Evaluated Kinetic Data for Combustion Modelling
Supplement I

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This compilation updates and expands a previous evaluation of kinetic data on elementary, homogeneous, gas phase reactions of neutral species involved in combustion systems [J. Phys. Chem. Ref. Data **21**, 411 (1992)]. The work has been carried out under the auspices of the European Community Energy Research and Development Program. Data sheets are presented for some 78 reactions and two tables in which preferred rate parameters are presented for reactions of ethyl, *i*-propyl, *t*-butyl, and allyl radicals are given. Each data sheet sets out relevant thermodynamic data, experimental kinetic data, references, and recommended rate parameters with their error limits. A table summarizing the recommended rate data is also given. The new reactions fall into two catagories: first, to expand the previous compilation relating largely to the combustion in air of methane, ethane and aromatic compounds; and second, provide data for some of the key radicals involved in the combustion of higher alkanes.

Key words: chemical kinetics; combustion; data evaluation; gas phase; rate constant.

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1. Introduction

This publication is the first supplement to the set of data sheets of critically evaluated data for combustion processes published in the Journal of Chemical Reference Data **21**, 411–734 (1992).

Both the previous and the present publication were prepared by the CEC Group on Evaluation of Kinetic Data for Combustion Modelling which was established as one of the projects within the European Community Energy Research and Development Program.

The original compilation was intended for use in computer modelling of the combustion of methane and ethane in air and it also dealt with a number of reactions of importance in the chemistry of exhaust gases, mainly involving NO_x, and in the combustion of aromatic compounds. This first supplement updates the original and extends it to cover the reactions of a number of radicals particularly important in the combustion of higher alkanes. It also provides a more extensive coverage of the reactions of nitrogen containing species.

In updating, a new data sheet has been provided for all reactions for which new data have been published since our previous work[1]. For reactions where no new data have become available, reference must be made back to the original compilation but the Summary Table, included in this supplement, contains the recommended rate parameters for all of the reactions evaluated by the group to date.

The general approach to updating has been to reproduce the tables of data from the previous data sheet, adding in the new data. However, for reactions where the data are particularly extensive and the new data are largely in agreement with our previous recommendations, only the new data are tabulated. In such cases the reader can gain a complete picture of the range and quality of the data from the graph (if presented) or must refer back to the original compilation[1]. In a very few instances where the new data consist of a single study agreeing with our previous recommendations, we have not updated, at this stage. For reasons given in 2.1 some of the combination/dissociation reactions dealt with in our previous publication are presented again despite there being no new data.

The formal cut-off point for the literature searching was January 1992, but the group continued to monitor the literature during the preparation of the manuscript and every attempt was made to incorporate more recent studies of importance, in particular the material presented at the 24th Symposium (International) on Combustion, held in 1992.

2. Guide to the Data Sheets

2.1. Scope and Reaction Ordering

For each reaction, a data sheet is presented setting out relevant thermodynamic data, rate coefficient measurements, an assessment 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[2]. 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.

In this present supplement, we have departed from this format in presenting data on the reactions of ethyl, *i*-propyl, *t*-butyl and allyl radicals. The reactions of these radicals are of key importance in modelling the combustion of higher alkanes but in most cases there are insufficient data to warrant production of a full data sheet. For most of the reactions of these species we have therefore presented our recommendations in the form of tables, with relevent comments on the preferred values, but without detailed display of the data.

These reactions are grouped in order 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
NH_3 Reactions
C Atom 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_3O_2 Radical Reactions
CH_3OH 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_3H_5 Radical Reactions
i-C_3H_7 Radical Reactions
C_3H_8 Reactions
t-C_4H_9 Radical 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.

An exception to this ordering is the placement of dissociation reactions immediately after their corresponding reverse reaction, the combination of the dissociation products. Thus the data sheet for the reaction

$$C_2H_6 + M \rightarrow 2CH_3 + M$$

will be found immediately following the data sheet for the reaction

$$CH_3 + CH_3 + M \rightarrow C_2H_6 + M.$$

This arrangement is followed wherever a full analysis of the pressure dependence of pairs of such reactions is carried out. In other cases where the data do not justify such a treatment or where only the combination or the decomposition reaction is dealt with, the normal ordering prevails.

In this supplement the data sheets on dissociation/combination reactions contain more extensive graphical presentation of the recommendations than was the case in the original publication in this series (CEC, 1992)[1]. For completeness, therefore, the data sheets for a number of such reactions, dealt with in CEC, 1992, are presented again in this present supplement with this enhanced graphical treatment.

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

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

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 ΔH° and ΔS° 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 thermodynamic data refer to a standard state of 1 atmosphere. The source of the thermodynamic data is discussed later in this Introduction.

The kinetic data for the reactions are summarized under the two headings (i) Rate Coefficient Measurements, and (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.

Among the Reviews and Evaluations there are a number which are referred to so frequently that rather than repetitively give their full reference, *in extenso*, we list them among the references in this Introduction and refer the reader back to this list. These reviews are those of the IUPAC Task Group[2–5], the NASA Panel[6] and our original publication referred to as CEC, 1992[1].

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

$$A + B + M \leftrightarrows AB + M,$$

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 fall-off curve" $[M]_c$ indicates the third body concentration for which the extrapolated $k_0[M]$ 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 on the rhs represent the Lindemann-Hinshelwood expression, and the additional broadening factor F, at not too high temperature, is approximately given by

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

where $N = 0.75 - 1.27 \log F_c$. The temperature dependence of F_c, which is sometimes significant, can be estimated by the procedure of Troe[7–9]. The results can usually be represented[9], approximately by an equation

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

where a, T^*, T^{**}, and T^{***} are constants. The first two terms are of importance for atmospheric conditions, but the last term in most cases becomes relevant only at high temperatures. In this way, the three quantities, k_0, k_∞, and F_c with

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

characterize the fall-off 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.

Theoretical predictions[7-9] 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[10] 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.

In a few instances, the rate constant for the reaction has been measured under conditions where it is almost certainly pressure dependent but where the measurements cannot be analysed to give values of k_0, k_∞, and F_c. In such cases an expression for k only is quoted.

To avoid ambiguity, the subscripts denoting infinite and zero pressure limiting rate constants have, in places, been written as superscripts e.g. $k^\infty{}_1$, $k^0{}_1$ rather than $k_{1\infty}$ and k_{10}.

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 $\Delta \log k = \pm X$ is equivalent to the statement that the range of values of k encompassed by these error limits may be found by multiplication and division of k 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 merit 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 the 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[11]. We have also made use of the NIST compilation[12] but that does not extend to temperatures sufficiently high for combustion modelling. The Sandia 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 has 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 at constants. The quality of the thermodynamic data rarely justify the use of expressions for K(T) involving more than three constants even through 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 K is very sensitive 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. Acknowledgments

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2.8. References

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3. Errata to Reference 1

We are grateful to a number of readers for drawing to our attention the following errors in our original set of data sheets (Ref. 1). There are also a number of minor typographical errors which are not listed.

$O + {}^3CH_2 \rightarrow CO + 2H$ $\rightarrow CO + H_2$	p.443.	The value of k in the first entry in the table of rate coefficients, measured by Vinckier and Debruyn should read 1.3×10^{-10} not 1.3×10^{-11}.
$H + CH_3 + M \rightarrow CH_4 + M$	p.428.	$k_0(\mathrm{He}) = 6.2 \times 10^{-29}\ (T/300)^{-1.8}$ not $k_0(\mathrm{He}) = 6.2 \times 10^{-29}\ (T/3000)^{-1.8}$.
$OH + C_2H_2 + M \rightarrow C_2H_2OH + M$	p.583.	k°_3 should read $5 \times 10^{-25}\ T^{-2}$ not $5 \times 10^{-35}\ T^{-2}$.
$OH + C_6H_5CH_3 \rightarrow H_2O + C_6H_5CH_2$	p.420.	Preferred values should read $k_1 = 8.6 \times 10^{-15} T\exp(-440/T)$ not $8.6 \times 10^{-15}\exp(-1440/T)$.
	p.599.	Preferred values should read $k_1 = 8.6 \times 10^{-15} T\exp(-440/T)$ not $8.6 \times 10^{-15}\exp(-440/T)$.
$OH + CO \rightarrow H + CO_2$	p.569.	There is a discrepancy between the line for the recommended value drawn on the graph and the expression quoted for the recommended value. The expression quoted should be used.
$HO_2 + CH_3 \rightarrow OH + CH_3O$	p.608.	The temperature range for the reliability of the preferred values should read 300–2500 K, not 600–1200 K.

4. Index of Reactions and Summary Table

4.1. Guide to the Summary Table

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 in that Table. 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.

4.2. Summary of Preferred Rate Data

TABLE 1. Bimolecular Reactions

Reaction	k/cm^3 molecule^{-1}s^{-1}	T/K	Error limits ($\Delta \log k$)
O Atom Reactions			
$O + H_2 \rightarrow OH + H$	$8.5 \times 10^{-20} T^{2.67} \exp(-3160/T)$	300–2500	± 0.5 at 300 K falling to ± 0.2 for $T > 500$ K
$O + OH \rightarrow O_2 + H$	$2.0 \times 10^{-11} \exp(112/T)$ $2.4 \times 10^{-11} \exp A(-353/T)$	220–500 1000–2000	± 0.2 ± 0.1
$O + HO_2 \rightarrow OH + O_2$	5.3×10^{-11}	300–1000	± 0.3 at 300 K rising to ± 0.5 at 1000 K
$O + H_2O_2 \rightarrow OH + HO_2$	$1.1 \times 10^{-12} \exp(-2000/T)$	300–500	± 0.3
$O + NO \rightarrow O_2 + N$	$1.14 \times 10^{-15} T^{1.13} \exp(-19200/T)$	1000–5000	± 0.3
$O + N_2 \rightarrow N + NO$	$3.0 \times 10^{-10} \exp(-38300/T)$	1400–4000	± 0.2
$O + NH \rightarrow NO + H$ $\rightarrow N + OH$	1.5×10^{-10}	1000–3380	± 0.5
$O + NH_3 \rightarrow OH + NH_2$	$1.6 \times 10^{-11} \exp(-3670/T)$	500–2500	± 0.5
$O + CH \rightarrow CO + H$ $\rightarrow CHO^+ + e$	6.6×10^{-11} $4.2 \times 10^{-13} \exp(-850/T)$	300–2000 300–2500	± 0.5 ± 0.5
$O + {}^3CH_2 \rightarrow CO + 2H$ $\rightarrow CO + H_2$	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.
$O + CH_3 \rightarrow HCHO + H$	1.4×10^{-10}	300–2500	± 0.2
$O + CH_4 \rightarrow OH + CH_3$	$1.2 \times 10^{-15} T^{1.56} \exp(-4270/T)$	300–2500	± 0.3 at 300 K falling to ± 0.15 at 2500 K
$O + CHO \rightarrow OH + CO$ $\rightarrow CO_2 + H$	5.0×10^{-11} 5.0×10^{-11}	300–2500 300–2500	± 0.3 ± 0.3
$O + HCHO \rightarrow OH + CHO$	$6.9 \times 10^{-13} T^{0.57} \exp(-1390/T)$	250–2200	± 0.1 at 250 K rising to ± 0.3 at 2200 K
$O + CH_3O \rightarrow O_2 + CH_3$ $\rightarrow OH + HCHO$	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
$O + CH_3OOH \rightarrow OH + CH_3O_2$ $\rightarrow OH + CH_2OOH$	$3.3 \times 10^{-11} \exp(-2390/T)$	300–1000	± 0.3 at 300 K rising to ± 0.5 at 100
$O + CN \rightarrow CO + N(^4S)$ $\rightarrow CO + N(^2D)$	1.7×10^{-11}	300–5000	± 0.2 at 300 K rising to ± 0.6 at 5000 K
$O + NCO \rightarrow NO + CO$ $\rightarrow O_2 + CN$	7.0×10^{-11}	1450–2600	± 0.8
$O + HCN \rightarrow NCO + H$ $\rightarrow CO + NH$ $\rightarrow OH + CN$	$2.3 \times 10^{-18} T^{2.1} \exp(-3075/T)$	450–2500	± 0.2 at 450 K rising to ± 0.3 at 2500 K
$O + C_2H \rightarrow CO + CH$	1.7×10^{-11}	300–2500	± 1.0
$O + C_2H_2 \rightarrow CO + {}^3CH_2$ $\rightarrow CHCO + H$	$1.2 \times 10^{-17} T^{2.1} \exp(-790/T)$ $k_2/k = 0.7 \pm 0.2$ over whole range.	295–2500	± 0.2
$O + C_2H_3 \rightarrow OH + C_2H_2$ $\rightarrow CO + CH_3$ $\rightarrow HCO + CH_2$	5×10^{-11}	300–2000	± 0.5

TABLE 1. Bimolecular Reactions — Continued

Reaction	k/cm^3 molecule^{-1}s^{-1}	T/K	Error limits ($\Delta \log k$)
$O + C_2H_4 \rightarrow CH_2CHO + H$ $\rightarrow HCO + CH_3$ $\rightarrow HCHO + CH_2$ $\rightarrow CH_2CO + H_2$	$2.25 \times 10^{-17} T^{1.88} \exp(-90/T)$ $k_1/k = 0.35 \pm 0.05$ at p> 3 Torr; $k_2/k = 0.6 \pm 0.10; k_4/k = 0.05 \pm 0.10$	300–2000	± 0.1 for $T < 1000$ K rising to ± 0.3 at 2000 K
$O + C_2H_5 \rightarrow CH_3CHO + H$ $\rightarrow HCHO + CH_3$	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
$O + C_2H_6 \rightarrow OH + C_2H_5$	$1.66 \times 10^{-15} T^{1.5} \exp(-2920/T)$	300–1200	± 0.3 at 300 K falling to ± 0.15 at 1200 K
$O + CHCO \rightarrow 2CO + H$	1.6×10^{-10}	300–2500	± 0.3
$O + CH_2CO \rightarrow CH_2O + CO$ $\rightarrow HCO + H + CO$ $\rightarrow HCO + HCO$	$3.8 \times 10^{-12} \exp(-680/T)$	230–500	± 0.3
$O + CH_3CO \rightarrow OH + CH_2CO$ $\rightarrow CO_2 + CH_3$	3.2×10^{-10} $k_1/k = 0.2 \pm 0.1$ at 298 K $k_2/k = 0.8 \pm 0.2$ at 298 K	298–1500	± 0.3 at 298 K rising to ± 1.0 at 1500 K
$O + CH_3CHO \rightarrow OH + CH_3CO$ $\rightarrow OH + CH_2CHO$	$9.7 \times 10^{-12} \exp(-910/T)$	298–1500	± 0.05 at 298 K rising to ± 0.5 at 1500 K
$O + C_2H_5OOH \rightarrow OH + C_2H_4OOH$ $\rightarrow OH + C_2H_5OO$	$3.3 \times 10^{-11} \exp(-2390/T)$ [estimate]	300–1000	± 0.3 at 300 K rising to ± 0.5 at 1000 K
$O + C_3H_5 \rightarrow CH_2CHCHO + H$ $\rightarrow HCHO + C_2H_3$	3.0×10^{-10} $<3 \times 10^{-11}$	300–1000 2000	± 0.2 over the range 300–600 K; ± 0.4 over the range 600–1000 K
$O + C_6H_6 \rightarrow OH + C_6H_5$ $\rightarrow C_6H_6O$	$(k_1 + k_2) = 5.9 \times 10^{-23} T^{3.8} \exp(-473/T)$ $k_2 = 3.7 \times 10^{-11} \exp(-2280/T)$	298–2000 298–1400	± 0.3 ± 0.3 at 298 K falling to ±0.2 at 1400 K.
$O + C_6H_5OH \rightarrow$ products	$2.1 \times 10^{-11} \exp(-1460/T)$	290–600	± 0.3
$O + C_6H_5CH_2 \rightarrow HCO + C_6H_6$ $\rightarrow C_6H_5CHO + H$ $\rightarrow CH_2O + C_6H_5$	5.5×10^{-10} No recommendation	300	± 0.3
$O + C_6H_5CH_3 \rightarrow$ products	$5.3 \times 10^{-15} T^{1.21} \exp(-1260/T)$	298–2800	± 0.1 at 298 K rising to ± 0.4 at 2800 K
$O + C_6H_5CHO \rightarrow OH + C_6H_5CO$ $\rightarrow OH + C_6H_4CHO$ $\rightarrow C_6H_5(O)CHO$	$1.0 \times 10^{-11} \exp(-910/T)$ No recommendation	298–1500	± 0.3 at 298 K rising to ± 0.7 at 1500 K
$O + p\text{-}C_6H_4(CH_3)_2 \rightarrow$ products	$5.1 \times 10^{-11} \exp(-1630/T)$	298–600	± 0.3
$O + C_6H_5C_2H_5 \rightarrow$ products	$2.8 \times 10^{-11} \exp(-1840/T)$	298–600	± 0.3
O_2 Reactions			
$O_2 + CH_4 \rightarrow HO_2 + CH_3$	$6.6 \times 10^{-11} \exp(-28630/T)$	500–2000	± 0.5 at 500 K rising to ± 1.0 at 2000 K
$O_2 + C_2H_6 \rightarrow HO_2 + C_2H_5$	$1.0 \times 10^{-10} \exp(-26100/T)$	500–2000	± 0.5 at 500 K rising to ± 1.0 at 2000 K

TABLE 1. Bimolecular Reactions — Continued

Reaction	k/cm^3 molecule^{-1}s^{-1}	T/K	Error limits ($\Delta \log k$)
$O_2 + HCHO \rightarrow HO_2 + HCO$	$1.0 \times 10^{-10} \exp(-20460/T)$	700–1000	± 0.5
$O_2 + CH_3CHO \rightarrow HO_2 + CH_3CO$	$5.0 \times 10^{-11} \exp(-19700/T)$	600–1100	± 0.5 at 600 K rising to ± 1.0 at 1100 K.
$O_2 + C_3H_6 \rightarrow HO_2 + CH_2CHCH_2$	$3.2 \times 10^{-12} \exp(-19700/T)$	600–1000	± 0.3 at 800 K rising to ± 0.5 at 600 K and 1000 K
$O_2 + C_6H_5CH_3 \rightarrow HO_2 + C_6H_5CH_2$	$3 \times 10^{-12} \exp(-20000/T)$	700–1200	± 0.7
H Atoms Reactions			
$H + O_2 \rightarrow OH + O$	$1.62 \times 10^{-10} \exp(-7470/T)$	300–5000	± 0.1 at 300 K rising to ± 0.5 at 5000 K
$H + O_2 + Ar \rightarrow HO_2 + Ar$	See Table 3		
$H + O_2 + H_2 \rightarrow HO_2 + H_2$	See Table 3		
$H + O_2 + N_2 \rightarrow HO_2 + N_2$	See Table 3		
$H + H + Ar \rightarrow H_2 + Ar$	See Table 3		
$H + H + H_2 \rightarrow H_2 + H_2$	See Table 3		
$H + OH + H_2O \rightarrow H_2O + H_2O$	See Table 3		
$H + OH + Ar \rightarrow H_2O + Ar$	See Table 3		
$H + OH + N_2 \rightarrow H_2O + N_2$	See Table 3		
$H + HO_2 \rightarrow H_2 + O_2$	$7.1 \times 10^{-11} \exp(-710/T)$	300–1000	± 0.3
$\rightarrow 2OH$	$2.8 \times 10^{-10} \exp(-440/T)$	300–1000	± 0.3
$\rightarrow H_2O + O$	$5.0 \times 10^{-11} \exp(-866/T)$	300–1000	± 0.3
$H + H_2O \rightarrow OH + H_2$	$7.5 \times 10^{-16} T^{1.6} \exp(-9270/T)$	300–2500	± 0.2
$H + H_2O_2 \rightarrow H_2 + HO_2$	$2.8 \times 10^{-12} \exp(-1890/T)$	300–1000	± 0.3
$\rightarrow OH + H_2O$	$1.7 \times 10^{-11} \exp(-1800/T)$	300–1000	± 0.3
$H + NO \rightarrow OH + N$	$3.6 \times 10^{-10} \exp(-24910/T)$	1500–4500	± 0.5
$H + NH \rightarrow H_2 + N$	1.7×10^{-11}	1500–2500	± 1.0
$H + NH_2 \rightarrow H_2 + NH$	1.0×10^{-11}	2000–3000	± 1.0
$H + CO + M \rightarrow HCO + M$	See Table 3		
$H + {}^3CH_2 \rightarrow H_2 + CH$	$1.0 \times 10^{-11} \exp(900/T)$	300–3000	± 0.7
$H + CH_3 \rightarrow H_2 + {}^1CH_2$	$1.0 \times 10^{-10} \exp(-7600/T)$	300–2500	± 1.0
$\rightarrow CH_4$	See Table 3		
$H + CH_4 \rightarrow H_2 + CH_3$	$2.2 \times 10^{-20} T^{3.0} \exp(-4045/T)$	300–2500	± 0.2 at 300 K and 2500 K reducing to ± 0.05 over range 500–1000 K
$H + CHO \rightarrow H_2 + CO$	1.5×10^{-10}	300–2500	± 0.3
$H + HCHO \rightarrow H_2 + HCO$	$2.1 \times 10^{-16} T^{1.62} \exp(-1090/T)$	300–1700	± 0.1 at 300 K rising to ± 0.3 at 1700 K
$H + CH_3O \rightarrow H_2 + HCHO$	3.0×10^{-11}	300–1000	± 0.5

TABLE 1. Bimolecular Reactions — Continued

Reaction	k/cm^3 molecule^{-1}s^{-1}	T/K	Error limits ($\Delta \log k$)
H + HNCO → NH_2 + CO	No recommendation		
→ H_2 + NCO	$3.4 \times 10^{-10}\ T^{-0.27} \exp(-10190/T)$	500–1000	± 1.0
H + NCO → NH + CO	8.7×10^{-11}	1400–1500	± 0.5
→ HCN + O			
H + C_2H_2 → H_2 + C_2H	$1.1 \times 10^{-10} \exp(-14000/T)$	1000–3000	± 1.0
→ C_2H_3	See Table 3		
H + C_2H_3 → H_2 + C_2H_2	2.0×10^{-11}	300–2500	± 0.5
→ C_2H_4	See Table 3		
H + C_2H_4 → H_2 + C_2H_3	$9.0 \times 10^{-10} \exp(-7500/T)$	700–2000	± 0.5
→ C_2H_5	See Table 3		
H + C_2H_5 → $2CH_3$	6.0×10^{-11}	300–2000	± 0.3 at 300 K rising to ± 0.7 at 2000 K
→ C_2H_6	See Table 3		
H + C_2H_6 → H_2 + C_2H_5	$2.4 \times 10^{-15}\ T^{1.5} \exp(-3730/T)$	300–2000	± 0.15 at 300 K rising to ± 0.3 at 2000 K
H + CHCO → CH_2 + CO	2.5×10^{-10}	300–2500	± 0.4
→ H_2 + C_2O			
→ HCCOH			
H + CH_2CO → CH_3 + CO	$3.0 \times 10^{-11} \exp(-1700/T)$	200–2000	± 0.5 at 200 K rising to ± 1.0 at 2000 K
→ CH_2CHO	k_2/k very small		
H + CH_3CHO → H_2 + CH_3CO	$6.8 \times 10^{-15}\ T^{1.16} \exp(-1210/T)$	300–2000	± 0.1 at 300 K rising to ± 0.4 at 2000 K
→ H_2 + CH_2CHO			
H + C_3H_5 → C_3H_6	$(k_1^\infty + k_2) = 2.8 \times 10^{-10}$	300–1000	± 0.2 at 300 K rising to ± 0.5 at 1000 K
→ C_2H_3 + CH_3			
→ H_2 + C_3H_4	3×10^{-11}	300–1000	± 0.5
H + C_6H_5 + M → C_6H_6 + M	See Table 3		
H + C_6H_6 → H_2 + C_6H_5	No recommendation		
→ C_6H_7	See Table 3		
H + C_6H_5O + M → C_6H_5OH + M	See Table 3		
H + C_6H_5OH → C_6H_5O + H_2	$1.9 \times 10^{-10} \exp(-6240/T)$	1000–1150	± 0.3
→ C_6H_6 + OH	$3.7 \times 10^{-11} \exp(-3990/T)$	1000–1150	± 0.3
H + $C_6H_5CH_2$ + M → $C_6H_5CH_3$ + M	See Table 3		
H + $C_6H_5CH_3$ → H_2 + $C_6H_5CH_2$	$3.6 \times 10^{-19}\ T^{2.63} \exp(-2210/T)$	600–2500	± 0.3
→ H_2 + $C_6H_4CH_3$	No recommendation		
→ C_6H_6 + CH_3	$9.6 \times 10^{-11} \exp(-4070/T)$	770–1100	± 0.3
→ $C_6H_6CH_3$	See Table 3		
H + p-$C_6H_4(CH_3)_2$ → products	5.8×10^{-13}	298	± 0.1
H + $C_6H_5C_2H_5$ → H_2 + $C_6H_5C_2H_4$	No recommendation		
→ $C_6H_6C_2H_5$	See Table 3		

TABLE 1. Bimolecular Reactions — Continued

Reaction	k/cm^3 molecule^{-1}s^{-1}	T/K	Error limits (Δ log k)
H_2 Reactions			
$H_2 + Ar \rightarrow 2H + Ar$	See Table 2		
$H_2 + H_2 \rightarrow 2H + H_2$	See Table 2		
OH Radical Reactions			
$OH + H_2 \rightarrow H_2O + H$	$1.7 \times 10^{-16}\ T^{1.6} \exp(-1660/T)$	300–2500	± 0.1 at 300 K rising to ± 0.3 at 2500 K
$OH + OH \rightarrow H_2O + O$	$2.5 \times 10^{-15}\ T^{1.14} \exp(-50/T)$	250–2500	± 0.2
$OH + OH + M \rightarrow H_2O_2 + M$	See Table 3		
$OH + HO_2 \rightarrow H_2O + O_2$	$4.8 \times 10^{-11} \exp(250/T)$	300–2000	± 0.2 at 300 K rising to ± 0.5 at 2000 K
$OH + H_2O_2 \rightarrow H_2O + HO_2$	$1.3 \times 10^{-11} \exp(-670/T)$	300–1000	± 0.2 at 300 K rising to ± 0.5 at 1000 K
$OH + NH \rightarrow NO + H_2$	8.0×10^{-11}	300–1000	± 0.5
$\rightarrow H_2O + N$			
$OH + NH_2 \rightarrow O + NH_3$	$3.3 \times 10^{-14}\ T^{0.405} \exp(-250/T)$	500–2500	± 0.5
$\rightarrow H_2O + NH$	No recommendation		
$OH + CO \rightarrow H + CO_2$	$1.05 \times 10^{-17}\ T^{1.5} \exp(250/T)$	300–2000	± 0.2 at 300 K rising to ± 0.5 at 2000 K
$OH + CH_3 \rightarrow H + CH_2OH$			
$\rightarrow H + CH_3O$	No recommendation		
$\rightarrow H_2O + {}^1CH_2$	$1.2 \times 10^{-11} \exp(-1400/T)$	300–1000	± 0.5
$\rightarrow CH_3OH$	See Table 3		
$OH + CH_4 \rightarrow H_2O + CH_3$	$2.6 \times 10^{-17}\ T^{1.83} \exp(-1400/T)$	250–2500	± 0.07 at 250 K rising to ± 0.15 at 1200 K
$OH + CHO \rightarrow H_2O + CO$	1.7×10^{-10}	300–2500	± 0.3
$OH + HCHO \rightarrow H_2O + CHO$	$5.7 \times 10^{-15}\ T^{1.18} \exp(225/T)$	300–3000	± 0.1 at 300 K rising to ± 0.7 at 3000 K
$OH + CN \rightarrow O + HCN$			
$\rightarrow NCO + H$	1.0×10^{-10}	1500–3000	± 0.5
$OH + HCN \rightarrow H_2O + CN$	$1.5 \times 10^{-11} \exp(-5400/T)$	1500–2500	± 0.5
$\rightarrow HOCN + H$	No recommendation		
$\rightarrow HNCO + H$			
$OH + CH_3OOH \rightarrow H_2O + CH_3OO$	$1.2 \times 10^{-12} \exp(130/T)$	300–1000	± 0.2 at 300 K rising to ± 0.4 at 1000 K
$\rightarrow H_2O + CH_2OOH$	$1.8 \times 10^{-12} \exp(220/T)$	300–1000	± 0.1 at 300 K rising to ± 0.3 at 1000 K
$OH + C_2H_2 \rightarrow H_2O + C_2H$	$1.0 \times 10^{-10} \exp(-6500/T)$	1000–2000	± 1.0
$\rightarrow H + CH_2CO$			
$\rightarrow C_2H_2OH$	See Table 3		
$OH + C_2H_4 \rightarrow H_2O + C_2H_3$	$3.4 \times 10^{-11} \exp(-2990/T)$	650–1500	± 0.5
$OH + C_2H_6 \rightarrow H_2O + C_2H_5$	$1.2 \times 10^{-17}\ T^{2.0} \exp(-435/T)$	250–2000	± 0.07 at 250 K rising to ± 0.15 at 2000 K

