence observed. The initial absolute concentrations of radicals were determined by measuring the yields of molecular hydrogen using mass spectrometry in the presence and in the absence of hydrogen atom scavengers.

(e) Isothermal discharge-flow reactor; total pressures 1.4–4.5 mbar. [CHO], [HO₂], and [OH] monitored by far-infrared laser magnetic resonance.

(f) Laser flash photolysis of glyoxal or formaldehyde at 308 nm; time-resolved dye laser absorption of CHO at 614.6 nm. Pressure range 10–30 Torr. Discrepan-cies with other results ascribed to differencies in the measured absorption cross section of CHO.

Preferred Values

k = 5.0·10⁻¹¹ at 300 K

Reliability

Δlog k = ± 0.3 at 300 K

Comments on Preferred Values

The recommended value and error limits cover scattered data available.

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$$HCHO(+M) \rightarrow CHO + H(+M) \qquad (1)$$
$$\rightarrow CO + H_2(+M) \qquad (2)$$
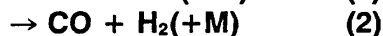
Thermodynamic Data

$\Delta H^\circ_{298} (1) = 377 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (1) = 121 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(1) = 1.19 \cdot 10^4 \ T^{0.879} \exp(-45400/T) \text{ atm}$

$\Delta H^\circ_{298} (2) = 5.3 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (2) = 109.3 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(2) = 1.36 \cdot 10^5 \ T^{0.37} \exp(-895/T) \text{ atm}$

Rate Coefficient Data ($k = k_1 + k_2$)

k [s^{-1}]	T [K]	Reference	Comments
Rate Coefficient Measurements			
$8.0 \cdot 10^{-8} \exp(-36300/T) \cdot [M]$	1400–2200	Schecker and Jost (1969)[1]	(a)
$3.5 \cdot 10^{-8} \exp(-17700/T) \cdot [M]$	1350–1900	Peeters and Mahnen (1973)[2]	(b)
$1.7 \cdot 10^{-10} \exp(-43800/T) \cdot [M]$	1070–1225	Aronowitz et al. (1977)[3]	(c)
$2.2 \cdot 10^{-8} \exp(-35600/T) \cdot [M]$	1700–2300	Bhaskaran et al. (1979)[4]	(d)
$6.0 \cdot 10^{-7} \exp(-43800/T) \cdot [M]$	1800–2500	Dean et al. (1979)[5]	(e)
$5.5 \cdot 10^{-8} \exp(-40800/T) \cdot [M]$	1600–3000	Dean et al. (1980)[6]	(f)
$4.2 \cdot 10^{-10} \exp(-14600/T) \cdot [M]$	1400–2000	Vandooren and Van Tiggelen (1981)[7]	(g)
$5.25 \cdot 10^{-9} \exp(-37700/T) \cdot [M]$	2200–2650	Saito et al. (1985)[8]	(h)
$k_1 = 2.08 \cdot 10^{-8} \exp(-39171/T) \cdot [M]$	1650–2200	Rimpel and Just (1988)[9]	(i)
$k_2 = 5.18 \cdot 10^{-10} \exp(-28100/T) \cdot [M]$	1900–2400		
Reviews and Evaluations			
$8.3 \cdot 10^{-8} \exp(-38500/T) \cdot [M]$	1000–3000	Warnatz (1984)[10]	(j)
$2.0 \cdot 10^{17} \ T^{-6.9} \exp(-48590/T) \cdot [M]$	1000–3000	Tsang and Hampson (1986)[11]	(k)

Comments

(a) Shock tube study of thermal decomposition of HCHO. Analysis by UV and IR absorption.

(b) Thermal decomposition of HCHO in a flame. Mass spectrometric analysis.

(c) Thermal decomposition of HCHO in a flow reactor. Gas chromatographic analysis.

(d) Shock tube study of HCHO decomposition. Analysis by resonance absorption.

(e) HCHO decay behind reflected shock wave monitored by IR emission.

(f) HCHO/O$_2$/Ar and HCHO/N$_2$/Ar mixtures investigated behind reflected shock waves; HCHO detected by IR emission. M = Ar.

(g) Thermal decomposition of HCHO in a flame. Mass spectrometric analysis.

(h) Thermal decomposition of HCHO behind reflected shock waves. HCHO decay and CO production determined by IR emission. H atom production measured by ARAS. M = Ar. Channel (2) appeared to have a smaller rate under the experimental conditions.

(i) Thermal decomposition of HCHO behind reflected shock wave. H atom production measured by ARAS. M = Ar.

(j) Based on the shock tube data of Schecker and Jost[1], Bhaskaran et al.[4], and Dean et al.[5,6].

(k) Theoretical calculation of k_1 in Ar using RRKM theory.

Preferred Values

$k_0(1) = 2.1 \cdot 10^{-8} \exp(-39200/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over range 1500–2500 K

Reliability

$\Delta \log k_0(1) = \pm 0.3$ over range 1500–2500 K

Comments on Preferred Values

The more recent shock tube data are in reasonable agreement near 2000 K and both Saito et al.[8] and Rimpel and Just[9] quote expressions for $k_0(1)$. Rimpel and Just give an expression for $k_0(2)$ for the molecular channel, which gives rates faster than obtained for $k_0(1)$ at temperatures near 2000 K, while Saito et al.[8] suggest that channel (2) is slower. The situation regarding channel (2) is therefore unclear and we are unable to recommend values for $k_0(2)$. The preferred expression for $k_0(1)$ is that of Rimpel and Just which gives values consistent with the other recent studies over the temperature range specified. The reaction is second order under all conditions where it has been studied and there is no information on fall-off.

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HCHO + M → HCO + H + M
→ H₂ + CO + M

T/K

EXPERIMENTAL DATA

————————— Schecker and Jost 1969
— — — — — Peeters and Mahnen 1973
— — — — Aronowitz et al 1977
— — — — — Bhaskaran et al 1979
— — — — Dean et al 1979
—·—·—·— Dean et al 1980
— — — — Vandooren and Van Tiggelen 1981
— — — — — Saito et al 1985
— — — — Rimpel and Just (k2) 1989
— — — — — Rimpel and Just (k1) 1989

————————— This Recommendation (k1) 1989

Log(k/cm³molecule⁻¹s⁻¹)

$10^3T^{-1}/K^{-1}$

$CH_2OH + O_2 \rightarrow CH_2O + HO_2$
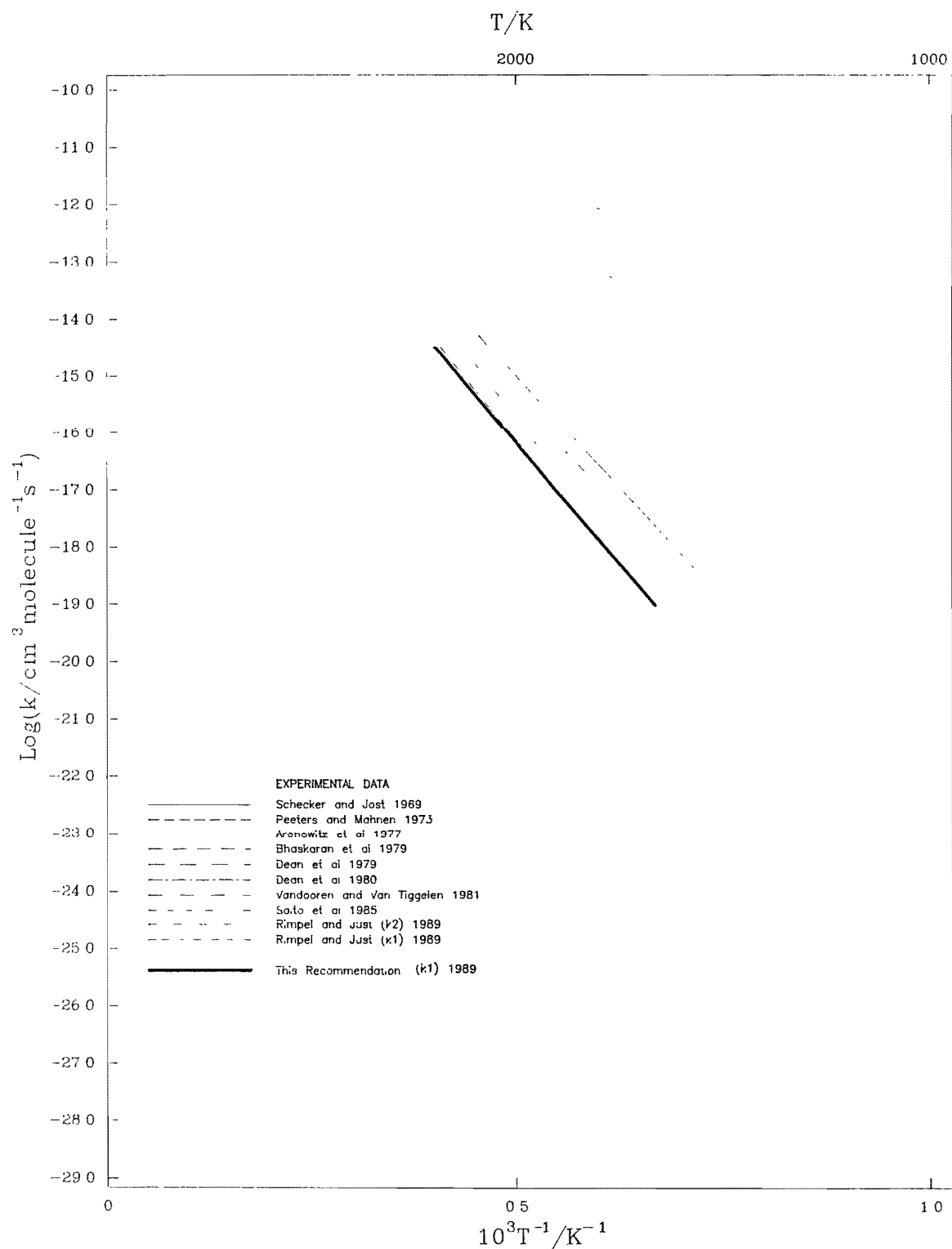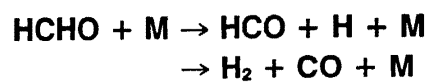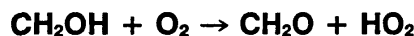
Thermodynamic Data

$\Delta H^\circ_{300}(1) = -87.94 \text{ kJ mol}^{-1}$
$\Delta S^\circ_{300}(1) = -14.14 \text{ J K}^{-1}\text{mol}^{-1}$
$K_p(300) = 2.08\cdot10^6$

Rate Coefficient Data

$k[\text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	$T[\text{ K }]$	Reference	Comments
Rate Coefficient Measurements			
$1.0\cdot10^{-11} \exp(-2640/T)$	453	Basevich *et al.* (1975)[1]	(a)
$1.7\cdot10^{-12} \exp(-3000/T)$	1800–1600	Westbrook and Dryer (1979)[3]	(b)
$2\cdot10^{-12}$	300	Radford (1980)[4]	(c)
$2.3\cdot10^{-10} \exp(-2525/T)$	1000–2000	Vandooren and van Tiggelen (1980)[5]	(d)
$1.7\cdot10^{-11}$	1300–1750	Tsuboi and Hashimoto (1981)[6]	(e)
$1.7\cdot10^{-11} \exp(-3620/T)$	(300–2000)	Dove and Warnatz (1983)[8]	(f)
$1.4\cdot10^{-12}$	298	Wang *et al.* (1984)[9]	(g)
$9.5\cdot10^{-12}$	298	Grotheer *et al.* (1985)[10]	(h)
$10.2\cdot10^{-12}$	296	Dobe *et al.* (1985)[11]	(i)
$8.6\cdot10^{-12}$	298	Payne *et al.* (1988)[12]	(j)
$2.5\cdot10^{-9} T^{-1}$ $+4.0\cdot10^{-10} \exp(-2525/T)$	298–682	Grotheer *et al.* (1988)[13]	(k)
$8.6\cdot10^{-12}$	300	Nesbitt *et al.* (1988)[14]	(l)
$7.5\cdot10^{-12}$	250		
$4.9\cdot10^{-12}$	239		
$3.3\cdot10^{-12}$	230		
$2.5\cdot10^{-12}$	215		
$8.8\cdot10^{-12}$	298	Pagsberg *et al.* (1989)[15]	(m)

Comments

(a) The rate coefficient for $CH_3OH + O$ was measured between 350–800 K in a discharge flow reactor under very large ($\approx 10^{15}$molecule cm^{-3}) concentrations of both reactants. The residence time was poorly defined. k was derived by simulating the stable end-product profiles as measured at 453 K. Therefore, the value on k is probably unreliable. It is quoted again in Ref. 2.

(b) The quoted expression has been used to simulate the profiles of stable endproducts, as measured for methanol oxidation in a turbulent flow reactor.

(c) Discharge flow reactor with $CH_3OH + Cl$ as CH_2OH source. Title reaction was isolated. k was obtained from relative HO_2 measurements (LMR) by varying the O_2 concentration for a fixed residence time. This actually yields k relative to the wall loss rate coefficient. This may introduce a considerable error. Radford was the first to show that this reaction is much faster than the corresponding $CH_3O + O_2$. Since then $CH_3OH/Cl/O_2$ has been widely used as HO_2 source.

(d) Mass spectrometric investigation of three low pressure (53 mbar) methanol flames (ϕ = 0.89, 0.36, 0.21). Aside from other labile species, CH_2OH/CH_3O has been detected. Unfortunately, the latter two species could not be discriminated and their calibration seems somewhat unclear.

(e) Shock tube at densities between $6\cdot10^{18}$ and $1.2\cdot10^{20}$ molecules cm^{-3}, Ar. Highly diluted methanol oxygen mixtures (ϕ = 0.2 to 2.0). Profiles for CH_3OH, H_2O, CO_2, CO, and CH_2O were measured by IR emission. k was obtained by simulating the system.

(f) Calculation study of the burning velocity of methanol/air mixtures. Title reaction is one of the 40 reaction set. This expression for k is also recommended in Ref. 8.

(g) Discharge flow reactor. Method very similar to Ref. 4 with the exception that HO_2 was monitored by OH ($A^2\Sigma \rightarrow X^2\pi$) photofragment emission. See comment (c) for disadvantages of the method. Further problems might have been introduced by the use of very high ($\sim 10^{14}$ molecules cm^{-3}) initial Cl_2 concentrations, so that subsequent reactions like $CH_2OH + Cl_2$ and $CH_2OH + CH_2OH$ might have played a role which was not accounted for.

(h) Discharge flow reactor. Source: $CH_3OH + Cl$. Title reaction was isolated. k from CH_2OH profiles, measured by a mass spectrometer. From absolute CH_2O measurements, it was concluded that this channel is major.

(i) Method as above (h), however CH_2OH monitored by LMR. From HO_2 built-up rates, it was concluded, that the HO_2 (+ CH_2O) channel is major. No pressure dependence for k in the range 0.7 to 6.5 mbar. This led to the suggestion that the reaction proceeds via an excited state of a bound intermediate.

(j) Method as above. Mass spectrometric CH_2OH detection.

(k) Method as above. Significant non-Arrhenius behaviour of k in the temperature range used. This led

to the interpretation of the reaction being composed of a path via an adduct and an abstraction path dominating at high temperatures. This picture is confirmed by the absence of a CH_2OH/CH_2OD isotope effect at ambient temperature.

(l) Method as above. Extension to temperatures below ambient. Large intercepts in the k^1 vs. [O_2] plots may indicate a wall problem, particularly at lower temperatures.

(m) Static reactor, 1000 mbar, Ar. CH_2OH source was CH_3OH + F. F atoms were produced from pulse radiolysis of SF_6. CH_2OH detection by UV absorption.

Preferred Values

$$k_1 = 2.6 \cdot 10^{-9} \ T^{-1} + 1.2 \cdot 10^{-10} \ \exp(-1800/T) \ cm^3 \ molecule^{-1} \ s^{-1} \ over \ range \ 300-1200 \ K$$

Reliability

$\Delta \log k_1 = \pm 0.1$ at 300 K increasing to $\pm$ 0.3 at 1000 K

Comments on Preferred Values

For the six most recent studies there is an exellent agreement at ambient temperature. The low temperature branch of Ref. 13 has been slightly adjusted to yield the mean of these studies.

For the abstraction channel a common fit for the measurements of Ref. 5 and Ref. 13 has been used.

For temperature below ambient, no recommendation is possible.

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$$CH_2OH + O_2 \rightarrow CH_2O + HO_2$$

$CH_3O(+M) \rightarrow HCHO + H(+M)$
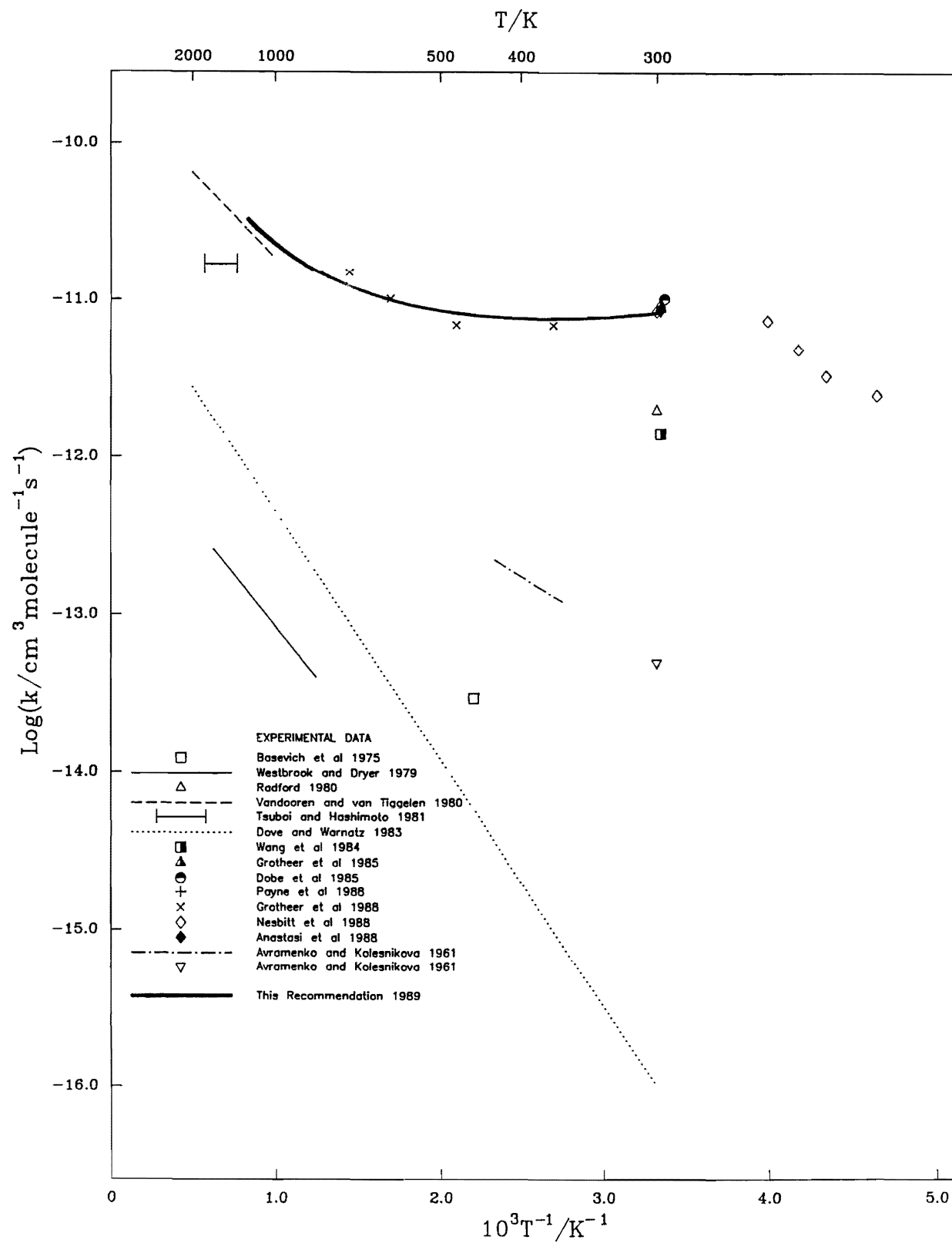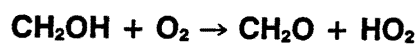
Thermodynamic Data

$\Delta H^\circ_{298} = 85.8 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} = 105 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p = 6.67 \cdot 10^4 \ T^{0.67} \exp(-10300/T) \text{ atm}$

Rate Coefficient Data

$k[\text{s}^{-1}]$	$T[\text{K}]$	Reference	Comments
Rate Coefficient Measurements			
No experimental data			
Reviews and Evaluations			
k_∞/s^{-1}			
$1.6 \cdot 10^{14} \exp(-13800/T)$	N/A	Batt (1979)[1]	(a)
$3.0 \cdot 10^{14} \exp(-13000/T)$	1000	Greenhill et al. (1986)[2]	(b)
$2.5 \cdot 10^{13} \exp(-13800/T)$	N/A	Batt (1987)[3]	(a)
$k_0/\text{cm}^3 \text{ molecule}^{-1}\text{s}^{-1}$			
$1.7 \cdot 10^{-10} \exp(-12640/T)$, [M] = N_2	300–2000	Warnatz (1984)[4]	(c)
$8.0 \cdot 10^{-9} \exp(-10830/T)$, [M] = N_2	600–1000	Greenhill et al. (1986)[2]	(b)
$3.16 \cdot 10^2 \ T^{-2.7} \exp(-15400/T)$	300–2000	Tsang and Hampson (1986)[5]	(d)

Comments

(a) Based on the thermochemistry and estimated A factor.

(b) Theoretical prediction using RRKM theory and taking into account fall-off effects. Similar treatment for CH_2OH decomposition.

(c) Based on the interpretation of complex mechanisms in shock tube studies of Bowman[6], Brabbs and Brokaw[7], and Tsuboi and Hashimoto[8], and flow system studies of Westbrook and Dryer[9].

(d) Based on k_∞ from Ref. 1 and RRKM calculations. Strong collision values given, as well as collision efficiency effects in tabular form.

Preferred Values

$k_0 = 3.16 \cdot 10^2 \ T^{-2.7} \exp(-15400/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
over range 300–1000 K

Reliability

$\Delta \log k = \pm 1.0$

Comments on Preferred Values

There are no direct measurement on this reaction. The reaction is under practically all conditions in combustion systems in the second-order region. The recent estimates of Greenhill et al.[2] and Tsang and Hampson[5] are in moderately good agreement and give values of k_0 which are considerably higher than earlier estimates. The recommendation of Tsang and Hampson is accepted. The recommended expression is the strong collision rate coefficient. For collision efficiency effects refer to Tsang and Hampson[5].

References

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$CH_3O + O_2 \rightarrow HCHO + HO_2$
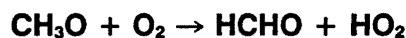
Thermodynamic Data
$\Delta H^\circ_{298} = -122$ kJ mol^{-1}
$\Delta S^\circ_{298} = 14.1$ J K^{-1}mol^{-1}
$K_p = 4.63\ T^{-0.28}\ \exp(+14500/T)$

Rate Coefficient Data

$k[$ cm^3 molecule^{-1} s^{-1}]	T [K]	Reference	Comments
Rate Coefficient Measurements			
$1.05 \cdot 10^{-13}\ \exp(-1310/T)$	413–628	Gutman, Sanders, and Butler (1982)[1]	(a)
$5.5 \cdot 10^{-14}\ \exp(-1000/T)$	298–450	Lorenz *et al*. (1985)[2]	(b)
Reviews and Evaluations			
$1.1 \cdot 10^{-13}\ \exp(-1310/T)$	298–630	CODATA (1984)[3]	(c)
$1.66 \cdot 10^{-11}\ \exp(-3610/T)$	300–2000	Warnatz (1984)[4]	(d)
$1.1 \cdot 10^{-13}\ \exp(-1310/T)$	413–608	Tsang and Hampson (1986)[5]	(e)
$3.9 \cdot 10^{-14}\ \exp(-900/T)$	200–300	NASA (1987)[6]	(f)

Comments

(a) Laser photolysis of CH_3ONO at 266 nm; CH_3O monitored by LIF. Psuedo first order conditions with excess O_2.

(b) Laser photolysis of CH_3ONO at 248 nm; CH_3O decay in excess O_2 monitored by LIF. k independent of pressure between 100 and 200 mbar.

(c) Based on data of Gutman *et al*.[1] and earlier relative rate studies.