TABLE 1. Bimolecular Reactions — Continued

Reaction	k/cm^3 molecule^{-1}s^{-1}	T/K	Error limits ($\Delta \log k$)
$OH + CH_2CO \rightarrow CH_2OH + CO$ $\rightarrow H_2CO + HCO$	1.7×10^{-11}	300–2000	± 1.0
$OH + CH_3CHO \rightarrow H_2O + CH_3CO$ $\rightarrow H_2O + CH_2CHO$	$3.9 \times 10^{-14}\, T^{0.73} \exp(560/T)$	250–1200	± 0.1 at 250 K rising to ± 0.3 at 1200 K
$OH + C_2H_5OOH \rightarrow H_2O + C_2H_5OO$ $\rightarrow H_2O + C_2H_4OOH$	$3.0 \times 10^{-12} \exp(190/T)$ [estimate]	250–1000	± 0.3 at 250 K rising to ± 0.7 at 1000 K
$OH + C_3H_5 \rightarrow H_2O + C_3H_4$	1.0×10^{-11}	300–1000	± 0.5
$\rightarrow CH_2CHCH_2OH$ $\rightarrow CH_2CHCHO + 2H$	$(k_2^{\infty} + k_3) = 2.5 \times 10^{-11}$	300–1000	± 0.3
$OH + C_6H_6 \rightarrow H_2O + C_6H_5$	$2.7 \times 10^{-16}\, T^{1.42} \exp(-730/T)$	400–1500	± 0.3
$\rightarrow H + C_6H_5OH$	$2.2 \times 10^{-11} \exp(-5330/T)$	1000–1150	± 0.3
$\rightarrow C_6H_6OH$	See Table 3		
$OH + C_6H_5OH \rightarrow C_6H_5(OH)_2$	See Table 3		
$\rightarrow H_2O + C_6H_5O$ $\rightarrow H_2O + C_6H_4OH$	1.0×10^{-11}	1000–1150	± 0.5
$OH + C_6H_5CH_3 \rightarrow H_2O + C_6H_4CH_2$	$8.6 \times 10^{-15}\, T \exp(-440/T)$	400–1200	± 0.5 at 400 K reducing to ± 0.3 at 1200 K
$\rightarrow C_6H_5CH_3OH$	See Table 3		
$OH + C_6H_5CHO \rightarrow H_2O + C_6H_5CO$ $\rightarrow H_2O + C_6H_4CHO$	1.3×10^{-11}	298–1500	± 0.1 at 298 K rising to ± 0.5 at 1500 K
$OH + p\text{-}C_6H_4(CH_3)_2 \rightarrow C_6H_4CH_2CH_3 + H_2O$	$6.4 \times 10^{-11} \exp(-1440/T)$	500–960	± 0.1
$\rightarrow p\text{-}C_6H_4(CH_3)_2OH$	See Table 3		
$OH + C_6H_5C_2H_5 \rightarrow HOC_6H_5C_2H_5$	See Table 3		
$\rightarrow H_2O + C_6H_5C_2H_4$ $\rightarrow H_2O + C_6H_4C_2H_5$	No recommendation		
H_2O Reactions			
$H_2O + M \rightarrow H + OH + M$	See Table 2		
HO_2 Radical Reactions			
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$7.0 \times 10^{-10} \exp(-6030/T) +$ $2.2 \times 10^{-13} \exp(820/T)$	550–1250	± 0.15 between 550–800 K rising to ± 0.4 at 1250 K
	$7.0 \times 10^{-10} \exp(-6030/T)$	850–1250	
$HO_2 + NH_2 \rightarrow NH_3 + O_2$ $\rightarrow HNO + H_2O$	2.6×10^{-11}	300–400	± 0.4
$HO_2 + CH_3 \rightarrow OH + CH_3O$	3×10^{-11}	300–2500	± 0.7
$\rightarrow O_2 + CH_4$	No recommendation		
$HO_2 + CH_4 \rightarrow H_2O_2 + CH_3$	$1.5 \times 10^{-11} \exp(-12440/T)$	600–1000	± 0.2 at 600 K rising to ± 0.3 at 1000 K
$HO_2 + HCHO \rightarrow H_2O_2 + CHO$	$5.0 \times 10^{-12} \exp(-6580/T)$	600–1000	± 0.5

TABLE 1. Bimolecular Reactions — Continued

Reaction	k/cm^3 molecule^{-1}s^{-1}	T/K	Error limits (Δ log k)
$HO_2 + CH_3O_2 \rightarrow CH_3OOH + O_2$	4.1×10^{-13} exp($790/T$)	298–700	± 0.1 at 298 K rising to
$\rightarrow HCHO + H_2O + O_2$	$k_1/k = 1.0 \pm 0.1$ over whole range		± 0.3 at 700 K
$HO_2 + C_2H_4 \rightarrow OH + C_2H_4O$	3.7×10^{-12} exp($-8650/T$)	600–900	± 0.15 at 600 K rising to ± 0.25 at 900 K
$HO_2 + C_2H_6 \rightarrow H_2O_2 + C_2H_5$	2.2×10^{-11} exp($-10300/T$)	500–1000	± 0.2 at 500 K rising to ± 0.3 at 1000 K
$HO_2 + CH_3CHO \rightarrow H_2O_2 + CH_3CO$	5.0×10^{-12} exp($-6000/T$)	900–1200	± 0.7
$HO_2 + C_3H_5 \rightarrow C_3H_6 + O_2$	4.4×10^{-12}	300–1000	± 0.3 over the range 600 K to 800 K rising to 0.5 at other temperatures
$\rightarrow$ CO + products	1.1×10^{-11}	500–900	± 0.3
$HO_2 + C_6H_5CH_3 \rightarrow H_2O_2 + C_6H_5CH_2$	6.6×10^{-13} exp($-7080/T$)	600–1000	± 0.3 at 750 K rising to ± 0.5 at 600 K and 1000 K
$\rightarrow H_2O_2 + C_6H_4CH_3$	9.1×10^{-12} exp($-14500/T$)	600–1000	± 1.0
$HO_2 + C_6H_5CH_2CH_3 \rightarrow H_2O_2 + C_6H_5CHCH_3$	4.4×10^{-13} exp($-5680/T$)	600–1000	± 0.3 at 750 K rising to ± 0.5 at 600 K and 1000 K
$\rightarrow H_2O_2 + C_6H_5CH_2CH_2$	5.3×10^{-12} exp($-9760/T$)	600–1000	± 0.5
$\rightarrow H_2O_2 + C_6H_4CH_2CH_3$	9×10^{-12} exp($-14500/T$)	600–1000	± 1.0
H_2O_2 Reactions			
$H_2O_2 + M \rightarrow 2OH + M$	See Table 2		
N Atom Reactions			
$N + O_2 \rightarrow NO + O$	1.5×10^{-14} T exp($-3270/T$)	298–5000	± 0.12 over range 300–1000 K rising to ± 0.3 over range 1000–5000 K
$N + OH \rightarrow NO + H$	4.7×10^{-11}	300–2500	± 0.1 at 300 K rising to ± 0.3 at 2500 K
$N + NO \rightarrow N_2 + O$	7.1×10^{-11} exp($-790/T$)	1400–4000	± 0.2
$N + CN \rightarrow N_2 + C$	3×10^{-10}	300–2500	± 1.0
$N + NCO \rightarrow NO + CN$	No recommendation		
$\rightarrow N_2 + CO$	3.3×10^{-11}	1700	± 0.5
NH Radical Reactions			
$NH + O_2 \rightarrow NO + OH$	$(k_1 + k_2) = 1.3 \times 10^{-13}$ exp($-770/T$)	270–550	± 0.25
$\rightarrow NO_2 + H$			
$\rightarrow HNO + O$	6.5×10^{-11} exp($-9000/T$)	2200–3500	± 0.5
$NH + NO \rightarrow N_2O + H$			
$\rightarrow HN_2 + O$	5.0×10^{-11}	270–380	± 0.2
$\rightarrow N_2 + OH$	2.8×10^{-10} exp($-6400/T$)	2220–3350	± 0.5
NH_2 Radical Reactions			
$NH_2 + O_2 \rightarrow$ products	$<3 \times 10^{-18}$	298	
$NH_2 + NO \rightarrow N_2 + H_2O$			
$\rightarrow N_2 + H + OH$	1.8×10^{-12} exp($650/T$)	220–2000	± 0.5
$\rightarrow N_2H + OH$	$(k_2 + k_3)/k \approx 0.12$ at 298 K		
$\rightarrow N_2O + H_2$			

TABLE 1. Bimolecular Reactions — Continued

Reaction	$k/\mathrm{cm^3\ molecule^{-1}s^{-1}}$	T/K	Error limits ($\Delta \log k$)
NH_3 Reactions			
$NH_3 + M \rightarrow NH_2 + H$	See Table 2		
$\rightarrow NH + H_2$	No recommendation		
C Atom Reactions			
$C + N_2 \rightarrow CN + N$	$8.7 \times 10^{-11} \exp(-22600/T)$	2000–5000	± 0.2
$\left.\begin{array}{l} C + NO \rightarrow CN + O \\ \quad\rightarrow CO + N \end{array}\right]$	2.5×10^{-11}	300	± 0.3
	8.0×10^{-11} $k_1/k_2 = 0.6 \pm 0.25$; $k_1/k = 0.4 \pm 0.25$ over range 1500–4050 K	1500–4050	± 0.3
$^1C_2$ and $^3C_2$ Radical Reactions	*See data sheets*		
CH Radical Reactions			
$\left.\begin{array}{l} CH + O_2 \rightarrow CHO + O \\ \quad\rightarrow CO + OH \end{array}\right]$	5.5×10^{-11}	300–2000	± 0.3 at 300 K rising to ± 0.5 at 2000 K
$\left.\begin{array}{l} CH + H_2 \rightarrow CH_2 + H \\ \quad\rightarrow CH_3 \end{array}\right]$	$2.4 \times 10^{-10} \exp(-1760/T)$	300–1000	± 0.3
$CH + H_2O \rightarrow$ products	$9.5 \times 10^{-12} \exp(380/T)$	300–1000	± 1.0
$\left.\begin{array}{l} CH + N_2 \rightarrow HCN + N \\ \quad\rightarrow CHN_2 \end{array}\right]$	$2.6 \times 10^{-12} \exp(-9030/T)$ at $p < 1$ atm.	2000–4000	± 0.3
$\left.\begin{array}{l} CH + NO \rightarrow CO + NH \\ \quad\rightarrow CN + OH \\ \quad\rightarrow HCN + O \end{array}\right]$	2.0×10^{-10}	300–4000	± 0.25
$CH + CO \rightarrow$ products	$4.6 \times 10^{-13} \exp(860/T)$	300–1000	± 1.0
$CH + CO_2 \rightarrow$ products	$5.7 \times 10^{-12} \exp(-345/T)$	300–1000	± 1.0
$CH + CH_4 \rightarrow$ products	$5.0 \times 10^{-11} \exp(200/T)$	200–700	± 1.0
$CH + C_2H_2 \rightarrow$ products	$3.5 \times 10^{-10} \exp(61/T)$	200–700	± 1.0
$CH + C_2H_4 \rightarrow$ products	$2.2 \times 10^{-10} \exp(173/T)$	200–700	± 1.0
$CH + C_2H_6 \rightarrow$ products	$1.8 \times 10^{-10} \exp(132/T)$	200–700	± 1.0
$CH + C_3H_8 \rightarrow$ products	$1.9 \times 10^{-10} \exp(240/T)$	300–700	± 1.0
$CH + n\text{-}C_4H_{10} \rightarrow$ products	$4.4 \times 10^{-10} \exp(28/T)$	250–700	± 1.0
$CH + i\text{-}C_4H_{10} \rightarrow$ products	$2.0 \times 10^{-10} \exp(240/T)$	300–700	± 1.0
$CH + \text{neo-}C_5H_{12} \rightarrow$ products	$1.6 \times 10^{-10} \exp(340/T)$	300–700	± 1.0
$CH + CH_3C_2H \rightarrow$ products	No recommendation		
$CH + CH_2O \rightarrow$ products	$1.6 \times 10^{-10} \exp(260/T)$	300–700	± 1.0

TABLE 1. Bimolecular Reactions — Continued

Reaction	k/cm^3 molecule^{-1}s^{-1}	T/K	Error limits (Δ log k)
$^3CH_2$ Radical Reactions			
$3CH_2 + O_2 \rightarrow CO + H + OH$ $\rightarrow CO_2 + H + H$ $\rightarrow CO + H_2O$ $\rightarrow CO_2 + H_2$ $\rightarrow HCHO + O$	$4.1 \times 10^{-11} \exp(-750/T)$	300–1000	± 0.1 at 300 K rising to ± 0.5 at 1000 K
$^3CH_2 + {}^3CH_2 \rightarrow C_2H_2 + H_2$ $\rightarrow C_2H_2 + 2H$	$2.0 \times 10^{-10} \exp(-400/T)$ $k_2/k = 0.9 \pm 0.1$ over range 300–3000 K.	300–3000	± 0.5
$^3CH_2 + CH_3 \rightarrow C_2H_4 + H$	7.0×10^{-11}	300–3000	± 0.3 at 300 K rising to ± 0.5 at 3000 K
$^3CH_2 + C_2H_2 \rightarrow C_3H_4$	See Table 3		
$^3CH_2 + C_2H_4 \rightarrow C_3H_6$ $\rightarrow c\text{-}C_3H_6$ $\rightarrow CH_2CHCH_2 + H$	See Table 3		
$^1CH_2$ Radical Reactions			
$^1CH_2 + Ar \rightarrow {}^3CH_2 + Ar$	6.0×10^{-12}	300–2000	± 0.3
$^1CH_2 + NO \rightarrow$ products	1.6×10^{-10}	290–650	± 0.2
$^1CH_2 + N_2 \rightarrow {}^3CH_2 + N_2$	1.0×10^{-11}	300–2000	± 0.3
$^1CH_2 + CH_4 \rightarrow {}^3CH_2 + CH_4$	1.2×10^{-11}	300–2000	± 0.4
$^1CH_2 + C_2H_2 \rightarrow {}^3CH_2 + C_2H_2$	8.0×10^{-11}	300–2000	± 0.4
$^1CH_2 + C_2H_4 \rightarrow {}^3CH_2 + C_2H_4$	4.0×10^{-11}	300–2000	± 0.4
$^1CH_2 + C_2H_6 \rightarrow {}^3CH_2 + C_2H_6$	3.6×10^{-11}	300–2000	± 0.4
$^1CH_2 + O_2 \rightarrow CO + H + OH$ $\rightarrow CO_2 + H_2$ $\rightarrow CO + H_2O$ $\rightarrow {}^3CH_2 + O_2$	5.2×10^{-11}	300–1000	± 0.3 at 300 K rising to ± 0.5 at 1000 K
$^1CH_2 + H_2 \rightarrow CH_3 + H$	1.2×10^{-10}	300–1000	± 0.1 at 300 K rising to ± 0.3 at 1000 K
$^1CH_2 + C_2H_2 \rightarrow CH_2CCH_2$ $\rightarrow CH_3CCH$ $\rightarrow CH_2CCH + H$	See Table 3		
$\rightarrow {}^3CH_2 + C_2H_2$	See earlier entry		
$^1CH_2 + C_2H_4 \rightarrow C_3H_6$	See Table 3		
$\rightarrow {}^3CH_2 + C_2H_4$	See earlier entry		
CH_3 Radical Reactions			
$CH_3 + M \rightarrow CH_2 + H + M$	See Table 2		
$CH_3 + O_2 \rightarrow CH_3O + O$	$2.2 \times 10^{-10} \exp(-15800/T)$	300–2500	± 0.5
$\rightarrow HCHO + OH$	$5.5 \times 10^{-13} \exp(-4500/T)$	1000–2500	± 0.5
$\rightarrow CH_3O_2$	See Table 3		
$CH_3 + H_2 \rightarrow CH_4 + H$	$1.14 \times 10^{-20}\, T^{2.74} \exp(-4740/T)$	300–2500	± 0.15 in the range 300–700 K ± 0.3 in the range 700–2500 K

TABLE 1. Bimolecular Reactions — Continued

Reaction	k/cm^3 molecule^{-1}s^{-1}	T/K	Error limits ($\Delta \log k$)
$CH_3 + CO + M \rightarrow CH_3CO + M$	See Table 3		
$CH_3 + CH_3 \rightarrow C_2H_5 + H$	$5 \times 10^{-11} \exp(-6800/T)$	1300–2500	± 0.6
$\rightarrow C_2H_4 + H_2$	No recommendation (see data sheets)		
$\rightarrow C_2H_6$	See Table 3		
$CH_3 + HCHO \rightarrow CH_4 + HCO$	$1.3 \times 10^{-31} T^{6.1} \exp(-990/T)$	300–2000	± 0.2
$CH_3 + C_2H_2 + M \rightarrow C_3H_5 + M$	See Table 3		
$\rightarrow CH_4 + C_2H$	No recommendation		
$CH_3 + C_2H_4 \rightarrow CH_4 + C_2H_3$	$6.9 \times 10^{-12} \exp(-5600/T)$	400–3000	± 0.5
$\rightarrow n\text{-}C_3H_7$	See Table 3		
$CH_3 + C_2H_5 \rightarrow CH_4 + C_2H_4$	1.9×10^{-12}	300–2000	± 0.4
$\rightarrow C_3H_8$	See Table 3		
$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5$	$2.5 \times 10^{-31} T^{6.0} \exp(-3043/T)$	300–1500	± 0.1 at 300 K rising to ± 0.2 at 1500 K
$CH_3 + CH_3CHO \rightarrow CH_4 + CH_3CO$	$3.3 \times 10^{-30} T^{5.6} \exp(-1240/T)$	300–1250	± 0.3
$\rightarrow CH_4 + CH_2CHO$	No recommendation (see data sheets)		
$CH_3 + C_3H_5 \rightarrow C_2H_5CHCH_2$	See Table 3		
$\rightarrow CH_4 + CH_2CCH_2$	3.5×10^{-13}	500–1200	± 0.5
CH_4 Reactions			
$CH_4 + M \rightarrow CH_3 + H + M$	See Table 2		
CHO Radical Reactions			
$CHO + Ar \rightarrow H + CO + Ar$	See Table 2		
$CHO + O_2 \rightarrow CO + HO_2$ $\rightarrow OH + CO_2$ $\rightarrow HCO_3$	5.0×10^{-12}	300–2500	± 0.3
$CHO + CHO \rightarrow HCHO + CO$	5.0×10^{-11}	300	± 0.3
HCHO Reactions			
$HCHO + M \rightarrow H + CHO + M$ $\rightarrow H_2 + CO + M$	See Table 2		
CH_2OH Reactions			
$CH_2OH + O_2 \rightarrow CH_2O + HO_2$	$2.6 \times 10^{-9} T^{-1.0} +$ $1.2 \times 10^{-10} \exp(-1800/T)$	300–1200	± 0.1 at 300 K rising to ± 0.3 at 1200 K
CH_3O Radical Reactions			
$CH_3O + M \rightarrow HCHO + H + M$	See Table 2		
$CH_3O + O_2 \rightarrow HCHO + HO_2$	$3.6 \times 10^{-14} \exp(-880/T)$	300–1000	± 0.1 at 500 K rising to ± 0.3 at 300 K and 1000 K

TABLE 1. Bimolecular Reactions — Continued

Reaction	k/cm^3 molecule^{-1}s^{-1}	T/K	Error limits ($\Delta \log k$)
CH_3O_2 Radical Reactions			
$CH_3O_2 + CH_3O_2 \rightarrow CH_3O + CH_3O + O_2$ $\rightarrow CH_3OH + HCHO + O_2$ $\rightarrow CH_3OOCH_3 + O_2$	$9.1 \times 10^{-14} \exp(420/T)$ $k_1/k_2 = 25 \exp(-1170/T)$; $k_3 = 0$ over whole range	298–700	± 0.1 at 298 K increasing to ± 0.3 at 700 K
$CH_3O_2 + C_3H_5 \rightarrow CH_3O + CH_2CHCH_2O$	2.0×10^{-11}	500–1200	± 0.5
CH_3OH Reactions			
$CH_3OH + Ar \rightarrow CH_3 + OH + Ar$ $\rightarrow CH_2OH + H + Ar$ $\rightarrow {}^1CH_2 + H_2O + Ar$	See Table 2		
CH_3OOH Reactions			
$CH_3OOH + M \rightarrow CH_3O + OH + M$	See Table 2		
CN Radical Reactions			
$CN + O_2 \rightarrow NCO + O$	$1.2 \times 10^{-11} \exp(210/T)$	290–4500	± 0.15 over the range 290–4500 K
$CN + H_2 \rightarrow HCN + H$	$3.2 \times 10^{-20}\, T^{2.87} \exp(-820/T)$	200–3500	± 0.2 at 200 K rising to ± 0.5 at 3500 K
$CN + H_2O \rightarrow HCN + OH$ $\rightarrow HOCN + H$	$1.3 \times 10^{-11} \exp(-3750/T)$	500–3000	± 0.3 at 500 K rising to ± 0.5 at 3000 K
$CN + CH_4 \rightarrow HCN + CH_3$	$1.5 \times 10^{-19}\, T^{2.64} \exp(150/T)$	290–1500	± 0.3
NCO Radical Reactions			
$NCO + M \rightarrow N + CO + M$	See Table 2		
$NCO + NO \rightarrow N_2O + CO$ $\rightarrow N_2 + CO_2$ $\rightarrow N_2 + CO + O$	$2.3 \times 10^{-6}\, T^{-1.73} \exp(-380/T)$	290–3000	± 0.25
C_2H Radical Reactions			
$C_2H + O_2 \rightarrow CO_2 + CH$ $\rightarrow 2CO + H$ $\rightarrow C_2HO + O$ $\rightarrow CO + HCO$	3.0×10^{-11}	300	± 0.5
$C_2H + H_2 \rightarrow C_2H_2 + H$	$1.8 \times 10^{-11} \exp(-1090/T)$	300–2500	± 0.3 at 300 K rising to ± 0.5 at 2500 K
$C_2H + C_2H_2 \rightarrow C_4H_2 + H$	1.5×10^{-10}	300–2700	± 0.5
$C_2H + CH_4 \rightarrow$ products	3.0×10^{-12}	298	± 1
$C_2H + C_2H_6 \rightarrow$ products	No recommendation		

TABLE 1. Bimolecular Reactions — Continued

Reaction	k/cm^3 molecule^{-1}s^{-1}	T/K	Error limits ($\Delta \log k$)
C_2H_3 Radical Reactions			
$C_2H_3 + M \rightarrow C_2H_2 + H + M$	See Table 2		
$C_2H_3 + O_2 \rightarrow HO_2 + C_2H_2$ $\rightarrow H_2CO + CHO$ $\rightarrow C_2H_3O + O$ $\rightarrow C_2H_3O_2$	9.0×10^{-12}	300–2000	± 0.3 over range 300–600 K; ± 0.5 over range 600–2000 K
C_2H_4 Reactions			
$C_2H_4 + M \rightarrow C_2H_2 + H_2 + M$ $\rightarrow C_2H_3 + H + M$	See Table 2		
C_2H_5 Radical Reactions			
$C_2H_5 + M \rightarrow C_2H_4 + H + M$	See Table 2		
$C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$	$1.7 \times 10^{-14} \exp(1100/T)$	600–1200	± 0.3
$C_2H_5 + H_2 \rightarrow C_2H_6 + H$	$5.1 \times 10^{-24}\, T^{3.6} \exp(-4250/T)$	700–1200	± 0.2 at 700 K rising to ± 0.6 at 1200 K
$C_2H_5 + C_2H_2 \rightarrow C_2H_5CHCH$	$5.6 \times 10^{-14} \exp(-3520/T)$	300–600	± 0.5
$C_2H_5 + C_2H_4 \rightarrow n\text{-}C_4H_9$	$1.8 \times 10^{-13} \exp(-3670/T)$	300–600	± 0.5
$C_2H_5 + C_2H_5 \rightarrow n\text{-}C_4H_{10}$	See Table 3		
$\rightarrow C_2H_6 + C_2H_4$	2.4×10^{-12}	300–1200	± 0.4
$C_2H_5 + C_2H_5CHO \rightarrow C_2H_6 + C_2H_5CO$	$2.9 \times 10^{-13} \exp(-3660/T)$	300–700	± 0.3
$C_2H_5 + C_3H_5 \rightarrow CH_3CH_2CH_2CHCH_2$	See Table 3		
$\rightarrow C_2H_6 + CH_2CCH_2$	$1.6 \times 10^{-12} \exp(66/T)$	500–1200	± 0.3
$\rightarrow C_2H_4 + C_3H_6$	$4.3 \times 10^{-12} \exp(66/T)$	500–1200	± 0.4
C_2H_6 Reactions			
$C_2H_6 + M \rightarrow CH_3 + CH_3 + M$	See Table 2		
CHCO Reactions			
$CHCO + O_2 \rightarrow CO_2 + HCO$ $\rightarrow 2CO + OH$ $\rightarrow C_2O + HO_2$ $\rightarrow CHO_2CO$	$2.7 \times 10^{-12} \exp(-430/T)$ M = He, 2 Torr	300–550	± 0.7
CH_2CHO Radical Reactions			
$CH_2CHO + O_2 \rightarrow HO_2 + CH_2CO$ $\rightarrow HCHO + CO + OH$ $\rightarrow O_2CH_2CHO$	$k_\infty = 2.6 \times 10^{-13}$ $k_2 = 3.0 \times 10^{-14}$	250–500 300	± 0.2 ± 0.3
CH_3CO Radical Reactions			
$CH_3CO + O_2 + M \rightarrow CH_3CO_3 + M$	See Table 3		
CH_3CHO Reactions			
$CH_3CHO + M \rightarrow CH_3 + HCO + M$	See Table 2		

TABLE 1. Bimolecular Reactions — Continued

Reaction	k/cm^3 molecule^{-1}s^{-1}	T/K	Error limits ($\Delta \log k$)
C_2H_5O Reactions			
$C_2H_5O + M \rightarrow HCHO + CH_3 + M$	See Table 2		
$\rightarrow CH_3CHO + H + M$			
$C_2H_5O + O_2 \rightarrow CH_3CHO + HO_2$	$1.0 \times 10^{-13} \exp(-830/T)$	300–1000	± 0.3 at 300 K rising to ± 0.5 at 1000 K
C_2H_5OOH Reactions			
$C_2H_5OOH + M \rightarrow C_2H_5O + OH + M$	See Table 2		
C_3H_5 Radical Reactions			
$C_3H_5 + M \rightarrow CH_2CCH_2 + H + M$	See Table 2		
$C_3H_5 + O_2 \rightarrow CH_2CCH_2 + HO_2$	$1.7 \times 10^{-12} \exp(-11400/T)$	600–1200	± 0.3 at 600 K rising to ± 0.5 at 1200 K
$\rightarrow$ CO + products	$7.6 \times 10^{-12} \exp(-9450/T)$	600–1200	± 0.3
$C_3H_5 + H_2 \rightarrow C_3H_6 + H$	$1.8 \times 10^{-19} T^{2.4} \exp(-9550/T)$	300–1100	± 0.7 at 300 K reducing to ± 0.3 at 1100 K
$C_3H_5 + CH_4 \rightarrow C_3H_6 + CH_3$	$6.6 \times 10^{-23} T^{3.4} \exp(-11670/T)$	300–1200	± 0.4
$C_3H_5 + C_2H_4 \rightarrow C_3H_6 + C_2H_3$	$6.6 \times 10^{-23} T^{3.4} \exp(-13120/T)$	600–1200	± 0.5
$\rightarrow$ c-$C_5H_8 + H$	$1.0 \times 10^{-13} \exp(-9620/T)$	600–1200	± 0.7
$C_3H_5 + C_2H_6 \rightarrow C_3H_6 + C_2H_5$	$3.9 \times 10^{-22} T^{3.3} \exp(-9990/T)$	300–1200	± 0.4
$C_3H_5 + C_3H_5 \rightarrow CH_2CHCH_2CH_2CHCH_2$	See Table 3		
$\rightarrow C_3H_6 + CH_2CCH_2$	$1.0 \times 10^{-13} \exp(132/T)$	300–1000	± 0.7
$C_3H_5 + C_3H_8 \rightarrow C_3H_6 + CH_3CH_2CH_2$	$3.9 \times 10^{-22} T^{3.3} \exp(-9990/T)$	300–1200	± 0.4 over the range 600 to 1000 K rising to ± 0.7 at other temperatures
$\rightarrow C_3H_6 + CH_3CHCH_3$	$1.3 \times 10^{-22} T^{3.3} \exp(-8660/T)$	300–1200	
C_3H_5 + 2-$C_4H_8 \rightarrow C_3H_6 + CH_2CHCHCH_3$	$6.6 \times 10^{-12} \exp(-8180/T)$	600–1000	± 0.5
$\rightarrow C_3H_6 + CH_3CCHCH_3$	$3.3 \times 10^{-23} T^{3.4} \exp(-12160/T)$	600–1000	± 0.5
$\rightarrow CH_2CHCH_2CH(CH_3)CHCH_3$	See Table 3		
C_3H_5 + i-$C_4H_{10} \rightarrow C_3H_6 + (CH_3)_2CHCH_2$	$5.9 \times 10^{-22} T^{3.3} \exp(-9990/T)$	300–1200	± 0.4 over the range 600 to 1000 K rising to ± 0.7 at other temperatures
$\rightarrow C_3H_6 + (CH_3)_3C$	$0.7 \times 10^{-22} T^{3.3} \exp(-7800/T)$	300–1200	
$C_3H_5 + HCHO \rightarrow C_3H_6 + HCO$	$1.2 \times 10^{-16} T^{1.8} \exp(-9155/T)$	300–1000	± 0.4
$C_3H_5 + C_6H_5CH_3 \rightarrow C_3H_6 + C_6H_5CH_2$	$3.3 \times 10^{-12} \exp(-8660/T)$	600–1000	± 0.4
i-C_3H_7 Radical Reactions			
i-$C_3H_7 + M \rightarrow C_3H_6 + H + M$	See Table 2		
i-$C_3H_7 + O_2 \rightarrow C_3H_6 + HO_2$	$3.3 \times 10^{-14} \exp(+1290/T)$	600–800	± 0.5
i-$C_3H_7 + H_2 \rightarrow C_3H_8 + H$	$1.3 \times 10^{-23} T^{3.28} \exp(-4360/T)$	300–1200	± 0.5
i-$C_3H_7 + C_2H_2 \rightarrow (CH_3)_2CHCHCH$	$5.3 \times 10^{-14} \exp(-3470/T)$	300–600	± 0.5
i-$C_3H_7 + C_2H_4 \rightarrow (CH_3)_2CHCH_2CH_2$	$7.5 \times 10^{-14} \exp(-3470/T)$	300–600	± 0.5

TABLE 1. Bimolecular Reactions — Continued

Reaction	k/cm^3 molecule^{-1}s^{-1}	T/K	Error limits ($\Delta \log k$)
i-C_3H_7 + i-C_3H_7 → C_6H_{14}	See Table 3	300–1000	± 0.1 at 300 K rising to ± 0.3 at 1000 K
→ C_3H_8 + C_3H_6	4.2 × 10^{-12}	300–1000	± 0.1 at 300 K rising to ± 0.5 at 1000 K
i-C_3H_7 + i-C_3H_7CHO → C_3H_8 + $(CH_3)_2CHCO$	6.6 × 10^{-14} exp($-3170/T$)	300–650	± 0.5
→ C_3H_8 + $(CH_3)_2CCHO$			
→ C_3H_8 + $CH_2CH(CH_3)CHO$	5.3 × 10^{-14} exp($-4780/T$)	500–650	± 0.5
C_3H_8 Reactions			
C_3H_8 + M → CH_3 + C_2H_5 + M	See Table 2		
t-C_4H_9 Radical Reactions			
t-C_4H_9 + M → i-C_4H_8 + H + M	See Table 2		
t-C_4H_9 + O_2 → i-C_4H_8 + HO_2	5 × 10^{-14} exp($+2115/T$)	600–800	± 0.5
t-C_4H_9 + H_2 → i-C_4H_{10} + H	3.1 × 10^{-26} $T^{4.24}$ exp($-4510/T$)	300–1200	± 0.5
t-C_4H_9 + C_2H_2 → $(CH_3)_3CCHCH$	1.2 × 10^{-13} exp($-4320/T$)	300–600	± 0.5
t-C_4H_9 + C_2H_4 → $(CH_3)_3CCH_2CH_2$	3.3 × 10^{-14} exp($-4020/T$)	300–650	± 0.5
t-C_4H_9 + t-C_4H_9 → C_8H_{18}	See Table 3		
→ i-C_4H_{10} + i-C_4H_8	1.2 × 10^{-7} $T^{-1.73}$	300–1000	± 0.15 at 300 K rising to ± 0.5 at 1000 K
t-C_4H_9 + t-C_4H_9CHO → i-C_4H_{10} + t-C_4H_9CO	1.0 × 10^{-14} exp($-3200/T$)	300–700	± 0.5
→ i-C_4H_{10} + $CH_2C(CH_3)_2CHO$	3.9 × 10^{-14} exp($-5540/T$)	500–700	± 0.5
C_6H_5 Radical Reactions			
C_6H_5 + M → C_2H_2 + C_4H_3 + M	see Table 2		
→ C_2H_3 + C_4H_2 + M			
→ linear-C_6H_5 + M			
C_6H_6 Reactions			
C_6H_6 + M → C_6H_5 + H + M	See Table 2		
→ C_4H_4 + C_2H_2 + M			
C_6H_5O Radical Reactions			
C_6H_5O + M → C_5H_5 + CO + M	See Table 2		
$C_6H_5CH_2$ Radical Reactions			
$C_6H_5CH_2$ + M → C_3H_3 + $2C_2H_2$ + M	See Table 2		
→ C_4H_4 + C_3H_3 + M			
→ C_5H_5 + C_2H_2 + M			
→ C_7H_7 + M			
$C_6H_5CH_3$ Reactions			
$C_6H_5CH_3$ + M → $C_6H_5CH_2$ + H + M	See Table 2		
→ C_6H_5 + CH_3 + M			

TABLE 1. Bimolecular Reactions — Continued

Reaction	k/cm^3 molecule^{-1}s^{-1}	T/K	Error limits ($\Delta \log k$)
p-$C_6H_4(CH_3)_2$ Reactions			
p-$C_6H_4(CH_3)_2 + M \rightarrow C_6H_4CH_2CH_3 + H + M$	See Table 2		
$C_6H_5C_2H_5$ Reactions			
$C_6H_5C_2H_5 + M \rightarrow C_6H_5CH_2 + CH_3 + M$ $\rightarrow C_6H_6 + C_2H_4 + M$ $\rightarrow C_6H_5CHCH_2 + H_2 + M$ $\rightarrow C_6H_5 + C_2H_5 + M$ $\rightarrow C_6H_5CHCH_3 + H + M$	See Table 2		

TABLE 2. Decomposition Reactions

Reaction	k_∞/s^{-1} $k_0/\mathrm{cm}^3\ \mathrm{molecule}^{-1}\ \mathrm{s}^{-1}$ F_c $k/\mathrm{s}^{-1} = \frac{k_0\, k_\infty\, [\mathrm{M}]}{k_0[\mathrm{M}] + k_\infty}\,\mathrm{F}$	T/K	Error limits ($\Delta \log k$)
$H_2 + Ar \rightarrow 2H + Ar$	$k_0 = 3.7 \times 10^{-10} \exp(-48350/T)$	2500–8000	± 0.3
$H_2 + H_2 \rightarrow 2H + H_2$	$k_0 = 1.5 \times 10^{-9} \exp(-48350/T)$	2500–8000	± 0.5
$H_2O + N_2 \rightarrow H + OH + N_2$	$k_0 = 5.8 \times 10^{-9} \exp(-52920/T)$	2000–6000	± 0.5
$H_2O_2 + M \rightarrow 2\ OH + M$	$k_0(Ar) = 3 \times 10^{-8} \exp(-21600/T)$	1000–1500	± 0.2
	$k_0(N_2) = 2 \times 10^{-7} \exp(-22900/T)$	700–1500	± 0.2
	$k_\infty = 3 \times 10^{14} \exp(-24400/T)$	1000–1500	± 0.5
	$F_c(Ar) = 0.5$	700–1500	$\Delta F_c = \pm 0.1$
$NH_3 + Ar \rightarrow NH_2 + H + Ar$	$k_0(1) = 7.4 \times 10^{-9} \exp(-41560/T)$	2000–3000	± 0.3
	$k_\infty(1) = 8.3 \times 10^{15} \exp(-55170/T)$	2000–3000	± 0.4
	$F_c = 0.58 \exp(-T/4581) + 0.42 \exp(-T/102)$	2000–3000	$\Delta F_c = \pm 0.1$
$CH_3 + M \rightarrow CH_2 + H + M$	$k_0 = 1.7 \times 10^{-8} \exp(-45600/T)$	1500–3000	± 0.5
$CH_4 + M \rightarrow CH_3 + H + M$	$k_0(Ar) = 7.5 \times 10^{-7} \exp(-45700/T)$	1000–1700	± 0.3
	$k_0(Ar) = 7.8 \times 10^{23}\ T^{-8.2} \exp(-59200/T)$	1700–5000	± 0.3
	$k_0(CH_4) = 1.4 \times 10^{-6} \exp(-45700/T)$	1000–2000	± 0.3
	$k_\infty = 2.4 \times 10^{16} \exp(-52800/T)$	1000–3000	± 0.5
	$F_c\ (Ar) = \exp(-T/1350) + \exp(-7830/T)$	1000–5000	$\Delta F_c = \pm 0.1$
	$F_c\ (CH_4) = 0.31 \exp(-T/90) + 0.69(-T/2210)$	1000–2000	$\Delta F_c = \pm 0.1$
$HCO + Ar \rightarrow H + CO + Ar$	$k_0 = 2.6 \times 10^{-10} \exp(-7930/T)$	600–2500	± 0.5
$HCHO + M \rightarrow H + CHO + M$	$k_0(Ar) = 2.7 \times 10^{12}\ T^{-5.54} \exp(-48660/T)$	1700–3200	± 0.3
$\rightarrow H_2 + CO + M$	$k_0(2)/k_0 = 0.7 \pm 0.4$	2000–3000	
$CH_3O + M \rightarrow HCHO + H + M$	$k_0 = 9.0 \times 10^{-11} \exp(-6790/T)$	300–1700	± 0.3
$CH_3OH + Ar \rightarrow CH_3 + OH + Ar$	$k_0 = 1.1 \times 10^{-7} \exp(-33080/T)$	1000–2000	± 0.3
$\rightarrow CH_2OH + H + Ar$	$k_\infty = 1.7 \times 10^{16} \exp(-45740/T)$	1000–2000	± 0.5
$\rightarrow {}^1CH_2 + H_2O + Ar$	$F_c = 0.18 \exp(-T/200) + 0.82 \exp(-T/1438)$	1000–2000	$\Delta F_c = \pm 0.1$
$CH_3OOH + M \rightarrow CH_3O + OH + M$	$k_\infty = 6 \times 10^{14} \exp(-21300/T)$	500–800	± 0.2 at 600 K rising to ± 0.5 at 500 and 800 K
$NCO + Ar \rightarrow N + CO + Ar$	$k_0 = 1.7 \times 10^{-9} \exp(-23500/T)$	1450–2600	± 0.4
$C_2H_3 + M \rightarrow C_2H_2 + H + M$	$k_0 = 6.9 \times 10^{17}\ T^{-7.5} \exp(-22900/T)$	500–2500	± 0.5
	$k_\infty = 2 \times 10^{14} \exp(-20000/T)$	500–2500	± 0.5
	$F_c = 0.35$	500–2500	$\Delta F_c = \pm 0.1$
$C_2H_4 + M \rightarrow C_2H_2 + H_2 + M$	$k_0(Ar,Kr) = 5.8 \times 10^{-8} \exp(-36000/T)$	1500–3200	± 0.3
$\rightarrow C_2H_3 + H + M$	$k_0(Ar) = 4.3 \times 10^{-7} \exp(-48600/T)$	1500–3200	± 0.5
$C_2H_5 + C_2H_6 \rightarrow C_2H_4 + H + C_2H_6$	$k_0 = 1.7 \times 10^{-6} \exp(-16800/T)$	700–900	± 0.3
	$k_\infty = 8.2 \times 10^{13} \exp(-20070/T)$	700–1100	± 0.3
	$F_c = 0.25 \exp(-T/97) + 0.75 \exp(-T/1379)$	700–1100	$\Delta F_c = \pm 0.1$
$C_2H_6 + M \rightarrow 2CH_3 + M$	$k_0(Ar) = 1.1 \times 10^{25}\ T^{-8.24} \exp(-47090/T)$	300–2000	± 0.5
	$k_0(N_2) = 1.1 \times 10^{25}\ T^{-8.24} \exp(-47090/T)$	300–2000	± 0.5
	$k_0(C_2H_6) = 4.5 \times 10^{-2} \exp(-41930/T)$	800–1000	± 0.5
	$k_\infty = 1.8 \times 10^{21}\ T^{-1.24} \exp(-45700/T)$	300–2000	± 0.3
	$F_c(Ar,N_2) = 0.38 \exp(-T/73) + 0.62 \exp(-T/1180)$	300–2000	$\Delta F_c = \pm 0.1$
	$F_c(C_2H_6) = 0.54 \exp(-T/1250)$	800–1000	$\Delta F_c = \pm 0.1$

TABLE 2. Decomposition Reactions — Continued

Reaction	k_∞/s^{-1} $k_0/\mathrm{cm}^3\ \mathrm{molecule}^{-1}\ \mathrm{s}^{-1}$ F_c $k/\mathrm{s}^{-1} = \dfrac{k_0\,k_\infty\,[\mathrm{M}]}{k_0[\mathrm{M}] + k_\infty}\,F$	T/K	Error limits ($\Delta \log k$)
$CH_3CO + M \rightarrow CH_3 + CO + M$	$k_0(\mathrm{He}) = 1.0 \times 10^{-8} \exp(-7080/T)$	400–500	± 0.2
	$k_0(\mathrm{Ar}) = 7.0 \times 10^{-18}$	353	± 0.4
	$k_\infty = 2.8 \times 10^{13} \exp(-8630/T)$	300–500	± 0.5
	$F_c(\mathrm{He}) = 0.5$	400–500	$\Delta F_c = \pm 0.1$
$CH_3CHO + M \rightarrow CH_3 + CHO + M$	$k(1\ \mathrm{atm.}) = 7 \times 10^{15} \exp(-41100/T)$ (pressure dependent region)	750–1200	± 0.4
$C_2H_5O + M \rightarrow HCHO + CH_3 + M$	$k_\infty = 8 \times 10^{13} \exp(-10830/T)$ [estimate]	300–600	± 1.0
$C_2H_5OOH + M \rightarrow C_2H_5O + OH + M$	$k_\infty = 4 \times 10^{15} \exp(-21600/T)$ [estimate]	400–800	± 0.3
$C_3H_5 + M \rightarrow CH_2CCH_2 + H + M$	$k_\infty = 1.5 \times 10^{11}\ T^{0.84} \exp(-30050/T)$	800–1500	± 0.3
$i\text{-}C_3H_7 + He \rightarrow C_3H_6 + H + He$	$k_0 = 3.6 \times 10^{-7} \exp(-14200/T)$	750–830	± 0.3
	$k_\infty = 8.76 \times 10^{7}\ T^{1.76} \exp(-17870/T)$	170–1000	± 0.3
	$F_c(\mathrm{He}) = 0.35$	750–830	$\Delta F_c = \pm 0.1$
$C_3H_8 + Ar \rightarrow CH_3 + C_2H_5 + Ar$	$k_0 = 1.3 \times 10^{-5} \exp(-32700/T)$	700–2000	± 0.5
	$k_\infty = 1.1 \times 10^{17} \exp(-42470/T)$	700–2000	± 0.3
	$F_c = 0.24 \exp(-T/1946) + 0.76 \exp(-T/38)$	700–2000	$\Delta F_c = \pm 0.2$
$t\text{-}C_4H_9 + M \rightarrow i\text{-}C_4H_8 + H + M$	$k_\infty = 8.3 \times 10^{13} \exp(-19200/T)$	300–800	± 0.5
$C_6H_5 + M \rightarrow C_2H_2 + C_4H_3 + M$ $\rightarrow C_2H_3 + C_4H_2 + M$	No recommendation		
$\rightarrow \text{linear-}C_6H_5 + M$	$4.0 \times 10^{13} \exp(-36700/T)$	1450–1900	± 0.4
$C_6H_6 + M \rightarrow C_6H_5 + H + M$ $\rightarrow C_4H_4 + C_2H_2 + M$	$9.0 \times 10^{15} \exp(-54060/T)$	1200–2500	± 0.4 at 1200 K reducing to ± 0.3 at 2500 K
$C_6H_5O + M \rightarrow C_5H_5 + CO + M$	$2.5 \times 10^{11} \exp(-22100/T)$	1000–1580	± 0.2
$C_6H_5CH_2 + M \rightarrow C_3H_3 + 2C_2H_2 + M$ $\rightarrow C_4H_4 + C_3H_3 + M$ $\rightarrow C_5H_5 + C_2H_2 + M$ $\rightarrow C_7H_7\ (\mathrm{BCH}) + M$	$5.1 \times 10^{13} \exp(-36370/T)$	1350–1900	± 0.3 at 1350 K rising to ± 0.5 at 1900 K
$C_6H_5CH_3 + M \rightarrow C_6H_5CH_2 + H + M$	$3.1 \times 10^{15} \exp(-44890/T)$	920–2200	± 0.3 at 920 K rising to ± 0.5 at 2200 K
$\rightarrow C_6H_5 + CH_3 + M$	$k_\infty = 7.8 \times 10^{18} \exp(-59400/T)$	1500–2000	± 0.7
$p\text{-}C_6H_4(CH_3)_2 + M \rightarrow$ $C_6H_4(CH_3)CH_2 + H + M$	$4.0 \times 10^{15} \exp(-42600/T)$	1400–1800	± 0.5
$C_6H_5C_2H_5 + M \rightarrow C_6H_5CH_2 + CH_3 + M$	$6.1 \times 10^{15} \exp(-37800/T)$	770–1800	± 0.1 at 770 K rising to ± 0.4 at 1800 K
$\rightarrow C_6H_6 + C_2H_4 + M$ $\rightarrow C_6H_5CHCH_2 + H_2 + M$ $\rightarrow C_6H_5 + C_2H_5 + M$ $\rightarrow C_6H_5CHCH_3 + H + M$	No recommendation		

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} = $\frac{k_0 k_\infty [\mathrm{M}]}{k_0[\mathrm{M}] + k_\infty} F$	T/K	Error limits ($\Delta \log k$)
$H + O_2 + Ar \rightarrow HO_2 + Ar$	$k_0 = 1.7 \times 10^{-30} T^{-0.8}$	300–2000	± 0.5
$H + O_2 + H_2 \rightarrow HO_2 + H_2$	$k_0 = 5.8 \times 10^{-30} T^{-0.8}$	300–2000	± 0.5
$H + O_2 + N_2 \rightarrow HO_2 + N_2$	$k_0 = 3.9 \times 10^{-30} T^{-0.8}$	300–2000	± 0.5
$H + H + Ar \rightarrow H_2 + Ar$	$k_0 = 1.8 \times 10^{-30} T^{-1.0}$	300–2500	± 0.5
$H + H + H_2 \rightarrow H_2 + H_2$	$k_0 = 2.7 \times 10^{-31} T^{-0.6}$	100–5000	± 0.5
$H + OH + H_2O \rightarrow H_2O + H_2O$	$k_0 = 3.9 \times 10^{-25} T^{-2.0}$	300–3000	± 0.5
$H + OH + Ar \rightarrow H_2O + Ar$	$k_0 = 2.3 \times 10^{-26} T^{-2.0}$	300–3000	± 0.3
$H + OH + N_2 \rightarrow H_2O + N_2$	$k_0 = 6.1 \times 10^{-26} T^{-2.0}$	300–3000	± 0.5
$H + CO + Ar \rightarrow HCO + Ar$	$k_0 = 5.3 \times 10^{-34} \exp(-370/T)$	300–2500	± 0.5
$H + CH_3 + M \rightarrow CH_4 + M$	$k_0(He) = 1.8 \times 10^{-24} T^{-1.8}$ $k_0(Ar) = 1.7 \times 10^{-24} T^{-1.8}$ $k_0(C_2H_6) = 8.6 \times 10^{-24} T^{-1.8}$ $k_\infty = 3.5 \times 10^{-10}$ $F_c(He,Ar) = 0.63 \exp(-T/3315) + 0.37 \exp(-T/61)$ $F_c(C_2H_6) = 0.71 \exp(-T/3079) + 0.29 \exp(-T/54)$	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
$H + C_2H_2 + He \rightarrow C_2H_3 + He$	$k_\infty = 1.4 \times 10^{-11} \exp(-1300/T)$ $k_0 = 3.3 \times 10^{-30} \exp(-740/T)$ $F_c = 0.44$	200–400 200–400 200–400	± 0.3 ± 0.5 ΔF_c = ± 0.1
$H + C_2H_3 + M \rightarrow C_2H_4 + M$	No recommendation		
$H + C_2H_4 + M \rightarrow C_2H_5 + M$	$k_0(He) = 1.3 \times 10^{-29} \exp(-380/T)$ $k_0(N_2) = 7.7 \times 10^{-30} \exp(-380/T)$ $k_\infty = 6.6 \times 10^{-15} T^{1.28} \exp(-650/T)$ $F_c = (He,N_2)\ 0.24 \exp(-T/40) + 0.76 \exp(-T/1025)$	300–800 300–800 200–1100 300–800	± 0.3 ± 0.3 ± 0.3 ΔF_c = ± 0.1
$H + C_2H_5 + M \rightarrow C_2H_6 + M$	No recommendation		
$H + C_3H_5 + M \rightarrow C_3H_6 + M$ $\rightarrow C_2H_3 + CH_3 + M$	$(k_1^\infty + k_2) = 2.8 \times 10^{-10}$	300–1000	± 0.2 at 300 K rising to ± 0.5 at 1000 K
$H + C_6H_5 + M \rightarrow C_6H_6 + M$	$k_\infty = 1.3 \times 10^{-10}$	1400–1700	± 0.5
$H + C_6H_6 + M \rightarrow C_6H_7 + M$	$k_\infty = 6.7 \times 10^{-11} \exp(-2170/T)$	300–1000	± 0,2
$H + C_6H_5O + M \rightarrow C_6H_5OH + M$	$k_\infty = 4.2 \times 10^{-10}$	1000	± 0.3
$H + C_6H_5CH_2 + M \rightarrow C_6H_5CH_3 + M$	$k_\infty = 4.3 \times 10^{-10}$	300–2000	± 0.2 at 300 K rising to ± 0.7 at 2000 K
$H + C_6H_5CH_3 + M \rightarrow C_6H_6CH_3 + M$	$k_\infty = 1.2 \times 10^{-13}$	298	± 0.2
$H + C_6H_5C_2H_5 + M \rightarrow C_6H_6C_2H_5 + M$	$k_\infty = 3.3 \times 10^{-13}$	298	± 0.1
$OH + OH + M \rightarrow H_2O_2 + M$	$k_0(N_2) = 6.1 \times 10^{-29} T^{-0.76}$ $k_0(H_2O) = 4 \times 10^{-30}$ $k_\infty = 1.2 \times 10^{-10} T^{-0.37}$ $F_c(N_2) = 0.5$	250–1400 300–400 200–1500 200–1500	± 0.4 ± 0.4 ± 0.5 ΔF_c = ± 0.2