(d) Based on earlier relative rate studies and estimates of k from shock tube and other high temperature studies.

(e) Accepts the recommendation from CODATA[3].

(f) Based on data of Lorenz *et al*.[2].

Preferred Values

$k = 6.7 \cdot 10^{-14}\ \exp(-1070/T)$ cm^3 molecule^{-1}s^{-1} over range 300–1000 K

Reliability
$\Delta \log k - \pm 0.2$ at 500 K increasing to ± 0.3 at 300 K and 1000 K
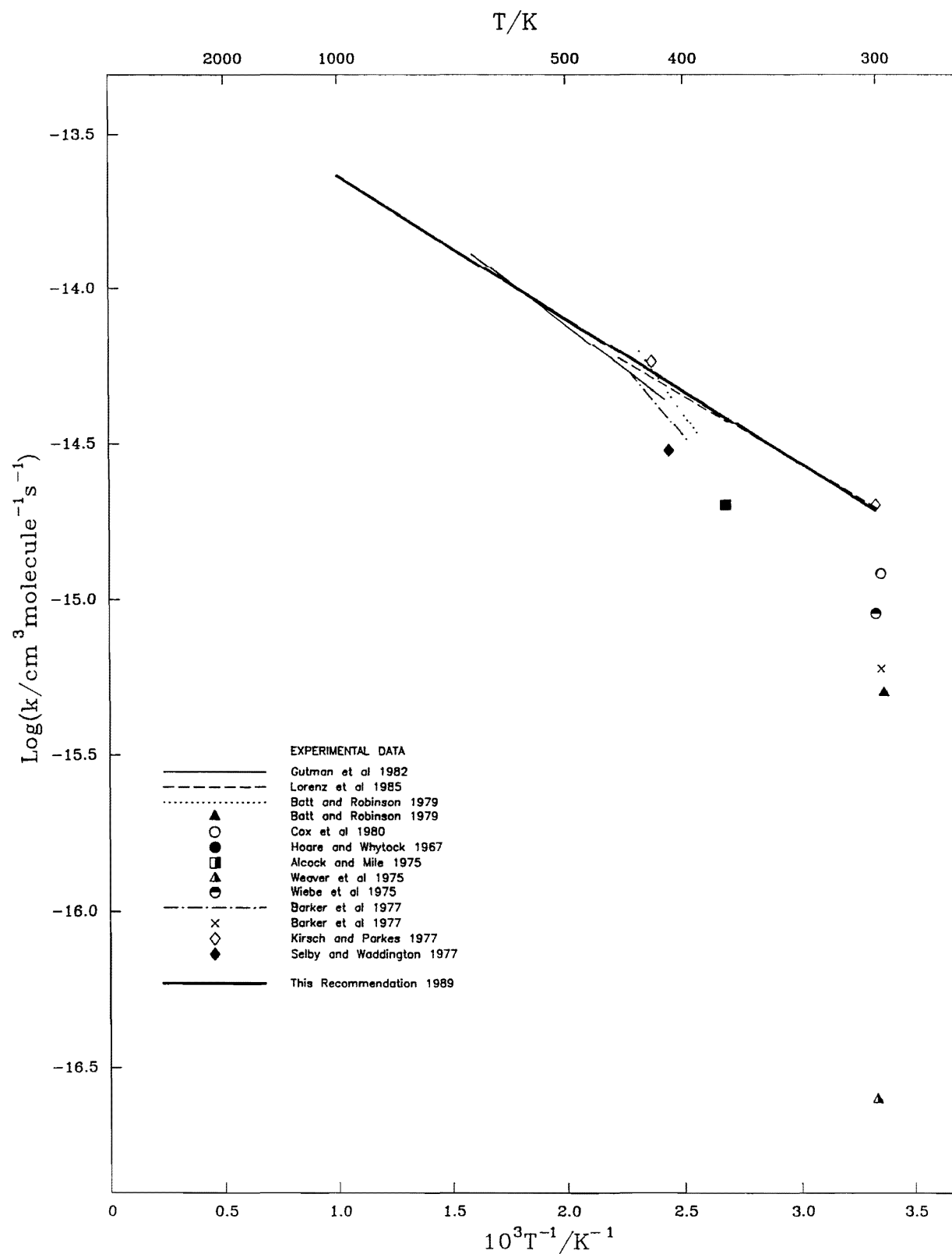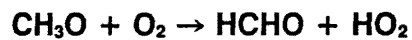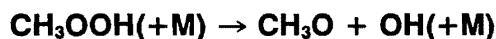
Comments on Preferred Values

The new data from Lorenz *et al*.[2] extend the temperature range for which direct measurements of k are available down to room temperature. The agreement with earlier relative rate measurements at 298 K is reasonable and both sets of direct measurements agree well near

450 K. The temperature dependence in the new study is lower than found by Gutman *et al*.[1] which may indicate non-Arrhenius behaviour; however in view of the limited range covered by the data and the uncertainties, we recommend an Arrhenius expression obtained by least squares fit to the data of Gutman *et al*.[1] and Lorenz *et al*.[2], applicable up to 1000 K.

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CH₃O + O₂ → HCHO + HO₂

EXPERIMENTAL DATA

————	Gutman et al 1982
– – – –	Lorenz et al 1985
··············	Batt and Robinson 1979
▲	Batt and Robinson 1979
○	Cox et al 1980
●	Hoare and Whytock 1967
▣	Alcock and Mile 1975
▵	Weaver et al 1975
⊖	Wiebe et al 1975
–·–·–·–	Barker et al 1977
×	Barker et al 1977
◇	Kirsch and Parkes 1977
◆	Selby and Waddington 1977
————	This Recommendation 1989

CH$_3$OOH(+M) $\rightarrow$ CH$_3$O + OH(+M)

Thermodynamic Data
$\Delta H^\circ_{298} = 180$ kJ mol^{-1}

Rate Coefficient Data

k[s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$k_\infty = 1.0 \cdot 10^{11} \exp(-16360/T)$	565–651	Kirk (1965)[1]	(a)
$k_\infty \leqslant 0.0085$	553	Kaiser *et al.* (1986)[2]	(b)
Reviews and Evaluations			
$k_\infty = 4 \cdot 10^{15} \exp(-21640/T)$	N/A	Benson (1981)[3]	(c)

Comments

(a) Pyrolysis of CH$_3$OOH in gas phase by toluene carrier method.

(b) Static pyrolysis of CH$_3$OOH; mass spectrometric detection of parent ion. Upper limit value. Recommended expression based on estimate by Benson[4] of activation energy of 190 kJ mol^{-1} was $6.5 \cdot 10^{14} \exp(-21640/T)$ s^{-1}.

(c) Based on thermochemistry together with an assumed temperature independent value for the reverse reaction.

Preferred Values

$k_\infty = 4 \cdot 10^{15} \exp(-21600/T)$ s^{-1} over range 400–1000 K

Reliability
$\Delta \log k_\infty = \pm 0.5$ at 600 K increasing to ± 1.0 at the end of range

Comments on Preferred Values
The earlier experimental data of Kirk give low values of both the activation energy and the A factor compared

with those expected from thermochemical kinetic considerations[4]. The author reported problems with heterogeneous reactions and these also are a potential problem in the work of Kaiser *et al.*[2]. The preferred values are based on experimentally derived Arrhenius expressions for decomposition of C$_7$-hydroperoxides[5], which agrees, within the stated uncertainty, with the value of k_∞ estimated from thermodynamic considerations. The main uncertainty arises from the unknown effects of fall-off on the rate at the temperatures where this reaction is important (500–700 K), which are almost certainly quite substantial, but not enough to account for the very low values of A and E_a reported by Kirk[1].

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$CN + O_2 \rightarrow NCO + O$
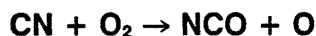
Thermodynamic Data

$\Delta H^\circ_{298} = -26.6 \text{kJ mol}^{-1}$

$\Delta S^\circ_{298} = -14.5 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p = 3.44 \cdot 10^{-4} \ T^{0.915} \exp(+3500/T)$

Rate Coefficient Data

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	$T[\text{ K }]$	Reference	Comments
Rate Coefficient Measurements			
$1.35 \cdot 10^{-11}$	300	Whyte and Phillips (1983)[1]	(a)
$1.25 \cdot 10^{-11}$ ($v = 1$)			
$7.9 \cdot 10^{-12}$	2400	Louge and Hanson (1984)[2]	(b)
$2.0 \cdot 10^{-11}$	300	Li, Sayah, and Jackson (1984)[3]	(c)
$2.4 \cdot 10^{-11}$ ($v = 1$)			
$2.6 \cdot 10^{-11}$	294	Lichtin and Lin (1985)[4]	(d)
$2.4 \cdot 10^{-11}$			
$8.1 \cdot 10^{-12}$	2195–3390	Thielen and Roth (1987)[5]	(e)
$1.86 \cdot 10^{-11}$	295	deJuan, Smith, and Veyret (1987)[6]	(f)
$1.82 \cdot 10^{-11}$	295	Anastasi and Hancock (1988)[7]	(g)
$1.25 \cdot 10^{-11} \exp(+205/T)$	294–761	Sims and Smith (1988)[8]	(h)
Reviews and Evaluations			
$4.0 \cdot 10^{-11} \exp(-450/T)$	290–400	Baulch *et al*. (1981)[9]	(i)
$1.1 \cdot 10^{-11} \exp(+205/T)$	290–760	CODATA (1989)[10]	(j)

Comments

(a) Fast flow system. CN radicals generated from $(CN)_2$ by ArF laser pulses. Decay of [CN, $v = 0$, $v = 1$] in excess O_2 monitored by laser induced fluorescence.

(b) Shock tube study on $O_2/(CN)_2/Ar$ mixtures. [CN] monitored by absorption at 388 nm. Data of [CN] analysed numerically in terms of 27 reaction mechanism. Fitting gives k. Sensitivity to assumed rate coefficient checked.

(c) Pulsed laser photolysis of $(CN)_2/Ar/O_2$ mixtures. [CN, $v = 0$, $v = 1$] monitored as a function of time by laser induced fluorescence.

(d) Pulsed laser photolysis of $ICN/O_2/Ar$ mixtures in flowing system. [CN] monitored as a function of time at both 388 nm and 619 nm, the latter giving the less precise of the two values of k tabulated.

(e) Shock wave study using reflected shocks in HCN/O_2 mixtures in Ar at 1.5–1.9 atm total pressure. [H], [O], [N] monitored by resonance absorption. [H], [O], [N] profiles computed from large reaction mechanism and fitted to experimental results. Sensitivity of fit to k checked.

(f) Laser pulsed photolysis of ICN in flow system with laser induced fluorescence determination of [CN]. Total pressure 10–30 Torr.

(g) Flash photolysis of $(CN)_2$ in Ar in flow system with laser induced fluorescence determination of [CN].

(h) Pulsed laser photolysis of flowing NCNO/Ar mixtures at 532 nm. [CN] monitored by laser induced fluorescence.

(i) Based on limited low temperature data.

(j) Accepts temperature coefficient of Sims and Smith[8].

Preferred Values

$k = 1.1 \cdot 10^{-11} \exp(+205/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over range 298–2500 K

Reliability

$\Delta \log k = \pm 0.25$ at 298 K rising to ± 0.5 at 2500 K

Comments on Preferred Values

Measurements up to 1981 have been reviewed[6]. Only more recent values are tabulated here.

At temperatures close to 300 K the available data range over a factor of $3^{1,3,4,6,7,8,11,12,13,14,15,16,19}$. The techniques used have been very similar and it has been suggested that the lower results might arise from population of the monitored v levels by quenching of higher v levels[3]. The most recent studies[3,4,6,7,8] are in reasonable agreement giving a mean value of $2.1 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
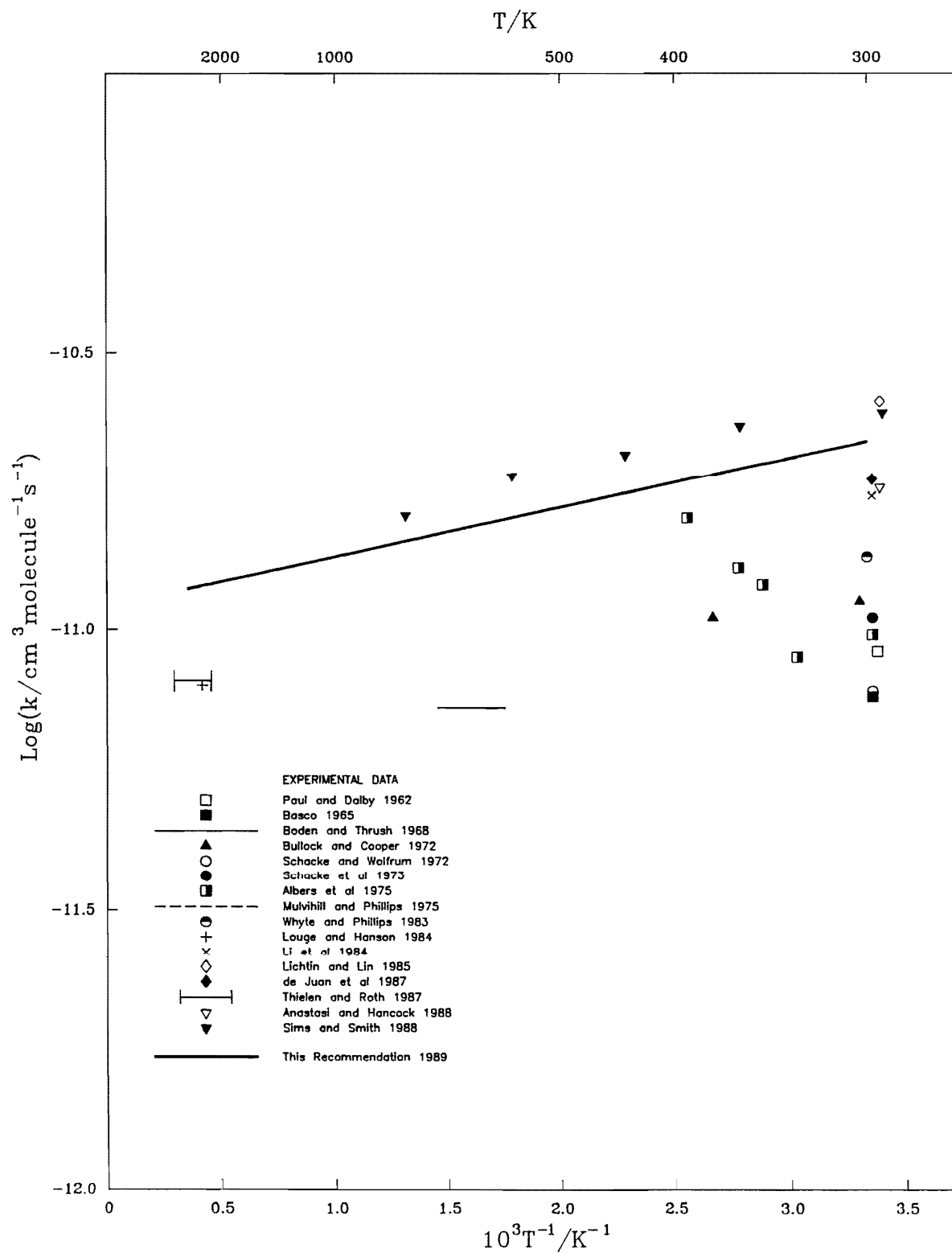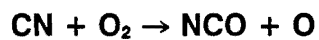
The measurements at higher temperatures are few and less precise but suggest that k has little or no temperature dependence[2,5,17]. This is in accord with the temperature dependence of k recently measured by Sims and Smith[8] which value we accept as the basis for the recommended expression.

The reaction has an alternative, highly exothermic channel giving $CO + NO$ ($\Delta H = -455 \text{ kJ mol}^{-1}$). The experimental evidence suggests that it is unimportant both at high and low temperatures[2,18].

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CN + O$_2$ → NCO + O

$$\text{CN} + \text{H}_2\text{O} \rightarrow \text{HCN} + \text{OH} \qquad (1)$$
$$\rightarrow \text{HOCN} + \text{H} \qquad (2)$$

Thermodynamic Data

ΔH^o_{298} (1) = -19.2 kJ mol^{-1}
ΔS^o_{298} (1) = -5.91 J K^{-1}mol^{-1}
K_p(1) = $4.79 \cdot 10^{-3}$ $T^{0.687}$exp($+2520/T$)

ΔH^o_{298} (2) = 15.1 kJ mol^{-1}
ΔS^o_{298} (2) = -28.78 J K^{-1}mol^{-1}
K_p(2) = $4.97 \cdot 10^{-5}$ $T^{0.941}$exp($-1493/T$)

Rate Coefficient Data ($k = k_1 + k_2$)

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$k_1 = 3.8 \cdot 10^{-11}$exp($-6700/T$)	850–2600	Szekely, Hanson, and Bowman (1984)[1]	(a)
$k_1 = 1.3 \cdot 10^{-11}$exp($-3750/T$)	518–1027	Jacobs *et al*. (1988)[2]	(b)
Reviews and Evaluations			
	–	Baulch *et al*. (1981)[3]	(c)

Comments

(a) Shock tube studies of C_2N_2/H_2O/Ar mixtures. [CN] and [OH] monitored by broad band absorption spectroscopy at 388 nm and narrow-line laser absorption at 306.67 nm respectively. Computer fit of data to assumed reaction mechanism shown to be sensitive to k_1. Values of k_1 from this study combined by authors with data of Fritz *et al*.[4] on the reverse reaction and with the equilibrium constant to obtain quoted expression for k_1.

(b) Laser photolysis at 193 nm of flowing C_2N_2/N_2 mixtures. [CN] in the $v = 0$ and $v = 1$ states and [OH] were monitored as function of time by laser induced fluorescence.

(c) Quotes early work of Paul and Dalby[5] which appears to give too high a value of k_1. No recommendation made.

Preferred Values

k_1 = $1.3 \cdot 10^{-11}$exp($-3750/T$) cm^3 molecule^{-1} s^{-1} over range 500–3000 K

Reliability

Δlog k_1 = $\pm$ 0.3 at 500 K rising to ± 0.5 at 3000 K.

Comments on Preferred Values

The recommended expression is that of Jacobs *et al*.[2]. If it is extrapolated to high temperatures it gives values of k_1 in good agreement with measured values of Szekely *et al*.[1]. The measurements of k_1 by Szekely *et al*.are likely to be valid but by combining them with data on the reverse reaction at lower temperatures and equilibrium data, they obtain an erroneous rate expression for k_1.

The other channel, (2) has been invoked to explain some features of nitrogen containing flames[6] but there is no direct evidence for its occurrence.

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CN + CH₄ → HCN + CH₃
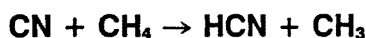
Thermodynamic Data

$\Delta H^{\circ}_{298} = -79.4 \text{ kJ mol}^{-1}$

$\Delta S^{\circ}_{298} = 7.18 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p = 9.79 \cdot 10^{-2} \, T^{0.546} \exp(+9570/T)$

Rate Coefficient Data

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	$T[\text{K}]$	Reference	Comments
Rate Coefficient Measurements			
$5.0 \cdot 10^{-13}$	293	Schacke, Wagner, and Wolfrum (1973)[1]	(a)
$1.1 \cdot 10^{-12}$, $CN_{v=1}$			
$5.6 \cdot 10^{-13}$	300	Li, Sayah, and Jackson (1984)[2]	(b)
$8.3 \cdot 10^{-13}$, $CN_{v=1}$			
$1.1 \cdot 10^{-12}$	294	Lichtin and Lin (1985)[3]	(c)
$7.8 \cdot 10^{-13}$	298	Balla and Pasternack (1987)[4]	(d)
Reviews and Evaluations			
–		Baulch et al. (1981)[5]	(e)

Comments

(a) Flash photolysis of $CH_4(0.037–0.4 \text{ Torr})/C_2N_2(0.05–0.2 \text{ Torr})/He$ mixtures. Total pressure 4–5 Torr, in a flowing system. [CN] monitored by kinetic absorption spectroscopy at 388 nm.

(b) Pulsed laser photolysis of $C_2N_2/Ar/CH_4$ mixtures. $[CN(v=0, v=1)]$ monitored as a function of time by laser induced fluorescence.

(c) Pulsed laser photolysis of $ICN/CH_4/Ar$ mixtures in flowing system. [CN] monitored as a function of time at 388 nm by laser induced fluorescence.

(d) Laser photolysis of $C_2N_2(0.05–0.3 \text{ Torr})/CH_4(0–0.15 \text{ Torr})$ mixtures with He, N_2, or Ar bath gas. Total pressures 1–200 Torr. [CN] decay and HCN formation monitored by diode laser absorption spectroscopy at 2015.22 cm^{-1} and 3280.987 cm^{-1} respectively.

(e) Review of all data up to 1980; no recommendation.

Preferred Values

$k = 1.5 \cdot 10^{-11} \exp(-940/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over range 260–400 K

Reliability

$\Delta \log k = \pm 0.3$ over range 260–400 K

Comments on Preferred Values

Experimental work on this reaction is largely confined to $T < 400$ K. The only higher temperature study by Boden and Thrush[6] yielded only an upper limit which does not correlate well with the lower temperature studies.

The results at 300 K range over a factor of 2 but the two studies of the temperature coefficient of k are in good agreement. The recommended values are based mainly on the work of Schacke et al.[9] and Bullock and Cooper[7,8].

The rate of the reaction is increased by vibrational excitation of the CN and several of the rate coefficients for $CN(v=1)$ have been determined[1,2,9].

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CN + CH$_4$ → CH$_3$ + HCN

NCO(+ M) → N + CO(+M)
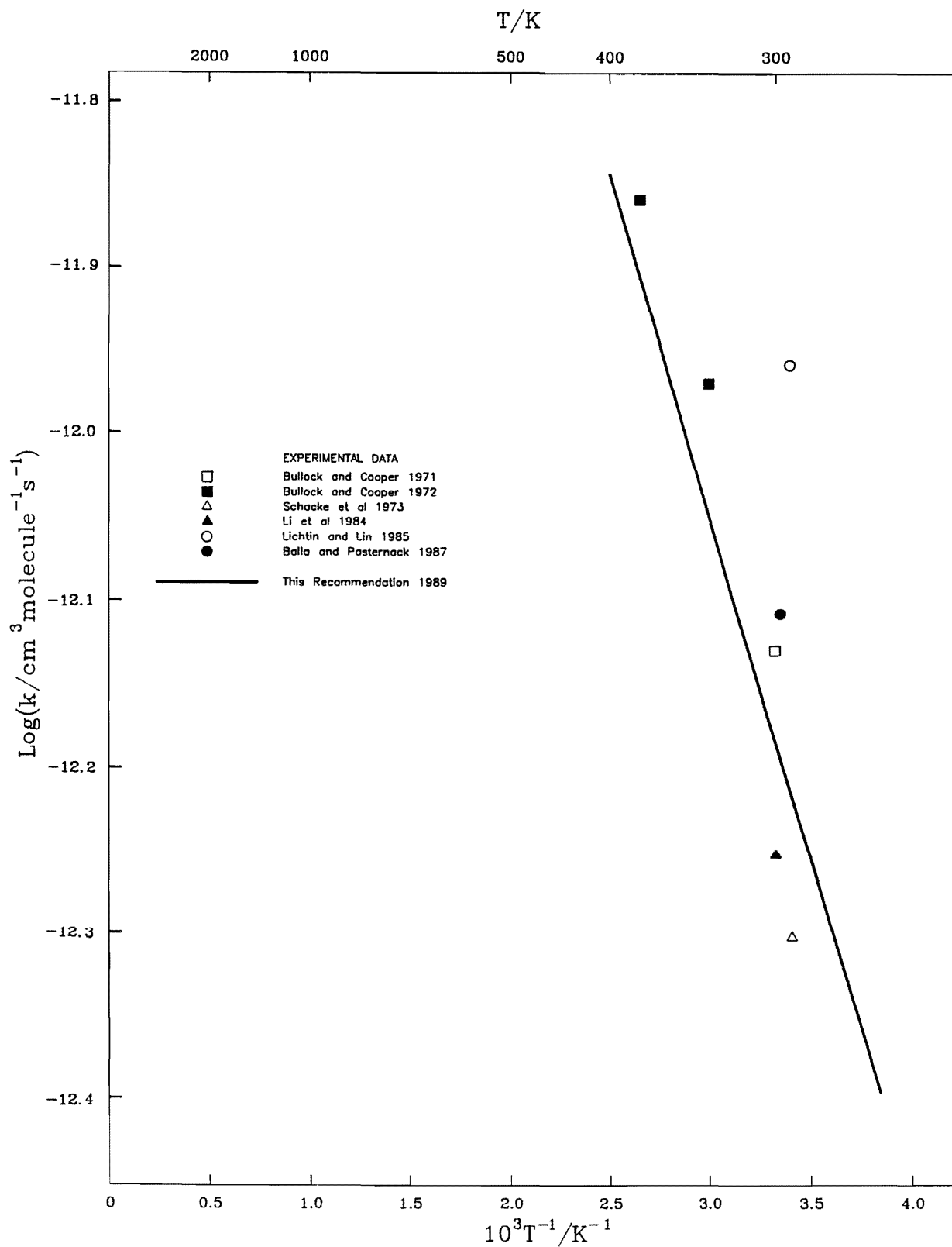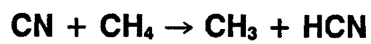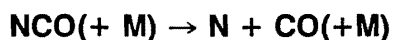
Thermodynamic Data

ΔH°_{298} = 203 kJ mol^{-1}

ΔS°_{298} = 119 J K^{-1}mol^{-1}

K_p = 5.49·10^6 $T^{-0.114}$ exp($-24560/T$) atm

Rate Coefficient Data

k[cm^3 molecule^{-1} s^{-1}]	T[K]	M	Reference	Comments
Reviews and Evaluations				
2.1·10^{-20}	1700	Ar	Lifshitz and Frenklach (1980)[1]	(a)
1.7·10^{-9} exp($-23450/T$)	1450–2600	Ar	Higashihara *et al*. (1983)[2]	(b)
1.7·10^{-11} $T^{0.5}$ exp($-20600/T$)	2240–2955	Ar	Colket (1984)[3]	(c)
8.1·10^{-8} exp($-31800/T$)	2150–2400	Ar	Louge and Hanson (1984)[4]	(d)
8.8·10^{-8} $T^{0.5}$ exp($-24000/T$)	2150–2400	Ar	Louge and Hanson (1984)[5]	(e)

Comments

(a) Shock tube study on C$_2$N$_2$/O$_2$/Ar mixtures. Computer simulations indicated induction period sensitive to this and 3 other reactions in 15 reaction mechanism. Only moderate agreement obtained between simulation and experiment.