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} = $\frac{k_0\, k_\infty\, [\mathrm{M}]}{k_0[\mathrm{M}] + k_\infty} F$	T/K	Error limits (Δ log k)
$OH + CH_3 + M \rightarrow CH_3OH + M$	$k_0(\mathrm{He}) = 2.3 \times 10^{-27}$ $k_0(\mathrm{Ar}) = 4.4 \times 10^{-4}\, T^{-8.2}$ $k_\infty = 1.0 \times 10^{-10}$ $F_c(\mathrm{Ar}) = 0.18 \exp(-T/200) + 0.82\ (-T/1438)$	300 1000–2000 300–2000 1000–2000	± 0.3 ± 0.5 ± 0.3 ΔF_c = ± 0.1
$OH + C_2H_2 + M \rightarrow C_2H_2OH + M$	See data sheet		
$OH + C_3H_5 + M \rightarrow CH_2CHCH_2OH + M$ $\rightarrow CH_2CHCHO + 2H + M$	$(k_1^\infty + k_2) = 2.5 \times 10^{-11}$	300–1000	± 0.3
$OH + C_6H_6 + M \rightarrow C_6H_6OH + M$	$k_\infty = 3.8 \times 10^{-12} \exp(-340/T)$	240–340	± 0.2
$OH + C_6H_5OH + M \rightarrow C_6H_5(OH)_2 + M$	$k_\infty = 2.8 \times 10^{-11}$	298	± 0.1
$OH + C_6H_5CH_3 + M \rightarrow HOC_6H_5CH_3 + M$	$k_\infty = 3.8 \times 10^{-12} \exp(180/T)$	200–300	± 0.4
$OH+C_6H_4(CH_3)_2+M \rightarrow C_6H_4(CH_3)_2OH+M$	$k_\infty = 1.4 \times 10^{-11}$	300	± 0.1
$OH+C_6H_5C_2H_5+M \rightarrow HOC_6H_5C_2H_5+M$	7.5×10^{-12} at $p \leqslant 1$ atm.	298	± 0.1
$^3CH_2 + C_2H_2 + M \rightarrow C_3H_4 + M$	$2.0 \times 10^{-11} \exp(-3330/T)$ at $p = \leqslant 10$ Torr.	300–1000	± 0.3
$^3CH_2 + C_2H_4 + M \rightarrow C_3H_6 + M$ $\rightarrow c\text{-}C_3H_6 + M$ $\rightarrow C_3H_5 + H + M$	$5.3 \times 10^{-12} \exp(-2660/T)$	300–1000	± 0.2 at 300 K rising to ± 0.3 at 1000 K
$^1CH_2 + C_2H_2 + M \rightarrow CH_2CCH_2 + M$ $\rightarrow CH_3CCH + M$ $\rightarrow CH_2CCH + H + M$	2.9×10^{-10} independent of p	300–1000	± 0.3 at 300 K rising to ± 0.7 at 1000 K
$^1CH_2 + C_2H_4 + M \rightarrow C_3H_6 + M$	1.6×10^{-10} independent of p	300–1000	± 0.2 at 300 K rising to ± 0.5 at 1000 K
$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$	$k_0(\mathrm{Ar}) = 1.55 \times 10^{-22}\, T^{-3.3}$ $k_0(\mathrm{N_2}) = 1.6 \times 10^{-22}\, T^{-3.3}$ $k_\infty = 1.3 \times 10^{-15}\, T^{1.2}$ $F_c = 0.466 - 1.30 \times 10^{-4}\, T$	300–800 300–800 300–800 300–800	± 0.3 ± 0.3 ± 0.3 ΔF_c = ± 0.1
$CH_3 + CO + M \rightarrow CH_3CO + M$	$k_0(\mathrm{He}) = 3.0 \times 10^{-34} \exp(-1910/T)$ $k_0(\mathrm{N_2}) = 4.2 \times 10^{-36}$ $k_\infty = 8.4 \times 10^{-13} \exp(-3460/T)$ $F_c(\mathrm{He}) = 0.5$ $F_c(\mathrm{N_2}) = 0.6$	400–500 300–350 300–500 400–500 300–350	± 0.2 ± 0.5 ± 0.5 ΔF_c = ± 0.1 ΔF_c = ± 0.1
$CH_3 + CH_3 + Ar \rightarrow C_2H_6 + Ar$	$k_\infty = 6.0 \times 10^{-11}$ $k_0 = 3.5 \times 10^{-7}\, T^{-7.0} \exp(-1390/T)$ $F_c = 0.38 \exp(-T/73) + 0.62 \exp(-T/1180)$	300–2000 300–2000 300–2000	± 0.3 ± 0.3 ΔF_c = ± 0.1
$CH_3 + C_2H_2 + M \rightarrow C_3H_5 + M$	$k_\infty = 1 \times 10^{-12} \exp(-3900/T)$	300–600	± 0.5
$CH_3 + C_2H_4 + M \rightarrow n\text{-}C_3H_7 + M$	$3.5 \times 10^{-13} \exp(\ \ 3700/T)$	300–600	± 0.3
$CH_3 + C_2H_5 + M \rightarrow C_3H_8 + M$	$k_\infty = 5.6 \times 10^{-11}$	300–2000	± 0.3
$CH_3 + C_3H_5 + M \rightarrow C_2H_5CHCH_2 + M$	$k_\infty = 1.7 \times 10^{-10}\, T^{-0.32} \exp(66/T)$	500–1200	± 0.2
$C_2H_5 + C_2H_5 + M \rightarrow n\text{-}C_4H_{10} + M$	$k_\infty = 1.9 \times 10^{-11}$	300–1200	± 0.3
$C_2H_5 + C_3H_5 + M \rightarrow CH_3CH_2CH_2CHCH_2 + M$	$k_\infty = 3.3 \times 10^{-11} \exp(66/T)$	500–1200	± 0.3

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} = $\frac{k_0 k_\infty [M]}{k_0[M] + k_\infty} F$	T/K	Error limits (Δ log k)
$CH_3CO + O_2 + M \rightarrow CH_3CO_3 + M$	2×10^{-12} for p = 1–4 Torr.	300	± 0.3
$C_3H_5 + C_3H_5 + M \rightarrow CH_2CHCH_2CH_2CHCH_2 + M$	$k_\infty = 1.7 \times 10^{-11} \exp(132/T)$ $k_\infty = 2.0 \times 10^{-11}$	300–600 600–1000	± 0.2 ± 0.4
C_3H_5 + 2-C_4H_8 + M $\rightarrow CH_2CHCH_2CH(CH_3)CHCH_3 + M$	$k_\infty = 1.0 \times 10^{-13} \exp(-9620/T)$	600–1200	± 0.7
i-C_3H_7 + i-C_3H_7 + M $\rightarrow (CH_3)_2CHCH_2CH_2 + M$	$k_\infty = 6.8 \times 10^{-12}$ to ± 0.3 at 1000 K	300–1000	± 0.1 at 300 K rising to ± 0.3 at 1000 K
t-C_4H_9 + t-C_4H_9 + M $\rightarrow C_8H_{18}$	$k_\infty = 5.2 \times 10^{-8}\ T^{-1.73}$	300–1000	± 0.15 at 300 K rising to ± 0.3 at 1000 K

5. Data Sheets

O + NO → O_2 + N

Thermodynamic Data
$\Delta H^\circ_{298} = 133$ kJ mol^{-1}
$\Delta S^\circ_{298} = -13.4$ J K mol^{-1}
$Kp = 7.6\cdot10^{-2}T^{0.126}\exp(-15930/T)$

Rate Coefficient Data

k/cm^3 molecule^{-1}s^{-1}	T/K	Reference	Comments
Rate Coefficient Measurements			
$6.03\cdot10^{-12}\exp(-19900/T)$	1575–1665	Kaufman and Decker, 1959[1]	(a)
$6.0\cdot10^{-13}$	5000	Wray and Teare, 1962[2]	(b)
$1.48\cdot10^{-14}$	3000	Clark *et al.*, 1969[3]	(c)
$3.89\cdot10^{-15}T\exp(-19450/T)$	2500–4100	Hanson *et al.*, 1974[4]	(d)
$2.89\cdot10^{-15}T\exp(-19450/T)$	1750–2100	McCullough, 1977[5]	(e)
Reviews and Evaluations			
$2.5\cdot10^{-15}T\exp(-19450/T)$	1000–3000	Baulch *et al.*, 1973[6]	(f)
$6.3\cdot10^{-15}T\exp(-20850/T)$	1500–5000	Hanson and Salimian, 1984[7]	(g)
$1.4\cdot10^{-15}T^{1.1}\exp(-19250)$	1000–5000	Cohen, 1991[8]	(g)

Comments

(a) Static reactor study using $[O_2]/[NO]$ mixtures in ratios from 0 to 40. Reaction progress monitored by UV absorption spectrometry of unreacted NO. Equilibrium of O atoms with O_2 was assumed.

(b) Shock tube study of $NO/O_2/Ar$ mixtures, with monitoring of NO behind the shock by absorption at 127 nm. Data fitting was performed with a detailed kinetic mechanism, however, only data acquired in $NO/O_2/Ar = 0.5\%/0.25\%/99.25\%$ mixtures near 5000 K were sufficiently insensitive to other rate constants to derive k.

(c) Reflected shock study of N_2O decomposition using mass spectrometric detection of NO, O_2 and O. k derived from small changes in measured NO concentration.

(d) Shock tube study of N_2O/Ar or N_2O/Kr mixtures with [NO] decays monitored at 5.3 μm. Rate constant derived by fitting observed [NO] decay to a detailed kinetic model.

(e) Flow tube study with NO/Ar mixtures, decomposition of NO as a function of flow rate monitored by chemiluminescence. Detailed modelling of kinetics and flow used to derive k.

(f) Based primarily on data for reverse reaction.

(g) Based on data from Refs. 1–5.

Preferred Values

$k = 1.14\cdot10^{-15}T^{1.13}\exp(-19200/T)$ cm^3 molecule^{-1} s^{-1} over range 1000–5000 K.

Reliability
$\Delta\log k = \pm0.3$.

Comments on Preferred Values

The experimental data available for this reaction are confined to temperatures above 1500 K. All of the studies are in good agreement. The data have been most recently reviewed by Hanson and Salimian[7] and by Cohen[8] who derive very similar expressions for k. We accept their analysis and recommend an expression for k very similar to Cohen's.

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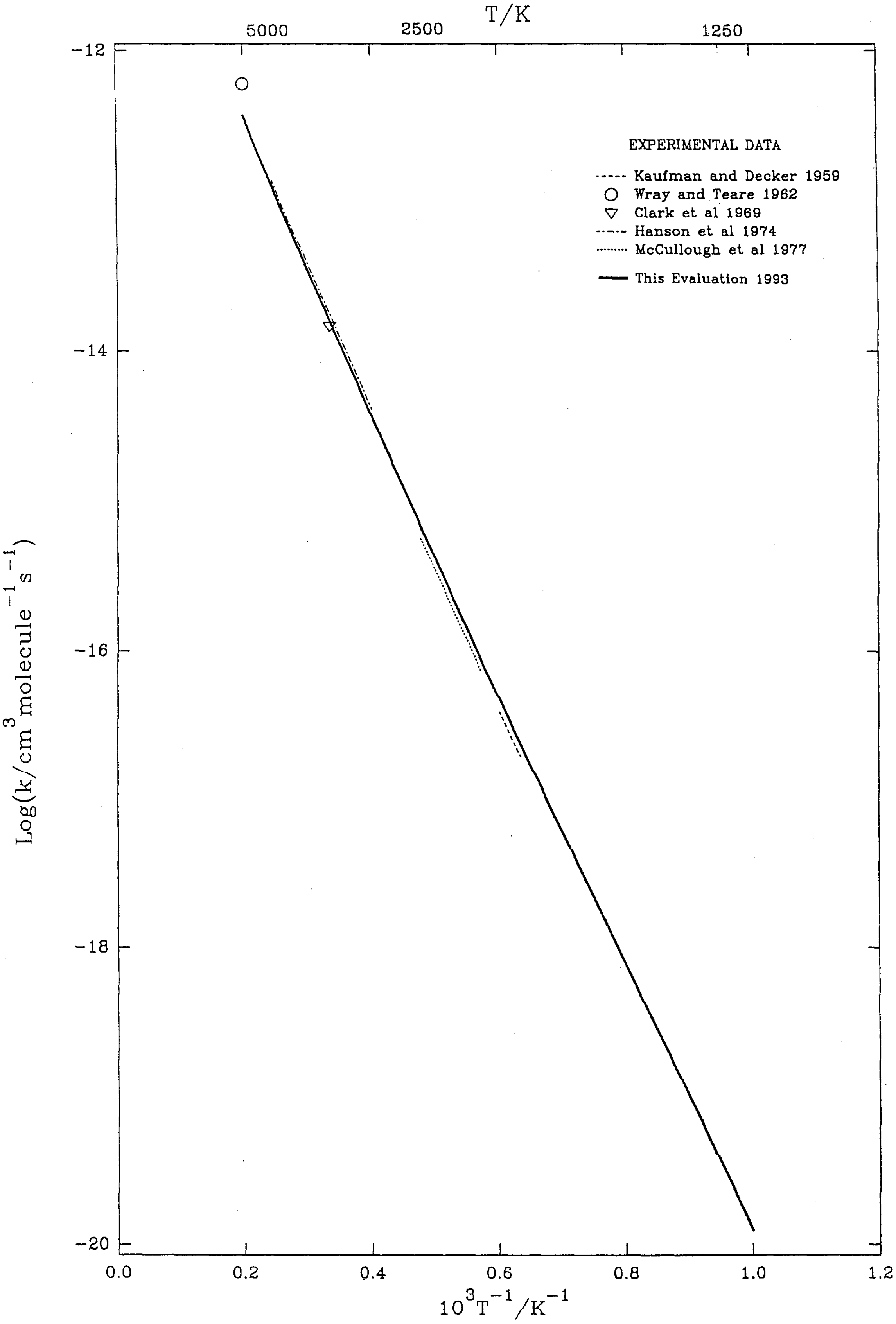
O + NO → O_2 + N


T/K
5000
2500
1250
−12
−14
−16
−18
−20
0.0
0.2
0.4
0.6
0.8
1.0
1.2
Log(k/cm³ molecule⁻¹ s⁻¹)
10³T⁻¹/K⁻¹
EXPERIMENTAL DATA
Kaufman and Decker 1959
Wray and Teare 1962
Clark et al 1969
Hanson et al 1974
McCullough et al 1977
This Evaluation 1993

$O + N_2 \rightarrow N + NO$

Thermodynamic Data
$\Delta H^\circ_{298} = 313.5$ kJ mol^{-1}
$\Delta S^\circ_{298} = 11.3$ J K^{-1} mol^{-1}
$Kp = 1.98\ T^{0.097}\exp(-37690/T)$

Rate Coefficient Data

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Comments
Rate Coefficient Measurements			
$1.1 \cdot 10^{-10}\exp(-38000/T)$	2000–3000	Duff and Davidson, 1959[1]	(a)
$2.82 \cdot 10^{-16}$	2880	Livesey, Roberts, and Williams, 1971[2]	(b)
$8.3 \cdot 10^{-11}\exp(-37900/T)$	1900–2250	Bachmaier, Eberius, and Just, 1973[3]	(c)
$2.2 \cdot 10^{-10}\exp(-37900/T)$	1900–2400	Iverach, Basden, and Kirov, 1973[4]	(d)
$3.0 \cdot 10^{-10}\exp(-38000/T)$	2120–2480	Harris, Nasralla, and Williams, 1976[5]	(e)
$1.25 \cdot 10^{-10}\exp(-38200/T)$	1880–2350	Blauwens, Smets, and Peeters, 1977[6]	(f)
$3.06 \cdot 10^{-10}\exp(-38370/T)$	2380–3850	Monat, Hanson, and Kruger, 1979[7]	(g)
$2.95 \cdot 10^{-10}\exp(-38370/T)$	2120–2230	Seery and Zabielski, 1980[8]	(h)
$3.0 \cdot 10^{-10}\exp(-38300/T)$	2400–4100	Thielen and Roth, 1984[9]	(i)
Reviews and Evaluations			
$1.3 \cdot 10^{-10}\exp(-38000/T)$	2000–5000	Baulch, Drysdale, and Horne, 1973[10]	(j)
$3.0 \cdot 10^{-10}\exp(-38370/T)$	2000–4000	Hanson and Salimian, 1984[11]	(k)
$4.3 \cdot 10^{-13}\ T^{0.8}\exp(-37370/T)$	1500–4100	Cohen, 1991[12]	(l)

Comments

(a) Determined by detailed analysis of the results from the single-pulse shock tube study of Glick *et al.*[13] in which NO was measured behind a shock wave through mixtures of air in an inert diluent.

(b) NO concentration profile measured by probe sampling and chemical analysis in the burned gas of an atmospheric pressure premixed propane-oxygen flame to which N_2 had been added. O atoms were assumed to be in equilibrium with OH which was measured by line absorption spectroscopy. Single value of k at the mean flame temperature was obtained by fitting to a simple mechanism and an A-factor calculated assuming an activation energy of 315 kJ mol^{-1}. However, [O] was overestimated by a factor of 2 owing to use of a low value for the OH oscillator strength leading to a factor of 2 underestimate in k. The corrected value reported here is based on the oscillator strength $f(0,0) = 1.10 \cdot 10^{-3}$ reported by Smith and Crosley[14].

(c) NO concentration profiles in atmospheric pressure premixed hydrocarbon-air flames measured by probe sampling and UV absorption spectroscopy. The expression for k obtained by fitting the rate of formation of NO in fuel-lean flames to the simple Zeldovich mechanism, assuming equilibrium concentrations of O atoms.

(d) NO concentration profiles in flat, premixed lean or slightly fuel-rich hydrocarbon-air flames measured by probe sampling and IR analysis. [O] calculated assuming equilibrium of O with O_2, CO and CO_2 which were also measured. Expression for k derived by fitting rate of NO formation to an extended Zeldovich mechanism.

(e) NO concentration profiles in the burned gas region of fuel-lean, premixed CH_4-O_2-N_2 flames measured by probe sampling and chemiluminescent detection. O atoms assumed to be in equilibrium with OH which was measured by line absorption spectroscopy. Assuming the activation energy recommended by Baulch *et al.*[10], the A-factor was adjusted to give the best fit of the data to an extended Zeldovich mechanism. However, as in reference (2), k was underestimated by a factor of 2 owing to use of a low value of the OH oscillator strength (see comment(b)). The reported expression for k was corrected to the value shown here using the oscillator strength given by Smith and Crosley[14].

(f) NO and O concentration profiles measured in post-flame region of low-pressure hydrocarbon-O_2-N_2 flames using molecular beam sampling mass spectrometry. Temperatures were inferred from partial equilibrium considerations and species concentration measurements. Rate coefficients obtained by fitting to the Zeldovich mechanism and found to agree to within ±20% of the expression previously recommended by Baulch *et al.*[10], which was the expression reported.

(g) Shock tube study. O atoms generated by pyrolysis of N_2O in $N_2/O_2/Kr$ mixtures optimised to maximise the sensitivity of the results to k. [NO] measured behind the incident shock wave by IR emission at 5.3 μm and absorption of CO laser radiation at 5.17 μm. Results fitted to a 9-step kinetic mechanism to derive k. Uncertainty estimated to be ±35% over the temperature range.

(h) NO and N_2 concentration profiles measured in post-flame region of low pressure CH_4-air flames using molecular beam sampling mass spectrometry and microprobe sampling with chemiluminescence analysis. [OH] profiles measured by resonance absorption and partial equilibrium assumptions used to infer [O]. Expression for k derived by fitting to Zeldovich mechanism.

(i) Shock tube study. O atoms generated by pyrolysis of N_2O in $N_2/N_2O/Ar$ mixtures. [O] and [N] measured by atomic resonance absorption spectroscopy as a function of time behind reflected shock wave to give k directly. Uncertainty in k estimated to be ±40%.

(j) Review of pre-1973 studies. Value derived from low temperature data for reverse reaction obtained by Clyne and Thrush[15,16] was revised downward by a factor of ~2 to accommodate results from the early shock tube studies of the forward reaction. Estimated uncertainty is $\Delta\log k = \pm0.3$.

(k) Comprehensive review of all previous direct and indirect determinations of k to 1980. Recommends rate expression determined by Monat *et al.*[7] Uncertainty estimated to be ±35%.

(l) Review of studies of the reaction in the forward and reverse direction since 1973. The recommended three-parameter Arrhenius expression for k is a fit to the experimental data of Monat *et al.*[7] and Thielen and Roth[9] for the forward reaction and the data of Davidson and Hanson[17] for the reverse reaction. Estimated uncertainty is $\Delta\log k = \pm0.3$.

Preferred Value

$k = 3.0\cdot10^{-10}\exp(-38300/T)$ cm^3 molecule^{-1} s^{-1} over the range 1400–4000 K.

Reliability

$\Delta\log k = \pm0.2$ over the range 1400–4000 K.

Comments on Preferred Values

There is complete agreement among all the studies in the value of the activation energy of the reaction, and with the exception of the result of Blauwens *et al.*[6], there is good agreement among the measurements of the A-factor made since 1973. The most direct determinations of k are considered to be those of Monat *et al.*[7] and Thielen and Roth[9] which are in excellent agreement and are the basis of the present recommendation. There have been two recent shock tube measurements of k for the reverse reaction at temperatures overlapping the range covered by Monat *et al.*[7] and Thielen and Roth[9]. The temperature dependent results of Davidson and Hanson[17] are entirely consistent with the equilibrium constant and the preferred rate for the forward reaction, but the temperature independent data for $k(N + NO)$ of Koshi *et al.*[18] are not.

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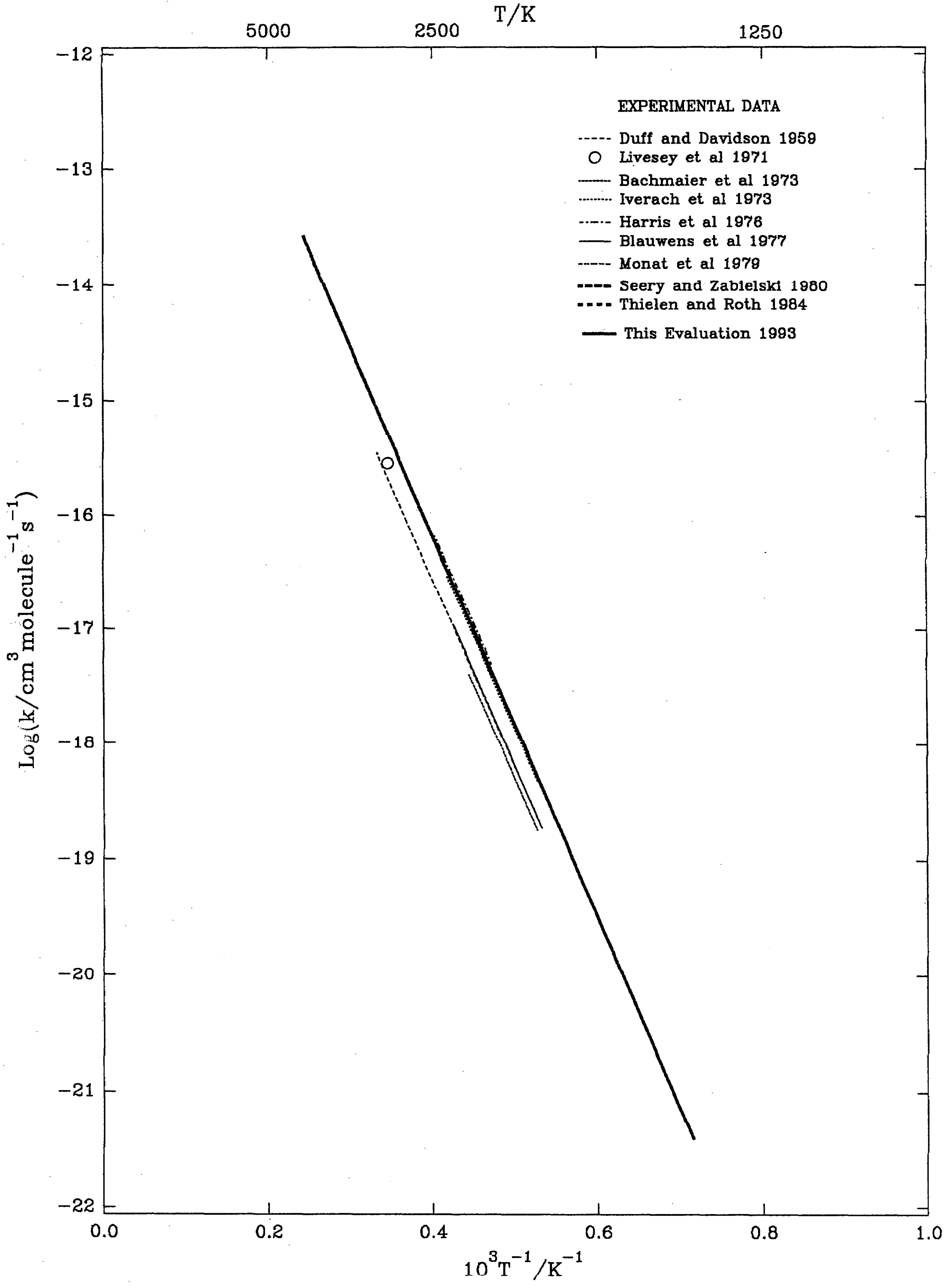
$O + N_2 \rightarrow N + NO$



$O + NH \rightarrow NO + H$ (1)
$\rightarrow OH + N$ (2)

Thermodynamic Data

$\Delta H^\circ_{298}(1) = -297.3$ kJ mol^{-1}
$\Delta S^\circ_{298}(1) = -16.8$ J K^{-1} mol^{-1}
$Kp(1) = 3.6 \cdot 10^{-10} T^{2.23} \exp(+38460/T)$

$\Delta H^\circ_{298}(2) = -94.2$ kJ mol^{-1}
$\Delta S^\circ_{298}(2) = -5.3$ J K^{-1} mol^{-1}
$Kp(2) = 1.5 \cdot 10^{-2} T^{0.40} \exp(+12140/T)$

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

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Comments
Rate Coefficient Measurements			
$1.5 \cdot 10^{-10}$	2730–3380	Mertens *et al.*, 1991[1]	(a)

Comments

(a) Shock tube study of HNCO/N_2O/Ar mixtures with NH($X^3\Sigma$) monitored at 336 nm by laser absorption. [NH] profiles fitted to reaction mechanism. [NH] shown to be sensitive to k and insensitive to value of the branching ratio.

Preferred Values

$k = 1.5 \cdot 10^{-10}$ cm^3 molecule^{-1} s^{-1} over the range 1000–3380 K.

Reliability

$\Delta \log k = \pm 0.5$ over the range 1000–3380 K.

Comments on Preferred Values

The only study of this reaction at elevated temperatures, by Mertens *et al.*[1], gives a temperature independent rate constant of $1.5 \cdot 10^{-10}$ cm^3 molecule^{-1} cm^{-1} over the range 2730–3380 K. Another study, by Temps[2], is reported in Ref. 1 to give a value of $8.3 \cdot 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K which would require an activation energy of approximately -8 kJ mol^{-1} for the two studies to be compatible. A temperature coefficient of k of this magnitude could possibly be accommodated by a combination of the error limits of the measurements and/or changes in the mechanism with temperature. However, we limit our recommendation to the value of Mertens *et al.*[1] extending their temperature range but increasing the error limits to take into account the possibility of a small temperature coefficient for k.

There are no experimental studies of the branching ratios. A theoretical study of Melius and Binkley[3] suggests that both channels are likely to be of comparable importance.

References

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

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

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Comments
Rate Coefficient Measurements			
$1.06 \cdot 10^{-14}$	297	Vaghjiani and Ravishankara, 1990[1]	(a)
Reviews and Evaluations			
$6.9 \cdot 10^{-13}\ T^{0.57} \exp(-1390/T)$	300–1000	CEC, 1992[2]	(b)

Comments

(a) Pulsed photolysis–resonance fluorescence technique. $O(^3P)$ generated by O_3 photolysis at 532 nm in the presence of excess CH_3OOH.
(b) Based on analogy with O + HCHO reaction.

Preferred Value

$k = 3.3 \cdot 10^{-11} \exp(-2390/T)$ cm^3 molecule^{-1} s^{-1} over the 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 room temperature data of Vaghjiani and Ravishankara[1] are the only reported experimental values of the rate constant for the reaction of $O(^3P)$ with CH_3OOH. The preferred temperature dependence is obtained assuming an *A*-factor for the reaction of O with CH_3OOH equal to that for O + CH_3OH, given in the evaluation of Herron[3]. Comparison with the rate constant for the reaction: $O + H_2O_2 = OH + HO_2$ ($1.7 \cdot 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K) indicates that abstraction of the peroxidic H is slower suggesting that channel (2) is dominant.

References

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

Thermodynamic Data

$\Delta H^\circ_{298}(1) = -200$ kJ mol^{-1}
$\Delta S^\circ_{298}(1) = 31.2$ J K^{-1} mol^{-1}
$Kp(1) = 7.31 \cdot 10^5 T^{-1.40} \exp(+23500/T)$

$\Delta H^\circ_{298}(2) = -80.4$ kJ mol^{-1}
$\Delta S^\circ_{298}(2) = 6.9$ J K^{-1} mol^{-1}
$Kp(2) = 1.17 T^{0.15} \exp(+9600/T)$

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

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Comments
Rate Coefficient Measurements			
$k_2/k = 0.5$	1000	Homann and Wellman, 1983[1]	(a)
$k_2/k = 0.6$	290–540	Peeters, Schaeker, and Vinckier, 1986[2]	(b)
$k_2/k = 0.8$	287	Peeters *et al.*, 1987[3]	(c)
$1.1 \cdot 10^{-19} T^{2.6} \exp(-330/T)$	290–1510	Mahmud and Fontijn, 1987[4]	(d)
$6.6 \cdot 10^{-11} \exp(-1900/T)$	370–876	Russell *et al.*, 1988[5]	(e)
$1.78 \cdot 10^{-10} \exp(-2714/T)$	850–1950	Michael and Wagner, 1990[6]	(f)
$k_2/k = 0.80$			
$2.3 \cdot 10^{-11} \exp(-1527/T)$	200–284	Bohn and Stuhl, 1990[7]	(g)
Reviews and Evaluations			
$3.6 \cdot 10^{-20} T^{2.8} \exp(-250/T)$	300–2500	CEC, 1992[8]	(h)

Comments

(a) Discharge flow ($O/C_2H_2/He$), nozzle beam sampling with mass spectrometric detection.
(b) Flow reactor, O generated by discharge through O_2, molecular beam sampling with mass spectrometric detection.
(c) 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.
(d) Flash photolysis, resonance fluorescence. O generated from photolysis of O_2 or CO_2.
(e) Laser flash photolysis, photoionization mass spectrometry. O generated from photolysis of SO_2, C_2H_2 from photolysis of C_2H_3Br.
(f) Flash photolysis, shock tube study. O atoms generated from photolysis of NO and detected by resonance absorption. Branching ratio from H yield of $O + C_2H_2$ vs H yield from $O + H_2$. An analysis of the available kinetic data gave $k = 1.2 \cdot 10^{-17} T^{2.09} \exp(-786/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 195–2500 K.
(g) O atoms generated by H_2 laser photolysis (160 nm) of NO and detected by the O + NO chemiluminescence.
(h) Review of all studies up to 1989.

Preferred Values

$k = 1.2 \cdot 10^{-17} T^{2.1} \exp(-786/T)$ cm^3 molecule^{-1} s^{-1} over range 195–2500 K.

$k_2/k = 0.7$ over range 300–2500 K.

Reliability

$\Delta \log k = \pm 0.2$

$\Delta\ (k_2/k) = \pm 0.2$

Comments on Preferred Values

The recent shock tube measurements of Michael and Wagner[6] are in excellent agreement with the data of Russell *et al.*[5], in the region in which they overlap and their recommendation, which incorporates earlier measurements, has been adopted. It appears that the measurements of Mahmud and Fontijn[4] are in error, especially in the middle temperature range.

Michael and Wagner's[6] determination of k_2/k is the most direct because the H yield was calibrated directly against that for O + H_2 but to obtain our recommended value, for a wide temperature range, their value has been combined with the lower temperature data of Peeters *et al.*[2,3] and Homann and Wellman[1].

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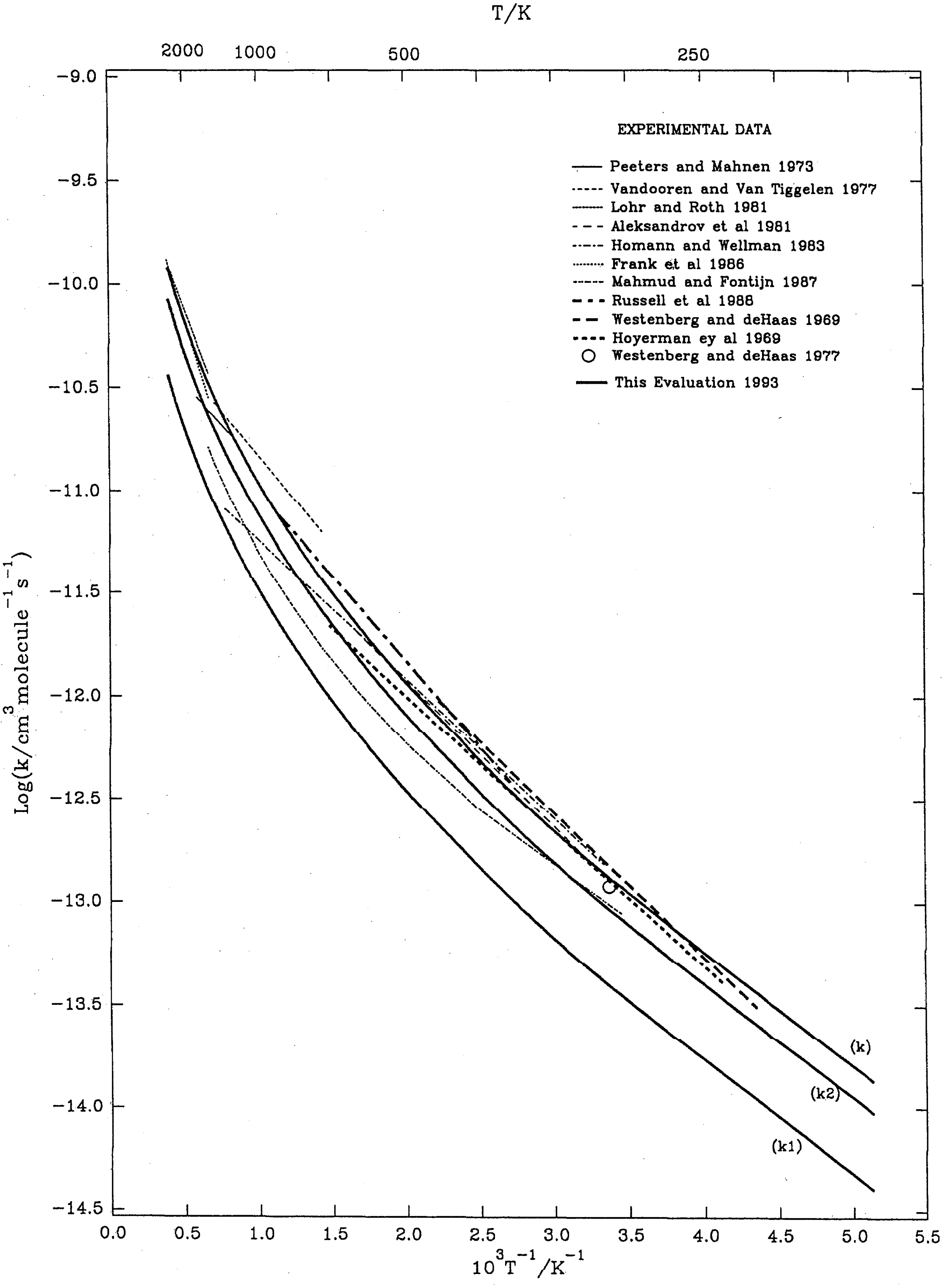
$O + C_2H_2 \rightarrow CO + {}^3CH_2$
$\rightarrow C_2HO + H$



$$\begin{aligned} \mathrm{O + C_2H_4} &\rightarrow \mathrm{CH_2CHO + H} && (1)\\ &\rightarrow \mathrm{HCO + CH_3} && (2)\\ &\rightarrow \mathrm{HCHO + CH_2} && (3)\\ &\rightarrow \mathrm{CH_2CO + H_2} && (4) \end{aligned}$$

Thermodynamic data

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

$\Delta H^\circ_{298}(2) = -112$ kJ mol^{-1}
$\Delta S^\circ_{298}(2) = 38.5$ J K^{-1} mol^{-1}
$Kp(2) = 4.5\cdot10^4\ T^{-0.114}\exp(+13100/T)$

$\Delta H^\circ_{298}(3) = -30.5$ kJ mol^{-1}
$\Delta S^\circ_{298}(3) = 33.9$ J K^{-1} mol^{-1}
$Kp(3) = 6.08\cdot10^4\ T^{-0.948}\exp(+3210/T)$

$\Delta H^\circ_{298}(4) = -353.0$ kJ mol^{-1}
$\Delta S^\circ_{298}(4) = -7.7$ J K^{-1} mol^{-1}
$Kp(4) = 0.369\ T^{0.143}\exp(+42280/T)$

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			
$1.3\cdot10^{-10}\exp(-2770/T)$	1052–2284	Klemm *et al.*, 1990[1]	(a)
Reviews and Evaluations			
$5.75\cdot10^{-18}T^{2.08}$	300–2000	CEC, 1992[2]	(b)

Comments

(a) High temperature study using the flash photolysis–shock tube technique. O atoms produced by photolysis of NO and monitored by atomic resonance absorption spectrometry. Pseudo first order decay of O in excess C_2H_4. Also give an expression for k based on data from Refs. 3–11 of $k = 9.3\cdot10^{-12}\exp(-752/T) + 1.5\cdot10^{-10}\exp(-3450/T)$ cm^3 molecule^{-1} s^{-1} over range 300–2300 K.

(b) Based on the analysis of Klemm *et al.*[3] of a large body of literature data.

Preferred Values

$k = 2.25\cdot10^{-17}T^{1.88}\exp(-92/T)$ cm^3 molecule^{-1} s^{-1} over range 300–2000 K.

$k_1/k = 0.35$ at P > 3 Torr and $T > 300$ K.
$k_2/k = 0.60$
$k_4/k = 0.05$

Reliability

$\Delta\log k = \pm0.1$ for $T < 1000$ K increasing to ±0.3 at 2000 K.
$\Delta k_1/k = \pm0.05$
$\Delta k_2/k = \pm0.10$
$\Delta k_4/k = \pm0.10$

Comments on Preferred Values

The new measurements of Klemm *et al.*[1] substantially extend the temperature range of the experimental data base, and agree reasonably well with the data from Mahmud *et al.*[12] at temperatures in the range 1100–1500 K. Klemm *et al.*[1] note that the discrepancy between the bi-exponential expression reported earlier by them[3] and that reported by Mahmud *et al.*[12] arises mainly from the lower temperature data of Mahmud *et al*[12]. Klemm *et al.*[1] give the following expression obtained from a fit to all the data including those of Mahmud *et al.*[12]: $k = 9.4\cdot10^{-12}\exp(-749/T) + 1.8\cdot10^{-10}\exp(-3740/T)$ cm^3 molecule^{-1} s^{-1}.

The preferred expression is derived by performing a three parameter, $A\ T^n\exp(B/T)$, fit to the curve generated from the bi-exponential expression of Klemm *et al.*[1] over the range 300–2000 K, from the data of Klemm *et al.*[3] and those in Refs. 4–11.

New data for the yield of H atoms[13] confirms that the branching ratio k_1/k is pressure dependent at low pressures. The recommendation based on earlier work of Smalley *et al.*[14] and Koda *et al.*[15,16] is unchanged.

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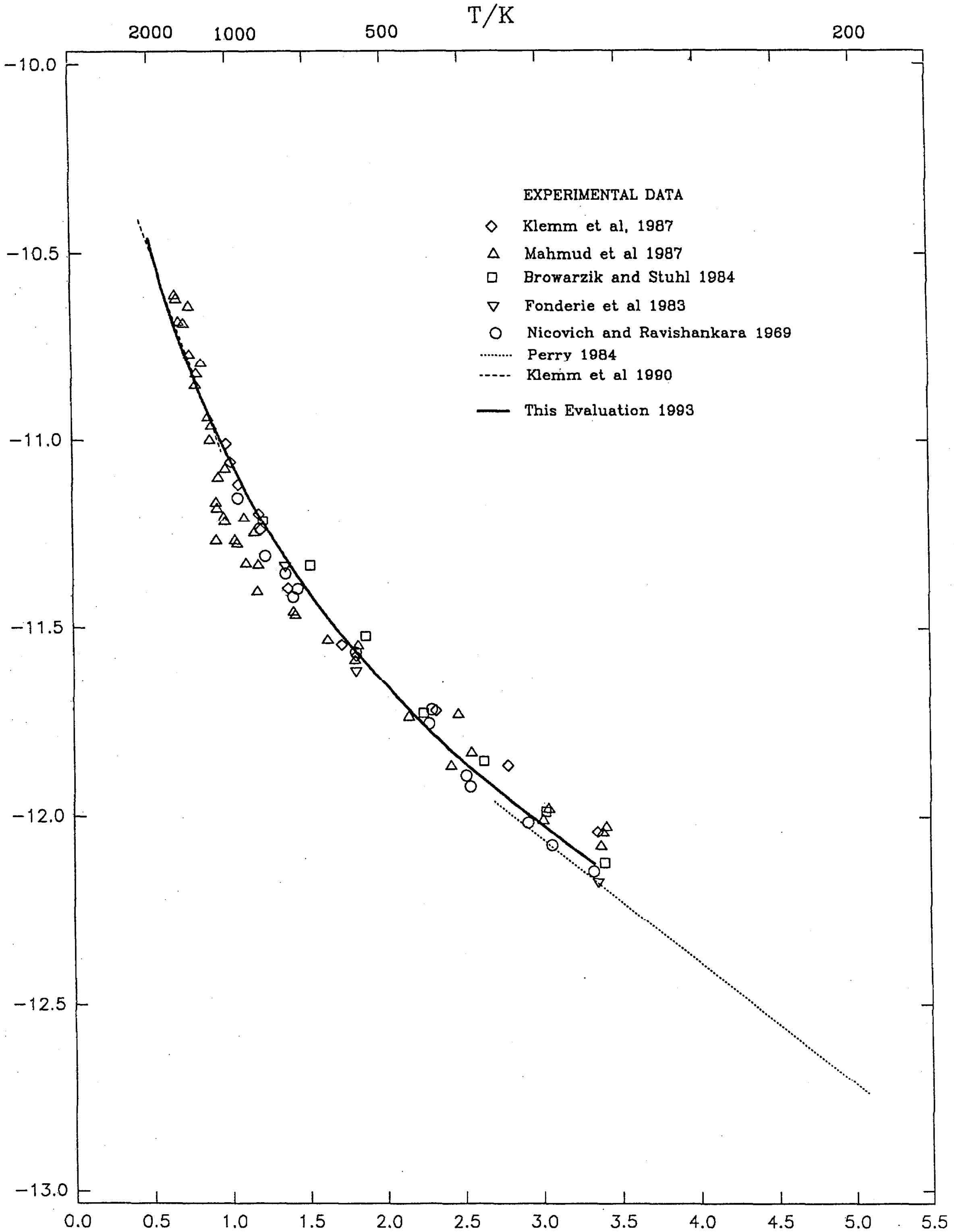
$$\mathrm{O + C_2H_4 \rightarrow CH_2CHO + H}$$
$$\mathrm{\rightarrow HCO + CH_3}$$
$$\mathrm{\rightarrow HCHO + CH_2}$$
$$\mathrm{\rightarrow CH_2CO + H_2}$$



$O + CH_3CO \rightarrow OH + CH_2CO$ (1)
$\rightarrow CO_2 + CH_3$ (2)

Thermodynamic Data

$\Delta H^\circ_{298}(1) = -239.3$ kJ mol^{-1}
$\Delta S^\circ_{298}(2) = -2.3$ J K^{-1} mol^{-1}
$Kp(1) = 9.4\cdot10^{-2}T^{0.27}\exp(+29400/T)$

$\Delta H^\circ_{298} = -474.0$ J K^{-1} mol^{-1}
$\Delta S^\circ_{298}(2) = -19.9$ J K^{-1} mol^{-1}
$Kp(2) = 3.0\cdot10^{-2}T^{0.07}\exp(+57700/T)$

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

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Comments
Rate Coefficient Measurements			
$3.2\cdot10^{-10}$	295	Miyoshi, Matsui, and Washida, 1989[1]	(a)
$k_1/k = 0.22$			
$k_2/k = 0.76$			
Reviews and Evaluations			
$3.3\cdot10^{-11}$	>300	Warnatz, 1984[2]	(b)
$1.6\cdot10^{-11}$	300–2500	Tsang and Hampson, 1986[3]	(c)
$1.0\cdot10^{-10}$	300–2000	Herron, 1988[4]	(d)

Comments

(a) Discharge flow system. Reactants and products monitored by photoionization mass spectrometry. k measured relative to $k(CH_3CO + O_2)$. $k_{ref}/k = (6.3 \pm 0.5)\cdot10^{-3}$ from the effect of $[O_2]$ on the yield of CH_3CO in the reaction of acetaldehyde in excess oxygen atoms. Given value of k based on $k(CH_3CO + O_2) = 2.0\cdot10^{-12}$ cm^3 molecule^{-1} s^{-1} from present evaluation. Branching ratio k_1/k from the yield of ketene and k_2/k from the yield of methyl radicals, both measured independently.

(b) Estimate.

(c) Estimate based on analogy of O atom reactions with alkyl radicals. Suggest channel (2) is dominant.

(d) As (c) but higher value preferred.

Preferred Value

$k = 3.2\cdot10^{-10}$ cm^3 molecule^{-1} s^{-1} over the range 298–1500 K.

$k_1/k = 0.2$ at 298 K.

$k_2/k = 0.8$ at 298 K.

Reliability

$\Delta\log k = \pm1.0$ at 1500 K reducing to ±0.3 at 298 K.

$\Delta k_1/k = \pm0.1$ at 298 K.

$\Delta k_2/k = \pm0.2$ at 298 K.

Comments on Preferred Values

The preferred values are based on the experimental measurements of Miyoshi *et al.*[1], which are consistent with the kinetics of other O-atom + radical reactions of similar type. In view of the rapid rate of this reaction, little, if any, temperature dependence of the rate is expected. The branching ratio, which is also based on the measurements of Miyoshi *et al.*[1], may change with temperature and the values can only be recommended with any confidence for room temperature.

References

[1] A. Miyoshi, H. Matsui, and N. Washida, J. Phys. Chem. **93**, 5813 (1989).

[2] J. Warnatz, in 'Combustion Chemistry', W.C. Gardiner, Jr., ed., Springer Verlag, New York p.197 (1984).

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

[4] J.T. Herron, J. Phys. Chem. Ref. Data **17**, 967 (1988).

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

Thermodynamic Data

$\Delta H^\circ_{298}(1) = -67.5$ kJ mol^{-1}
$\Delta S^\circ_{298}(1) = 25.6$ J K^{-1} mol^{-1}
$Kp = 2.2 \cdot 10^3 T^{-0.614} \exp(+7780/T)$

$\Delta H^\circ_{298}(2) = -19.8$ kJ mol^{-1}
$\Delta S^\circ_{298}(2) = 26.6$ J K^{-1} mol^{-1}
$Kp = 9.6 \cdot 10^2 T^{-0.455} \exp(+2050/T)$

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

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Comments
Rate Coefficient Measurements			
$3.9 \cdot 10^{-13}$	295	Miyoshi, Matsui, and Washida, 1989[1]	(a)
Reviews and Evaluations			
$9.7 \cdot 10^{-12} \exp(-910/T)$	298–1500	CEC, 1992[2]	(b)

Comments

(a) Discharge flow system. Reactants and products monitored by photoionization mass spectrometry. Pseudo first order decay of CH_3CHO in excess oxygen atoms.
(b) See Comments on Preferred Values.

Preferred Value

$k = 9.7 \cdot 10^{-12} \exp(-910/T)$ cm^3 molecule^{-1} s^{-1} over the 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

The new room temperature data agree with previous measurements within the experimental uncertainty. There is no change in the preferred values which are based on the low temperature data of Mack and Thrush[3], Michael and Lee[4] and Singleton *et al.*[5]. No information is available on the branching ratio. If it is assumed that $k_2 = 1/2\, k(O + C_2H_6)$ 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.*[6]. The contribution of the second channel is negligible at $T < 500$ K, where the only reliable studies were conducted.

References

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

Comment

There are no experimental data for the reaction of $O(^3P)$ with C_2H_5OOH. The same rate expression as for the $O + CH_3OOH$ reaction is recommended: $k = 3.3 \cdot 10^{-11} \exp(-2390/T)$ cm^3 molecule^{-1} s^{-1}, with channel (2) dominant.

$O + C_6H_6 \rightarrow OH + C_6H_5$ (1)
$O + C_6H_6\ (+ M) \rightarrow C_6H_6O\ (+ M)$ (2)

Thermodynamic Data

$\Delta H^\circ_{298}(1) = 35.3\ \mathrm{kJ\ mol^{-1}}$	$\Delta H^\circ_{298}(2) = -428.5\ \mathrm{kJ\ mol^{-1}}$
$\Delta S^\circ_{298}(1) = 41.7\ \mathrm{J\ K^{-1}\ mol^{-1}}$	$\Delta S^\circ_{298}(2) = -115.4\ \mathrm{J\ K^{-1}\ mol^{-1}}$
$Kp(1) = 9.8 \cdot 10^4\ T^{-0.88} \exp(-4701/T)$	$Kp(2) = 4.3 \cdot 10^{-6}\ T^{-0.20} \exp(+51411/T)\ \mathrm{atm^{-1}}$

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

$k/\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$	T/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, Oganesyan, and Nalbandyan, 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]	(a)
$1.8 \cdot 10^{-11} \exp(-2214/T)$	298–462	Colussi *et al.*, 1975[6]	(e)
$1.8 \cdot 10^{-11} \exp(-2003/T)$	299–392	Atkinson and Pitts, 1975[7]	(e)
$1.7 \cdot 10^{-11} \exp(-2010/T)$	299–440	Atkinson and Pitts, 1979[8]	(f)
$4.6 \cdot 10^{-11} \exp(-2470/T)$	298–867	Nicovich, Gump, and Ravishankara, 1982[9]	(g)
$k_1 = 5.3 \cdot 10^{-10} \exp(-3020/T)$	1600–2300	Hsu, Lin, and Lin, 1984[10]	(h)
$3.5 \cdot 10^{-11} \exp(-2250/T)$	300–670	Tappe, Schiephake, and Wagner, 1989[11]	(i)
$k_2 = 4 \cdot 10^{-11} \exp(-2350/T)$	1200–1450	Leidreiter and Wagner, 1989[12]	(j)
$k_2 = 5.4 \cdot 10^{-11} \exp(-2611/T)$	600–1300	Ko, Adusei, and Fontijn, 1991[13]	(k)
Reviews and Evaluations			
$2.5\text{–}10^{-11} \exp(-2130/T)$	298–600	Cvetanovic, 1987[14]	(l)
$1.2\text{–}10^{-22}\ T^{3.68} \exp(-570/T)$	300–1000	CEC, 1992[15]	(m)

Comments

(a) Pulse 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) Phase shift, O + NO chemiluminescence. O atoms are generated by Hg photosensitized decomposition of NO_2.

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

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

(h) 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.

(i) Flow reactor, mass spectrometric detection of O-atoms produced by microwave discharge in O_2. O-atom concentration in excess by factors 32–80. Total pressure range: 2.4–11.6 mbar, T-range: 300–870 K. At temperatures above 670 K an upward curvature of the Arrhenius plot is observed. Authors therefore recommend a rate expression only up to $T \approx 670$ K.

(j) Reaction studied under well isolated conditions (100–160 ppm benzene) behind incident shock waves at total densities of about $1\text{–}10^{-5}\ \mathrm{mol\ cm^{-3}}$. Thermal decomposition of ozone (6–25 ppm) was used as O atom source. $O(^3P)$-atoms monitored by ARAS at 130.5 nm. Values of k_2 from this work found to fit well with extrapolation of lower temperature data for k from Refs. 6–9.

(k) High temperature fast flow reactor study. $O(^3P)$ generated by 193 nm photolysis of SO_2 and monitored by resonance fluorescence in excess C_6H_6. Results for rate of removal of $O(^3P)$ consistent with low temperature data and with higher temperature results of Leidreiter and Wagner[12]. It is concluded that the same reaction channel is dominant up to 1400 K (channel 2) and fit to all these data gives expression for k_2 very similar to that recommended here.

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

(m) Fit to the data from Refs. 1–10.

Preferred Values

$k = 5.9 \cdot 10^{-23}\ T^{3.8} \exp(-473/T)$ cm^3 molecule^{-1} s^{-1} over range 300–2000 K.

$k_2 = 3.7 \cdot 10^{-11} \exp(-2280/T)$ cm^3 molecule^{-1} s^{-1} over range 298–1400 K.

Reliability

$\Delta\log k = \pm 0.3$ over range 298–2000 K.

$\Delta\log k_2 = \pm 0.3$ at 298 K falling to ± 0.2 at 1400 K.

Comments on Preferred Values

There is a large variety of studies on benzene oxidation in the lower temperature range, up to ≈ 900 K. The shock tube data for the higher temperature range are derived from reaction systems with reduced sensitivity. The preferred value for k_2 is based mainly on the measurements of Refs. 5–9, 11, 12, 15. From the excellent agreement between these data and from thermochemical arguments (see also Ref. 12) it is concluded that below about 1500 K reaction pathway (1) plays only a minor role with respect to the addition channel (2).

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[15] CEC, 1992 (see references in Introduction).

$O + C_6H_5OH \rightarrow$ products

Rate Coefficient Data

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Comments
Rate Coefficient Measurements			
$2.1 \cdot 10^{-11} \exp(-1455/T)$	292–873	Frerichs *et al.*, 1990[1]	(a)

Comments

(a) Flow reactor, mass spectrometric detection, O atoms produced in microwave discharge of O_2. O atom concentration in excess by factors 70–580. Total pressure range: 2.3–3.4 mbar.

Preferred Values

$k = 2.1 \cdot 10^{-11} \exp(-1455/T)$ cm^3 molecule^{-1} s^{-1} over range 290–600 K.

Reliability

$\Delta\log k = \pm 0.3$ over range 290–600 K.

Comments on Preferred Values

The preferred value is based on the only available measurement of Ref. 1. It is restricted to temperatures below 600 K. At higher temperatures this study indicates an upward curvature of the Arrhenius plot.

References

[1] H. Frerichs, R. Koch, V. Schliephake, M. Tappe, and H.Gg. Wagner, Zeits. f. Phys. Chemie N.F. **166**, 145 (1990).

$$\mathrm{O + C_6H_5CHO \rightarrow OH + C_6H_5CO} \quad (1)$$
$$\mathrm{\rightarrow OH + C_6H_4CHO} \quad (2)$$
$$\mathrm{O + C_6H_5CHO\ (+\ M) \rightarrow C_6H_5(O)CHO\ (+\ M)} \quad (3)$$

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

k/cm^3 molecule^{-1}s^{-1}	T/K	Reference	Comments
Rate Coefficient Measurements			
$4.8 \cdot 10^{-13}$	298	Filby and Gusten, 1978[1]	(a)

Comments

(a) Discharge flow; time resolved EPR detection of O in excess benzaldehyde. Pressure = 4.7 Torr He.

Preferred Values

$k_1 = 1.0 \cdot 10^{-11}\exp(-910/T)$cm^3 molecule^{-1} s^{-1} over range 298–1500 K.