(b) Shock tube study on HCN/O$_2$/Ar and HCN/O$_2$/NO$_2$/Ar mixtures. Detailed induction time data simulated using large reaction mechanisms in which title reaction and NCO + O → CO + NO are key reactions.

(c) Shock tube study on C$_2$N$_2$/O$_2$/Ar mixtures. Experimental [NO] profiles simulated using 8 reaction mechanism. Adjusting title k by factor of 3 hardly affected [CN] profile.

(d) Shock tube study of C$_2$N$_2$/O$_2$/Ar and C$_2$N$_2$/O$_2$/Ar mixtures. Analysis of [NO] profile in former and [CN] in latter gave k(NCO + O)/k(NCO + Ar) = 10$^{-3.07}$exp($+31800/T$). Quoted expression calculated using k(NCO + O) = 7.0·10^{-11} cm^3 molecule^{-1} s^{-1} (this review).

(e) Shock tube study of C$_2$N$_2$/N$_2$O/Ar mixtures. Analysis of [NCO], in conjunction with own earlier results (see (d)) gave k(NCO + O)/k(NCO + Ar) = 10$^{-3.1}$ $T^{0.5}$exp($+24000/T$). Quoted expression calculated using k(NCO + O) = 7.0·10^{-11} cm^3 molecule^{-1} s^{-1} (this review).

Preferred Values

k = 1.7·10^{-9} exp($-23500/T$) cm^3 molecule^{-1} s^{-1} for M = Ar over the range 1450–2600 K

Reliability

Δlog k = ± 0.4 over the range 1450–2600 K

Comments on Preferred Values

We recommend the expression obtained by Higashihara *et al*.[2] from analysis of a fairly detailed induction period data set over a wide temperature range, and subsequently corroborated by Louge and Hanson[4,5]. The result of Lifshitz and Frenklach[1] can be considered as a preliminary value and the experimental data of Colket[3] were hardly sensitive to the rate of this reaction.

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$$NCO + NO \rightarrow N_2O + CO \quad (1)$$
$$\rightarrow N_2 + CO_2 \quad (2)$$
$$\rightarrow N_2 + CO + O \quad (3)$$

Thermodynamic Data

$\Delta H_{298}^\circ (1) = -278$ kJ mol^{-1}

$\Delta S_{298}^\circ (1) = -25.4$ J K^{-1}mol^{-1}

$K_p(1) = 0.164 \ T^{-0.190} \exp(+33400/T)$

$\Delta H_{298}^\circ (2) = -643$ kJ mol^{-1}

$\Delta S_{298}^\circ (2) = -37.5$ J K^{-1}mol^{-1}

$K_p(2) = 7.22 \cdot 10^{-2} \ T^{-0.295} \exp(+77300/T)$

$\Delta H_{298}^\circ (3) = -111$ kJ mol^{-1}

$\Delta S_{298}^\circ (3) = 107$ J K^{-1}mol^{-1}

$K_p(3) = 2.96 \cdot 10^6 \ T^{-0.219} \exp(+13100/T)$ atm

Rate Coefficient Data ($k = k_1 + k_2 + k_3$)

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$1.66 \cdot 10^{-12}$	1329–1846	Fifer and Homes (1982)[1]	(a)
$1.69 \cdot 10^{-11} \exp(+197/T)$	294–538	Perry (1985)[2]	(b)
$3.4 \cdot 10^{-11}$	295	Hancock and McKendrick (1986)[3]	(c)

Comments

(a) Shock tube study of HCN/NO$_2$/Ar mixtures. [NO$_2$] monitored by absorption at 450 nm. [NO$^\bullet$], [OH$^\bullet$], and [NO$_2^\bullet$] monitored by emission at 237, 307, and 427.5 nm respectively. Value of k obtained is only an estimate from computer modelling of reaction mechanism.

(b) Flowing system. NCO produced by pulsed laser photolysis of HCNO/Ar/NO mixtures. Decay of [NCO] monitored using laser induced fluorescence at 416.8 nm.

(c) NCO produced by infrared multiphoton dissociation of phenyl isocyanate. Decay of [NCO] in large excess of NO monitored by laser induced fluorescence at 438.48 nm. This work supersedes earlier similar studies[4,5] in which vibrational excitation of NCO may have influenced results.

Preferred Values

$k = 1.7 \cdot 10^{-11} \exp(+200/T)$ cm^3 molecule^{-1} s^{-1} over range 300–600 K

Reliability

$\Delta \log k = \pm 0.5$ over range 300–600 K

Comments on Preferred Values

The preferred expression is that of Perry[2] which is in good agreement with the results of Hancock and McKendrick[3] at ambient temperatures. These are the only direct measurements and therefore we assign fairly large error limits. The only available value of k at higher temperatures is a very indirect determination which is an order of magnitude lower than that obtained by extrapolation of our recommended expression. We therefore limit our recommendation to the low temperature region.

There have been no studies of the branching ratios. Both Perry[2] and Hancock and McKendrick[3] have suggested that reaction (1) is the dominant channel as (2) and (3) are likely to have significant energy barriers, reaction (2) proceeding via a triplet surface and (3) requiring a 1,3 oxygen migration via a 4 centre transition state. Furthermore, Hancock and McKendrick[3] observe no NO + O recombination afterglow in their experiments, thus suggesting the absence of channel (3).

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$$C_2H + O_2 \rightarrow CH + CO_2 \quad (1)$$
$$\rightarrow H + 2\ CO \quad (2)$$
$$\rightarrow O + C_2HO \quad (3)$$
$$\rightarrow CHO + CO \quad (4)$$
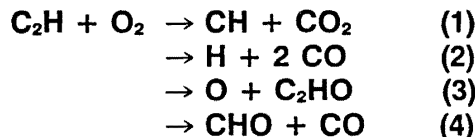
Thermodynamic Data

ΔH°_{298} (1) = -360 kJ mol^{-1}

ΔS°_{298} (1) = 15.8 J K^{-1}mol^{-1}

K_p (1) = 4.69·10^2 $T^{-0.158}$ exp($+43400/T$)

ΔH°_{298} (3) = -134 kJ mol^{-1}

ΔS°_{298} (3) = 2.67 J K^{-1}mol^{-1}

K_p (3) = 2.70·10^{-2} $T^{0.616}$ exp($+16200/T$)

ΔH°_{298} (2) = -564 kJ mol^{-1}

ΔS°_{298} (2) = 97.2 J K^{-1}mol^{-1}

K_p (2) = 6.41·10^4 $T^{0.176}$ exp ($+67700/T$)atm

ΔH°_{298} (4) = -628 kJ mol^{-1}

ΔS°_{298} (4) = 9.65 J K^{-1}mol^{-1}

K_p (4) = 1.79·10^2 $T^{-0.596}$ exp($+15300/T$)

Rate Coefficient Data ($k = k_1 + k_2 + k_3 + k_4$)

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$\approx 3.3 \cdot 10^{-12}$	320	Lange and Wagner (1975)[1]	(a)
$1.7 \cdot 10^{-11}$ exp($-5032/T$)	1400–2600	Shaub and Bauer (1978)[2]	(b)
$2.1 \cdot 10^{-11}$	300	Renlund et al. (1981, 1982)[3,4]	(c)
$k_3 = 1.0 \cdot 10^{-12}$	295	Laufer and Lechleider (1984)[5]	(d)
$k_4 = 4.0 \cdot 10^{-12}$			
$4.2 \cdot 10^{-11}$	298	Stephens et al. (1987)[6]	(e)
Reviews and Evaluations			
$8.3 \cdot 10^{-11}$	> 300	Warnatz (1984)[7]	
$5.0 \cdot 10^{-12}$	300–2500	Tsang and Hampson (1986)[8]	

Comments

(a) Flow reactor; C_2H from microwave discharge of C_2HBr/He; mass spectrometric product analysis. Total pressure 4.1 Torr. [C_2HO] observed, no CHO or C_2O detected; (3) supposed to be the main reaction channel. Lower limit of k.

(b) Shock heating of $C_2H_2/O_2/Ar$ mixtures. Final product concentrations by gas chromatography. Numerical modelling of 17 reaction mechanism.

(c) UV or IR photodissociation of C_2HCF_3, C_2HCHO, C_2H_2, or C_2HBr. Observation of $CH(A^2\Delta - X^2\Pi)$ and $CO(a^{13}\Sigma \pm a^3\Pi)$ chemiluminescence at 432.6 nm and 790 nm and of $CO_2(\Delta\nu_3 = 1)$ emission at 2300 cm^{-1}. Total pressures 0.2–2.0 Torr He or Ar. CO and CH emissions independent of the nature of the buffer gas (He, Ar, N$_2$, or Xe) and of its pressure (0.6–100 Torr). They propose the formation of an intermediate peroxy species with enough vibrational energy to allow significant rearrangements of the nuclei during the course of the reaction.

(d) Flash photolysis of CF_3C_2H; gas chromatographic sampling; [CO] by absorption at 154.4 nm. Reaction rates indendent of pressure in the range 50–600 Torr (He or N$_2$). Lack of CHO detection in Ref. 1 explained by low detection limit and fast consumption of CHO.

(e) Flash photolysis of CF_3C_2H at 193 nm; IR absorption of ground state C_2H at 3594.4 cm^{-1}. Total pressure 20 Torr He; SF$_6$ added to ensure rapid vibrational relaxation of C_2H.

Preferred Values

$k = 3.0 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 300 K

Reliability

$\Delta\log k = \pm 0.5$ at 300 K

Comments on Preferred Values

The larger rate coefficient based on Refs. 3,4,6 is taken as the recommendation due to the modern methods used. From the measurements of Laufer and Lechleider[5] the product channel (4) seems to be the most important one which is similar to channel (2) at high temperature.

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$C_2H + H_2 \rightarrow H + C_2H_2$
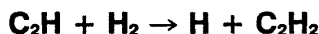
Thermodynamic Data

$\Delta H^\circ_{298} = -116$ kJ mol^{-1}

$\Delta S^\circ_{298} = -22.5$ J K^{-1}mol^{-1}

$K_p = 1.38 \cdot 10^{-4} \ T^{0.866} \exp(+14300/T)$

Rate Coefficient Data

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$\approx 1.7 \cdot 10^{-13}$	320	Lange and Wagner (1975)[1]	(a)
$1.5 \cdot 10^{-13}$	298	Laufer and Bass (1979)[2]	(b)
$9.3 \cdot 10^{-12}$	625–3400	Tanzawa and Gardiner (1980) [3]	(c)
$1.2 \cdot 10^{-11}$	300	Renlund *et al.* (1981)[4]	(d)
$1.3 \cdot 10^{-11}$	1800–2500	Koike and Morinaga (1981)[5]; corr. by Gardiner *et al.* (1985)[6]	(e)
$3.9 \cdot 10^{-13}$	298	Okabe (1981)[7]	(f)
$1.2 \cdot 10^{-11}$	2300–3200	Kiefer *et al.* (1983)[8]	(g)
$4.8 \cdot 10^{-13}$	298	Stephens *et al.* (1987)[9]	(h)
Reviews and Evaluations			
$2.5 \cdot 10^{-11} \exp(-1564/T)$	300–3000	Warnatz (1984)[10]	
$1.9 \cdot 10^{-11} \exp(-1443/T)$	300–2800	Gardiner *et al.* (1985)[6]	
$1.8 \cdot 10^{-11} \exp(-1455/T)$	300–2500	Tsang and Hampson (1986) [11]	

Comments

(a) Flow reactor; C_2H from microwave discharge of C_2HBr/He. Mass spectrometric product analysis. Total pressure 4.2 Torr. Lower limit of k.

(b) VUV flash photolysis of C_2H_2 with and without added H_2; [C_4H_2] by gas chromatographic sampling and VUV absorption at 144.6 nm. Total pressures 20 or 700 Torr He.
$k(C_2H + H_2)/k(C_2H + C_2H_2) = 4.9 \cdot 10^{-3}$. Given value based on $k(C_2H + C_2H_2) = 3.1 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

(c) Modelling study of C_2H_2 pyrolysis in shock tubes, flow reactors, and bulb dissociation experiments. Wrong data transcription in the table; corrected in Ref. 6.

(d) UV or IR flash photolysis of C_2H_2, C_2HBr, or C_2HCHO. $CH(A^2\Delta - X^2\Pi)$ and CO_2 chemiluminescence at 432.6 nm and 2300 cm^{-1}. Total pressures 200–800 mTorr Ar or He. k measured relative to reaction with O_2. The authors do not exclude the possibility of C_2H reacting from an excited state.

(e) Shock heating of C_2H_2, C_2H_2/H_2, or C_2H_4 in 0.5 atm Ar. Absorption measurements at 216 nm and 230 nm. Numerical modelling of 25 reaction mechanism, k adjusted to fit the absorption profile of C_4H_2. Wrong thermochemical data for C_2H; correction in Ref. 6.

(f) Photolysis of C_2H_2 at 147 nm. [C_4H_2], [C_2H_4], and [C_2H_2] by absorption measurements at $\approx$ 165 nm, 174.4 nm, and 151.9 nm. Relative rate $k(C_2H + H_2)/k(C_2H + C_2H_2) = 1/130$. Given value of k based on $k(C_2H + C_2H_2) = 5 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

(g) Pyrolysis of C_2H_4/Kr mixtures behind incident shock waves; laser schlieren measurements. Total pressure 200–750 Torr. Numerical modelling of 29 reaction mechanism based on Ref. 3. k adjusted.

(h) Flash photolysis of CF_3C_2H at 193 nm. Ground state C_2H monitored by IR absorption at 3594.4 cm^{-1}. Total pressure 20 Torr He; SF_6 added to ensure rapid vibrational relaxation of C_2H.

Preferred Values

$k = 2.5 \cdot 10^{-11} \exp(-1564/T)$ cm^3 molecule^{-1} s^{-1} over range 300–2500 K

Reliability

$\Delta \log k = \pm 0.3$ at 300 K rising to ± 0.7 at 2500 K

Comments on Preferred Values

The recommendation of Warnatz[10] is adopted. It gives a good representation of the high and low temperature data available.

References

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[6]W. C. Gardiner, T. Tanzawa, T. Koike, and K. Morinaga, Bull. Chem. Soc. Jpn. **58**, 1851 (1985).

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[10]J. Warnatz, in "Combustion Chemistry", ed. W. C. Gardiner, Springer-Verlag, New York (1984).

[11]W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data **15**, 1087 (1986).

C₂H + H₂ → C₂H₂ + H

$C_2H + C_2H_2 \rightarrow H + C_4H_2$
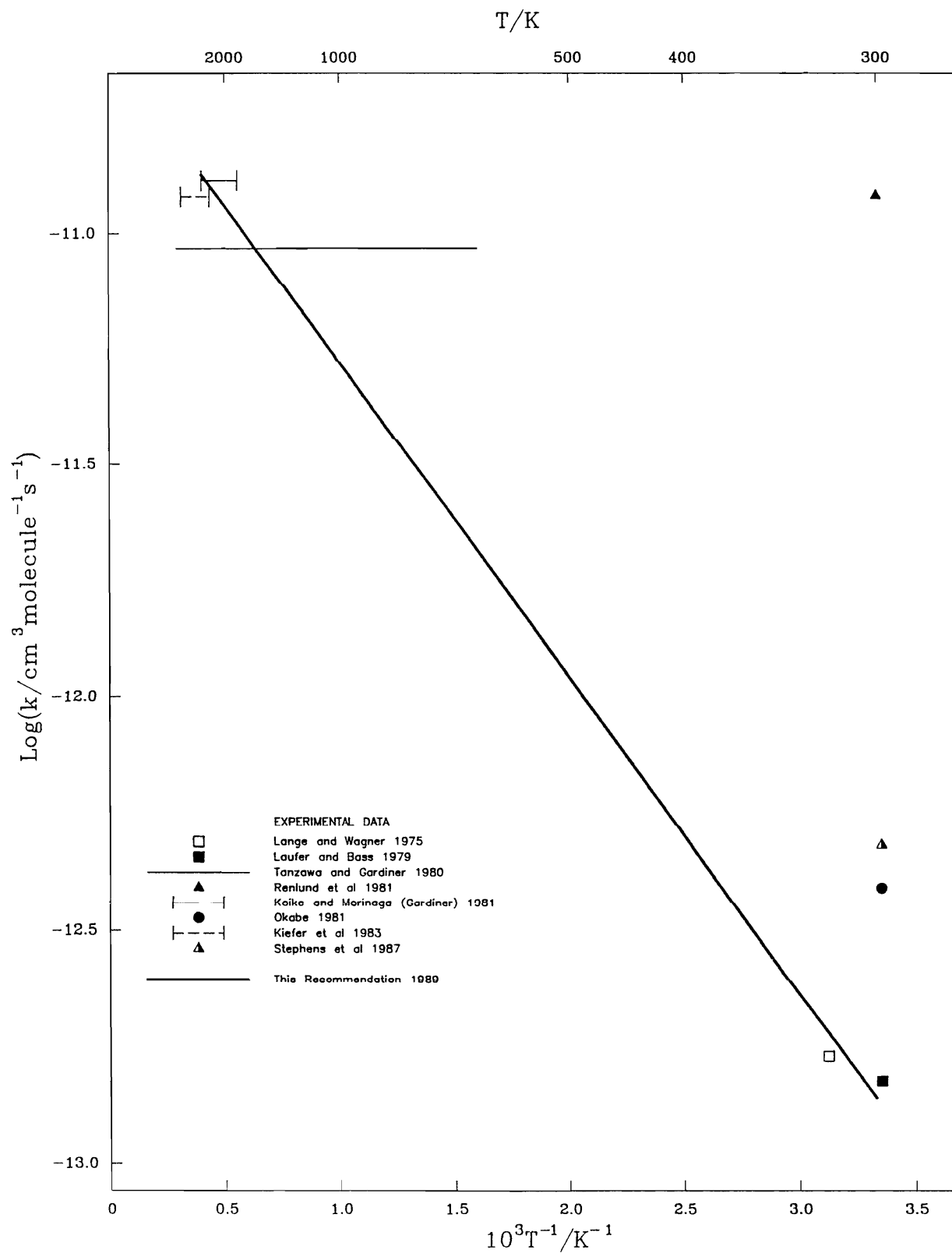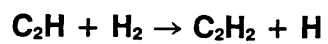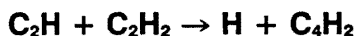
Thermodynamic Data
$\Delta H^\circ_{298} = -102 \text{ kJ mol}^{-1}$
$\Delta S^\circ_{298} = -43.5 \text{ J K}^{-1}\text{mol}^{-1}$
$K_p = 4.46 \cdot 10^{-7} T^{1.43} \exp(+12600/T)$

Rate Coefficient Data

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	$T[\text{K}]$	Reference	Comments
Rate Coefficient Measurements			
$\approx 5 \cdot 10^{-11}$	320	Lange and Wagner (1975)[1]	(a)
$3.1 \cdot 10^{-11}$	298	Laufer and Bass (1979)[2]	(b)
$(5-6.6) \cdot 10^{-11}$	2300–2700	Frank and Just (1980)[3]	(c)
$1.5 \cdot 10^{-10}$	298	Stephens *et al*. (1987)[4]	(d)
Reviews and Evaluations			
$4.0 \cdot 10^{-11}$	300–2500	Tsang and Hampson (1986)[5]	

Comments

(a) Flow reactor; mass spectrometric product analysis. C_2H from microwave discharge of C_2HBr/He. Total pressure 4.1 Torr. C_4H_2 identified as main product. Lower limit of k.

(b) VUV flash photolysis of C_2H_2. C_4H_2 formation observed by gas chromatographic sampling and absorption measurement at 144.6 nm. Total pressures 20 and 700 Torr He.

(c) Thermal decomposition of C_2H_2 and C_4H_2 behind reflected shock waves. [H] by atomic resonance absorption spectroscopy at 121.5 nm. Total pressures 1.5–4 bar Ar.

(d) Flash photolysis of C_2H_2 at 193 nm; $[C_2H]$ monitored by IR absorption at 3594.4 cm^{-1}. Total pressure 20 Torr He; SF_6 added to ensure rapid vibrational relaxation of C_2H.

Preferred Values

$k = 5 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over range 300–2700 K.

Reliability
$\Delta \log k = \pm 0.3$ over total range.

Comments on Preferred Values
The recommended rate coefficient is consistent with most of the experimental material available.

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[1] W. Lange and H. Gg. Wagner, Ber. Bunsenges. Phys. Chem. 79, 165 (1975).

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[3] P. Frank and Th. Just, Comb. Flame 38, 231 (1980).

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[5] W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data 15, 1087 (1986).

$C_2H + CH_4 \rightarrow$ Products

Rate Coefficient Data

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	$T[\text{K}]$	Reference	Comments
Rate Coefficient Measurements			
$4.8 \cdot 10^{-12}$	298	Renlund *et al*. (1981)[1]	(a)
$1.2 \cdot 10^{-12}$	297	Laufer (1981)[2]	(b)
$1.6 \cdot 10^{-12}$	298	Okabe (1981)[3]	(c)
Reviews and Evaluations			
$3.0 \cdot 10^{-12} \exp(-250/T)$	300–2500	Tsang and Hampson (1986) [4]	

Comments

(a) Flash photolysis of C_2H_2, C_2HBr, or C_2HCO at 193 nm, or of C_2HCO at 953 cm^{-1}. $CH(A^2\Delta)$ from $C_2H + O_2$ reaction monitored by chemiluminescence at 432.6 nm, with and without added CH_4, $[CO_2]$ monitored by chemiluminescence at 2300 cm^{-1}. Total pressures 200–800 mTorr Ar or He.

(b) VUV flash photolysis of C_2HCF_3. Gas chromatographic sampling, $[C_2H_2]$ by absorption spectroscopy at 152 nm. k independent of pressure between 20 and 700 Torr.

(c) Photolysis of C_2H_2 at 147 nm; $[C_4H_2]$, $[C_2H_4]$, and $[C_2H_2]$ by absorption spectroscopy at $\approx$ 165 nm, 174.4 nm, and 151.9 nm, respectively. Relative rates $k(C_2H + CH_4)/k(C_2H + C_2H_2) = 4.2/130$. k based on $k(C_2H + C_2H_2) = 5 \cdot 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}.

Preferred Values

$k = 2.0 \cdot 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K

Reliability

$\Delta \log k = \pm 1$ at 298 K

Comments on Preferred Values

The preferred value is based on all of the available data but wide error limits are suggested.