Reliability

$\Delta\log k = \pm 0.7$ at 1500 K reducing to ± 0.3 at 298 K.

Comments on Preferred Values

The only experimental kinetic data for this reaction are at room temperature. The k value is essentially identical to that for the reaction of O atoms with acetaldehyde, indicating that the main channel is H– abstraction from the carbonyl group. The preferred rate expression applies to channel (1) and is based on the room temperature measurement and the temperature dependence for O + CH_3CHO (see this evaluation). There is no direct information on the alternative channels (2) and (3) where O attacks the aromatic ring. The importance of these channels can be assessed from the O + C_6H_6 reaction. Applying the recommended expression from this evaluation for $k(\mathrm{O} + \mathrm{C_6H_6}) = 1.2 \cdot 10^{-22}T^{3.68}\exp(-570/T)$cm^3 molecule^{-1} s^{-1} to the other channels, $(k_2 + k_3)$ is approximately a factor of 40 lower than k_1 at 300 K but the rates are about equal to 1000 K.

References

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$O + p\text{-}C_6H_4(CH_3)_2 \rightarrow$ 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]	(b)
$3.9 \cdot 10^{-11} \exp(-1540/T)$	298–600	Nicovich, Gump, and Ravishankara, 1982[4]	(c)
$4.3 \cdot 10^{-11} \exp(-1540/T)$	298–868	Frerichs *et al.*, 1989[5]	(d)
Reviews and Evaluations			
$2.6 \cdot 10^{-11} \exp(-1409/T)$	298–600	Cvetanovic, 1987[6]	(e)
$2.6 \cdot 10^{-11} \exp(-1409/T)$	298–600	CEC, 1992[7]	(f)

Comments

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

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

(c) Flash photolysis–resonance fluorescence. O atoms from VUV photolysis of O_2. Diluent N_2 or Ar at 76 mbar.

(d) Flow reactor with mass spectrometric detection, O atoms produced by microwave discharge in O_2. O atom concentration in excess by factors 45–172. Total pressure range: 2.2–4.5 mbar.

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

(f) Accepts evaluation of Cvetanovic.[6]

Preferred Values

$k = 5.1 \cdot 10^{-11} \exp(-1630/T)$ cm^3 molecule^{-1} s^{-1} over range 298–600 K.

Reliability

$\Delta \log k = \pm 0.3$ over range 298–600 K.

Comments on Preferred Values

In our previous recommendation the evaluation of Cvetanovic[6] was accepted. The new study of Frerichs *et al.*[5] provides further reliable results over an extended temperature range. The preferred value is based on the measurements of Refs. 2–5 but is still restricted to temperatures below 600 K. Above this value, the results of two studies[4,5] indicate an upward curvature of the Arrhenius plot which requires further study.

References

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

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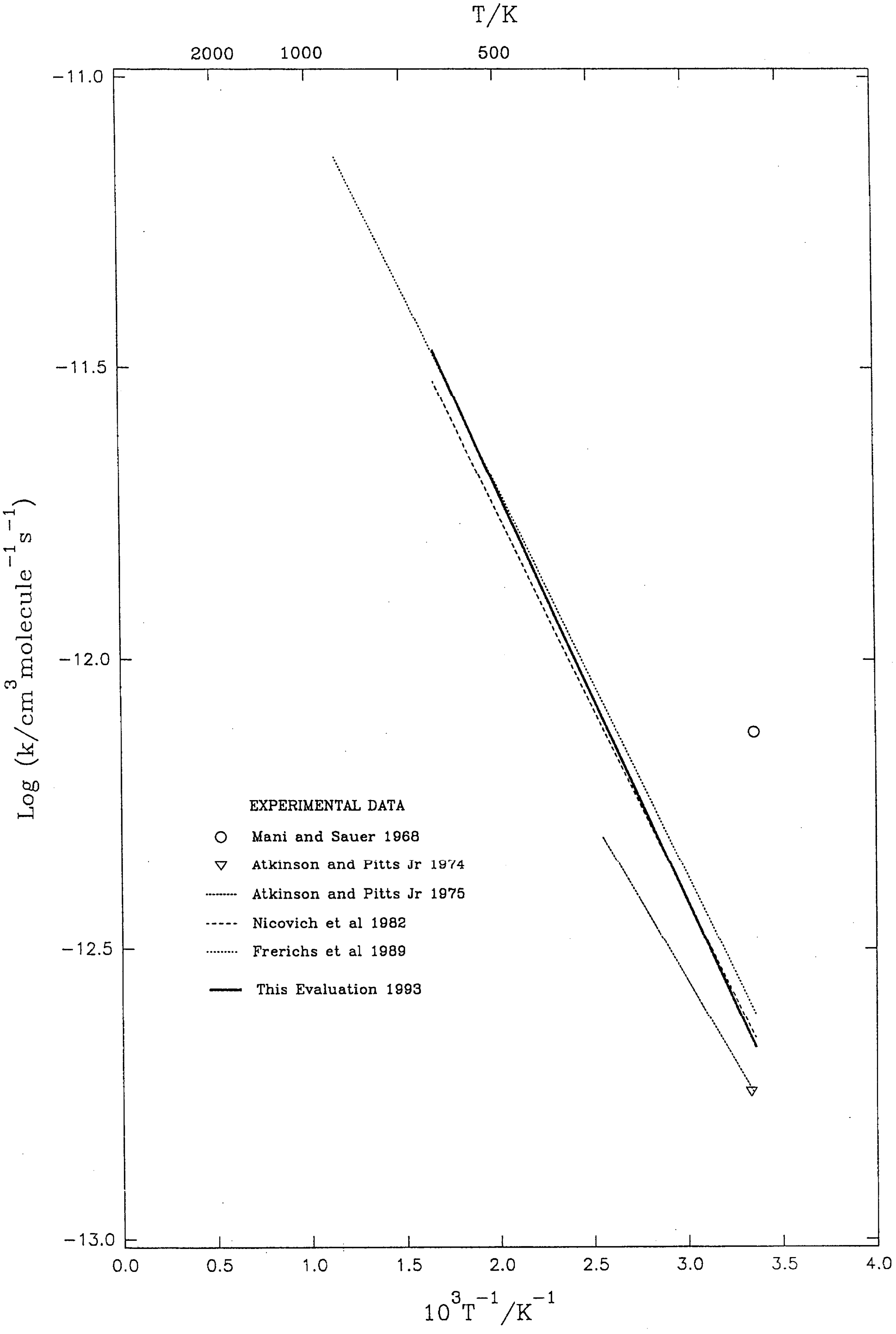
[5] H. Frerichs, V. Schliephake, M. Tappe, and H.Gg. Wagner, Zeits. f. Phys. Chemie N.F. **165**, 9 (1989).

[6] R.J. Cvetanovic, J. Phys. Chem. Ref. Data **16**, 261 (1987).

[7] CEC, 1992 (see references in Introduction).

O + p-$C_6H_4(CH_3)_2$ → products



$O + C_6H_5CH_3 \rightarrow$ products

Rate Coefficient Data

k/cm^3 molecule^{-1} s^{-1}	T/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]	(d)
$1.4 \cdot 10^{-11} \exp(-1560/T)$	299–392	Atkinson and Pitts, 1975[6]	(d)
$8.3 \cdot 10^{-12} \exp(-1359/T)$	373–648	Furuyama and Ebara, 1975[7]	(e)
$1.6 \cdot 10^{-11} \exp(-1535/T)$	299–440	Atkinson and Pitts, 1979[8]	(f)
$1.7 \cdot 10^{-10} \exp(-3625/T)$	1700–2800	McLain, Jachimowski, and Wilson, 1979[9]	(g)
$4.3 \cdot 10^{-11} \exp(-1910/T)$	298–932	Nicovich, Gump, and Ravishankara, 1982[10]	(h)
$2.8 \cdot 10^{-11} \exp(-1770/T)$	306–630	Tappe, Schliephake, and Wagner, 1989[11]	(i)
Reviews and Evaluations			
$2.7 \cdot 10^{-11} \exp(-1720/T)$	298–932	Cvetanovic, 1987[12]	(j)
$5.3 \cdot 10^{-15}\, T^{1.21} \exp(-1260/T)$	298–2800	CEC, 1992[13]	(k)

Comments

(a) O atoms from Hg photosensitized decomposition of N_2O. Ratio derived from relative k data in competitive studies. Reference reaction was O + cyclopentene → products. Evaluated by Cvetanovic.[12]

(b) Same method as in (a). Reference reaction was O + benzene → products. Evaluated by Cvetanovic.[12]

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

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

(g) 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. Arrhenius expression for the product channel $C_6H_5CH_2$ + OH estimated by comparison with data for benzene.

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

(i) Flow reactor with mass spectrometric detection, O-atoms produced by microwave discharge in O_2. O atom concentration in excess by factors 86–518. Total pressure range: 3.9–11.9 mbar. T-range: 300–870 K. At temperatures above 630 K an upward curvature of the Arrhenius plot is observed.

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

(k) See Comments on Preferred Values.

Preferred Values

$k = 5.3 \cdot 10^{-15}\, T^{1.21} \exp(-1260/T)$ 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

Our previous recommendations remain unchanged.[13]

The results of nine studies (Refs. 2–6, 8–11) in which the rate coefficient for total O consumption by toluene was measured, 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.

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[12] R.J. Cvetanovic, J. Phys. Chem. Ref. Data **16**, 261 (1987).

[13] CEC, 1992 (see references in Introduction).

$O + C_6H_5C_2H_5 \rightarrow$ 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)
$2.8 \cdot 10^{-11} \exp(-1840/T)$	300–600	Tappe *et al*., 1989[3]	(c)
Reviews and Evaluations			
$1.0 \cdot 10^{-13}$	298	Cvetanovic, 1987[4]	(d)
$1.0 \cdot 10^{-13}$	298(1 bar)	CEC, 1992[5]	(e)

Comments

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

(b) Ratio derived from relative k data in competition experiments. Reference reaction was O + benzene → products. $p \approx 1$ bar. Evaluated by Cvetanovic.[4]

(c) Flow reactor with mass spectrometric detection, O-atoms produced by microwave discharge in O_2. O-atom concentration in excess by factors 107–346. Total pressure range: 2.2–4.3 mbar. T-range: 300–870 K. At temperatures above 600 K an upward curvature of the Arrhenius plot is observed.

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

(e) Accepts the evaluation of Cvetanovic.[4]

Preferred Values

$k = 2.8 \cdot 10^{-11} \exp(-1840/T)$ cm^3 molecule^{-1} s^{-1} over range 298–600 K.

Reliability

$\Delta \log k = \pm 0.3$ over range 298–600 K.

Comments on Preferred Values

The preferred expression is that obtained in the recent study of Tappe *et al*.[3] which is in reasonable agreement at 300 K with the earlier results of Grovenstein and Mosher[2] which were the basis of our previous recommendations.[5]

References

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[3] M. Tappe, V. Schliephake, and H.Gg. Wagner, Zeits.f. Phys. Chemie N.F. **162**, 129 (1989).
[4] R.J. Cvetanovic, J. Phys. Chem. Ref. Data **16**, 261 (1987).
[5] CEC, 1992 (see references in Introduction).

$O_2 + C_3H_6 \rightarrow HO_2 + CH_2CHCH_2$

Thermodynamic Data

$\Delta H^\circ_{298} = 151.7$ kJ mol^{-1}
$\Delta S^\circ_{298} = 37.4$ J K^{-1} mol^{-1}
$Kp = 0.488 T^{-0.01} \exp(-18170/T)$

Rate Coefficient Data

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Comments
Rate Coefficient Measurements			
$3.2 \cdot 10^{-12} \exp(-19670/T)$	673–793	Stothard and Walker, 1991[1]	(a)
Reviews and Evaluations			
$1 \cdot 10^{-10} \exp(-23950/T)$	–	Tsang, 1991[2]	(b)

Comments

(a) Oxidation of C_3H_6 under conditions where chain length is low. k obtained by equating rate of initiation to rate of termination, which was determined directly. Minor corrections (<20%) made for radical branching reactions.

(b) Estimate based on view that rate of abstraction should be similar to that of secondary C—H in alkanes.

Preferred Value

$k = 3.2\cdot10^{-12}\exp(-19700/T)$ cm^3 molecule^{-1} s^{-1} over range 600–1000 K.

Reliability

$\Delta\log k = \pm0.3$ at 800 K rising to ±0.5 at 1000 K and 600 K.

Comments on Preferred Values

Although there are no other independent data to compare with the one available experimental study[1], the rate coefficient values are in excellent agreement with those of the analogous reaction $O_2 + HCHO \rightarrow HO_2 + HCO$ for which $k = 3.4\cdot10^{-11}\exp(-19580/T)$ cm^3 molecule^{-1} s^{-1} was obtained[3] between 713 and 813 K, the enthalpies of reaction being the same within ±4 kJ mol^{-1}. The low A factor for $O_2 + C_3H_6$ is consistent with loss of entropy of activation due to the emerging electron-delocalized allyl radical.

References

[1] N.D. Stothard and R.W. Walker, J. Chem. Soc., Faraday Trans. **87**, 241 (1991).

[2] W. Tsang, J. Phys. Chem. Ref. Data **20**, 231 (1991).

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$O_2 + C_6H_5CH_3 \rightarrow HO_2 + C_6H_5CH_2$

Thermodynamic Data

$\Delta H^\circ_{298} = 165.0$ kJ mol^{-1}

$\Delta S^\circ_{298} = 23.9$ J K^{-1} mol^{-1}

$Kp = 1.93\cdot T^{0.331}\exp(-19860/T)$

Rate Coefficient Data

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Comments
Rate Coefficient Measurements			
$5.5\cdot10^{-10}\exp(-19100/T)$	~1000	Bittker, 1988[1]	(a)
$5\cdot10^{-10}\exp(-20800/T)$	1000–1200	Emdee, Brezinsky, and Glassman, 1992[2]	(b)

Comments

(a) Reported by Emdee *et al.* in Ref. 2. Based on computer modelling fit in studies of toluene oxidation at about 1000 K.

(b) Based on computer modelling fit to data obtained on the oxidation of toluene at atmospheric pressure between 1100 and 1200 K. Authors claim high sensitivity of the rate of toluene consumption to the value for k and hence estimate value of k. Activation energy estimated from reaction endothermicity, and pre-exponential factor adjusted to achieve best fit to the rate of toluene consumption. At 1100 K the value of k is a factor of about 5 lower than recommended by Bittker. Mechanism still very uncertain and very complex, and any radical branching not isolated will result in high values of k.

Preferred Value

$k = 3\cdot10^{-12}\exp(-20{,}000/T)$ cm^3 molecule^{-1} s^{-1} over range 700–1200 K.

Reliability

$\Delta\log k = \pm0.7$ over range 700–1200 K.

Comments on Preferred Values

Although the activation energies given by Bittker[1] and by Emdee *et al.*[2] are reasonable since $\Delta H \approx E$, the A factor is probably about two orders of magnitude too high. Directly determined values of $k_{1f} = 3.4\cdot10^{-11}\exp(-19580/T)$ cm^3 molecule^{-1} s^{-1} for $HCHO + O_2 \rightarrow HCO + HO_2$[3] and $k_{1p} = 3.2\cdot10^{-12}\exp(-19670/T)$ cm^3 molecule^{-1} s^{-1} for $C_3H_6 + O_2 \rightarrow C_3H_5 + HO_2$[4] confirm the validity of $\Delta H \approx E$ for the primary initiation reaction $RH + O_2 \rightarrow R + HO_2$. However, A for $C_6H_5CH_3 + O_2$ is a factor of 10 greater than A_{1f} and a factor of 100 greater than A_{1p}. Stothard and Walker[4] have suggested that $A_{1f}/A_{1p} \approx 10$ is reasonable and arises from an increased loss of entropy of activation due to electron delocalization in the emerging allyl radical. Formation of the benzyl radical also involves electron delocalization and the recommendation is thus based on equal A factors for $C_3H_6 + O_2$ and $C_6H_5CH_3 + O_2$. Support[5] for this view comes from the value of $k(HO_2 + HCHO \rightarrow HCO + H_2O_2)/k(HO_2 + C_6H_5CH_3 \rightarrow C_6H_5CH_2 + H_2O_2) = 14$ at 750 K, the two reactions having the same activation energy to within 4 kJ mol^{-1}, so that the difference in rate constants arises mostly from the much lower A factor for $HO_2 + C_6H_5CH_3$.

In addition, thermochemical calculation of the rate constant for the reverse reaction, $HO_2 + C_6H_5CH_2 \rightarrow O_2 + C_6H_5CH_3$

from the Emdee *et al.* data[2] gives a value of $3.5\cdot10^{-10}$ cm^3 molecule^{-1} s^{-1} at 1100 K which is at least a factor of 10 too high and compares with $k = 3.3\cdot10^{-12}$ between 700 and 800 K determined experimentally for $C_3H_5 + HO_2 \rightarrow C_3H_6 + O_2$. Use of the recommended value of k gives a value of $2.0\cdot10^{-12}$ cm^3 molecule^{-1} s^{-1} for the reverse reaction, $HO_2 + C_6H_5CH_2 \rightarrow C_6H_5CH_3 + O_2$.

References

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$H + O_2 \rightarrow OH + O$

Thermodynamic Data

$\Delta H^\circ_{298} = 70.2$ kJ mol^{-1}
$\Delta S^\circ_{298} = 24.9$ J K^{-1} mol^{-1}
$Kp = 3.02\cdot10^{2}T^{-0.374}\exp(-8620/T)$

Rate Coefficient Data

k/cm^3 molecule^{-1}s^{-1}	T/K	Reference	Comments
Rate Coefficient Measurements			
$9.96\cdot10^{-10}\exp(-11427/T)$	1900–2650	Fujii and Shin, 1988[1]	(a)
$1.55\cdot10^{-10}\exp(-7440/T)$	1450–3370	Masten *et al.*, 1990[2]	(b)
$2.64\cdot10^{-7}T^{-0.927}\exp(-8493/T)$	1050–2700	Yuan *et al.*, 1991[3]	(c)
$1.15\cdot10^{-10}\exp(-6917/T)$	1102–2055	Shin and Michael, 1991[4]	(d)
$1.55\cdot10^{-10}\exp(-7270/T)$	2050–5305	Du and Hessler, 1992[5]	(e)
Reviews and Evaluations			
$3.3\cdot10^{-10}\exp(-8456/T)$	300–2500	CEC, 1992[6]	(f)

Comments

(a) The concentration growth of OH radicals was measured in rich shock-heated H_2–O_2–Ar mixtures by cw laser absorption spectroscopy.

(b) Shock tube study. OH was detected by OH laser absorption. Additional H atom production was measured with ARAS. Combination of these results with those of Pirraglia *et al.*[9] gives $k = 5.84\cdot10^{-8}T^{-0.7}\exp(-8580/T)$ cm^3 molecule^{-1} s^{-1}.

(c) A shock tube/laser absorption/detailed modelling study. Total pressure 1.57–3.43 atm. H_2/O_2 was diluted in Argon. The reaction progress was measured *in situ* by state-selective laser absorption of OH radicals.

(d) Laser photolysis/shock tube study. H– or D–atom detection by atomic resonance absorption spectroscopy (ARAS). Total density during shock in range $(1.668–3.364)\cdot10^{+18}$ cm^{-3}.

(e) Tunable laser/flash absorption technique used to monitor OH in shock heated H_2/O_2/Ar or Kr mixtures. Results were combined with previous measurements[2,4,9] to give the expression $k = 1.62\cdot10^{-10}\exp(-7474/T)$ cm^3 molecule^{-1} s^{-1} over range 960–5300 K.

(f) Based on earlier evaluation of Baulch *et al.*[7] and results of Frank and Just[8] and Pirraglia *et al.*[9]

Preferred Values

$k = 1.62\cdot10^{-10}\exp(-7474/T)$ over range 300–5000 K.

Reliability

$\Delta\log k = \pm0.2$ at 300 K rising to ±0.5 at 5000 K.

Comments on Preferred Values

The expression derived by Du and Hessler[5] is preferred. It lies within the error limits of the previous CEC recommenations[6] but incorporates the new results of Fujii and Shin[1], Masten *et al.*[2] and Shin and Michael[4] and extends the temperature range.

References to earlier results shown on the graph may be found in CEC, 1992[6].

References

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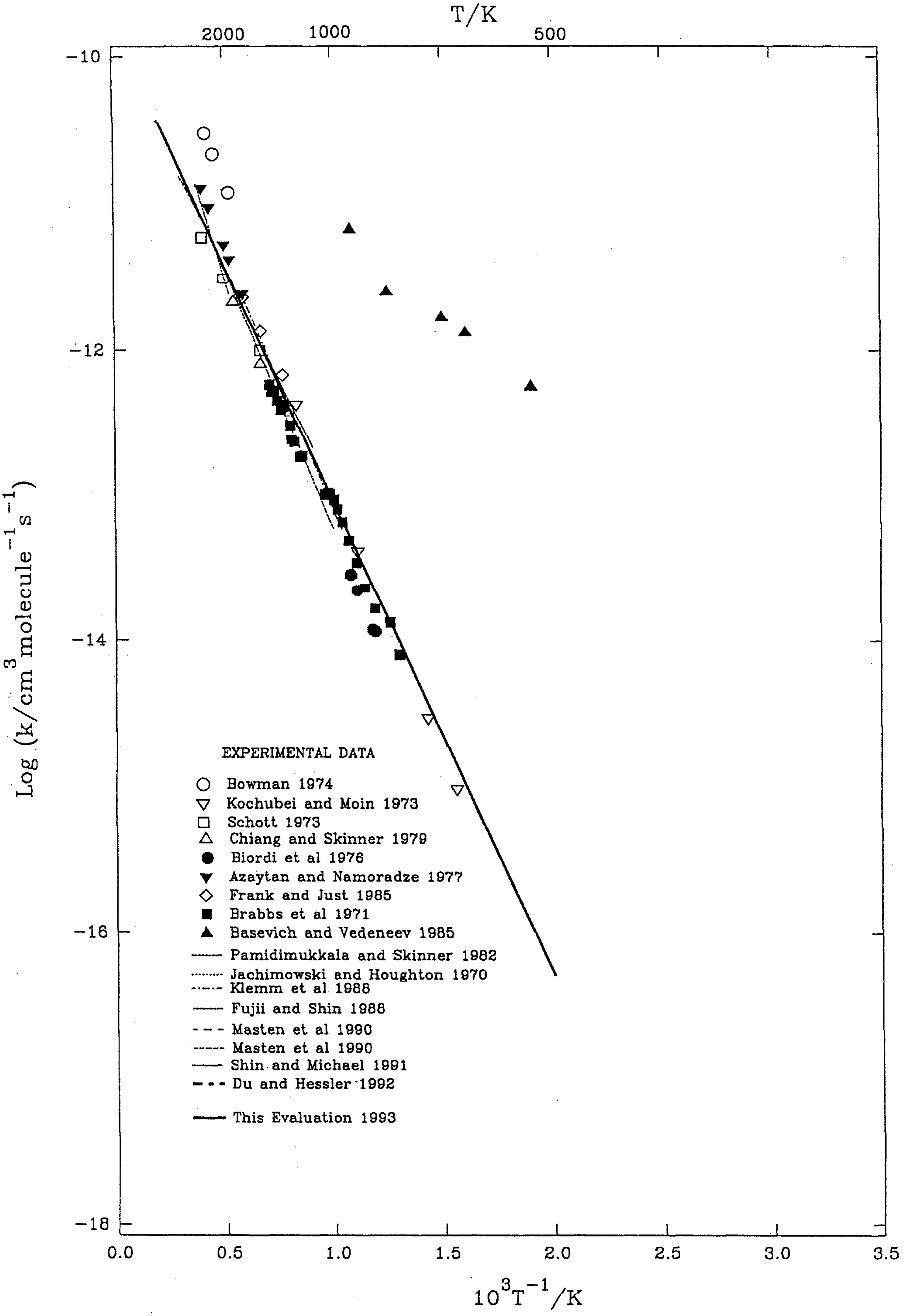
[9] A.N. Pirraglia, J.V. Michael, J.W. Sutherland, and R.B. Klemm, J. Phys. Chem. **93**, 282 (1989).

$H + O_2 \rightarrow OH + O$



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

Thermodynamic Data

$\Delta H^\circ_{298} = -208$ kJ mol^{-1}

$\Delta S^\circ_{298} = -90.6$ J K^{-1} mol^{-1}

$Kp = 6.9\cdot10^{-3}T^{-0.95}\exp(+24800/T)$ atm^{-1}

Rate Coefficient Data

k/cm^6 molecule^{-2} s^{-1}	T/K	p/Torr	M	Reference	Comments
Rate Coefficient Measurements					
$0.99\cdot10^{-32}$	800	100–243	N_2	Hanning-Lee *et al.*, 1991[1]	(a)
$2.95\cdot10^{-32}$	825	100–243	N_2		
$3.45\cdot10^{-32}$	850	100–243	N_2		
Reviews and Evaluations					
$1.8\cdot10^{-29}T^{-1}$	300–2500		O_2, N_2	Tsang and Hampson, 1986[2]	(b)
$1.7\cdot10^{-30}T^{-0.8}$	300–2000		Ar	CEC, 1992[3]	(c)
$3.9\cdot10^{-30}T^{-0.8}$	300–2000		N_2		
$5.8\cdot10^{-30}T^{-0.8}$	300–2000		H_2		

Comments

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

(b) Based on evaluations by the CODATA[4] and NASA[5] Groups.

(c) See comments on Preferred Values.

Preferred Values

$k = 1.7\cdot10^{-30}T^{-0.8}$ cm^6 molecule^{-2} s^{-1} over range 300–2000 K for M = Ar.

$k = 5.8\cdot10^{-30}T^{-0.8}$ cm^6 molecule^{-2} s^{-1} over range 300–2000 K for M = H_2.

$k = 3.9\cdot10^{-30}T^{-0.8}$ cm^6 molecule^{-2} s^{-1} over range 300–2000 K for M = N_2.

Reliability

$\Delta\log k = \pm0.5$ over range 300–2000 K.

Comments on Preferred Values

The recommendations are unchanged from our previous evaluation which were based largely on the recommendations of Baulch *et al.*[6]. The new data of Hanning-Lee *et al.*[1] are in agreement within the error limits.

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

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[6] 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).

$H + NO \rightarrow OH + N$

Thermodynamic Data
$\Delta H^\circ_{298} = 203.1$ kJ mol^{-1}
$\Delta S^\circ_{298} = 11.6$ J K^{-1} mol^{-1}
$Kp = 24.4\ T^{-0.257}\exp(-24560/T)$

Rate Coefficient Data

k/cm^3 molecule^{-1}s^{-1}	T/K	Reference	Comments
Rate Coefficient Measurements			
$5.76 \cdot 10^{-10}\exp(-23940/T)$	2530–3020	Bradley and Craggs, 1975[1]	(a)
$4.28 \cdot 10^{-10}\exp(-24560/T)$	2200–3250	Duxbury and Pratt,1975[2]	(b)
$8.32 \cdot 10^{-11}\exp(-24510/T)$	2400–3500	Ando and Asaba, 1976[3]	(c)
$3.71 \cdot 10^{-10}\exp(-25410/T)$	2400–4200	Flower *et al*.. 1977[4]	(d)
$2.89 \cdot 10^{-10}\exp(-24760/T)$	1750–2040	McCullough *et al*., 1977[5]	(e)
Reviews and Evaluations			
$2.82 \cdot 10^{-10}\exp(-24560/T)$	1750–4200	Hanson and Salimian. 1984[6]	(f)

Comments

(a) Shock tube study with fluorescence detection of NO at 226 nm and OH at 306.4 nm. Computer simulation of concentration profiles used to derive rate constant.

(b) Shock tube study using highly diluted H_2/NO/Ar mixtures with monitoring of NO, OH, NH_3 and NH in absorption. Computer modelling of [OH] and [NO] profiles used to derive rate constant.

(c) Reanalysis of the data of Koshi *et al*.[7], who carried out a shock tube study on NO/H_2/Ar mixtures, monitoring [O] by NO/O chemiluminescence at 650 nm and [NO] in emission at 5.22 μm.

(d) Shock tube study of NO/H_2/inert gas mixtures. IR emission from NO and H_2O at 5.3 and 6.3 μm monitored. Comparison of computed with experimental profiles used to derive k.

(e) Dilute mixtures of NO/H_2/Ar passed through alumina packed flow reactor heated to temperatures in the range 1750–2040. Fractional decomposition of NO monitored as a function of flow rate using chemiluminescence detection.

(f) Based on Duxbury and Pratt[2], Flower *et al*.[4], McCullough *et al*.[5].

Preferred Values

$k = 3.6 \cdot 10^{-10}\exp(-24910/T)$ cm^3 molecule^{-1} s^{-1} over the range 1500–4500 K.

Reliability
$\Delta\log k = \pm 0.5$.

Comments on Preferred Values

All of the studies of this reaction are in good agreement on the temperature coefficient of k but the absolute values show considerable scatter in the temperature region where the studies overlap.

Our recommendations are based on the studies of Duxbury and Pratt[2], Flower *et al*.[4], and McCullough *et al*.[5] and are very similar to those of Hanson and Salimian[6]. The temperature coefficient from the three studies[2,4,5] was averaged and a pre-exponential factor was derived from the temperature coefficient and a mean value of k at 2500 K.

The recommended expressions for k for the forward and reverse reactions give an expression for the equilibrium constant considerably different from the thermodynamic expression but within the substantial error limits of the kinetic data.

References

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[4] W.L. Flower, R.K. Hanson, and C.H. Kruger, Comb. Sci. Tech. **15**, 115 (1977).
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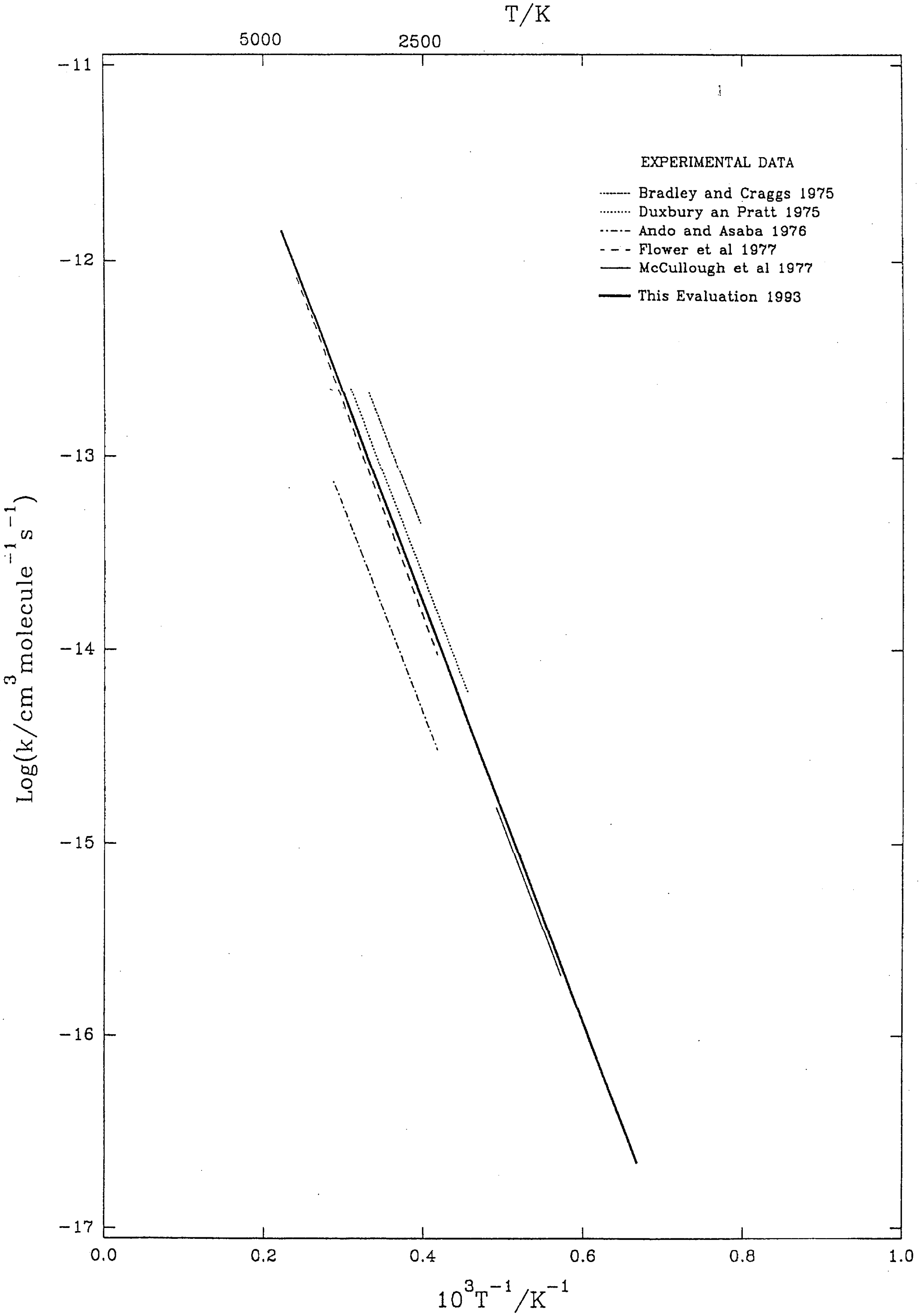
H + NO → OH + N


T/K
5000
2500
−11
−12
−13
−14
−15
−16
−17
0.0
0.2
0.4
0.6
0.8
1.0
Log(k/cm³molecule⁻¹s⁻¹)
10³T⁻¹/K⁻¹
EXPERIMENTAL DATA
Bradley and Craggs 1975
Duxbury an Pratt 1975
Ando and Asaba 1976
Flower et al 1977
McCullough et al 1977
This Evaluation 1993

H + CO (+ M) → HCO (+ M)

Thermodynamic data
$\Delta H^\circ_{298} = -63.9$ kJ mol^{-1}
$\Delta S^\circ_{298} = -20.9$ J K^{-1} mol^{-1}
$Kp = 1.5 \cdot 10^{-2} T^{-1.0} \exp(+7560/T)$ atm^{-1}

Rate Coefficient Data

k/cm^3 molecule^{-1} s^{-1}	T/K	[M]/molecule cm^{-3}	References	Comments
Rate Coefficient Measurements				
Low Pressure Range				
$[\mathrm{Ar}](7.2 \pm 1.1) \cdot 10^{-35}$	298	$(1.9\text{–}5.2) \cdot 10^{19}$	Hikida, Eyre and Dorfman, 1971[1]	(a)
$[\mathrm{H_2}](1.1 \pm 0.2) \cdot 10^{-34}$		$(0.7\text{–}4.5) \cdot 10^{19}$		
$[\mathrm{He}]3.3 \cdot 10^{-34}$	298	$(1.6\text{–}8.1) \cdot 10^{18}$	Bennet and Blackmore, 1971[2]	(b)
$[\mathrm{He}]4.7 \cdot 10^{-35}$	298	$(3.4\text{–}19) \cdot 10^{18}$	Ahumada, Michael, and Osborne, 1972[3]	(c)
$[\mathrm{Ne}]4.1 \cdot 10^{-35}$		$(3.3\text{–}19) \cdot 10^{18}$		
$[\mathrm{Ar}]5.3 \cdot 10^{-35}$		$(1.7\text{–}19) \cdot 10^{18}$		
$[\mathrm{Kr}]7.3 \cdot 10^{-35}$		$(3.2 \cdot 19) \cdot 10^{18}$		
$[\mathrm{H_2}]7.5 \cdot 10^{-35}$		$(1.8\text{–}19) \cdot 10^{18}$		
$[\mathrm{H_2}]6.3 \cdot 10^{-34}$	773		Baldwin *et al.*, 1972[4]	(d)
$[\mathrm{H_2}]2.2 \cdot 10^{-33} \exp(-1064/T)$	298–373	$(0.7\text{–}4.5) \cdot 10^{19}$	Wang, Eyre, and Dorfman, 1973[5]	(e)
$[\mathrm{Ar}](2.7 \pm 0.2) \cdot 10^{-34}$	425	$(0.6\text{–}1.7) \cdot 10^{17}$	Campbell and Handy, 1978[6]	(f)
$[\mathrm{N_2}](4.0 \pm 0.3) \cdot 10^{-34}$		$(7.0\text{–}7.9) \cdot 10^{16}$		
$[\mathrm{H_2}](1.0 \pm 0.1) \cdot 10^{-34}$	298	$2.5 \cdot 10^{19}$	Hochanadel, Sworsky, and Ogren, 1980[7]	(g)
$[\mathrm{CO}](9.9 \pm 2.5) \cdot 10^{-35}$		$(2.5\text{–}7.4) \cdot 10^{19}$		
$[\mathrm{CH_4}](1.6 \pm 0.2) \cdot 10^{-34}$		$2.5 \cdot 10^{19}$		
Reviews and Evaluations				
$k_0 = [\mathrm{H_2}]1.6 \cdot 10^{-34} T^{0.11}$	1400–3000		Browne, White, and Smookler, 1969[8]	(h)
$k_0 = [\mathrm{H_2}]2.0 \cdot 10^{-33} \exp(-850/T)$	298–773		Baulch *et al.*, 1976[9]	(i)
$k_0 = [\mathrm{H_2}]1.4 \cdot 10^{-33} \exp(-760/T)$	1100		Cherian *et al.*, 1981[10]	(j)
$k_0 = [\mathrm{H_2}]1.9 \cdot 10^{-33} \exp(-842/T)$	300–2000		Warnatz, 1984[11]	(k)
$k_0 = [\mathrm{N_2}]1.74 \cdot 10^{-27} T^{-1.82} \exp(-1856/T)$	800–2500		Tsang and Hampson, 1986[12]	(l)

Comments

(a) H atoms generated by pulse radiolysis of H_2 and detected by Lyman-α spectrophotometry. Diffusion of H atoms to the wall taken into account.

(b) Fast-flow study. H atoms were generated by a hot tungsten wire or by a high-pressure microwave discharge and detected by ESR.

(c) H atoms formed by mercury photosensitization of H_2 and monitored by Lyman-α absorption spectrophotometry. Steady state conditions and decay of [H] followed after the end of the light pulse.

(d) Thermal reaction of $H_2/CO/O_2$ mixtures. Study of the second explosion limit in KCl and CsCl coated vessels.

(e) Pulse radiolysis of H_2. H monitored by Lyman-α spectrophotometry. An activation energy of $E_2 = 2.0 \pm 0.4$ kcal mol^{-1} was determined. The value of the pre-exponential factor given here is based on the k_0 data from Ref. 1.

(f) Discharge flow stirred reaction study of O_2-H_2-CO-N_2 (or Ar) mixtures. The experiments were conducted over the ranges $90 \leq [\mathrm{CO}]/[\mathrm{O}] \leq 950$ and $0.2 \leq [\mathrm{H}]/[\mathrm{O}] \leq 3$.

(g) Flash photolysis of H_2O vapour in the presence of CO. [HCO] monitored by UV absorption at 230 nm. The competing reaction $\mathrm{H} + \mathrm{HCO} \rightarrow \mathrm{H_2} + \mathrm{CO}$ is significant during the formation of HCO. From the amount of H_2O photodissociated (using the H_2O + CH_4 system as an actinometer) and a computer modelling of the formation and decay rates of HCO values of k were obtained.

(h) Expression recommended for modelling of shock heated $H_2/CO/O_2$ mixtures. Evaluation based on data from Ref. 7.

(i) Evaluation of the literature up to 1975.

(j) Modelling of CO oxidation in flames.

(k) Review of literature rate data.

(l) Data evaluation and construction of RRKM fall-off curves.

Preferred Values

$k_0 = [\mathrm{Ar}]5.3 \cdot 10^{-34} \exp(-370/T)$ cm^3 molecule^{-1} s^{-1} over range 300–2500 K.

Reliability
$\Delta \log k_0 = \pm 0.5$ for M = Ar over range 300–2500 K.

Comments on Preferred Values
The absolute values of k_0 close to room temperature and the temperature dependence of k_0 remain considerably uncertain. Most previous evaluations of the temperature dependence have been based on the reverse dissociation reaction. Here, we have converted the recommended k_0 values for the dissociation reaction to recombination using the calculated equi-

librium constant as given above. The preferred values of k_0 are consistent with an average energy transferred per collision of 20 $[T/300]$ cm^{-1}. Figure 1 shows the temperature dependence of k_0 from several sources together with our recommendation.

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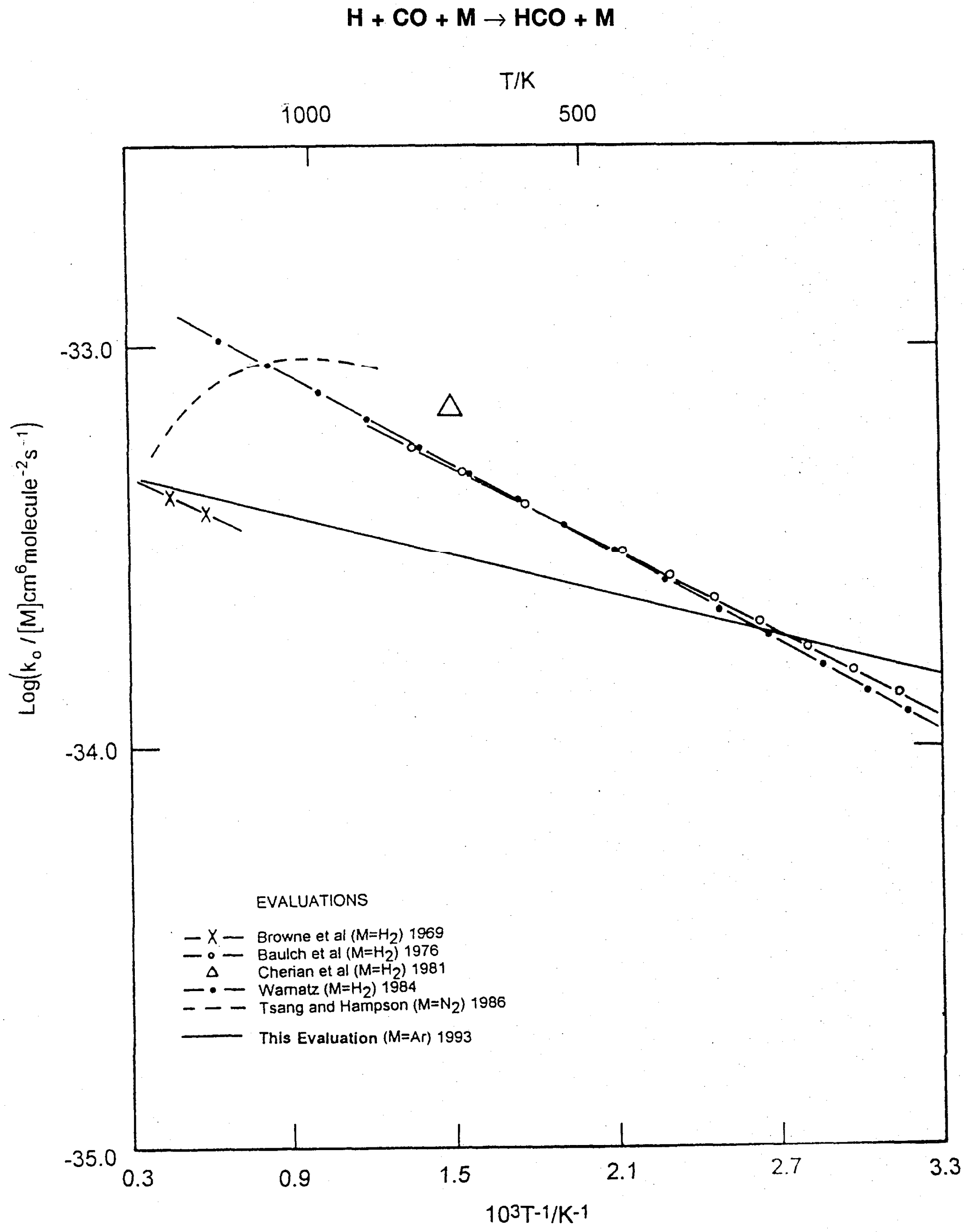

HCO (+ M) → H + CO (+ M)

Thermodynamic data

$\Delta H^\circ_{298} = 63.9$ kJ mol^{-1}
$\Delta S^\circ_{298} = 20.9$ J K^{-1} mol^{-1}
$Kp = 6.6\cdot10^{+1}T^{1.0}\exp(-7560/T)$ atm

Rate Coefficient Data

k/s^{-1}	T/K	[M]/molecule cm^{-3}	References	Comments
Rate Coefficient Measurements				
Low Pressure Range				
$[\mathrm{Ar}]2.6\cdot10^{-10}\exp(-7400/T)$	1400–2200		Schecker and Jost, 1969[1]	(a)
$[\mathrm{Ar}]3.3\cdot10^{-11}T^{0.5}\exp(-14400/T)$	1350–1900		Bowman, 1970[2]	(b)
$[\mathrm{Ar}]2.5\cdot10^{-10}\exp(-7340/T)$	1700–2710	$(2.4\text{–}4.5)\cdot10^{18}$	Dean *et al.*, 1979[3]	(c)
$[\mathrm{Ar}]1.7\cdot10^{-9}\exp(-7699/T)$	1350–1450	$(1.6\text{–}2.8)\cdot10^{17}$	de Guertechin *et al.*, 1983[4]	(d)
$[\mathrm{He}]3.80\cdot10^{-7}T^{-1}\exp(-8600/T)$	637–832	$(3.5\text{–}7.1)\cdot10^{16}$	Timonen *et al.*, 1987[5]	(e)
$[\mathrm{Ar}]3.09\cdot10^{-7}T^{-1}\exp(-8555/T)$		$7.1\cdot10^{16}$		
$[\mathrm{N_2}]3.07\cdot10^{-7}T^{-1}\exp(-8555/T)$		$7.1\cdot10^{16}$		
$[\mathrm{H_2}]5.79\cdot10^{-7}T^{-1}\exp(-8555/T)$		$7.1\cdot10^{16}$		
$[\mathrm{Ne,Ar}]8.3\cdot10^{-11}\exp(-8455/T)$	1800–2740	$1.0\cdot10^{18}$	Cribb, Dove, and Yamazaki, 1992[6]	(f)
Reviews and Evaluations				
$k_o = [\mathrm{Ar}]1.2\cdot10^{-10}\exp(-7550/T)$	1000–1700		Browne *et al.*, 1969[7]	(g)
$k_o = [\mathrm{Ar}]4.2\cdot10^{-10}\exp(-8455/T)$	700–2500		Warnatz, 1984[9]	(h)
$k_o = [\mathrm{N_2}]8.5\cdot10^{-3}T^{-2.14}$ $\exp(-10278/T)$	1000–2000		Tsang and Hampson, 1986[10]	(i)

Comments

(a) Shock tube study of the thermal dissociation of H_2CO. The reactant was monitored by UV absorption at 366 nm and by IR emission at 3.5 μm.
(b) Shock tube study of CH_4-O_2 mixtures in Ar. The reaction was followed by IR emission from CO, CO_2 and H_2O and by the laser schlieren method. Modelling with 14 reactions.
(c) Pyrolysis of 0.1%, 0.5% and 1% CH_2O in Ar. CH_2O monitored by IR emission at 3.5 μm behind reflected shocks.
(d) Thermal decomposition of HCO in a molecular beam. Kinetics followed by mass spectrometry.
(e) HCO radicals were generated by 308 nm photodissociation of CH_3CHO in a heatable tubular quartz reactor. The [HCO] decay was monitored using a photoionization mass spectrometer. The rates were measured from 637 K to 832 K and extrapolated from 300 K to 3000 K using an RRKM model adapted to treat the extremely sparse density of vibrational states of HCO.
(f) Thermal decomposition of methanol studied by laser schlieren densitometry and dynamic mass spectrometry. Modelling with a mechanism of 28 reactions.
(g) Numerical analysis of C_2H_2-O_2 flames measured previously[8]. The analysis includes rich and lean C_2H_2 flames and rich C_2H_2 flames with added CO or H_2.
(h) Review of literature rate data.
(i) Data evaluation. The recommended value is based on rate data for the reverse process.

6

Preferred Values

$k_o = [\mathrm{Ar}]2.6\cdot10^{-10}\exp(-7930/T)$ s^{-1} over range 600–2500 K.

Reliability

$\Delta\log k_o = \pm0.5$ for M = Ar over range 600–2500 K.

Comments on Preferred Values

All available measurements have been done in the low pressure region. The present recommended values for k_o are based on a theoretical analysis[11] of the data of Refs. 1, 3 and 5. In order to reproduce the absolute values and the temperature dependence of k_o, an average energy transferred per collision of $-\langle\Delta E\rangle = 20\,[T/300]$ cm^{-1} was employed. In this way collisional efficiencies between 0.065 to 0.050 between 600 K and 2500 K were obtained. The figure shows the given experimental data together with the data of recent compilations and the recommended expression for k_o.

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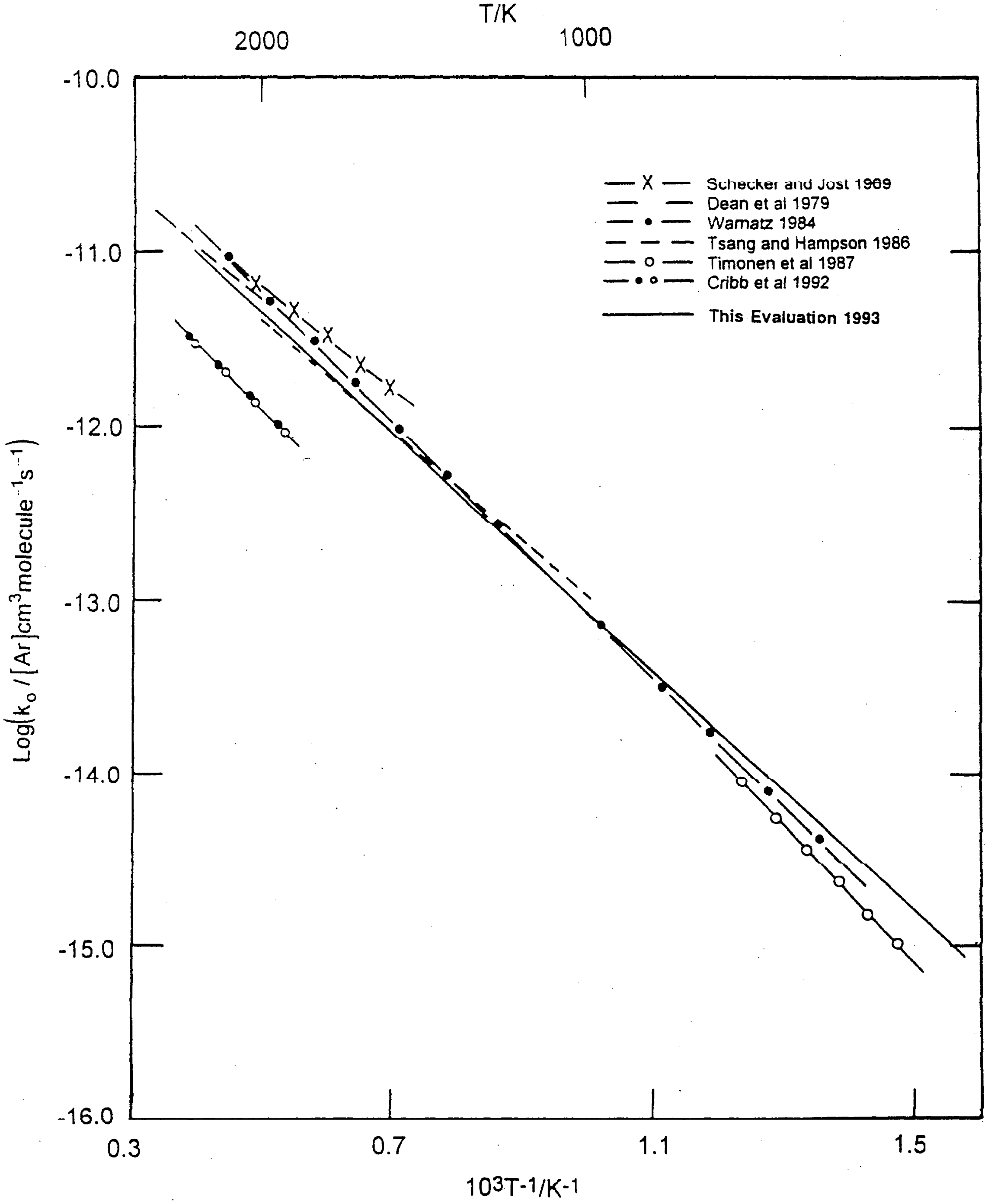
HCO + M → H – CO – M


T/K
2000
1000
-10.0
-11.0
-12.0
-13.0
-14.0
-15.0
-16.0
0.3
0.7
1.1
1.5
$\text{Log}(k_o\,/[\text{Ar}]\text{cm}^3\text{molecule}^{-1}\text{s}^{-1})$
$10^3T^{-1}/K^{-1}$
Schecker and Jost 1969
Dean et al 1979
Warnatz 1984
Tsang and Hampson 1986
Timonen et al 1987
Cribb et al 1992
This Evaluation 1993