References

[1] A. M. Renlund, F. Shokoohi, H. Reisler, and C. Wittig, Chem. Phys. Lett. **84**, 293 (1981).

[2] A. H. Laufer, 15th Int. Symp. Free Radicals, Ingonish Beach, Canada (1981).

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[4] W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data **15**, 1087 (1986).

$C_2H + C_2H_6 \rightarrow C_2H_2 + C_2H_5$
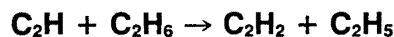
Thermodynamic Data

$\Delta H^\circ_{298} = -133$ kJ mol^{-1}

$\Delta S^\circ_{298} = 16.2$ J $K^{-1}mol^{-1}$

$K_p = 4.04 \cdot T^{0.906} \exp(+12640/T)$

Rate Coefficient Data

k[cm^3 $molecule^{-1}$ s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$6.5 \cdot 10^{-12}$	298	Laufer (1981)[1]	(a)
Reviews and Evaluations			
$6.0 \cdot 10^{-12}$	300–2500	Tsang and Hampson (1986)[2]	

Comments

(a) Photolysis of C_2H_2 at 147 nm; $[C_4H_2]$, $[C_2H_4]$, and $[C_2H_2]$ by absorption spectroscopy at $\approx$ 165 nm, 174.4 nm, and 151.9 nm, respectively. Relative rates $k(C_2H + CH_4)/k(C_2H + C_2H_2) = 4.2/130$. k based on $k(C_2H + C_2H_2) = 5 \cdot 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}.

Preferred Values

No recommendation.

References

[1] A. H. Laufer, 15th Int. Symp. Free Radicals, Ingonish Beach, Canada (1981).

[2] W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data **15**, 1087 (1986).

$C_2H_3(+M) \rightarrow C_2H_2 + H(+M)$

Thermodynamic Data
$\Delta H^\circ_{298} = 158 \text{ kJ mol}^{-1}$
$\Delta S^\circ_{298} = 171 \text{ J K}^{-1}\text{mol}^{-1}$
$K_p = 2.43 \ T^{1.5} \exp(-18900/T)\text{atm}$

Rate Coefficient Data

$k[\text{s}^{-1}]$	$T[\text{K}]$	[M] [molecule cm^{-3}]	Reference	Comments
Rate Coefficient Measurements				
Intermediate Fall-off Range				
$1.3 \cdot 10^{-9}\exp(-15800/T)$ [Ar]	1200–1700	$2 \cdot 10^{19}$ (Ar)	Benson and Haugen (1967)[1]	(a)
$1.6 \cdot 10^{-11}\exp(-19000/T)$ [Ar]	1100–1500	$1.7 \cdot 10^{19}$ (Ar)	Skinner, Sweet, and Davis (1971)[2]	(b)
$3 \cdot 10^{-12}$ [C$_2$H$_4$]	1500	$2 \cdot 10^{17}$ (C$_2$H$_4$)	Peeters and Mahnen (1973)[3]	(c)
$2.7 \cdot 10^{-9}\exp(-16100/T)$ [C$_2$H$_4$]	1800–2400	$5 \cdot 10^{18}$ (C$_2$H$_4$)	Jachimowski (1977)[4]	(d)
$2.6 \cdot 10^{-9}\exp(-15800/T)$ [Ar]	1300 -2000	$(1-9) \cdot 10^{15}$ (Ar)	Coats and Williams (1979)[5]	(e)
Reviews and Evaluations				
$k_0 = 5.0 \cdot 10^{-9}\exp(-16120/T)$	500–2500	(Ar)	Warnatz (1984)[6]	(f)
$k_\infty = 1.6 \cdot 10^{14}\exp(-19120/T)$	500–2500			
$k_0 = 6.9 \cdot 10^{17}T^{-7.49}\exp(-22917/T)$	>600	(N$_2$)	Tsang and Hampson (1986)[7]	(g)

Comments

(a) Analysis of available experimental data on the hydrogenation of C_2H_2 and the pyrolysis of C_2H_4.

(b) Pyrolysis of dilute mixtures of C_2H_4, C_2H_4/C_2D_4, $C_2H_2D_2$ in Ar in a shock tube. No dependence of k on pressure observed, suggested that the reaction was in the high pressure range. Here represented as a pressure-proportional rate coefficient.

(c) Molecular beam sampling, mass spectrometric analysis of C_2H_4 flames at 40 Torr.

(d) Oxidation of C_2H_4 behind incident shock waves. Monitored IR emission from CO and CO$_2$, and chemiluminescence from $O + CO \rightarrow CO_2 + h\nu$. k mainly derived from induction time modelling of a 11 step mechanism.

(e) Study of n-heptane/O$_2$/Ar mixtures behind incident and reflected shock waves. Monitored IR emission from CO, CO$_2$, and chemiluminescence from OH, CH, and C$_2$.

(f) Evaluation of literature data.

(g) Evaluation of literature data. RRKM calculation of fall-off curve (misprinted table).

Preferred Values

$k_0 = 6.9 \cdot 10^{17} \ T^{-7.5} \exp(-22900/T) \text{ cm}^{-3} \text{ molecule}^{-1} \text{ s}^{-1}$
over range 500–2500 K (in Ar and N$_2$)
$k_\infty = 2 \cdot 10^{14}\exp(-20000/T) \text{ s}^{-1}$ over range 500–2500 K
$F_c = 0.35$ over range 500–2500 K

Reliability
$\Delta \log k_0 = \pm 0.5$ over range 500–2500 K
$\Delta \log k_\infty = \pm 0.5$ over range 500–2500 K
$\Delta F_c = \pm 0.1$ over range 500–2500 K

Comments on Preferred Values
There are no sufficiently direct measurements for this reaction. The preferred value for k_0 follows the analysis by Tsang and Hampson[7] based on a RRKM fit of the reverse reaction. The preferred value for k_∞ follows the evaluation by Warnatz [6]. An RRKM modelling of the reaction from this evaluation with the potential energy surface calculated by Harding *et al.*[8] leads to $k_\infty = 1.1 \cdot 10^{14}\exp(-20000/T) \text{ s}^{-1}$ which is sufficiently close to the recommended value. As long as no more direct measurement are available, more elaborate specification of the T dependence of F_c appears premature.

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[3] J. Peeters and G. Mahnen, Comb. Inst. Europ. Symp., 53 (1973).
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[7] W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data 15, 1087 (1987).
[8] L. B. Harding, A. F. Wagner, J. M. Bowman, G. C. Schatz, and K. Christoffel, J. Phys. Chem. 86, 4312 (1982).

$$C_2H_3 + O_2 \rightarrow C_2H_2 + HO_2 \quad (1)$$
$$\rightarrow H_2CO + CHO \quad (2)$$
$$\rightarrow C_2H_3O_2 \quad (3)$$
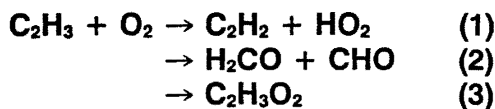
Thermodynamic Data

ΔH^o_{298} (1) $= -49$ kJ mol^{-1}
ΔS^o_{298} (1) $= -6.7$ J K^{-1}mol^{-1}
K_p(1) $= 1.69 \cdot 10^{-2} \, T^{0.55} \exp(+5940/T)$

ΔH^o_{298} (2) $= -360$ kJ mol^{-1}
ΔS^o_{298} (2) $= 6.6$ J K^{-1}mol^{-1}
K_p(2) $= 23.1 \, T^{-0.33} \exp(+43000/T)$

No thermodynamic data available for channel (3)

Rate Coefficient Data ($k = k_1 + k_2 + k_3$)

k[cm^3 molecule^{-1} s^{-1}]	T [K]	Reference	Comments
Rate Coefficient Measurements			
$k_1 = 1.7 \cdot 10^{-12}$	1726	Cooke and Williams (1971)[1]	(a)
$k_2 = 6.6 \cdot 10^{-12} \exp(+125/T)$	291–602	Slagle et al. (1984)[2]	(b)
$k = 1.0 \cdot 10^{-11}$	298	Krueger and Weitz (1988)[3]	(c)
$k_3 = 2.5 \cdot 10^{-12}$	298	Munk et al. (1987)[4]	(d)
Reviews and Evaluations			
$k_1 = 1.7 \cdot 10^{-12}$	1000–2000	Warnatz (1984)[5]	(e)
$k_1 = 2.0 \cdot 10^{-13}$	–	Tsang and Hampson (1986)[6]	(f)
$k_3 = 1.0 \cdot 10^{-11}$	–		

Comments

(a) Shock tube study of C_2H_4, $CH_4 + O_2$ mixtures. Based on simulation of reaction mechanism.

(b) Excimer laser flash photolysis (193 nm) – photoionisation mass spectrometry at 0.76–3.60 Torr. Monitored C_2H_3, CHO, H_2CO. No signals corresponding to products of channel (1), therefore $k_1 \ll k_2$. Similar conclusion by Baldwin and Walker[7].

(c) Excimer laser flash photolysis (248 nm) – diode laser spectroscopy on C_2H_4 in $C_2H_3I/HCl/O_2$ mixtures at ≈ 7 Torr.

(d) Pulse radiolysis with variety C_2H_3 precursors, pressure ≈ 1 atm. Monitored disappearance of C_2H_3 and the build-up of a long-lived product at 230 and 270 nm. Latter ascribed to a product X of $C_2H_3 + O_2$, presumed to be $C_2H_3O_2$; the rate coefficient was deduced from the product build-up.

(e) Based on the observation that HO_2 forming reactions of R $+ O_2$ have small pre-exponential factors of $\approx 2 \cdot 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

(f) Determined by analogy with C_2H_5.

Preferred Values

$k_2 = 9.0 \cdot 10^{-12}$ cm^3 molecule^{-1} s^{-1} over range 300–2000 K

Reliability

$\Delta \log k_2 = \pm 0.3$ over range 300–600 K; ± 0.5 over range 600–2000 K

Comments on Preferred Values

There is no direct evidence for the involvement of channel (1). There is excellent agreement between the data of Slagle et al.[2] and Krueger and Weitz[3]. It is curious that Munk et al.[4] record a slower reaction at higher pressures; it is possible that they were not observing the formation of $C_2H_3O_2$ but of a secondary product.

References

[1] D. F. Cooke and A. Williams, 13th Symp. (Int.) Combust., 757 (1971).
[2] I. R. Slagle, J.-Y. Park, M. C. Heaven, and D. Gutman, J. Am. Chem. Soc. **106**, 4356 (1984).
[3] H. Krueger and E. Weitz, J. Chem. Phys. **88**, 1608 (1988).
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$$C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2 \quad (1)$$
$$\rightarrow C_2H_5O_2 \quad (2)$$

Thermodynamic Data

$\Delta H^\circ_{298} (1) = -54.3 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} (1) = -8.5 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p(1) = 1.19 \cdot 10^{-1} \, T^{0.183} \exp(+6550/T)$

Rate Coefficient Data ($k = k_1 + k_2$)

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	$T[\text{ K }]$	Reference	Comments
Rate Coefficient Measurements			
$k_1 = 2.1 \cdot 10^{-13}$	295	Plumb and Ryan (1981)[1]	(a)
$1.5 \cdot 10^{-14} \exp(+1660/T)$	294–1002	Slagle, Feng, and Gutman (1984)[2]	(b)
$k_1 = 1.8 \cdot 10^{-14} \exp(+760/T)$	593–753	McAdam and Walker (1987)[3]	(c)
$k_1/k_2 < 0.01$	298	Niki *et al.* (1982)[4]	(d)
Reviews and Evaluations			
$k_1 = 2 \cdot 10^{-13}$	298	CODATA (1984)	(e)
$k_1 = 3.3 \cdot 10^{-12} \exp(-2510/T)$	700 2000	Warnatz (1984)	(f)
$k_1 = 1.4 \cdot 10^{-12} \exp(-1950/T)$	300–2500	Tsang and Hampson (1986)	(g)

Comments

(a) Discharge-flow system with He carrier gas. C_2H_5 produced from Cl + C_2H_5 and [C_2H_6] and [C_2H_4] measured directly by mass spectrometry. Rate coefficient determined from yields of C_2H_4 and shown to be independent of pressure over range 0.6–10 Torr.

(b) Slow-flow system, radicals produced by Cl + C_2H_6 reaction with pulsed formation of Cl from IR multiphoton induced decomposition of $CFCl_3$. Reactants and products monitored in real time using photoionization mass spectrometry. Rate expression has been calculated here from high-pressure values of k for the overall reaction.

(c) Thermal oxidation of C_2H_5CHO in a static system. Yields of C_2H_4 and C_2H_6 were determined by GC analysis for the early stages of the reaction. Ratio of rate coefficients determined to be $k_1/k(C_2H_5 + C_2H_5CHO) = 6.76 \cdot 10^{-2} \exp(+4414/T)$. The above value of k_1 is derived by taking $k(C_2H_5 + C_2H_5CHO) = 2.7 \cdot 10^{-13} \exp(-3656/T)$ cm³ molecule⁻¹ s⁻¹ as evaluated by McAdam and Walker[3] from literature data.

(d) FTIR study of the photo-oxidation of C_2H_6 initiated by Cl_2 in the presence of O_2/N_2 mixtures at total pressures of 760 Torr. Rate coefficient ratio derived from the analysis of CH_3CHO, C_2H_5OH and C_2H_4 products.

(e) Based on data of Plumb and Ryan[1].

(f) Based on an analysis of data prior to study of Plumb and Ryan[1].

(g) Based on data of Baldwin *et al.*[7].

Preferred Values

$k_1 = 1.7 \cdot 10^{-14} \exp(+1100/T)$ cm³ molecule⁻¹ s⁻¹ over range 600–1200 K

Reliability

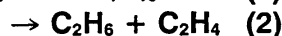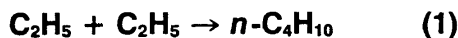$\Delta \log k_1 = \pm 0.3$ over range 600–1200 K

Comments on Preferred Values

For temperatures about 600 K we have chosen to represent k_1, by a compromise between the results reported by McAdam and Walker[3] and those we have derived from the data of Slagle *et al.*[2].

Over the wider temperature range 300–1000 K a recent experimental and theoretical study by Wagner *et al.*[8] recommends a mechanism involving activated $C_2H_5O_2^*$ radicals and its isomerization to $C_2H_4O_2H^*$ radicals, followed by decomposition of this radical to the products C_2H_4 and HO_2. These authors have also derived complicated analytical functional forms to their mechanism to explain the observed rate dependences over the temperature range 300–1000 K. More work is required to confirm the details of the mechanism of the $C_2H_5 + O_2$ reaction.

References

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$$C_2H_5 + C_2H_5 \rightarrow n\text{-}C_4H_{10} \quad (1)$$
$$\rightarrow C_2H_6 + C_2H_4 \quad (2)$$

Thermodynamic Data

ΔH°_{298} (1) $= -296$ kJ mol^{-1}
ΔS°_{298} (1) $= -160.4$ kJ mol^{-1}

ΔH°_{298} (2) $= -266$ kJ mol^{-1}
ΔS°_{298} (2) $= -55.1$ J K^{-1}mol^{-1}
K_p(2) $= 1.87 \cdot 10^{-5}$ $T^{0.628}$ exp($+3220/T$)

Rate Coefficient Data ($k = k_1 + k_2$)

k[cm^3 molecule^{-1} s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$1.5 \cdot 10^{-11}$	296	Parkes and Quinn (1976)[1]	(a)
$2.4 \cdot 10^{-11}$	296	Adachi, Basco, and James (1979)[2]	(b)
$9.3 \cdot 10^{-12}$	803	Corbel, Marquaire, and Côme (1981)[3]	(c)
$2.0 \cdot 10^{-11}$	296	Demissy and Lesclaux (1982)[4]	(d)
$2.2 \cdot 10^{-11}$	903	Pacey and Wimalasena (1984)[5]	(e)
$1.9 \cdot 10^{-11}$	296	Munk et al. (1986)[6]	(f)
$1.63 \cdot 10^{-11}$	300–373	Arthur (1986)[7]	(g)
$1.69 \cdot 10^{-11}$	308	Anastasi and Arthur (1987)[8]	(h)
Reviews and Evaluations			
$k_1 = 2.3 \cdot 10^{-12}$	300–1250	Warnatz (1984)[9]	(ı)
$k_1 = 1.8 \cdot 10^{-11}$	300–2500	Tsang and Hampson (1986)[10]	(i)
$k_2 = 2.3 \cdot 10^{-12}$	300–2500		

Comments

(a) Molecular modulation spectroscopic study. C_2H_5 produced from photolysis of $(C_2H_5N)_2$ in presence of N_2 and monitored by UV absorption spectroscopy. k obtained from computer simulation of concentration profiles.

(b) Flash photolysis of mixtures of $(C_2H_5N)_2$ and n-C_5H_{12}. [C_2H_5] monitored by UV absorption spectroscopy.

(c) Pyrolysis of C_2H_6 in a continuous-flow stirred-tank reactor with end-product analyses by GC. k determined from a fit of rates of formation of C_2H_4 as a function of residence time in the reactor, based on a mechanism of 6 elementary reactions.

(d) Flash photolysis – laser resonance absorption study of NH_2 reactions in presence of C_2H_5. NH_2 produced from photolysis of NH_3, and [NH_2] monitored by absorption at 597.73 nm. C_2H_5 produced from H + C_2H_4. k(NH_2 + C_2H_5) and k(C_2H_5 + C_2H_5) derived from a fit of [NH_2] profiles.

(e) Pyrolysis of C_2H_6 in a flow system with end-product analyses by GC. k determined from a fit of the rates of formation of C_2H_4 as a function of residence time in the reactor, based on a mechanism of 12 elementary reactions. Preliminary results: P.D. Pacey and J.H. Wimalasena, Chem. Phys. Lett. **76**, 433 (1980).

(f) Pulse radiolysis study with [C_2H_5] monitored by UV absorption. C_2H_5 produced from H + C_2H_4. k derived from computer simulations of [C_2H_5] profiles in real time.

(g) Same experimental procedure as for comment (a).

(h) Same experimental procedure as for comment (a), preliminary results reported by N.L. Arthur and C. Anastasi, Bull. Soc. Chim. Belg. **92**, 647 (1983).

(i) Based on literature data prior to 1981.

Preferred Values

$k_\infty = 1.9 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1} over range 300–1200 K
$k_2 = 2.4 \cdot 10^{-12}$ cm^3 molecule^{-1} s^{-1} over range 300–1200 K

Reliability
$\Delta \log k_1 = \pm 0.3$ over range 300–1200 K
$\Delta \log k_2 = \pm 0.4$ over range 300–1200 K

Comments on Preferred Values

The preferred rate coefficient is the mean of the results of Parkes and Quinn[1], Adachi et al.[2], Demissy and Lesclaux[4], Pacey and Wimalasena[5], Munk et al.[6], Arthur[7], and Anastasi and Arthur[8] which are all in substantial agreement. The preferred branching ratio, k_2/k was then calculated from the disproportionation-combination ratio, $k_2/k_1 = 0.14$, which is widely accepted[11] at low temperatures and which appears to be applicable at higher temperatures as well[12].

There are very few reliable studies of this reaction at temperatures above 1200 K, hence the restricted range over which the preferred rate coefficients are recommended.

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$$C_2H_5 + C_2H_5 \rightarrow n\text{-}C_4H_{10}$$
$$\rightarrow C_2H_6 + C_2H_4$$

T/K

EXPERIMENTAL DATA

□ Parkes and Quinn 1976
■ Adachi et al 1979
△ Corbel et al 1981
▲ Demissy and Lesclaux 1982
○ Pacey and Wimalasena 1984
● Monk et al 1986
—— Arthur 1986
▲ Anastasi and Arthur 1987

—— This Recommendation (k1) 1989

—— This Recommendation (k2) 1989

(k1)

(k2)

$\text{Log}(k/cm^3 molecule^{-1}s^{-1})$

$10^3T^{-1}/K^{-1}$

$C_2H_6(+M) \rightarrow CH_3 + CH_3(+M)$
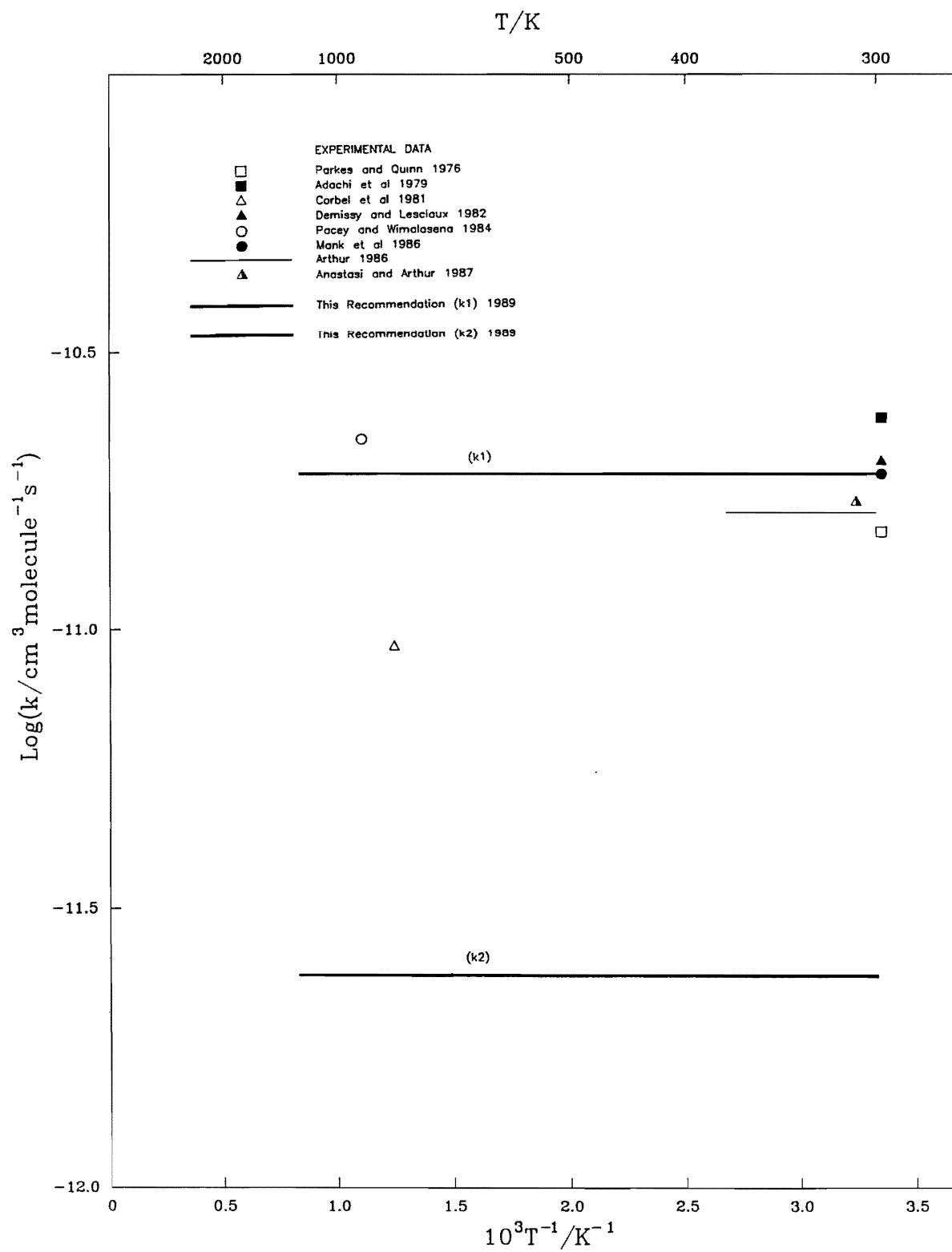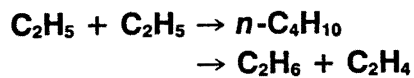
Thermodynamic Data

$\Delta H^\circ_{298} = 375 \text{ kJ mol}^{-1}$

$\Delta S^\circ_{298} = 159 \text{ J K}^{-1}\text{mol}^{-1}$

$K_p = 4.15 \cdot 10^9 \ T^{-0.236} \exp(-45700/T)\text{atm}$

Rate Coefficient Data

$k[\text{s}^{-1}]$	$T[\text{K}]$	[M] [molecule cm^{-3}]	Reference	Comments
Rate Coefficient Measurements				
Intermediate Fall-off Range				
$1.2 \cdot 10^{-7}$	823	$7.9 \cdot 10^{16}$ (C_2H_6)	Lin and Back (1966)[1]	(a)
$1.3 \cdot 10^{-7}$		$1.9 \cdot 10^{17}$		
$1.4 \cdot 10^{-7}$		$7.0 \cdot 10^{17}$		
$6.7 \cdot 10^{-6}$	893	$4.4 \cdot 10^{17}$		
$8.4 \cdot 10^{-6}$		$2.3 \cdot 10^{18}$		
$8.9 \cdot 10^{-6}$		$4.9 \cdot 10^{18}$		
$1.7 \cdot 10^{-4}$	999	$9.7 \cdot 10^{15}$		
$5.7 \cdot 10^{-4}$		$1.1 \cdot 10^{17}$		
$1.0 \cdot 10^{-3}$		$8.2 \cdot 10^{17}$		
$4.1 \cdot 10^{-7}$	839	$7.6 \cdot 10^{15}$ (C_2H_6)	Trenwith (1966,1967,1979)[2]	(b)
$1.5 \cdot 10^{-7}$		$1.3 \cdot 10^{17}$		
$2.5 \cdot 10^{-7}$		$3.2 \cdot 10^{18}$		
$2.3 \cdot 10^{-3}$	873	$5.1 \cdot 10^{15}$		
$1.2 \cdot 10^{-6}$		$1.1 \cdot 10^{17}$		
$1.9 \cdot 10^{-6}$		$1.6 \cdot 10^{18}$		
$4.8 \cdot 10^{-6}$	913	$3.4 \cdot 10^{16}$		
$1.7 \cdot 10^{-5}$		$8.8 \cdot 10^{17}$		
$2.4 \cdot 10^{-5}$		$7.0 \cdot 10^{18}$		
$3.5 \cdot 10^{-8}$	813	$1.2 \cdot 10^{17}$ (C_2H_6)	Scacchi *et al.* (1971)[3]	(c)
$5.8 \cdot 10^{-8}$		$6.2 \cdot 10^{17}$		
$7.7 \cdot 10^{-8}$		$2.5 \cdot 10^{18}$		
$2.0 \cdot 10^{15} \exp(-44280/T)$	1400–2200	$5.0 \cdot 10^{17}$ (Ar)	Izod *et al.* (1971)[4]	(d)
$2.1 \cdot 10^{-7}$	838	$3.0 \cdot 10^{17}$ (C_2H_6)	Clark and Quinn (1976)[5]	(e)
$4.2 \cdot 10^{-7}$		$7.6 \cdot 10^{18}$		
$4.8 \cdot 10^{-7}$		$2.1 \cdot 10^{19}$		
	1300–2500	$(6.6-26.5) \cdot 10^{17}$ (Ar)	Olson *et al.* (1979)[6]	(f)
$2.8 \cdot 10^{15} \exp(-42400/T)$	1240–1500	$1.3 \cdot 10^{16}$ (Ar)	Chiang and Skinner (1981)[7]	(g)
$2.0 \cdot 10^{-7}$	841	$1.1 \cdot 10^{17}$ (C_2H_6)	Kanan *et al.* (1983)[8]	(h)
$2.5 \cdot 10^{-7}$		$2.1 \cdot 10^{17}$		
$7.6 \cdot 10^{-7}$	871	$5.4 \cdot 10^{16}$		
$1.1 \cdot 10^{-6}$		$1.6 \cdot 10^{17}$		
$2.0 \cdot 10^{-6}$		$4.2 \cdot 10^{18}$		
$5.7 \cdot 10^{-6}$	913	$5.2 \cdot 10^{16}$		
$1.3 \cdot 10^{-5}$		$2.0 \cdot 10^{17}$		
$6.2 \cdot 10^{-6}$	902	$1.1 \cdot 10^{17}$ (C_2H_6)	Pacey and Wimalasena (1984)[9]	(i)
$7.0 \cdot 10^{-6}$		$3.2 \cdot 10^{17}$		
$1.1 \cdot 10^{-5}$		$1.1 \cdot 10^{18}$		
$3.4 \cdot 10^{-5}$	938	$5.4 \cdot 10^{17}$ (H_2)	Cao and Back (1984)[10]	(j)
$4.6 \cdot 10^{-5}$		$1.8 \cdot 10^{18}$		
$5.2 \cdot 10^{-5}$		$3.4 \cdot 10^{18}$		
$2.6 \cdot 10^{-4}$	998	$5.1 \cdot 10^{17}$		
$4.2 \cdot 10^{-4}$		$2.0 \cdot 10^{18}$		
$3.6 \cdot 10^{-4}$		$3.2 \cdot 10^{18}$		
$8.0 \cdot 10^{-4}$	1038	$5.0 \cdot 10^{17}$		
$1.1 \cdot 10^{-3}$		$1.1 \cdot 10^{18}$		
$2.4 \cdot 10^{-3}$		$2.8 \cdot 10^{18}$		
High Pressure Range				
$7.9 \cdot 10^{16} \exp(-45040/T)$	1200–1430	$(9-33) \cdot 10^{18}$	Burcat *et al.* (1973)[11]	(h)
$5.2 \cdot 10^{16} \exp(-44700/T)$	840–913	$(3.4-77.6) \cdot 10^{17}$ (C_2H_6)	Trenwith (1979)[2]	(b)
Reviews and Evaluations				
$k_\infty = 2.4 \cdot 10^{16} \exp(-44010/T)$	750–1500		Baulch and Duxbury (1980)[12]	(l)
$k_0 = [\text{Ar}] \ 1.7 \cdot 10^{-5} \exp(-34280/T)$	800–2500		Warnatz (1984)[13]	(m)
$k_\infty = 2.4 \cdot 10^{16} \exp(-44020/T)$	750–2000			
$k_\infty = 3.2 \cdot 10^{22} \ T^{-1.79} \exp(-45834/T)$	300–1400		Tsang and Hampson (1986)[14]	(n)
$k_\infty = 3.0 \cdot 10^{22} \ T^{-1.79} \exp(-45834/T)$	300–1400		Tsang (1989)[15]	(o)

Comments

(a) Static reactor, dissociation of pure ethane with measurement of the rate of production of methane and butane. Extrapolation to the high pressure limit and comparison with earlier work.

(b) Ethane dissociation studied in static reactor. Product analysis by gas chromatography. Extrapolation to the high pressure limit. Relative efficiencies of different bath gases: $k_0(M)/k_0(C_2H_6)$ = 0.25 (N_2), 0.33 (O_2), 0.17 (He), 0.18 (Ne), 0.26 (Ar), 0.30 (Kr), 0.88 (H_2O).

(c) Pyrolysis of ethane in static reactor. Analysis of initiation of the reaction using manometric and gas chromatographic measurements.

(d) Pyrolysis of CO/O_2/ethane/azomethane/Ar mixtures in a shock tube. The reaction was followed by measuring emission from CO and CO_2. Modelling with 8 reactions.

(e) Static reactor study of dissociation in pure ethane. Gas chromatographic analysis of reaction products.

(f) Shock tube study of ethane dissociation in Ar using laser-absorption and laser-schlieren measurements. Modelling of mechanism. Data near 1300 K are markedly lower than recombination results and shock wave results from Ref. 7. Better agreement with Ref. 7 at higher temperatures. Extrapolation to the high pressure limit uncertain due to fall-off effects.

(g) Shock tube study of ethane decomposition in Ar measuring H atom concentrations from $CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5$, $C_2H_5 \rightarrow C_2H_4 + H$ sequence.

(h) Ethane pyrolysis in static reactor with gas chromatographic analysis. Enhanced hydrogen recombination at activated vessel surface. Results in good agreement with Ref. 2.

(i) Ethane pyrolysis in a flow system with gas chromatographic product analysis. Evaluation of induction periods.

(j) Pyrolysis of ethane in static reactor. Product analysis by gas chromatography. Collision efficiencies of Xe and H_2 relative to C_2H_6 have been measured.

(h) Single-pulse shock tube study of ethane dissociation in Ar, measurement of methane production rate. Analysis of earlier shock tube work, extrapolation to the high pressure limit. Data neglected in later work by one of the authors[7].

(l) Complete review of earlier literature.

(m) Data evaluation and simplified fall-off construction.

(n) Data evaluation and construction of RRKM fall-off curves.

(o) See comment (n).

Preferred Values

k_∞ = $1.8 \cdot 10^{21}$ $T^{-1.24}$ exp($-45700/T$) s^{-1} over range 300–2000 K

k_0 = [Ar] $1.1 \cdot 10^{25}$ $T^{-8.24}$ exp($-47090/T$) s^{-1} over range 300–2000 K

k_0 = [C_2H_6] $4.5 \cdot 10^{-2}$ exp($-41930/T$) s^{-1} over range 800–1000 K

F_c = 0.38 exp($-T/73$)} + 0.62 exp($-T/1180$) for M = Ar over range 300–2000 K

F_c = 0.54 exp($-T/1250$) for M = C_2H_6 over range 800–1000 K

Reliability

$\Delta\log k_\infty$ = $\pm$ 0.3 over range 300–2000 K

$\Delta\log k_0$ = $\pm$ 0.5 for M = Ar over range 300–2000 K

$\Delta\log k_0$ = $\pm$ 0.5 for M = C_2H_6 over range 800–1000 K
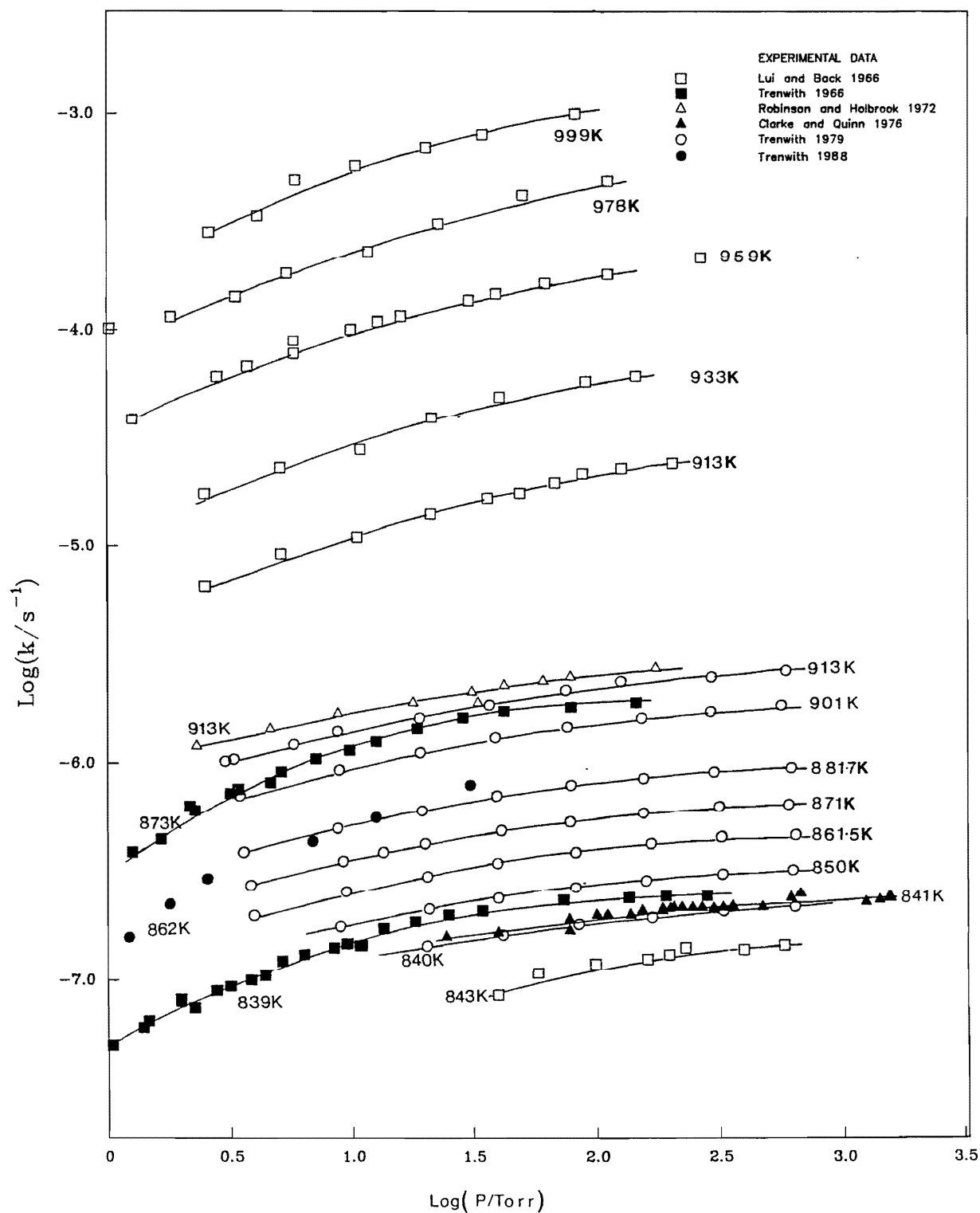
ΔF_c = $\pm$ 0.1 for M = Ar over range 300–2000 K

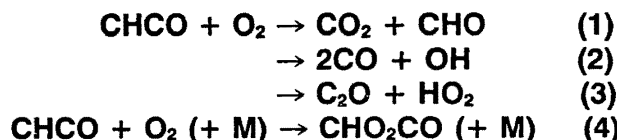ΔF_c = $\pm$ 0.1 for M = C_2H_6 over range 800–1000 K

Comments on Preferred Values

The preferred values for k_∞ and k_0 (for M = Ar) have been derived from the recommended rate coefficients of the reverse reaction 2 CH_3 + M $\rightarrow$ C_2H_6 + M from this evaluation and the given expression of the equilibrium constant. They are based on the combined evaluation of dissociation and recombination data given in the review of Ref. 16 which assumes a nearly temperature independent rate coefficient k_∞ for the reverse recombination over the range 300–2000 K. The expressions for k_0 and F_c also follow the combination of experimental and theoretical data analysed in Ref. 16. The preferred values obtained in this way are in good agreement with the available dissociation experiments. They are not influenced by the numerous mechanistic complications of the high temperature shock tube studies of this dissociation.

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$C_2H_6 + M \rightarrow CH_3 + CH_3 + M$

$$CHCO + O_2 \rightarrow CO_2 + CHO \qquad (1)$$
$$\rightarrow 2CO + OH \qquad (2)$$
$$\rightarrow C_2O + HO_2 \qquad (3)$$
$$CHCO + O_2 (+ M) \rightarrow CHO_2CO (+ M) \qquad (4)$$

Thermodynamic Data

$\Delta H^\circ_{298} (1) = -527.6$ kJ mol^{-1}
$\Delta S^\circ_{298} (1) = -20.9$ J K^{-1}mol^{-1}
$K_p(1) = 0.847 \ T^{-0.041} \exp(+63459/T)$

$\Delta H^\circ_{298} (2) = -359.7$ kJ mol^{-1}
$\Delta S^\circ_{298} (2) = 119.5$ J K^{-1}mol^{-1}
$K_p(2) = 7.17 \cdot 10^8 \ T^{-0.081} \exp(+42842/T)$atm

Rate Coefficient Data ($k = k_1 + k_2 + k_3 + k_4$)

k[cm^3 molecule^{-1} s^{-1}]	Temperature [K]	Reference	Comments
Rate Coefficient Measurements			
$3.7 \cdot 10^{-14}$	296	Jones and Bayes (1973)[1]	(a)
($M = N_2$, 2 Torr)			
$2.7 \cdot 10^{-12} \exp(-430/T)$	–	Peeters, Schaekers,	
($M = $ He, 2 Torr)		and Vinckier (1986)[2]	(b)

Comments

(a) Discharge flow study; O atoms generated by N + NO. CHCO produced as intermediate from C$_2$H$_2$ with [CHCO] and [O] measured by photoionisation mass spectrometry. [CHCO] measured in presence and absence of O$_2$, and k(CHCO + O$_2$)/k(CHCO + O) = 0.018 ± 0.003 at 296 K obtained from a Stern-Volmer plot. Used k(CHCO + O) = $2.0 \cdot 10^{-12}$ cm^3 molecule^{-1} s^{-1}, obtained by Jones and Bayes[3] in a related study. Data obtained at total pressures of 2 Torr (mostly N$_2$).

(b) Reported by Peeters, Schaekers, and Vinckier[2]. No experimental details given. Radical concentrations measured by molecular beam mass spectroscopy. [CHCO]-time profile measured in presence and absence of molecular O$_2$. No temperature range quoted, but Peeters et al.[4] use the expression in the range 300–550 K.

Preferred Values

$k = 2.7 \cdot 10^{-12} \exp(-430/T)$ cm^3 molecule^{-1} s^{-1} over range 300–550 K (M = He, 2 Torr)

Reliability

$\Delta \log k = \pm 0.7$ over range 300–550 K

Comments on Preferred Values

Kinetic data on this reaction are very limited, and no products have been suggested. k may be pressure-dependent, although no dependency was reported. Both studies involved total pressures of about 2 Torr, but different inert gases. The k values differ by a factor of about 20 at 296 K, but use of k(CHCO + O) = $1.16 \cdot 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 296 K obtained by Vinckier et al.[4] with Jones and Bayes' ratio gives $k = 2.1 \cdot 10^{-12}$ cm^3 molecule^{-1} s^{-1} which is only a factor of 3 greater than $k = 6.3 \cdot 10^{-13}$ cm^3 molecule^{-1} s^{-1} obtained from the expression given by Peeters et al.[2]. This factor is probably within the combined experimental error involved in the two determinations, particularly as experimental conditions are uncertain.

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$$CH_2CHO + O_2 \rightarrow CH_2CO + HO_2 \quad (1)$$
$$\rightarrow HCHO + CO + OH \quad (2)$$
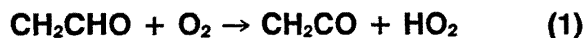
Thermodynamic Data

ΔH°_{298} (1) = -66.5 kJ mol^{-1}
ΔS°_{298} (1) = -20.5 J K^{-1}mol^{-1}
$K_p(1)$ = $0.344\ T^{0.592}\ \exp(+7960/T)$

ΔH°_{298} (2) = -212.6 kJ mol^{-1}
ΔS°_{298} (2) = 126.7 J K^{-1}mol^{-1}
$K_p(2)$ = $5.5 \cdot 10^8\ T^{-0.62}\ \exp(+25160/T)$ atm

Rate Coefficient Data $(k = k_1 + k_2)$

k[cm^3 molecule^{-1} s^{-1}]		T [K]	Reference	Comments
Rate Coefficient Measurements				
$2.7 \cdot 10^{-14}\ \exp(+668/T)$ (100 Torr He)		300–500	Lorenz *et al.* (1984)[1]	(a)
$2.46 \cdot 10^{-13}$	(100 Torr N$_2$)	295	Gutman and Nelson (1983)[2]	(b)
$2.50 \cdot 10^{-13}$	(90 Torr SF$_6$)	295		

Comments

(a) Laser photolysis of CH$_3$OCH=CH$_2$ at 193 nm; laser induced fluorescence detection of CH$_2$CHO at 337 nm. Reaction is pressure dependent between 10 and 280 mbar (M = He). Fall-off curve analysis using F_c = 0.6 gave k_∞ = $(2.6 \pm 0.5) \cdot 10^{-13}$ cm^3 molecule^{-1} s^{-1} and k_0 = $2 \pm 2 \cdot 10^{-30}$ cm^6 molecule^{-2} s^{-1}. Yield of OH product = 20% as determined by LIF, at 25 mbar He and 298 K.

(b) Laser photolysis of CH$_3$OCH=CH$_2$ at 193 nm; laser induced fluorescence detection of CH$_2$CHO at 337 nm. Reaction is pressure dependent between 1.5 and 100 Torr. Data given are for highest pressures of N$_2$ and SF$_6$ used. Data for lower pressure presented in figure.

Preferred Values

k_∞ = $2.6 \cdot 10^{-13}$ cm^3 molecule^{-1} s^{-1} over range 250–500 K
k_2 = $3.0 \cdot 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 300 K

Reliability

$\Delta \log k_\infty$ = $\pm$ 0.5 at 1000 K reducing to $\pm$ 0.2 at 300 K
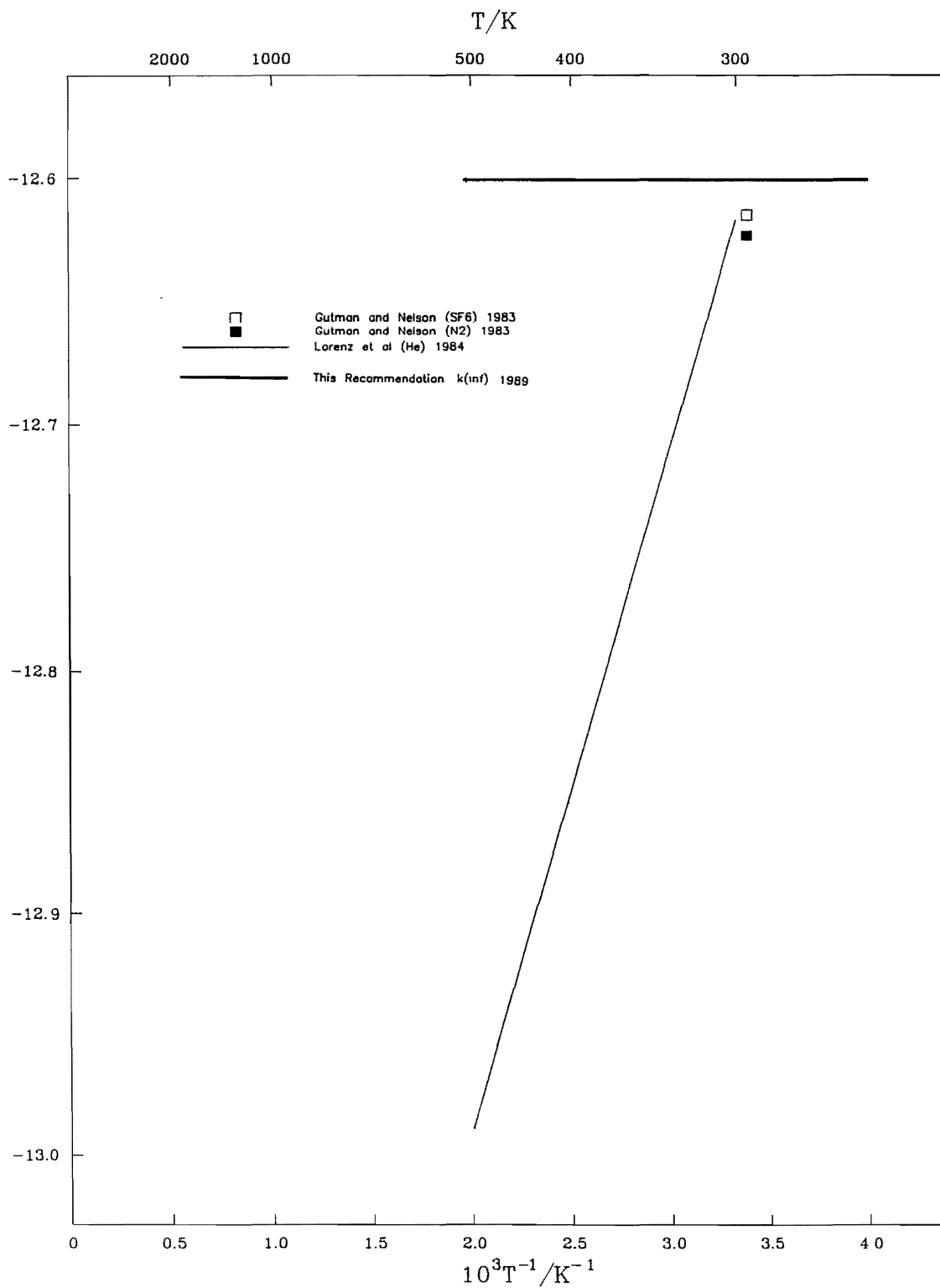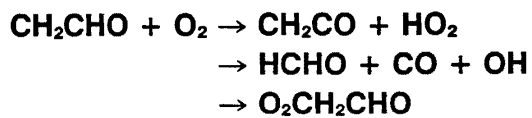$\Delta \log k_2$ = $\pm$ 0.3 at 300 K
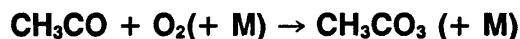
Comments on Preferred Values

The results of the two studies of this reaction using the laser photolysis-LIF technique are in excellent agreement where measurements are under comparable conditions. Both studies show that there is a pressure effect consistent with an addition reaction as one of the channels. The observation of OH product at low pressure indicates a possible bimolecular channel as well. The preferred value for k_∞ is based on the values of k at pressures $\geqslant 100$ Torr He, N$_2$ or SF$_6$ from both studies at 292–300 K. The recommended value of k_2 may apply to low pressures only since the pressure dependence of the OH yield is not established.

The temperature dependence of the rate coefficient at higher temperatures is difficult to define because of fall-off effects. The data indicate little variation of k_∞ with temperature up to 500 K. Lack of data at low pressures and the possibility of a bimolecular channel precludes the recommendation of a value for k_0.

References

[1] K. Lorenz, D. Rhäsa, R. Zellner, and B. Fritz, Ber. Bunsenges. Phys. Chem. **89**, 341 (1985).
[2] D. Gutman and H. H. Nelson, J. Phys. Chem. **87**, 3902 (1983).

$$CH_2CHO + O_2 \rightarrow CH_2CO + HO_2$$
$$\rightarrow HCHO + CO + OH$$
$$\rightarrow O_2CH_2CHO$$

CH₃CO + O₂(+ M) → CH₃CO₃ (+ M)

Rate Coefficient Data

k[cm³ molecule^{-1} s^{-1}]		T[K]	Reference	Comments
Rate Coefficient Measurements				
$2 \cdot 10^{-12}$		298	McDade *et al*. (1982)[1]	(a)
Reviews and Evaluations				
$3 \cdot 10^{-12}$		298	Tsang and Hampson (1986)[2]	(b)
$2 \cdot 10^{-12}$	(1–4 Torr)	298	IUPAC (1989)[3]	(c)
$5 \cdot 10^{-12}$	(k_∞)	200–300		

Comments

(a) Flash photolysis of CH₃COCH₃ or CH₃COCH₂COCH₃–photoionisation mass spectrometric detection of CH₃CO in excess O₂. Independent of pressure 1–4 Torr.

(b) Based on results of McDade *et al*.[1]

(c) Based on results for analogous reaction of C₂H₅ with O₂.

Preferred Values

$k = 2 \cdot 10^{-12}$ cm³ molecule^{-1} s^{-1} at 298 K

Reliability

$\Delta \log k = \pm 0.3$ at 298 K

Comments on Preferred Values

There is only one direct study of this reaction which was conducted at room temperature. The rate coefficient obtained is comparable to that found for the reaction of C₂H₅ under similar conditions. The latter reaction has a substantial negative temperature coefficient, a pressure dependence, and an additional channel forming HO₂. The same complex kinetic behaviour probably applies to CH₃CO + O₂, but in the absence of data, we can only recommend a value for k at 298 K.

References

[1] C. E. McDade, T. M. Lenhardt, and K. D. Bayes, J. Photochem. **20**, 1 (1982).

[2] W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data **15**, 1087 (1986).

[3] R. Atkinson *et al*., IUPAC Task Group on Data Evaluation (1989).

CH₃CHO (+ M) → CH₃ + CHO (+ M)
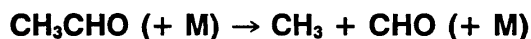
Thermodynamic Data
$\Delta H^\circ_{298} = 361$ kJ mol^{-1}
$\Delta S^\circ_{298} = 117$ J K^{-1}mol^{-1}
$K_p = 5.92 \cdot 10^9 \, T^{-0.417} \exp(-43100/T)$ atm

Rate Coefficient Data

k[s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$2.0 \cdot 10^{15} \exp(-39800/T)$	753–813	Liu and Laidler (1968)[1]	(a)
$7.1 \cdot 10^{15} \exp(-41100/T)$	1000–1200	Colket *et al*. (1975)[2]	(b)
Reviews and Evaluations			
$2.0 \cdot 10^{15} \exp(-39800/T)$	500–2000	Warnatz (1984)[3]	(c)

Comments

(a) Static reactor. Pyrolysis of CH₃CHO; k determined from time dependence of product C₂H₆ and C₂H₄.

(b) Turbulent flow reactor at 1 atm pressure. $M = N_2$. k determined as in (a).

(c) Based on expression of Liu and Laidler[1].

Preferred Values

$k = 7.1 \cdot 10^{15} \exp(-41100/T)$ s^{-1} over range 750–1200 K at 1 atm pressure

Reliability

$\Delta \log k = \pm 0.4$ over range 750–1200 K

Comments on Preferred Values

Preferred value is based on the data of Colket et al.[2] which are in good agreement with the earlier work. The reaction is in the fall-off region in the specified temperature region and the expression applies to 1 atm pressure only.

References

[1]M. T. H. Liu and K. J. Laidler, Can. J. Chem. **46**, 479 (1968).
[2]M. B. Colket, D. W. Naegeli, and I. Glassman, Int. J. Chem. Kin. **7**, 223 (1975).
[3]J. Warnatz, in "Combustion Chemistry", ed. W. C. Gardiner, Springer-Verlag, New York (1984).

$C_2H_5O(+ M) \rightarrow HCHO + CH_3 (+ M)$

Thermodynamic Data

$\Delta H^\circ_{298} = 70.0 \text{ kJ·mol}^{-1}$

Comments

There are no reliable experimental data for the thermal decomposition of C_2H_5O. Leggett and Thynne[1] studied pyrolysis of $(C_2H_5O)_2$ and extracted a rate coefficient for decomposition of C_2H_5O over the range 422–449 K of $1.4 \cdot 10^{12} \exp(-11120/T)$ s^{-1}, independent of pressure. Since the reaction is almost certainly in the fall-off region

under their conditions, this result is doubtful. In a recent review, Batt[2] has suggested the following expression for the high pressure limit: $k_\infty = 8.0 \cdot 10^{13} \exp(-10830/T)$ s^{-1}.

References

[1]C. Leggett and J. C. J. Thynne, Trans. Faraday Soc. **63**, 2504 (1967).
[2]L. Batt, Int. Rev. Phys. Chem. **6**, 53 (1987).

$C_2H_5O + O_2 \rightarrow CH_3CHO + HO_2$

Thermodynamic Data

$\Delta H^\circ_{298} = -152.5 \text{ kJ·mol}^{-1}$

Rate Coefficient Data

$k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$	T [K]	Reference	Comments
Rate Coefficient Measurements			
$8.0 \cdot 10^{-15}$	296	Gutman, Sanders, and Butler (1982)[1]	(a)
$9.8 \cdot 10^{-15}$	353		
$1.2 \cdot 10^{-13} \exp(-924/T)$	225–393	Zabarnick and Heicklen (1985)[2]	(b)
Reviews and Evaluations			
$8.0 \cdot 10^{-15}$	298	CODATA (1984)[3]	(c)

Comments

(a) Laser photolysis of C_2H_5ONO at 266 nm; C_2H_5O monitored by LIF. Psuedo first order conditions with excess O_2.

(b) Steady state photolysis of C_2H_5ONO at 366 nm in the presence of O_2 and NO. k measured relative to $C_2H_5O + NO \rightarrow$ products; i.e. $k/k(C_2H_5O + NO) = 6.8 \cdot 10^{-3} \exp(-924/T)$. Pressure > 155 Torr, $M = N_2$.

(c) Based on data of Gutman et al.[1].

Preferred Values

$k = 1.0 \cdot 10^{-13} \exp(-830/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over range 300–1000 K

Reliability

$\Delta \log k = \pm 0.3$ at 300 K rising to ± 0.5 at 1000 K

Comments on Preferred Values

The only direct measurements of k from Ref. 1 agree reasonably well with the recent relative rate study, but show a smaller temperature dependence, although the range of temperature covered is small. In view of the limited range covered and the uncertainties in the measurements, we recommend an Arrhenius expression based on an average of k values from the two studies at 353 K and an A-factor equal to that for the $CH_3O + O_2$ reaction.

References

[1]D. Gutman, N. Sanders, and J. E. Butler, J. Phys. Chem. **86**, 66 (1982).
[2]S. Zabarnick and J. Heicklen, Int. J. Chem. Kin. **18**, 455 (1985).
[3]CODATA evaluation, Supplement II, J. Phys. Chem. Ref. Data **13**, 1259 (1984).
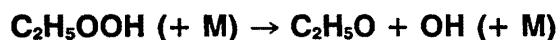
C_2H_5OOH (+ M) → C_2H_5O + OH (+ M)

Thermodynamic Data

$\Delta H^\circ_{298} = 180.0$ kJ mol^{-1}

Comment

There are no experimental data for the thermal decomposition of C_2H_5OOH. The high pressure limit rate constant $k_\infty = 4.0 \cdot 10^{15} \exp(-21600/T)$ s^{-1} is recommended by analogy with the decomposition of CH_3OOH.

C_6H_5(+ M) → C_2H_2 + C_4H_3(+ M)   (1)
→ C_2H_3 + C_4H_2 (+ M)   (2)
→ linear-C_6H_5 (+ M)   (3)
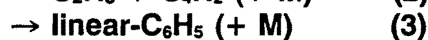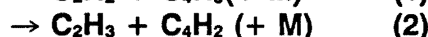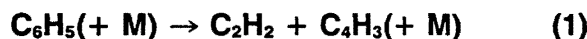
Thermodynamic Data

ΔH°_{298} (1) = 325.0 kJ mol^{-1}

ΔS°_{298} (1) = 185.6 J K^{-1}mol^{-1}

K_p(1) = $9.7 \cdot 10^9$ $T^{0.16}$ exp(39600/T) atm

ΔH°_{298} (2) = 425.2 kJ mol^{-1}

ΔS°_{298} (2) = 193.3 J K^{-1}mol^{-1}

K_p(2) = $9.2 \cdot 10^{10}$ $T^{-0.06}$ exp(-51680/T) atm

ΔH°_{298} (3) = 97.2 kJ mol^{-1}

ΔS°_{298} (3) = 261.9 J K^{-1}mol^{-1}

K_p(3) = $7.9 \cdot 10^{25}$ $T^{-3.56}$ exp($-41176/T$)

Rate Coefficient Data ($k = k_1 + k_2 + k_3$)

k[s^{-1}]	T[K]	Reference	Comments
Rate Coefficient Measurements			
$k_1 + k_2 = 1.2 \cdot 10^{15} \exp(-41265/T)$	1570–1790	Rao and Skinner (1984)[1]	(a)
$k_1 = 1.6 \cdot 10^{15} \exp(-41265/T)$	1900–2400	Kiefer *et al*. (1985)[2]	(b)
$k_3 = 3.5 \cdot 10^{13} \exp(-32700/T)$	1500–2400	Colket (1987)[3]	(c)
$5.0 \cdot 10^{13} \exp(-36736/T)$	1500–1900	Rao and Skinner (1988)[4]	(d)
$k_3 = 3.0 \cdot 10^{13} \exp(-36736/T)$	1500–1900		(e)
$k_3 = 4.5 \cdot 10^{13} \exp(-36500/T)$	1450–1730	Braun-Unkhoff *et al*. (1989)[5]	(f)

Comments

(a) Dissociation of chlorobenzene behind reflected shock waves at total pressures of about 2.7 bar. Hydrogen atom production was monitored by ARAS during pyrolysis of 10 ppm chlorobenzene in argon. From the measured profiles it was deduced that the hydrogen atoms are formed in a secondary reaction step. Therefore it was not possible to discriminate between reaction pathway (1) or (2). An Arrhenius expression is evaluated for the overall process $C_6H_5 \rightarrow C_2H_2 + C_4H_2 + H$.

(b) Mixtures of 1 and 2 mol% benzene in krypton have been studied in a shock tube at $0.2 < p < 1$ atm using the laser schlieren technique. The measured density gradient profiles and some time-of-flight mass spectra were modelled by a 26 step reaction mechanism. RRKM calculations are also presented. A high pressure limiting rate coefficient for reaction pathway (1) was derived at total pressures around 1 bar. For total pressures of 0.47 and 0.2 bar second-order rate coefficient expressions are deduced, indicating significant fall-off behaviour for the lower pressure regime.

(c) Single-pulse shock tube experiments on acetylene and vinylacetylene pyrolysis for the temperature range 1100–2400 K at total pressures of about 8 bar. Initial concentrations of the hydrocarbon in argon ranged from 100 ppm to 4%. Gas samples were collected and analyzed using gas chromatography. The rate coefficients for the ring formation process n-C_4H_3 (+ C_2H_2) → linear-C_6H_5 → C_6H_5 were deduced by applying a comprehensive reaction mechanism. The rate coefficient for reaction (3) was calculated using a heat of formation for the linear-C_4H_3 radical of 582 kJ/mol. No sensitivity calculations of reaction (3) are given.

(d) Highly dilute mixtures of C_6D_6, C_6H_5Cl, C_6H_5Br, and C_6H_5I were pyrolyzed behind incident shock waves at $p = 0.4$ atm. The formation of H and D atoms was monitored by the ARAS technique. RRKM calculations were carried out to evaluate unimolecular fall-off rate expressions. Rate coefficient expressions for the dissociation of phenyl radicals were deduced from the pyrolysis of chloro- and bromobenzene. From these experiments it was found that about 18% of the phenyl radicals dissociate in some way without formation of H atoms, while the remainder produces

hydrogen atoms, presumably via a linear-C_6H_5 radical.

(e) Experimental conditions of (d). From the iodobenzene results it was found necessary to introduce additional reactions into the model, especially the dissociation of iodobenzene into phenyl and iodine atoms, which has been measured by Robaugh and Tsang[6]. RRKM caculations indicate that the phenyl dissociation should proceed with a rate constant approaching the limiting high pressure value.

(f) Dissociation of phenyl radicals behind reflected shock waves has been investigated by monitoring H atoms with ARAS. The density range was (1.0–1.7)$\cdot 10^{-5}$ mol cm^{-3}. Nitrosobenzene C_6H_5NO served as thermal source for the phenyl radicals. The test gas mixtures consisted of argon with relative concentrations of 1 to 100 ppm nitrosobenzene. For a first order formation rate in the early stage of the phenyl decomposition a value for the activation energy of 306 ± 8 kJ/mol was found. From thermodynamic data together with the experimental value for the activation energy it is impossible to attribute the high temperature H-atom formation to a direct decomposition pathway of phenyl. Therefore a two step reaction mechanism, starting with isomerisation from the aromatic phenyl to a linear structure, which dissociates immediately to products which include H atoms, has been assumed. The experimental rate expression for the isomerisation reaction is in good accord with the findings of Ref. 4.

Preferred Values

$k_3 = 4.0\cdot 10^{13} \exp(-36700/T)$ s^{-1} over range 1450–1900 K
Presumably not far from k_∞

Reliability
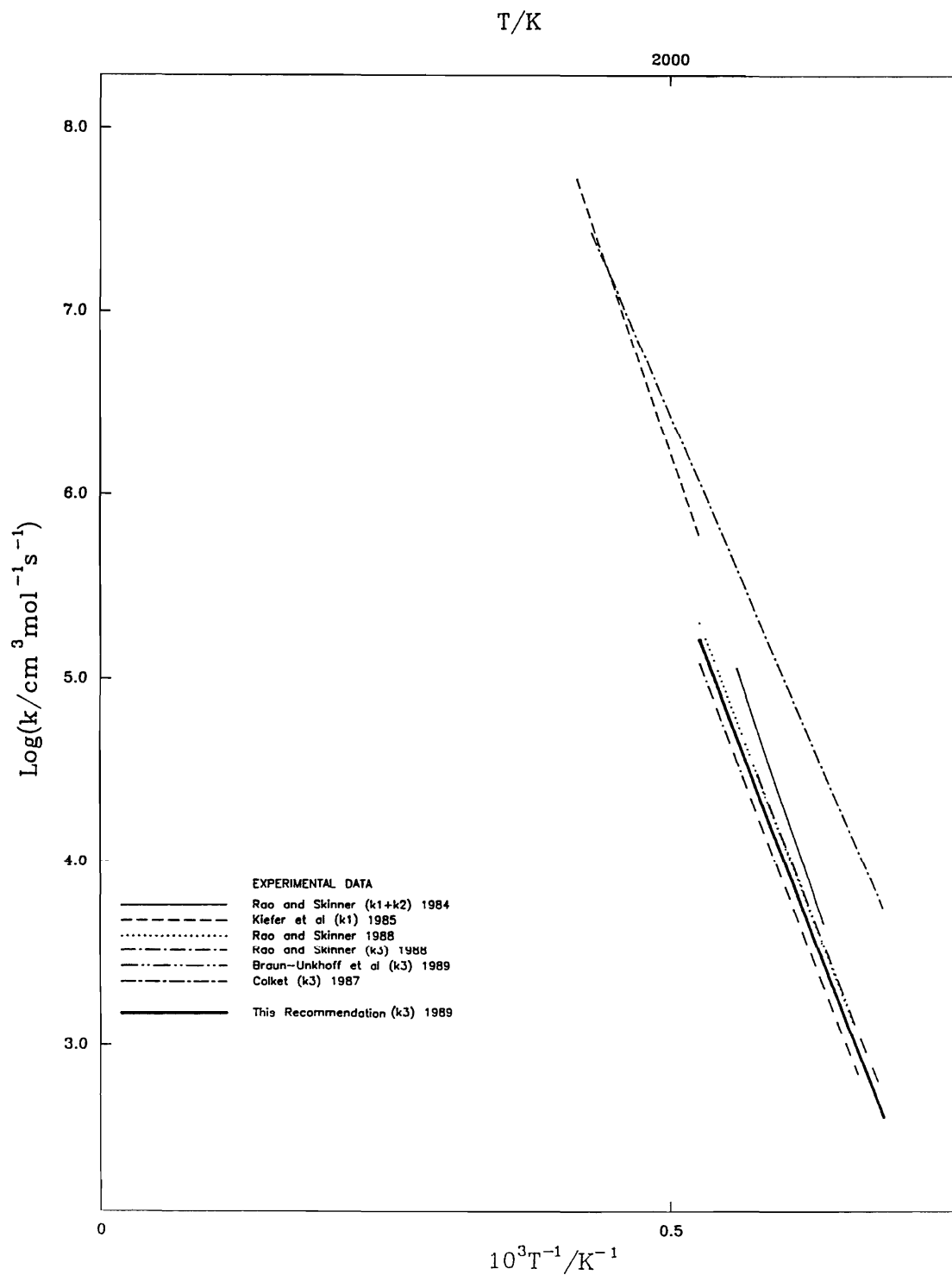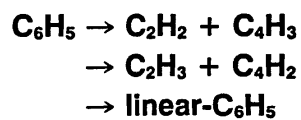$\Delta\log k = \pm 0.4$ over whole range
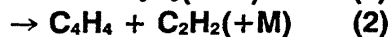
Comments on Preferred Values

The heats of reaction for different decomposition pathways of phenyl give values on the order of 335 to 502 kJ/mol. These findings are incompatible with a high activation energy of about 306 kJ/mol. For the linear aliphatic structure C_6H_5 a value of about 586 ± 12.6 kJ/mol for the heat of formation was estimated by applying Benson's method[7]. Together with 329–340 kJ/mol[6,8] for the heat of formation for the phenyl radical, values of 255–268 kJ/mol are found for the heat of reaction for pathway (3), which are compatible with the experimentally derived apparent activation energy of about 306 kJ/mol (Refs. 4 and 5). Consequently a rate coefficient for only the isomerisation reaction (3) is recommended.

RRKM calculations[4,9] indicate that at temperatures around 1500 K and at total pressures of about 1 bar the rate of reaction (3) is not far from the high pressure limiting value ($k/k_\infty = 0.5$–0.7).

References

[1] V. S. Rao and G. B. Skinner, J. Phys. Chem. **88**, 5990 (1984).
[2] J. H. Kiefer, L. J. Mizerka, M. R. Patel, and H.-C. Wei, J. Phys. Chem. **89**, 2013 (1985).
[3] M. B. Colket, 21st Symp. (Int.) Combust., 851 (1987).
[4] V. S. Rao and G. B. Skinner, J. Phys. Chem. **92**, 2442 (1988).
[5] M. Braun-Unkhoff, P. Frank, and Th. Just, 22nd Symp. (Int.) Combust., 1053 (1989).
[6] D. Robaugh and W. Tsang, J. Phys. Chem. **90**, 5363 (1986).
[7] S. W. Benson, in "Thermochemical Kinetics", J. Wiley, New York (1976).
[8] D. F. McMillen and D. M. Golden, Ann. Rev. Phys. Chem. **33**, 493 (1983).
[9] M. J. S. Dewar, W. C. Gardiner, Jr., M. Frenklach, and I. Oref, J. Am. Chem. Soc. **109**, 4456 (1987).

$$C_6H_5 \rightarrow C_2H_2 + C_4H_3$$
$$\rightarrow C_2H_3 + C_4H_2$$
$$\rightarrow \text{linear-}C_6H_5$$

T/K

EXPERIMENTAL DATA

Rao and Skinner (k1+k2) 1984
Kiefer et al (k1) 1985
Rao and Skinner 1988
Rao and Skinner (k3) 1988
Braun–Unkhoff et al (k3) 1989
Colket (k3) 1987

This Recommendation (k3) 1989

$$C_6H_6(+ M) \rightarrow H + C_6H_5(+ M) \qquad (1)$$
$$\rightarrow C_4H_4 + C_2H_2(+M) \qquad (2)$$

Thermodynamic Data

ΔH°_{298} (1) = 463.5 kJ mol^{-1}

ΔS°_{298} (1) = 133.7 J K^{-1}mol^{-1}

$K_p(1)$ = 9.7·10^5 $T^{0.45}$ exp($-$55840/T) atm

ΔH°_{298} (2) = 451.9 kJ mol^{-1}

ΔS°_{298} (2) = 210.4 J K^{-1}mol^{-1}

$K_p(2)$ = 1.1·10^{12} $T^{-0.10}$ exp($-$54940/T) atm

Rate Coefficient Data ($k = k_1 + k_2$)

$k[s^{-1}]$	$T[K]$	Reference	Comments
Rate Coefficient Measurements			
k_1 = 3.2·10^{15} exp($-$53342/T)	1300–1700	Fujii and Asaba (1972)[1]	(a)
k_1 = 1.6·10^{15} exp($-$51329/T)	1200–1900	Fujii and Asaba (1977)[2]	(b)
3.9·10^9 exp($-$18935/T)	1400–2200	Singh and Kern (1983)[3]	(c)
k_1 = 7.0·10^{13} exp($-$47807/T)	1630–1940	Rao and Skinner (1984)[4]	(d)
k_1 = 4.6·10^{13}exp($-$44787/T)	1515–2500	Kern *et al*. (1984)[5]	(e)
k_2 = 1.3·10^{14}exp($-$44284/T)	1515–2500		
k_1 = 5.0·10^{15}exp($-$54300/T)	1600–2300	Hsu, Lin, and Lin (1984)[6]	(f)
k_1 = 2.0·10^{17} exp($-$59381/T)	1900–2400	Kiefer *et al*. (1975)[7]	(g)
k_1 = 9.3·10^{14}exp($-$53342/T)	1500–1900	Rao and Skinner (1988)[8]	(h)

Comments

(a) Rich mixtures of benzene and oxygen were pyrolyzed in a single pulse shock tube. The reaction progress was followed by light absorption (formation of biphenyl in the wavelength range of 315 to 600 μm) and IR emission (formation of CO in the wavelength range of 3000 to 5000 μm) behind incident shock waves. The products were also analyzed by GC. The experimental data could be modelled by a simple reaction scheme in the initial stage.

(b) The high temperature pyrolysis of benzene was studied in a single pulse shock tube. Gas samples were heated by reflected shock waves; the products were analyzed by GC. The reaction progress was also followed by light absorption at 200–600 nm (benzene, biphenyl). The experimental data are explained by a chain mechanism consisting of 7 elementary reactions (channel (1)).

(c) The pyrolysis of mixtures of 2.1–5% benzene diluted with neon was studied behind reflected shock waves. Products were analyzed by recording time-of-flight mass spectra. The data could be reproduced from a five step reaction mechanism. The first order rate expression as presented in the table has been calculated for a density of 2.6·10^{-6} mol cm^{-3} from the second order rate coefficient evaluated by the authors.

(d) Dilute mixtures of 3–20 ppm C$_6$D$_6$ were pyrolyzed behind reflected shock waves at 2 < p < 3 atm. The formation of D atoms was monitored by time resolved ARAS. A six step reaction mechanism was used to model the experimental data. The rate coefficient for H atom production was determined by using approximate isotope effect calculations.

(e) The rate coefficients for both product channels were derived in a collaborative study on C$_6$H$_6$ and C$_6$D$_6$ pyrolysis using three independent shock tube methods:

time-of-flight mass spectrometry, time resolved ARAS, and laser schlieren density gradient profiles.

(f) The oxidation of benzene under fuel lean conditions was studied behind reflected shock waves using a stabilized cw CO laser to monitor CO production. The formed CO was modelled by a 25 step mechanism. A rate coefficient for channel (1) was determined.

(g) Mixtures of 1 and 2 mol% benzene in krypton have been heated in a shock tube at 0.2 < p < 1 atm using the laser schlieren technique. The measured density gradient profiles and some time-of-flight mass spectra were modelled by a 26 step reaction mechanism. RRKM calculations are also presented. A high pressure limiting rate coefficient for reaction pathway (1) was derived.

(h) The rate coefficient for the production of H atoms in channel (1) was derived from approximate isotope effect calculations. Highly dilute mixtures of C$_6$D$_6$, C$_6$H$_5$Cl, C$_6$H$_5$Br, and C$_6$H$_5$I were pyrolyzed behind incident shock waves at p = 0.4 atm. The formation of H and D atoms was monitored by the ARAS technique. RRKM calculations were carried out to account for unimolecular fall-off and to distinguish the rate constant for dissociation of C$_6$H$_6$ to that for the dissociation of C$_6$D$_6$.

Preferred Values

k = 9.0·10^{15} exp($-$54060/T) s^{-1} over range 1200–2500 K

Reliability

log k = ± 0.4 at 1200 K reducing to ±0.3 at 2000 K

Comments on Preferred Values

From the present data a first order rate expression for benzene decomposition is evaluated. Although most of the experimental work is interpreted by the authors as indicating that the H-atom producing reaction channel (1)

is the dominant one, it should be mentioned that the diagnostic methods of many of the experiments do not permit a distinction between product channels. Consequently a rate coefficient for the overall reaction is recommended.

References

[1]N. Fujii and T. Asaba, 14th Symp. (Int.) Combust., 433 (1972).
[2]N. Fujii and T. Asaba, J. Fac. Eng., Univ. Tokyo, Ser. B 34, 189 (1977).

[3]H. J. Singh and R. D. Kern, Comb. Flame **54**, 49 (1983).
[4]V. S. Rao and G. B. Skinner, J. Phys. Chem. **88**, 5990 (1984).
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[6]D. S. Hsu, C. Y. Lin, and M. C. Lin, 20th Symp. (Int.) Combust., 623 (1984).
[7]J. H. Kiefer, L. J. Mizerka, M. R. Patel, and H. C. Wei, J. Phys. Chem. **89**, 2013 (1985).
[8]V. S. Rao and G. B. Skinner, J. Phys. Chem. **92**, 2442 (1988).

$$C_6H_6 + M \rightarrow C_6H_5 + H + M$$
$$\rightarrow C_4H_4 + C_2H_2 + M$$

C_6H_5O (+ M) → c-C_5H_5 + CO (+ M)
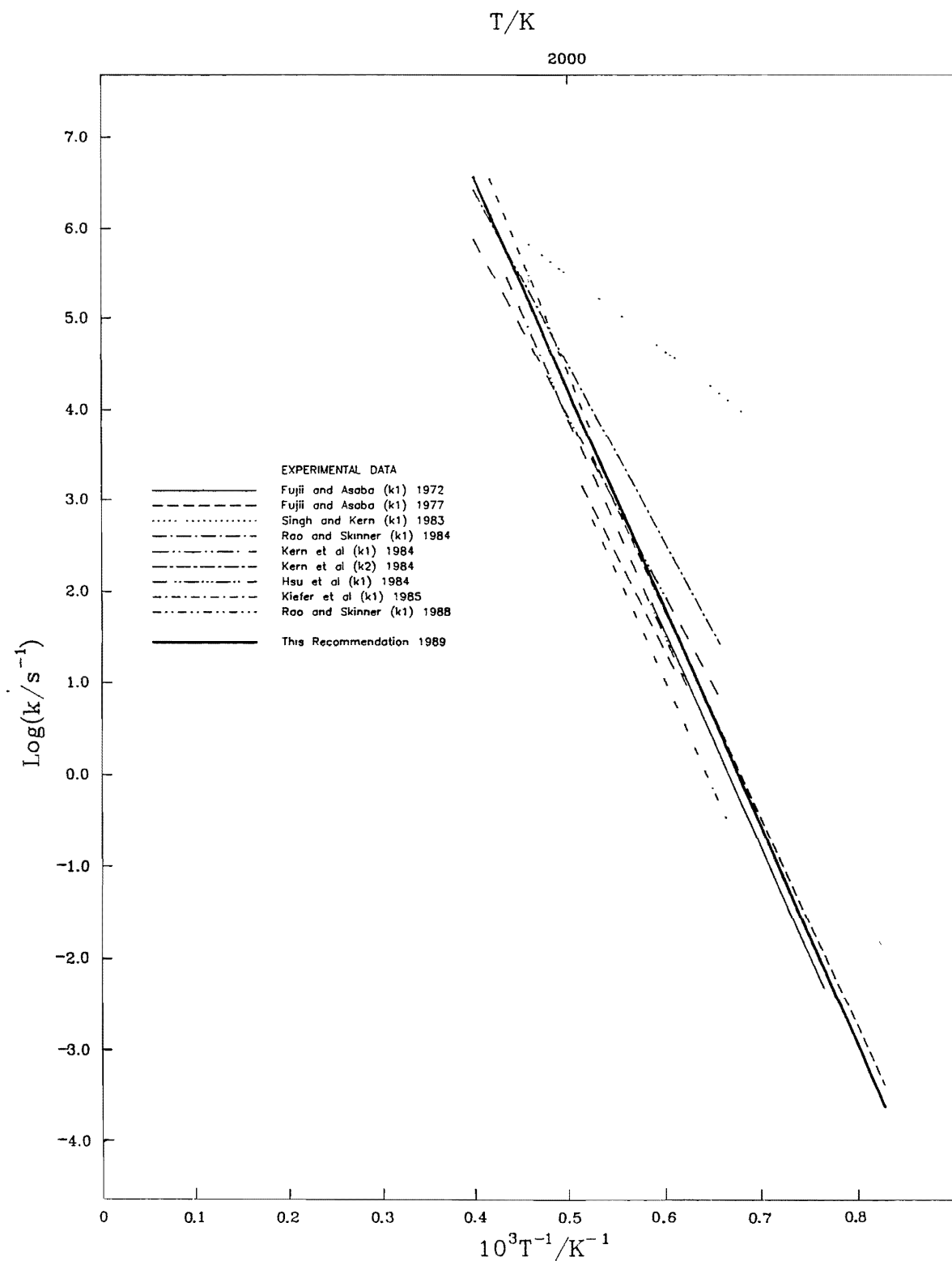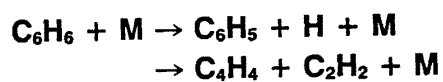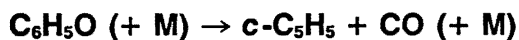
Thermodynamic Data
$\Delta H^\circ_{298} = 94.5 \text{ kJ mol}^{-1}$
$\Delta S^\circ_{298} = 184.2 \text{ J K}^{-1}\text{mol}^{-1}$
$K_p = 1.1 \cdot 10^{11} \, T^{-0.446}\exp(-11561/T)$ atm

Rate Coefficient Data

$k[\text{s}^{-1}]$	$T[\text{K}]$	Reference	Comments
Rate Coefficient Measurements			
10 ± 5	1000	Colussi *et al.* (1977)[1]	(a)
$1.0 \cdot 10^{12}\exp(-24000/T)$	1010–1430	Lin and Lin (1985)[2]	(b)
$2.5 \cdot 10^{11}\exp(-22100/T)$	1000–1580	Lin and Lin (1986)[3]	(c)

Comments

(a) Pyrolysis of phenyl allyl ether in a VLPP reactor. Above 983 K the ether is mostly decomposed so that the phenoxy radical decays are isolated. Mass spectrometric detection of radical fragments (at m/e = 41 and 94). No experimental data reported. Based on thermochemical grounds, a decomposition mechanism via a bicyclic radical intermediate is proposed.

(b) Pyrolysis of phenyl methyl ether (anisole) in high dilution (0.1% and 0.5% in Ar) in a shock tube between 1010 and 1430 K and 0.5–0.9 atm. k_1 is deduced from CO profiles (probed by resonance absorption, cw CO laser) by assuming that anisole decomposition and phenoxy decomposition are the only important reactions.

(c) Extension of the above study[2]. Same method. The kinetic mechanism is extended and the deduction of k is based on computer simulation.

Preferred Values

$k = 2.5 \cdot 10^{11}\exp(-22100/T) \text{ s}^{-1}$ over range 1000–1580 K
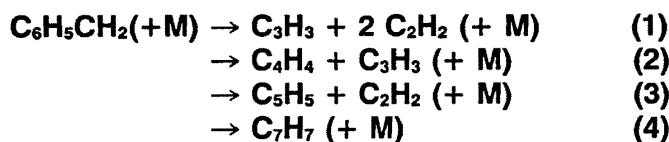
Reliability
$\Delta\log k = \pm 0.2$

Comments on Preferred Values
The preferred expression is that one of Lin and Lin[3].

References

[1]A. J. Colussi, F. Zabel, and S. W. Benson, Int. J. Chem. Kin. **9**, 161 (1977).
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$$C_6H_5CH_2(+M) \rightarrow C_3H_3 + 2\ C_2H_2\ (+\ M) \qquad (1)$$
$$\rightarrow C_4H_4 + C_3H_3\ (+\ M) \qquad (2)$$
$$\rightarrow C_5H_5 + C_2H_2\ (+\ M) \qquad (3)$$
$$\rightarrow C_7H_7\ (+\ M) \qquad (4)$$

Thermodynamic Data

$\Delta H^\circ_{298} (2) = 428.1$ kJ mol^{-1}

$\Delta S^\circ_{298} (2) = 213.2$ J K^{-1}mol^{-1}

$K_p(2) = 2.3 \cdot 10^{-19}\ T^{11.26}\ \exp(-50752/T)$ atm

$\Delta H^\circ_{298} (3) = 463.6$ kJ mol^{-1}

$\Delta S^\circ_{298} (3) = 179.1$ J K^{-1}mol^{-1}

$K_p(3) = 1.7 \cdot 10^{10}\ T^{-0.13}\ \exp(-56155/T)$ atm

Rate Coefficient Data ($k = k_1 + k_2 + k_3 + k_4$)

$k[\text{s}^{-1}]$	$T[\text{K}]$	Reference	Comments
Rate Coefficient Measurements			
$2.0 \cdot 10^{16}\ \exp(-51357/T)$	1500–1800	Astholz *et al.* (1981)[1]	(a)
$k_2 + k_3 = 1.6 \cdot 10^{14}\ \exp(-42698/T)$	1550–2020	Astholz and Troe (1982)[2]	(b)
$k_2 + k_3 = 2.5 \cdot 10^{17}\ \exp(-53402/T)$	1550–2020		(c)
$k_1 = 1.0 \cdot 10^{14}\exp(-42674/T)$	1300–1800	Mizerka and Kiefer (1986)[3]	(d)
$2.0 \cdot 10^{15}\ \exp(-42048/T)$	1400–1900	Mueller-Markgraf and	
$+1.0 \cdot 10^{10}\ \exp(-21409/T)$		Troe (1987)[4]	(e)
$k_1 = 1.8 \cdot 10^{14}\exp(-42674/T)$	1600–2100	Pamidimukkala *et al.* (1987)[5]	(f)
$5.4 \cdot 10^{16}\ \exp(-50327/T)$	1430–1740	Rao and Skinner (1987)[6]	(g)
$1.6 \cdot 10^{10}\ \exp(-22491/T)$	1250–1900	Mueller-Markgraf and	
$+2.0 \cdot 10^{15}\ \exp(-42048/T)$		Troe (1988)[7]	(h)
$k_4 = 1.3 \cdot 10^{13}\ \exp(-34600/T)$	1350–1800	Braun-Unkhoff *et al.* (1989)[8]	(i)

Comments

(a) The temporal absorption of toluene and benzyl were monitored during the thermal dissociation of toluene behind reflected shock waves. Rate expressions for the benzyl decay were determined for the density range $(1–5) \cdot 10^{-5}$ mol cm^{-3}. The presented rate expression corresponds to $1 \cdot 10^{-5}$ mol cm^{-3}. The determination of the overlapping absorption profiles was performed on the assumption of high thermal stability of the benzyl radical.

(b) Toluene pyrolysis behind shock waves. Experimental setup as in comment (a). From the product analysis of Smith[9] it was assumed that two dissociation channels (2) and (3) compete during thermal decay of benzyl. The density range covered was $1.4 \cdot 10^{-6}$ to $1.5 \cdot 10^{-4}$ mol cm^{-3}. The presented rate expression corresponds to the lowest density value.

(c) Same as in comment (b). The rate expression corresponds to a density of $1.5 \cdot 10^{-4}$ mol cm^{-3}.

(d) Investigation of high temperature pyrolysis of ethylbenzene in shock waves with the laser schlieren technique. Benzyl and methyl radicals are found as the dominant products of the dissociation process. For modelling the schlieren profiles it is assumed that benzyl dissociation ultimately generates acetylene and the propargyl radical (1). High stability of the benzyl radical leads to a rate expression just slightly below that of Refs. 1 and 2.

(e) High temperature UV absorption spectra of benzyl radicals were monitored over the wavelength range 190–330 nm following shock wave induced thermal decomposition of different precursor molecules (benzyl iodide, benzyl chloride, and methyl benzyl ketene). It was found that benzyl radicals exhibit an unexpected low thermal stability. The marked curvature of the Arrhenius plot, together with the lack of any systematic dependence of the rate coefficient on the concentration, is considered as indicating the contribution of two benzyl fragmentation pathways with very different activation energies.

(f) The thermal decomposition of toluene has been investigated by time-of-flight mass spectrometry and by laser schlieren densitometry behind shock waves at total pressures of 0.2–0.5 bar. It is found that the dissociation of toluene proceeds mainly by C—C scission to phenyl and methyl. This result involves the assumption that benzyl radicals have a high stability which makes the concurrent reaction pathway leading to benzyl and hydrogen atoms reversible.

(g) Dilute mixtures of deuterated ethylbenzene in argon were pyrolyzed behind incident shock waves at total pressures around 0.55 bar. H and D atom concentrations were monitored by ARAS. A first order rate constant was found for the dissociation of benzyl into smaller fragments.

(h) Benzyl radicals were generated by the thermal decomposition of benzyl iodide into benzyl and iodide atoms. Benzyl concentration was monitored by UV absorption. From the results, which are in good agreement with previous findings (Ref. 4) it is concluded that the evaluated Arrhenius expressions cannot be definitely attributed to the product channels (2) and (3).

(i) Investigation of benzyl decomposition behind reflected shock waves in highly diluted mixtures of benzyliodide with argon. Hydrogen atoms were monitored by ARAS. The temperatures ranged between 1300 and 1800 K at total pressured around 2 bar. In each experiment the initial concentrations of benzyliodide were determined by monitoring the iodine atom concentration with ARAS during benzyliodide decay. This procedure of applying very low initial concentrations of the benzyl precursor ($[X]$ = 0.5–5 ppm) allowed to evaluate a reaction scheme for the initiation reaction(s) and for some fast subsequent reaction steps. Thermodynamic considerations favour a fast intramolecular rearrangement of the benzyl radical to structures like the bicycloheptadienyl radical, the tropylium radical or an open chain structure, from which fast hydrogen abstraction occurs. Therefore the deduced Arrhenius expression is considered to describe the rate limiting isomerization reaction step.

Preferred Values

$k = 5.1 \cdot 10^{13} \exp(-36370/T)$ s^{-1} over range 1350–1900 K

Reliability

$\Delta \log k = \pm 0.3$ at 1350 K increasing to ± 0.5 at 1900 K

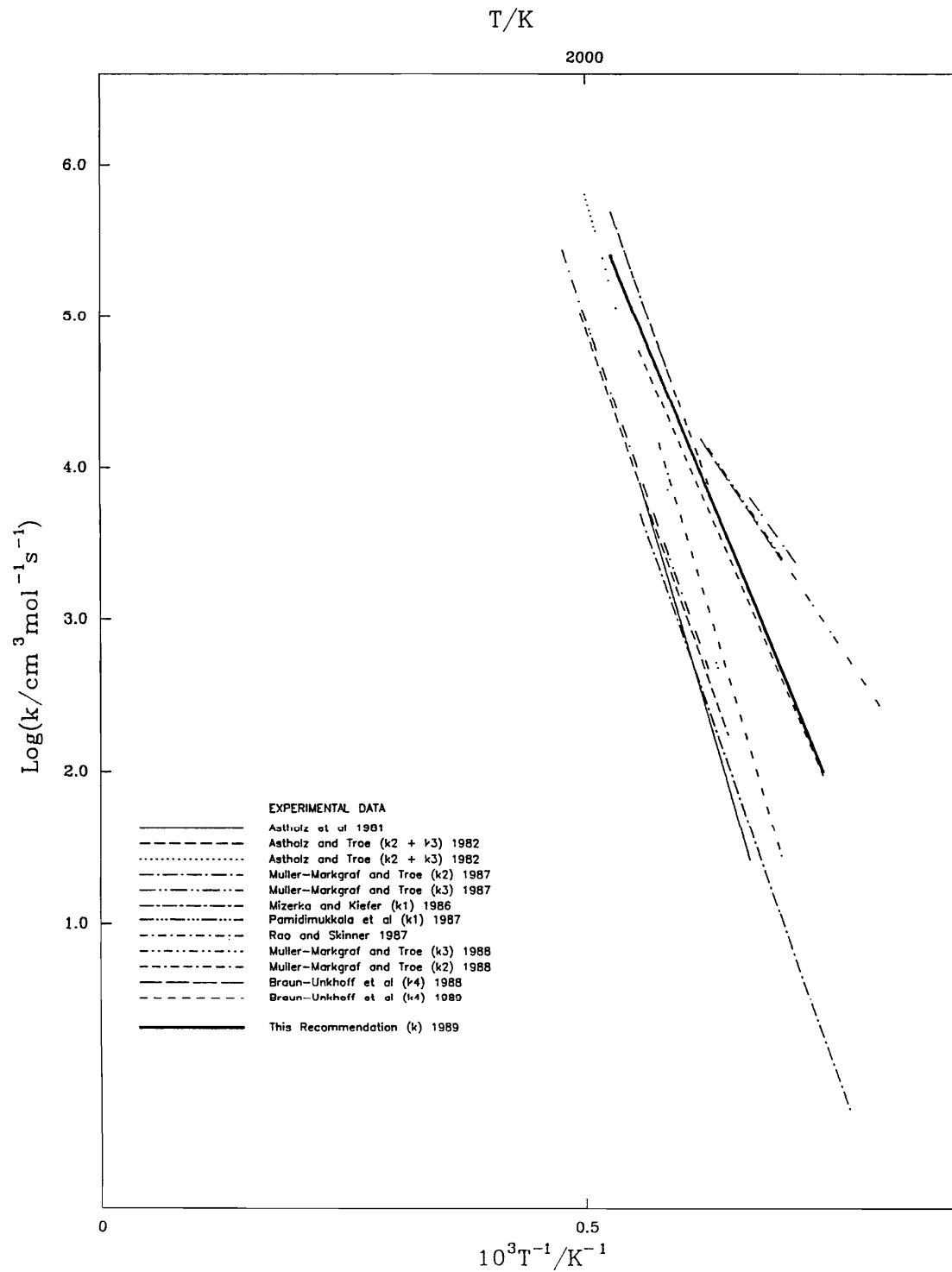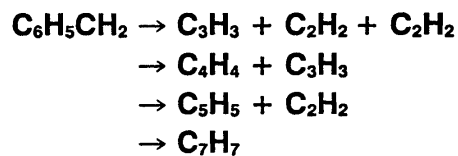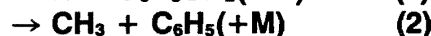*Comments on Preferred Values*

The recommended rate coefficient has been evaluated from the only direct measurements of benzyl radical absorption[4,7] and of H-atom production during benzyl decay[8] at elevated temperatures. The product distribution measurements of Smith[9] give evidence for benzyl decomposing predominantly via reaction pathways (2) and (3), but no direct specific measurements of intermediates other than H atoms during the decomposition process are available. The ARAS measurements of Braun-Unkhoff *et al.*[8] indicate that the decay of benzyl leads to the formation of H atoms in considerable amounts. Therefore it was necessary to reinterprete the benzyl decay rates reported by Mueller-Markgraf and Troe[4,7]. The reevaluation was done by Hippler *et al.*[10] by taking the recombination reaction $C_7H_7 + H \rightarrow C_7H_8$ ($k_2 = 2 \cdot 10^{14}$ cm^3 mol^{-1} s^{-1}) into account. Their resulting Arrhenius plot for the thermal decay of benzyl is now in good accord with the one derived in Ref. 8 on the basis of the production of H atoms during the benzyl decomposition. Therefore the recommended rate expression is considered to apply to the overall dissociation process of benzyl radicals.

References

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$$C_6H_5CH_2 \rightarrow C_3H_3 + C_2H_2 + C_2H_2$$
$$\rightarrow C_4H_4 + C_3H_3$$
$$\rightarrow C_5H_5 + C_2H_2$$
$$\rightarrow C_7H_7$$

EXPERIMENTAL DATA

Astholz et al 1981
Astholz and Troe (k2 + k3) 1982
Astholz and Troe (k2 + k3) 1982
Muller–Markgraf and Troe (k2) 1987
Muller–Markgraf and Troe (k3) 1987
Mizerka and Kiefer (k1) 1986
Pamidimukkala et al (k1) 1987
Rao and Skinner 1987
Muller–Markgraf and Troe (k3) 1988
Muller–Markgraf and Troe (k2) 1988
Braun–Unkhoff et al (k4) 1988
Braun–Unkhoff et al (k4) 1989

This Recommendation (k) 1989

$$C_6H_5CH_3(+M) \rightarrow H + C_6H_5CH_2(+M) \quad (1)$$
$$\rightarrow CH_3 + C_6H_5(+M) \quad (2)$$

Thermodynamic Data

ΔH°_{298} (1) = 367.9 kJ mol^{-1}

ΔS°_{298} (1) = 110.9 J K^{-1}mol^{-1}

K_p(1) = 5.6·10^1 $T^{1.488}$ exp($-44030/T$) atm

ΔH°_{298} (2) = 424.1 kJ mol^{-1}

ΔS°_{298} (2) = 162.5 J K^{-1}mol^{-1}

K_p(2) = 2.1·10^{10} $T^{-0.50}$ exp($-51450/T$) atm

Rate Coefficient Data ($k = k_1 + k_2$)

$k[s^{-1}]$	$T[K]$	Reference	Comments
Rate Coefficient Measurements			
$k_1 = 2.0·10^{13}$ exp($-38900/T$)	1011–1138	Szwarc (1948)[1]	(a)
$k_1 = 2.5·10^{12}$ exp($-37091/T$)	1011–1122	Takahashi (1960)[2]	(b)
$k_1 = 1.3·10^{18}$ exp($-52340/T$)	1185–1206		
$k_1 = 6.3·10^{14}$ exp($-42778/T$)	913–1143	Price (1962)[3]	(c)
$k_2 = 3.4·10^{14}$ exp($-40262/T$)	1073–1373	Errede and DeMaria (1964)[4]	(d)
$k_1 = 9.2·10^{15}$ exp($-44737/T$)	920–970	Brooks et al. (1971)[5]	(e)
$k_1 = 1.7·10^{14}$ exp($-41268/T$)	1410–1730	Rao and Skinner (1984)[6]	(f)
$k_1 = 2.0·10^{15}$ exp($-44393/T$)	1500–1900	Mueller-Markgraf and Troe (1986)[7]	(g)
$k_1 = 8.1·10^{12}$ exp($-36534/T$)	1300–1800	Mizerka and Kiefer (1986)[8]	(h)
$k_2 = 4.0·10^{11}$exp($-45291/T$)	1300–1800		(h)
$k_2 = 8.9·10^{12}$ exp($-36534/T$)	1600–2100	Pamidimukkala et al. (1987)[9]	(i)
$k_1 = 2.8·10^{15}$ exp($-44730/T$)	1450–1900	Brouwer et al. (1988)[10]	(j)
$k_1 = 3.6·10^{15}$ exp($-45000/T$)	1380–1700	Braun-Unkhoff et al. (1989)[13]	(m)
Reviews and Evaluations			
$k_1 = 3.2·10^{15}$ exp($-44439/T$)	920–1140	Benson and O'Neal (1970)[11]	(k)
$k_1 = 2.7·10^{14}$exp($-41722/T$)	1050–1600	Rao and Skinner (1984)[6]	(l)

Comments

(a) Pyrolysis of toluene and xylene in a flow system at pressure between 3 and 20 mbar.

(b) Flow system with mass spectrometric analysis. It was concluded that the curvature of the Arrhenius plot for channel (1) was caused mainly by competitive reactions.

(c) The flow system study (pressure 8–28 mbar) revealed that the toluene decay was strongly surface controlled at temperatures below 1000 K. The reported Arrhenius parameters for reaction (1) were derived from the isolated homogeneous reaction.

(d) Flow system study. Rate coefficient parameters for reaction pathway (2) were deduced from the rate of benzene formation during the decompostion of xylene between 1070 and 1370 K. Due to the indirect method which was used in this study, the results were criticized by Benson and O'Neal (Ref. 11): the obtained preexponential factor and the activation energy seem unlikely for this reaction.

(e) Pyrolysis of toluene/nitrogen mixtures in a static system at total pressures below 300 mbar ($p_{toluene} \leq 30$ mbar). Stable compounds analysis by gas chromatography.

(f) Shock tube study with initial mixtures of toluene-d_8/Ar and neopentane/toluene-d_8/Ar mixtures. D and H atoms are monitored as function of time by ARAS. Investigation covered a temperature range from 1200–1460 K for neopentane/toluene, and from 1410–1730 K for toluene experiments at total pres-

sures of about 3 bar. The authors recommend an isotope correction factor of 1.5 for the evaluation of k_H of channel (1). The estimated uncertainty for k_H, k_D is about log $k = \pm 0.2$.

(g) In an earlier shock tube study on toluene decomposition using light absorption of toluene and benzyl in the 200–350 nm range (Ref. 12) rate constants were derived on the assumption that the benzyl radical exhibits sufficient thermal stability. The measurements were reinterpreted and superseded by experimental results on benzyl decomposition (Ref. 7). These experiments indicate an unexpectedly low thermal stability of the benzyl radical. With these results, from a reinterpretation of the experiments of Ref. 12 rate coefficients for channel (1) were derived for the density range (1–3)·10^{-5}mol cm^{-3}. The given Arrhenius expression in the present table corresponds to 1.05·10^{-5}mol cm^{-3}.

(h) Shock tube study on high temperature pyrolysis of ethylbenzene with the laser schlieren technique. Rate expressions for channels (1) and (2) have been included into the reaction system by the authors and originate from their unpublished LS measurements of toluene pyrolysis.

(i) Two independent shock tube techniques (time-of-flight mass spectrometry and laser schlieren densitometry) were used to investigate the high temperature pyrolysis of toluene in mixtures with Kr and Ne, respectively. A rate coefficient for the formation of methyl and phenyl (channel (2)) was deduced at total pressures around 0.5 bar. A high pressure limiting

rate coefficient of $1.2 \cdot 10^{16} \exp(-47505/T)$ s^{-1} has also been calculated for reaction pathway (2).

(j) The thermal decomposition of toluene has been reinvestigated in shock waves detecting toluene, benzyl, and benzyl fragment concentrations by UV absorption spectrometry. The results give evidence for dominant toluene dissociation to benzyl radicals and H atoms (channel (1)). The derived thermally averaged rate coefficient for channel (1) is consistent with specific rate constants $k(E,J)$ from laser excitation experiments.

(k) Reevaluation of earlier flow system results in the pressure range 2–22 Torr. The preferred parameters for reaction pathway (1) are obtained by accepting the rate constant of Ref. 6 and scaling the parameters to fit the thermodynamic enthalpy.

(l) See comment (f). The limiting high pressure rate constant for toluene decomposition (channel (1)) is derived from RRKM calculations and $k_H - 1.5 \cdot k_D$.

(m) Decomposition of toluene and nitrosobenzene highly diluted in argon behind reflected shock waves. The hydrogen atom formation was followed by ARAS. Nitrosobenzene served as thermal source of phenyl radicals in the seperate study of the phenyl decomposition mechanism. The results for phenyl dissociation indicated that the main product channel is the H atom abstraction channel (1) and that the rate coefficient for channel (2) should not exceed $0.2 \cdot k_1$. The rate expression for channel (1) is in excellent agreement with the results of Brouwer et al.[10].

Preferred Values

$k_1 = 3.1 \cdot 10^{15} \exp(-44890/T)$ s^{-1} over range 920–2200 K

Reliability

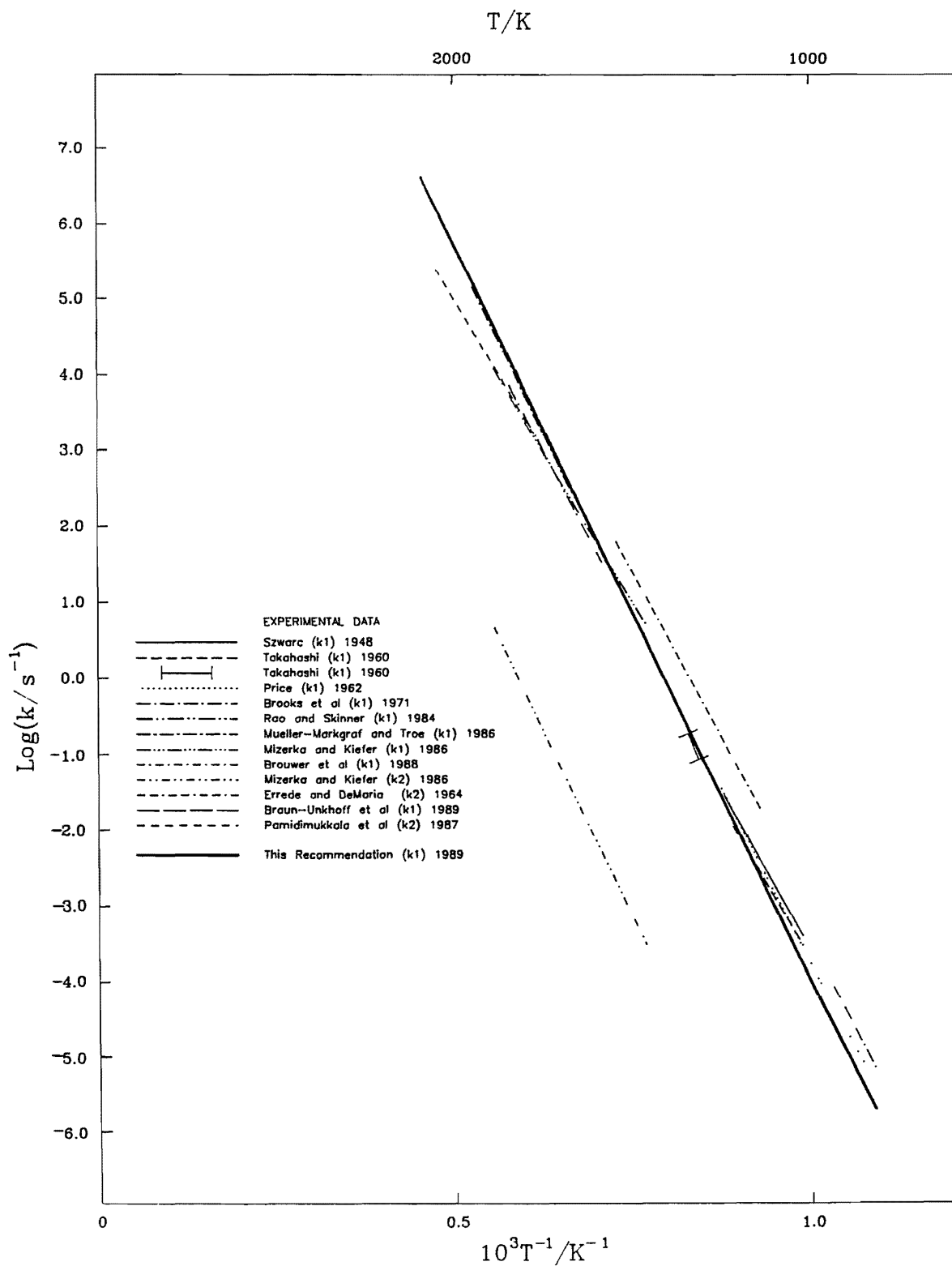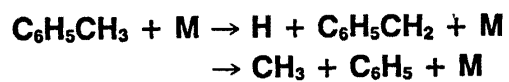$\Delta \log k_1 = \pm 0.5$ at 2200 K reducing to ± 0.3 at 900 K
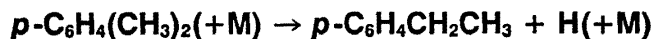
Comments on Preferred Values

There exists a large variety of studies on toluene pyrolysis in the lower temperature range up to approximately 1000 K. But most of these studies were conducted under experimental conditions under which bimolecular reactions of toluene leading to bibenzyl and other compounds dominate. The investigation of unimolcular decomposition of toluene becomes less difficult at temperatures above 900 K. Most of the available data give evidence for the product channel (1) leading to benzyl radicals and hydrogen atoms. From some of the experiments in conjunction with the calculated limiting high pressure rate coefficient it can be deduced that the recommended Arrhenius expression covers a density range of about $(1-3) \cdot 10^{-5}$ mol cm^{-3}, very close to the high pressure limit. The experimental data for the second decomposition channel leading to phenyl and methyl radicals (channel (2)) are insufficient to permit a recommendation of a rate expression. Thermochemical arguments together with the findings of some of the authors give evidence that the rate for this channel should not exceed 10 to 20% of the rate for channel (1) for $T \leq 2000$ K.

References

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$$C_6H_5CH_3 + M \rightarrow H + C_6H_5CH_2 + M$$
$$\rightarrow CH_3 + C_6H_5 + M$$

T/K

EXPERIMENTAL DATA

———————	Szwarc (k1) 1948
– – – – –	Takahashi (k1) 1960
⊢——⊣	Takahashi (k1) 1960
··············	Price (k1) 1962
—·—·—·—	Brooks et al (k1) 1971
—··—··—··	Rao and Skinner (k1) 1984
—·—·—·—	Mueller–Markgraf and Troe (k1) 1986
—···—···—	Mizerka and Kiefer (k1) 1986
—··—··—··	Brouwer et al (k1) 1988
—···—···—	Mizerka and Kiefer (k2) 1986
———————	Errede and DeMaria (k2) 1964
———————	Braun–Unkhoff et al (k1) 1989
– – – – –	Pamidimukkala et al (k2) 1987
———————	This Recommendation (k1) 1989

$10^3T^{-1}/K^{-1}$

p-C$_6$H$_4$(CH$_3$)$_2$(+M) $\rightarrow$ p-C$_6$H$_4$CH$_2$CH$_3$ + H(+M)

Rate Coefficient Data

$k[\text{s}^{-1}]$	$T[\text{K}]$	Reference	Comments
Rate Coefficient Measurements			
$5.0 \cdot 10^{13} \exp(-38300/T)$	1018–1133	Szwarc (1948)[1]	(a)
$9.3 \cdot 10^{13} \exp(-38200/T)$	1213–1383	Errede and DeMaria (1962)[2]	(b)
$4.0 \cdot 10^{14} \exp(-40100/T)$	1400–1800	Brouwer *et al.* (1984)[3]	(c)
$3.2 \cdot 10^{15} \exp(-42600/T)$	1400–1800		(d)
$4.0 \cdot 10^{15} \exp(-42600/T)$	1400–1800		(e)

Comments

(a) Flow reactor at pressure of 2.7–20 mbar.

(b) Fast flow pyrolysis.

(c) Shock tube study. Reactants highly diluted in Ar. UV absorption at 266.5 nm of para-methyl-benzyl. [Ar] $\approx 1.3 \cdot 10^{18}$ cm^{-3}.

(d) Same method as in (c). [Ar] $\approx 3.7 \cdot 10^{19}$ cm^{-3}.

(e) Same method as in (c). [Ar] $\approx 1.1 \cdot 10^{20}$ cm^{-3}.

Preferred Values

$k_\infty \approx 4.0 \cdot 10^{15} \exp(-42600/T)$ s^{-1} over range 1400–1800 K
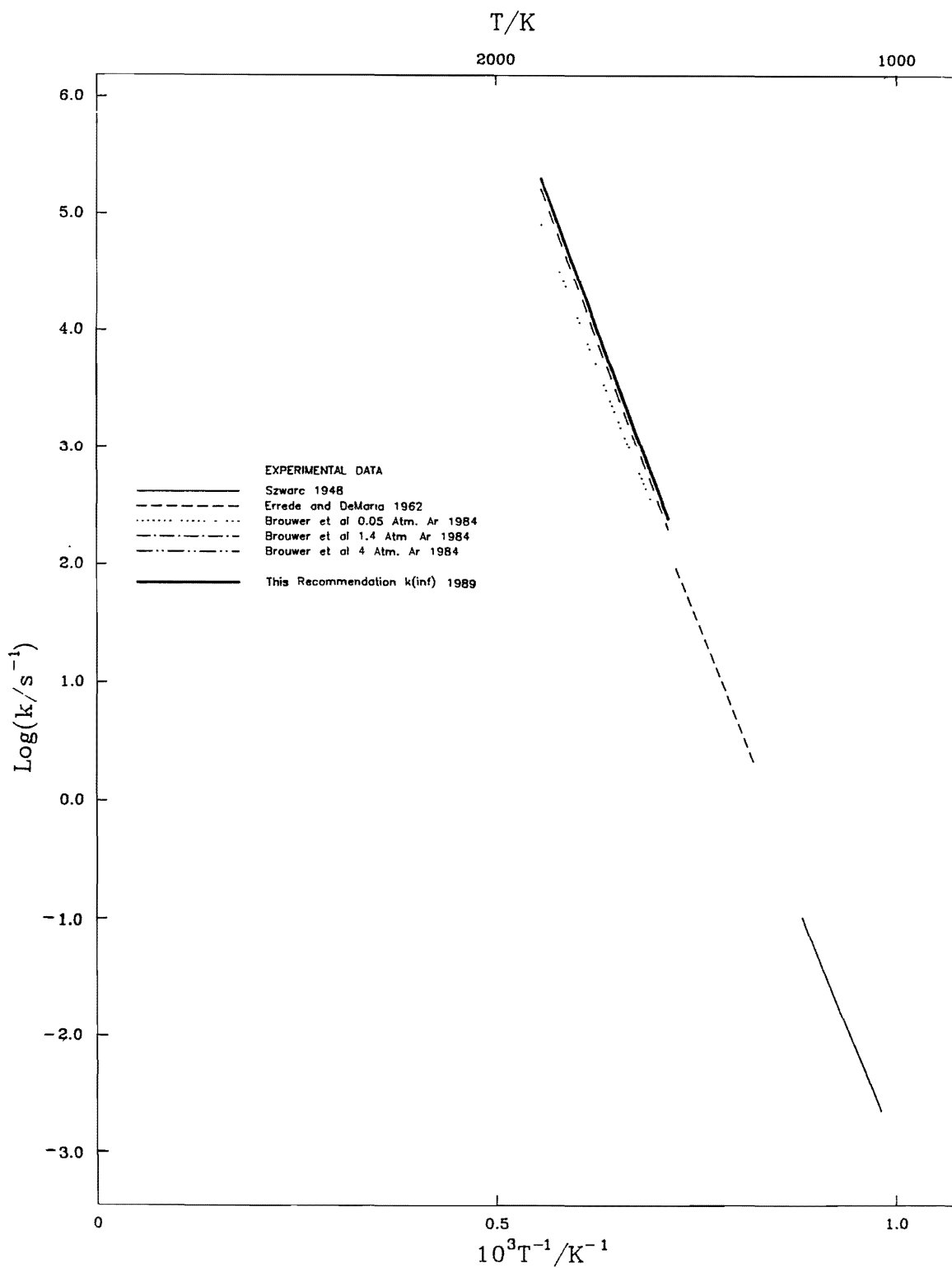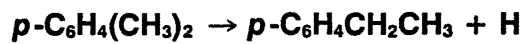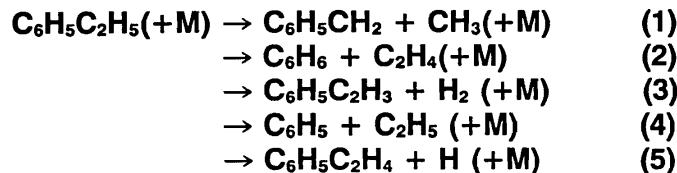
Reliability
$\Delta \log k = \pm 0.5$

Comments on Preferred Values

It has been assumed that in the temperature range 1400–1800 K the rate coefficient given by Brouwer *et al.*[3] for the highest pressure is close to the high pressure limit k_∞. The data given for the lower densities are in the fall-off region.

References

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BAULCH *ET AL.*

$$p\text{-}C_6H_4(CH_3)_2 \rightarrow p\text{-}C_6H_4CH_2CH_3 + H$$

$$C_6H_5C_2H_5(+M) \rightarrow C_6H_5CH_2 + CH_3(+M) \qquad (1)$$
$$\rightarrow C_6H_6 + C_2H_4(+M) \qquad (2)$$
$$\rightarrow C_6H_5C_2H_3 + H_2 (+M) \qquad (3)$$
$$\rightarrow C_6H_5 + C_2H_5 (+M) \qquad (4)$$
$$\rightarrow C_6H_5C_2H_4 + H (+M) \qquad (5)$$

Thermodynamic Data

$\Delta H^\circ_{298} (1) = 315.9$ kJ mol^{-1}
$\Delta S^\circ_{298} (1) = 149.9$ J K^{-1}mol^{-1}
$K_p(1) = 4.0\cdot10^8 \, T^{-0.134} \exp(-38330/T)$ atm

$\Delta H^\circ_{298} (2) = 105.6$ kJ mol^{-1}
$\Delta S^\circ_{298} (2) = 128.1$ J K^{-1}mol^{-1}
$K_p(2) = 4.0\cdot10^8 \, T^{-0.642} \exp(-12930/T)$ atm

$\Delta H^\circ_{298} (3) = 117.6$ kJ mol^{-1}
$\Delta S^\circ_{298} (3) = 115.3$ J K^{-1}mol^{-1}
$K_p(3) = 5.7\cdot10^4 \, T^{0.578} \exp(-14280/T)$ atm

$\Delta H^\circ_{298} (4) = 415.9$ kJ mol^{-1}
$\Delta S^\circ_{298} (4) = 179.7$ J K^{-1}mol^{-1}
$K_p(4) = 4.8\cdot10^{13} \, T^{-1.427} \exp(-50560/T)$ atm

$\Delta H^\circ_{298} (5) = 341.4$ kJ mol^{-1}
$\Delta S^\circ_{298} (5) = 110.3$ J K^{-1}mol^{-1}
$K_p(5) = 5.2\cdot10^2 \, T^{1.125} \exp(-40900/T)$ atm

Rate Coefficient Data $(k = k_1 + k_2 + k_3 + k_4 + k_5)$

$k[\mathrm{s}^{-1}]$	$T[\mathrm{K}]$	Reference	Comments
Rate Coefficient Measurements			
$k_1 = 1.0\cdot10^{13}\exp(-31800/T)$	888–1018	Szwarc (1949)[1]	(a)
$k_1 = 4.0\cdot10^{14} \exp(-35300/T)$	876–1000	Esteban et al. (1963)[2]	(b)
$k_1 = 5.0\cdot10^{14}\exp(-34800/T)$	906–1010	Crowne et al. (1969)[3]	(c)
$k_1 = 5.0\cdot10^{14} \exp(-35300/T)$	910–1089	Clark and Price (1970)[4]	(d)
$k_2 = 1.1\cdot10^9 \exp(-26000/T)$	910–1089		
$k_3 = 5.0\cdot10^{12} \exp(-32200/T)$	910–1089		
$k_1 = 2.0\cdot10^{15}\exp(-36700/T)$	800–1100	Ebert et al. (1978)[6]	(e)
$k_4 = 1.0\cdot10^{16}\exp(-41800/T)$	800–1100		
$k_1 = 7.1\cdot10^{15}\exp(-37400/T)$	990–1190	McMillen et al. (1980)[7]	(f)
$k_1 = 2.0\cdot10^{15} \exp(-36600/T)$	1053–1234	Robaugh and Stein (1981)[8]	(g)
$k_1 = 2.5\cdot10^{14} \exp(-35200/T)$	770–820	Brooks et al. (1982)[9]	(h)
$k_1 = 5.0\cdot10^{15} \exp(-37500/T)$	873–998	Davis (1983)[10]	(i)
$k_1 = 1.3\cdot10^{17}\exp(-40900/T)$	1250–1600	Brouwer et al. (1983)[11]	(j)
$k_5 = 2.5\cdot10^{12}\exp(-30100/T)$	1250–1600		(k)
$k_1 = 2.0\cdot10^{15} \exp(-36600/T)$	1000–1110	Grela and Colussi (1985)[12]	(l)
$k_1 = 3.1\cdot10^{13}\exp(-30200/T)$	1300–1800	Mizerka and Kiefer (1986)[13]	(m)
$k_1 = 3.5\cdot10^{15}\exp(-36900/T)$	1200–1650	Mueller-Markgraf and Troe (1988)[14]	(n)
Reviews and Evaluations			
$k_1 = 2.0\cdot10^{15}\exp(-36700/T)$	876–1018	Benson and O'Neal (1970)[5]	(o)

Comments

(a) Pyrolysis of ethylbenzene in the presence of excess of toluene in a flow reactor at pressure between 10 and 22 mbar.

(b) Pyrolysis of ethylbenzene in the presence of excess of aniline in a flow reactor at pressure between 12.5 and 17.9 mbar.

(c) Stirred flow reactor at pressure between 8 and 18 mbar. Gas analysis by GC.

(d) Toluene carrier flow system at pressure between 26 and 48 mbar. Gas analysis by GC.

(e) Flow reactor study at pressure between 0.13–1.3 mbar and at normal pressure. GC- and TOF-analysis of the reaction products.

(f) Very low pressure pyrolysis in a Knudsen cell reactor at pressure between $1.3\cdot10^{-5}$–$1.3\cdot10^{-3}$ mbar. Mass spectrometric analysis of the reaction products. Rate expression for high pressure limit.

(g) Very low pressure pyrolysis at pressure lower than $1.3\cdot10^{-3}$ mbar in a stirred flow reactor. Rate expression for high pressure limit. Gas analysis by mass spectrometry.

(h) Static reactor at pressure between 10–65 mbar. GC analysis.

(i) Conventional flow equipment at atmospheric pressure. Analysis by rate of formation of toluene.

(j) Shock tube. High dilution by argon. UV-absorption of ethylbenzene and reaction products. $2.4\cdot10^{18}$ | $\wedge$ |
$\leq 1.4\cdot10^{20}$ cm^{-3}. Rate expression for $4.8\cdot10^{19}$ | $\wedge$
$\leq 1.4\cdot10^{20}$ cm^{-3}.

(k) Shock tube. High dilution by argon. UV-absorption of ethylbenzene and reaction products. $1.8\cdot10^{10}$ | $\wedge$
$\leq 1.5\cdot10^{20}$ cm^{-3}. Rate expression for $4.2\cdot10^{10}$ | $\wedge$
$\leq 1.5\cdot10^{20}$ cm^{-3}.

(l) Very low pressure pyrolysis in a stirred reactor. Mass spectrometric analysis of the reaction products. Rate expression for high pressure limit.

(m) Shock tube. Laser schlieren technique. Density range $4.3 \cdot 10^{17} – 4.2 \cdot 10^{18}$ cm^{-3}.

(n) Shock tube. High dilution by argon. UV-absorption between 190–330 nm. $1.2 \cdot 10^{19} \leq$ [Ar] $\leq 1.4 \cdot 10^{20}$ cm^{-3}.

(o) Critical evaluation of kinetic data on gas phase unimolecular reactions.

Preferred Values

$k_1 = 7.1 \cdot 10^{15} \exp(-37800/T)$ s^{-1} over range 770–1800 K

Reliability

$\Delta \log k_1 = \pm 0.4$ at 1800 K reducing to ± 0.1 at 770 K

Comments on Preferred Values

The preferred value is based on the data of Szwarc[1], Esteban *et al.*[2], Crowne *et al.*[3], Clark and Price[4], Ebert *et al.*[6], McMillen *et al.*[7], Robaugh and Stein[8], Brooks *et al.*[9], Davis[10], Brouwer *et al.*[11], Grela and Colussi[12], Mizerka and Kiefer[13], Mueller-Markgraf and Troe[14], and Benson and O'Neal[5]. It is assumed that the given expression for k_1 represents values close to the high pressure limit.

Insufficient experimental data are available for the other channels (2)–(5) to allow recommended rate expressions.

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