$H + CH_3 (+ M) \rightarrow CH_4 (+ M)$

hermodynamic Data

$\Delta H^\circ_{298} = -439$ kJ mol^{-1}

$\Delta S^\circ_{298} = -123$ J K^{-1} mol^{-1}

$Kp = 1.76\cdot10^{-4}T^{-1.06}\exp(+52700/T)$ atm^{-1}

Rate Coefficient Data

/cm^3 molecule^{-1}s^{-1}	T/K	[M]/molecule cm^{-3}	Reference	Comments
ate Coefficient Measurements				
ow Pressure Range				
$[He]3.2\cdot10^{-29}$	504	$(4.8\text{–}76.6)\cdot10^{17}$	Brouard *et al.*, 1985[1]	(a)
$[He]4.0\cdot10^{-29}$	300–600	$(4.8\text{–}163.5)\cdot10^{17}$	Brouard *et al.*, 1989[2]	(a)
termediate Fall-off Range				
$6.6\cdot10^{-12}$	298	$(5.2\text{–}10.0)\cdot10^{16}(Ar)$	Brown *et al.*, 1966[3]	(b)
$1.7\cdot10^{-11}$	293	$2.2\cdot10^{17}(He)$	Dodonov *et al.*, 1969[4]	(c)
$3.9\cdot10^{-12}$	290	$2.7\cdot10^{17}(Ar)$	Halstead *et al.*, 1970[5]	(d)
$6.6\cdot10^{-12}$		$5.4\cdot10^{17}$		
$1.8\cdot10^{-12}$	303–603	$2.0\cdot10^{16}(H_2)$	Teng and Jones, 1972[6]	(e)
$2.0\cdot10^{-12}$	300	$2.4\cdot10^{16}(He)$	Michael *et al.*, 1973[7]	(f)
$5.5\cdot10^{-12}$		$8.1\cdot10^{16}$		
$8.0\cdot10^{-12}$		$11.1\cdot10^{16}$		
$1.8\cdot10^{-12}$	503–753	$1.3\cdot10^{17}(Ar)$	Camilleri *et al.*, 1974[8]	(g)
$3.6\cdot10^{-12}$		$2.6\cdot10^{17}$		
$3.0\cdot10^{-12}$	295	$2.0\cdot10^{17}(He)$	Pratt and Veltmann, 1974[9]	(h)
$7.4\cdot10^{-12}$		$4.9\cdot10^{17}$		
$6.7\cdot10^{-12}$	321	$2.4\cdot10^{17}(He)$	Pratt and Veltmann, 1976[10]	(h)
$5.2\cdot10^{-12}$	415	$1.9\cdot10^{17}$		
$3.4\cdot10^{-12}$	521	$1.5\cdot10^{17}$		
$0.53\cdot10^{-10}$	308	$0.94\cdot10^{18}(C_2H_6)$	Cheng and Yeh, 1977[11]	(i)
$1.8\cdot10^{-10}$		$3.1\cdot10^{18}$		
$2.5\cdot10^{-10}$		$9.4\cdot10^{18}$		
$2.8\cdot10^{-10}$		$25.1\cdot10^{18}$		
$3.0\cdot10^{-10}$		$72.1\cdot10^{18}$		
$2.6\cdot10^{-12}$	640–818	$9.8\cdot10^{16}(Ar)$	Sepehrad *et al.*, 1979[12]	(j)
$4.7\cdot10^{-12}$		$18.5\cdot10^{16}$		
$2.0\cdot10^{-10}$	296	$2.5\cdot10^{17}(N_2, H_2)$	Sworski *et al.*, 1980[13]	(k)
$1.52\cdot10^{-11}$	504	$4.8\cdot10^{17}(He)$	Brouard *et al.*, 1985[1]	(a)
$1.86\cdot10^{-11}$		$9.6\cdot10^{17}$		
$3.44\cdot10^{-11}$		$19.3\cdot10^{17}$		
$5.31\cdot10^{-11}$		$38.5\cdot10^{17}$		
$7.75\cdot10^{-11}$		$76.7\cdot10^{17}$		
$2.26\cdot10^{-11}$	301	$0.81\cdot10^{18}(He)$	Brouard *et al.*, 1989[2]	(a)
$3.52\cdot10^{-11}$		$1.6\cdot10^{18}$		
$6.36\cdot10^{-11}$		$3.3\cdot10^{18}$		
$14.0\cdot10^{-11}$		$9.8\cdot10^{18}$		
$18.2\cdot10^{-11}$		$16.3\cdot10^{18}$		
$1.35\cdot10^{-11}$	401	$0.61\cdot10^{18}$		
$2.52\cdot10^{-11}$		$1.2\cdot10^{18}$		
$4.44\cdot10^{-11}$		$2.4\cdot10^{18}$		
$10.1\cdot10^{-11}$		$8.4\cdot10^{18}$		
$14.4\cdot10^{-11}$		$14.7\cdot10^{18}$		
$2.11\cdot10^{-11}$	601	$1.7\cdot10^{18}$		
$3.78\cdot10^{-11}$		$4.9\cdot10^{18}$		
$6.18\cdot10^{-11}$		$11.4\cdot10^{18}$		
High Pressure Range				
$1.5\cdot10^{-10}$	300	$(1.6\text{–}32.2)\cdot10^{18}(Ar,SF_6)$	Patrick *et al.*, 1980[14]	(l)
$3.5\cdot10^{-10}$	504	$(4.8\text{–}76.7)\cdot10^{17}(He)$	Brouard *et al.*, 1985[1]	(a)
$4.7\cdot10^{-10}$	300	$(8.1\text{–}16.4)\cdot10^{18}(He)$	Brouard and Pilling, 1986[15]	(a)
$4.7\cdot10^{-10}$	300–600	$(8.1\text{–}16.4)\cdot10^{18}(He)$	Brouard *et al.*, 1989[2]	(a)

$H + CH_3\ (+ M) \rightarrow CH_4\ (+ M)$ — Continued

Rate Coefficient Data

k/cm^3 molecule^{-1}s^{-1}	T/K	[M]/molecule cm^{-3}	Reference	Comments
Reviews and Evaluations				
$k_0 = [Ar]\ 2.2 \cdot 10^{-21} T^{-3}$	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)
$k_\infty = 4.23 \cdot 10^{-8} T^{-0.82} \exp(-159/T)$	300–2500		Steward *et al.*, 1989[18]	(o)
$k_\infty = 2.0 \cdot 10^{-9} T^{-0.4}$	300–1100		Tsang, 1989[19]	(p)
$k_0 = [He] 6.2 \cdot 10^{-29} (T/300)^{-1.8}$	300–1000		Cobos and Troe, 1990[21]	(q)
$k_0 = [C_2H_6] 3.0 \cdot 10^{-28} (T/300)^{-1.8}$	300–1000			
$F_c(He) = \exp(-0.45\text{-}T/3230)$	300–1000			
$F_c(C_2H_6) = \exp(-0.34\text{-}T/3035)$	300–1000			
$k_\infty = 3.5 \cdot 10^{-10}$	300–1000			
$k_0 = [He] 6.2 \cdot 10^{-29} (T/300)^{-1.8}$	300–1000		CEC, 1992[25]	(r)
$k_0 = [Ar] 6.0 \cdot 10^{-29} (T/300)^{-1.8}$	300–1000			
$k_0 = [C_2H_6] 3.0 \cdot 10^{-28} (T/300)^{-1.8}$	300–1000			
$F_c(He,Ar) = (-0.45\text{-}T/3231)$	300–1000			
$F_c(C_2H_6) = \exp(-0.34\text{-}T/3053)$	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 $H + C_2H_4$ system. CH_3 generated by $H + C_2H_5 \rightarrow 2CH_3$. ESR detection of H.

(c) Mass spectrometric study of species distribution in diffusion cloud; CH_3 generated from $H + C_2H_4$, $H + C_3H_6$; H generated in discharge.

(d) Discharge flow study of $H + C_2H_4$ system; used GC analysis of CH_4, C_2H_6, C_3H_8, and C_4H_{10}.

(e) Discharge flow study of $H + C_2H_4$ system, products analysed by GC and simulated by numerical integration.

(f) Comparison of $H + C_2H_4$ 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 $H + C_2H_6$ system. GC detection of CH_4, C_2H_4, and C_3H_8. Rate coefficients from fitting the reaction scheme using numerical integration. Assumed k_1 independent of temperature.

(h) Discharge flow study of $H + C_2H_4$ system. Products detected by mass spectrometry. Rate coefficients by fitting 7 reaction scheme using numerical integration.

(i) Steady-state Hg photosensitisation of C_2H_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_2O/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.*[20] 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.*[20] to derive the recommended expression.

(q) Theoretical calculation based on k_0 calculations from Ref. 22, the representation of fall-off curves from Ref. 23, and the k_∞ treatment from Ref. 24. Collision efficiencies β_c at 300 K of 0.07 for M = He and of 0.15 for $M = C_2H_6$ point to particularly inefficient energy transfer for which $\langle \Delta E \rangle$ 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. 24 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 $F_c^{sc} = \exp(-0.09\text{-}T/3320)$.

(r) See Comments on Preferred Values.

Preferred Values

k_0 = [He]$6.2 \cdot 10^{-29}$ $(T/300)^{-1.8}$ cm^3 molecule^{-1} s^{-1} over range 300–1000 K.

k_0 = [Ar]$6.0 \cdot 10^{-29}$ $(T/300)^{-1.8}$ cm^3 molecule^{-1} s^{-1} over range 300–1000 K.

k_0 = [C_2H_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.

$F_c = 0.63 \exp(-T/3315) + 0.37 \exp(-T/61)$ for M = He, Ar over range 300–1000 K.

$F_c = 0.71 \exp(-T/3079) + 0.29 \exp(-T/54)$ for M = C_2H_6 over range 300–1000 K.

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

No measurements for this reaction have been reported since our previous compilation[25]. Therefore, the preferred values for k_0 and k_∞ of Ref. 25 remain unaltered, but the format of the F_c has been modified. In Fig. 1 representative fall-off curves are shown. Recombination and dissociation rate data are related via the above given equilibrium constant.

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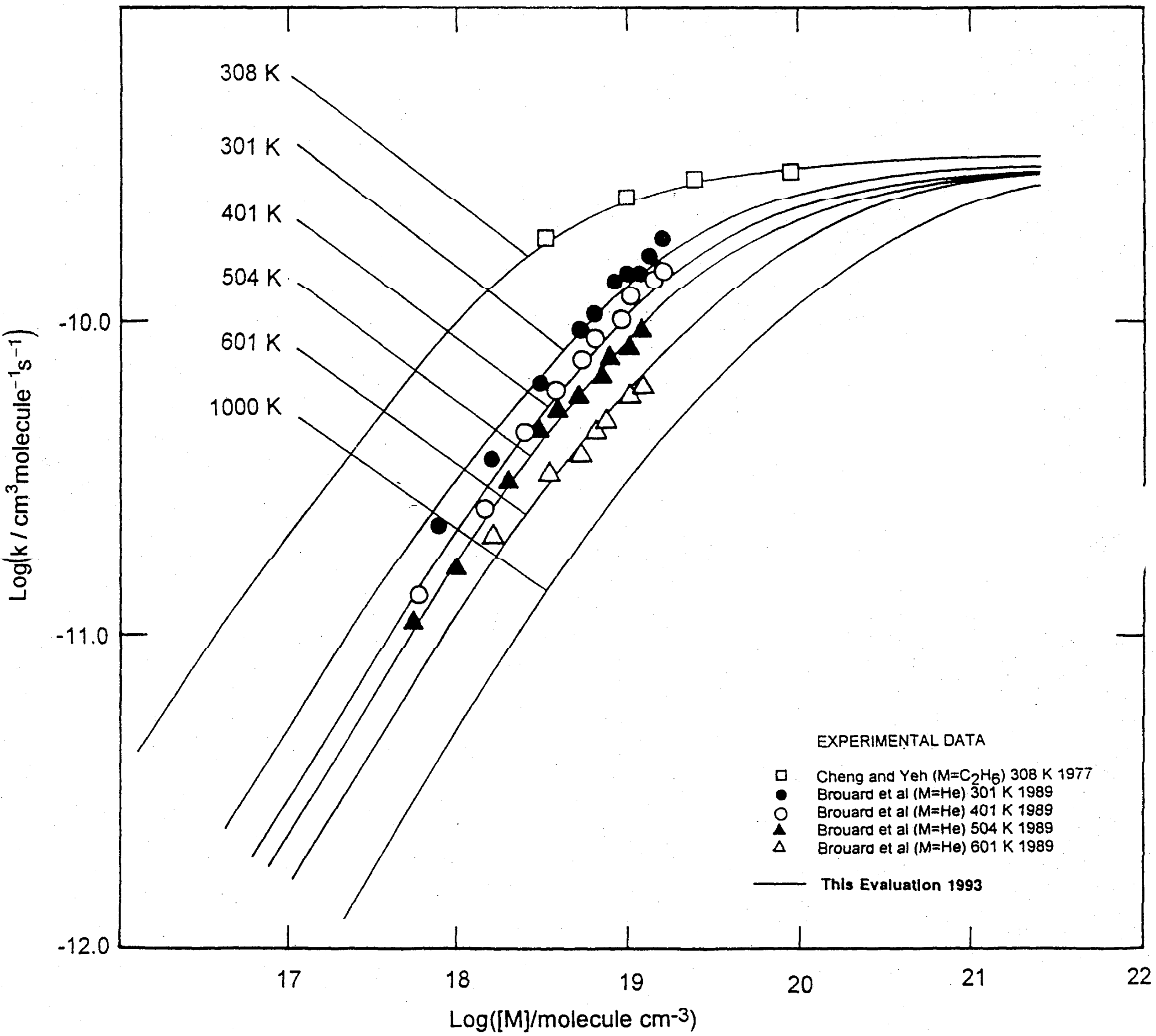
308 K
301 K
401 K
504 K
601 K
1000 K
-10.0
-11.0
-12.0
Log(k / cm^{3}molecule^{-1}s^{-1})
17
18
19
20
21
22
Log([M]/molecule cm^{-3})
EXPERIMENTAL DATA
□ Cheng and Yeh (M=C_2H_6) 308 K 1977
● Brouard et al (M=He) 301 K 1989
○ Brouard et al (M=He) 401 K 1989
▲ Brouard et al (M=He) 504 K 1989
△ Brouard et al (M=He) 601 K 1989
—— This Evaluation 1993

CH_4 (+ M) → CH_3 + H (+ M)

Thermodynamic data
$\Delta H^\circ_{298} = 439$ kJ mol^{-1}
$\Delta S^\circ_{298} = 123$ J K^{-1} mol^{-1}
$Kp = 5.68\cdot10^{3}T^{1.06}\exp(-52700/T)$ atm

Rate Coefficient Data

k/s^{-1}	T/K	[M]/molecule cm^{-3}	Reference	Comments
Rate Coefficient Measurements				
Low Pressure Range				
$[Ar]3.3\cdot10^{-7}\exp(-44800/T)$	1850–2500	$(3.3–90.0)\cdot10^{19}$	Hartig *et al.*, 1971[1]	(a)
$[Ar]6.8\cdot10^{-8}\exp(-44900/T)$	1726–2134	$3\cdot10^{18}$	Klemm *et al.*, 1992[2]	(b)
$[Ar]5.7\cdot10^{-7}\exp(-46770/T)$	1794–2326	$(2–15)\cdot10^{18}$	Davidson *et al.*, 1992[3]	(c)
$[Ar,Kr]3.2\cdot10^{23}T^{-8.106}\exp(-59084/T)$	1600–4200	$(6.5–18)\cdot10^{17}$	Kiefer and Kumaran, 1993[4]	(d)
Intermediate Fall-Off Range				
$2.5\cdot10^{13}\exp(-48300/T)$	1850–2500	$3.3\cdot10^{19}$(Ar)	Hartig *et al.*, 1971[1]	(a)
$4.0\cdot10^{14}\exp(-50800/T)$		$9.0\cdot10^{20}$(Ar)		
$1.4\cdot10^{12}\exp(-51800/T)$	1750–2575	$5.0\cdot10^{17}$(Ar)	Dean and Kistiakowsky, 1971[5]	(e)
$3.8\cdot10^{13}\exp(-47100/T)$	1750–2700	$4.0\cdot10^{19}$(Ar)	Napier and Subrahmanyan, 1972[6]	(f)
$4.0\cdot10^{9}\exp(-31700/T)$	2000–2700	$2.4\cdot10^{18}$(Ne)	Vompe, 1973[7]	(g)
$4.7\cdot10^{12}\exp(-46900/T)$	1700–2300	$6.0\cdot10^{18}$(Ar)	Roth and Just, 1975[8]	(h)
$2.3\cdot10^{8}\exp(-32500/T)$	2000–2700	$6.0\cdot10^{17}$(Ar)	Gardiner *et al.*, 1975[9]	(i)
$2.3\cdot10^{9}\exp(-32500/T)$		$6.0\cdot10^{18}$(Ar)		
$0.74\cdot10^{-8}$	995	$0.5\cdot10^{18}$(CH_4)	Chen *et al.*, 1975[10]	(j)
$1.32\cdot10^{-8}$		$3.2\cdot10^{18}$		
$2.82\cdot10^{-8}$		$7.2\cdot10^{18}$		
$0.39\cdot10^{-7}$	1038	$0.3\cdot10^{17}$		
$1.38\cdot10^{-7}$		$3.1\cdot10^{18}$		
$2.57\cdot10^{-7}$		$6.9\cdot10^{18}$		
$0.98\cdot10^{-7}$	1068	$0.23\cdot10^{18}$		
$4.9\cdot10^{-7}$		$2.1\cdot10^{18}$		
$8.71\cdot10^{-7}$		$6.7\cdot10^{18}$		
$0.69\cdot10^{-6}$	1103	$0.43\cdot10^{18}$		
$2.06\cdot10^{-6}$		$2.0\cdot10^{18}$		
$3.86\cdot10^{-6}$		$6.5\cdot10^{18}$		
$1.8\cdot10^{12}\exp(-44500/T)$	1875–2240	$1.2\cdot10^{19}$(Ar)	Bowman, 1975[11]	(k)
$2.2\cdot10^{12}\exp(-45400/T)$	2000–2700	$6.0\cdot10^{18}$(Ar)	Heffington *et al.*, 1977[12]	(l)
$6\cdot10^{12}\exp(-45400/T)$		$17\cdot10^{18}$		
$2.3\cdot10^{11}\exp(-43200/T)$	1950–2770	$1.4\cdot10^{18}$(Ar)	Tabayashi and Bauer, 1979[13]	(m)
$9.1\cdot10^{11}\exp(-43200/T)$		$5.4\cdot10^{18}$		
$1.13\cdot10^{-5}$	1098	$2.0\cdot10^{20}$(He)	Barnes, Pratt, and Wood, 1989[14]	(n)
$1.37\cdot10^{-5}$		$3.3\cdot10^{20}$		
$2.52\cdot10^{-5}$	1123	$6.5\cdot10^{19}$		
$3.17\cdot10^{-5}$		$1.9\cdot10^{20}$		
$4.12\cdot10^{-5}$		$3.2\cdot10^{20}$		
$5.30\cdot10^{-5}$	1148	$3.2\cdot10^{19}$		
$8.30\cdot10^{-5}$		$1.9\cdot10^{20}$		
$10.1\cdot10^{-5}$		$3.2\cdot10^{20}$		
$4.44\cdot10^{-6}$	1073	$1.0\cdot10^{20}$(Ar)		
$5.28\cdot10^{-6}$		$3.4\cdot10^{20}$		
$9.80\cdot10^{-6}$	1098	$6.6\cdot10^{19}$		
$1.20\cdot10^{-5}$		$2.0\cdot10^{20}$		
$1.46\cdot10^{-5}$		$3.3\cdot10^{20}$		
$1.87\cdot10^{-5}$	1123	$3.2\cdot10^{19}$		
$2.31\cdot10^{-5}$		$6.5\cdot10^{19}$		
$3.19\cdot10^{-5}$		$1.9\cdot10^{20}$		
$4.32\cdot10^{-5}$	1148	$3.2\cdot10^{19}$		
$5.39\cdot10^{-5}$		$6.3\cdot10^{19}$		
$3.04\cdot10^{-6}$	1073	$3.4\cdot10^{19}$(CH_4)		
$5.11\cdot10^{-6}$		$1.4\cdot10^{20}$		
$4.93\cdot10^{-6}$		$3.4\cdot10^{20}$		
$8.25\cdot10^{-6}$	1098	$3.3\cdot10^{19}$		
$1.52\cdot10^{-5}$		$1.3\cdot10^{20}$		
$1.55\cdot10^{-5}$		$3.3\cdot10^{20}$		
$2.27\cdot10^{-5}$	1123	$3.2\cdot10^{19}$		

CH_4 (+ M) → CH_3 + H (+ M) — Continued

Rate Coefficient Data

k/s^{-1}	T/K	[M]/molecule cm^{-3}	Reference	Comments
$3.63\cdot10^{-5}$		$1.3\cdot10^{20}$		
$4.20\cdot10^{-5}$		$3.2\cdot10^{20}$		
$6.03\cdot10^{-5}$	1148	$3.2\cdot10^{19}$		
$8.50\cdot10^{-5}$		$1.3\cdot10^{20}$		
$1.20\cdot10^{-4}$		$3.2\cdot10^{20}$		
High Pressure Range				
$1.3\cdot10^{15}\exp(-52300/T)$	1850–2500	$(3.3–90.0)\cdot10^{19}$(Ar)	Hartig *et al.*, 1971[1]	(a)
$2.8\cdot10^{16}\exp(-54100/T)$	995–1103	$(0.43–7.2)\cdot10^{18}(CH_4)$	Chen *et al.*, 1975[7]	(j)
$1.75\cdot10^{16}\exp(-53000/T)$	1073–1148	$(3.2–33.4)\cdot10^{19}(CH_4)$	Barnes, Pratt, and Wood, 1989[14]	(n)
Reviews and Evaluations				
$k_\infty = 2.0\cdot10^{15}\exp(-52300/T)$			Benson and O'Neal, 1970[15]	(o)
$k_0 = [Ar]3.3\cdot10^{-7}\exp(-44500/T)$	1500–3000		Warnatz, 1984[16]	(p)
$k_\infty = 1.0\cdot10^{15}\exp(-50500/T)$	1000–3000			
$k_\infty = 3.7\cdot10^{15}\exp(-52200/T)$	300–2500		Tsang and Hampson, 1986[17]	(q)
$k_\infty = 3.7\cdot10^{17}T^{-0.558}\exp(-52782/T)$	300–2500		Stewart *et al.*, 1989[18]	(r)
$k_0 = [Ar]7.5\cdot10^{-7}\exp(-45700/T)$	1000–3000		Cobos and Troe, 1990[19]	(s)
$k_0 = [CH_4]1.4\cdot10^{-6}\exp(-45700/T)$	1000–3000			
$k_\infty = 2.4\cdot10^{16}\exp(-52800/T)$	1000–3000			
$F_c(Ar) = \exp(-0.45\text{-}T/3230)$	1000–3000			
$F_c(CH_4) = \exp(-0.37\text{-}T/2210)$	1000–3000			
$k_0 = [Ar]1.2\cdot10^{-6}\exp(-47000/T)$	1000–3000		CEC, 1992[23]	(t)
$k_0 = [CH_4]1.4\cdot10^{-5}\exp(-48100/T)$	1000–2000			
$k_\infty = 2.4\cdot10^{16}\exp(-52800/T)$	1000–3000			
$F_c(Ar) = \exp(-0.45\text{-}T/3231)$	1000–3000			
$F_c(CH_4) = \exp(-0.37\text{-}T/2210)$	1000–3000			
$k_0 = [Ar]7.8\cdot10^{23}T^{-8.2}$ $\exp(-59200/T)$	1700–5000		Cobos and Troe, 1992[24]	(u)
$F_c(Ar) = \exp(-T/1350)$ $+ \exp(-7834/T)$	1000–5000			
$k_\infty = 2.46\cdot10^{16}\exp(-52800/T)$	1000–5000			

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 tube study of the pyrolysis of CH_4. H atoms monitored directly using atomic resonance absorption spectroscopy. Absolute H concentration determined using calibration by N_2O/H_2/Ar mixtures. Modelling with 17 reactions. RRKM and master equation calculations.

(c) Study of the decomposition of CH_4 in reflected shock waves. CH_3 concentrations detected by narrow-line-width laser absorption at 216.6 nm. Reaction mechanism with 38 reactions.

(d) Study of the pyrolysis of CH_4 in incident shock waves with the laser-schlieren technique. Measurements in mixtures of 2% CH_4-Kr, 2% CH_4-Ar and 0.5% CH_4-Ar at pressures of 230–660 Torr have been done between 2800–4300 K. RRKM analysis of data between 1600–4200 K.

(e) Shock wave study of CH_4/O_2/CO/Ar mixtures. The reaction was followed by measuring infrared emissions from CO and O_2.

(f) The CH_4 pyrolysis was investigated by a shock waves technique.

(g) Shock wave study of CH_4/Ne mixtures. The reaction was analysed by time-of-flight mass spectrometry.

(h) Direct measurements of the time dependent H atom concentration during the pyrolysis of CH_4/Ar mixtures using shock waves technique.

(i) Pyrolysis of CH_4 in shock waves. The reaction was followed by time-of-flight mass spectrometry, infrared laser absorption, and laser schlieren technique.

(j) Pyrolysis of CH_4 in a static system. Initial rates based on analysis of H_2, C_2H_6, and C_2H_4. k_∞ values extrapolated with RRKM theory.

(k) 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.

(l) Shock waves study of CH_4 pyrolysis. The reaction was followed monitoring the CH_4 emission and absorption at 3.392 μm.

(m) Shock waves measurements of CH_4/Ar mixtures. Modelling of 12 reactions.

(n) Pyrolysis of CH_4 at very early stages (0.003–0.05% reaction) in a quartz-lined flow reactor. Reactant and products (ethane, ethylene, acetylene, and propylene) detected by gas chromatography.

(o) Review of literature previous to 1966.

(p) Review of literature previous to 1980.

(q) The k_∞ recommended is based on the Hartig *et al.*[1] results scaled up by a factor 3.

(r) Single-channel hindered Gorin model RRKM calculations of the CH_4 decomposition with a fit to experimental results.

(s) 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 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. 20, fall-off expression from Ref. 21 and SACM-modified PST calculations from Ref. 22 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}.

(t) Critical evaluation of gas phase chemical reactions for use in modelling combustion processes.

(u) Re-analysis of the kinetic data from Refs. 3 and 4 in terms of the theory of unimolecular reactions[20,21]. The analysis leads to an energy transferred per collision of 50 ± 20 cm^{-1} for M = Ar over the temperature range 1000–5000 K.

Preferred Values

$k_0 = [Ar]7.5 \cdot 10^{-7}\exp(-45700/T)$ over range 1000–1700 K.

$k_0 = [Ar]7.8 \cdot 10^{23}T^{-8.2}\exp(-59200/T)$ over range 1700–5000 K.

$k_0 = [CH_4]1.4 \cdot 10^{-6}\exp(-45700/T)$ over range 1000–2000 K

$k_\infty = 2.4 \cdot 10^{16}\exp(-52800/T)$ over range 1000–3000 K

$F_c = \exp(-T/1350) + \exp(-7834/T)$ for M = Ar over range 1000–5000 K.

$F_c = 0.31\exp(-T/91) + 0.69\exp(-T/2207)$ for $M = CH_4$ over range 1000–2000 K.

Reliability

$\Delta\log k_0 = \pm 0.3$ over range 1000–5000 K.

$\Delta\log k_\infty = \pm 0.5$ over range 1000–3000 K.

$\Delta F_c = \pm 0.1$ over range 1000–5000 K (M = Ar).

$\Delta F_c = \pm 0.1$ over range 1000–2000 K ($M = CH_4$).

Comments on Preferred Values

The recommended values for k_0 result from a detailed analysis of the experimental data from Refs. 1,3,4,8,10–13 in terms of the theory of unimolecular reaction[20–22] as given in Refs. 19 and 24. From this evaluation a $\beta_c = 0.11$ was derived near 1000 K for $M = CH_4$[19] and β_c from 0.06 to 0.006 between 1000 to 5000 K for M = Ar[24]. These last values are consistent with an average energy transferred per collision of 50 ± 20 cm^{-1}. The recommended k_∞ values are consistent with a nearly temperature independent k_∞ of $3.5 \cdot 10^{-10}$ cm^3 molecule^{-1} s^{-1} for the reverse association reaction. Figures 1 and 2 show the temperature dependence of k_0 and k_∞ respectively. Figure 3 shows a set of fall-off curves over the range 300–4300 K for the recombination $H + CH_3 \rightarrow CH_4$[24]. The high temperature dissociation rate coefficients were converted to recombination rate coefficients with the k_c given above. Finally, in Fig. 4 dissociation fall-off curves for $M = CH_4$[19] are depicted.

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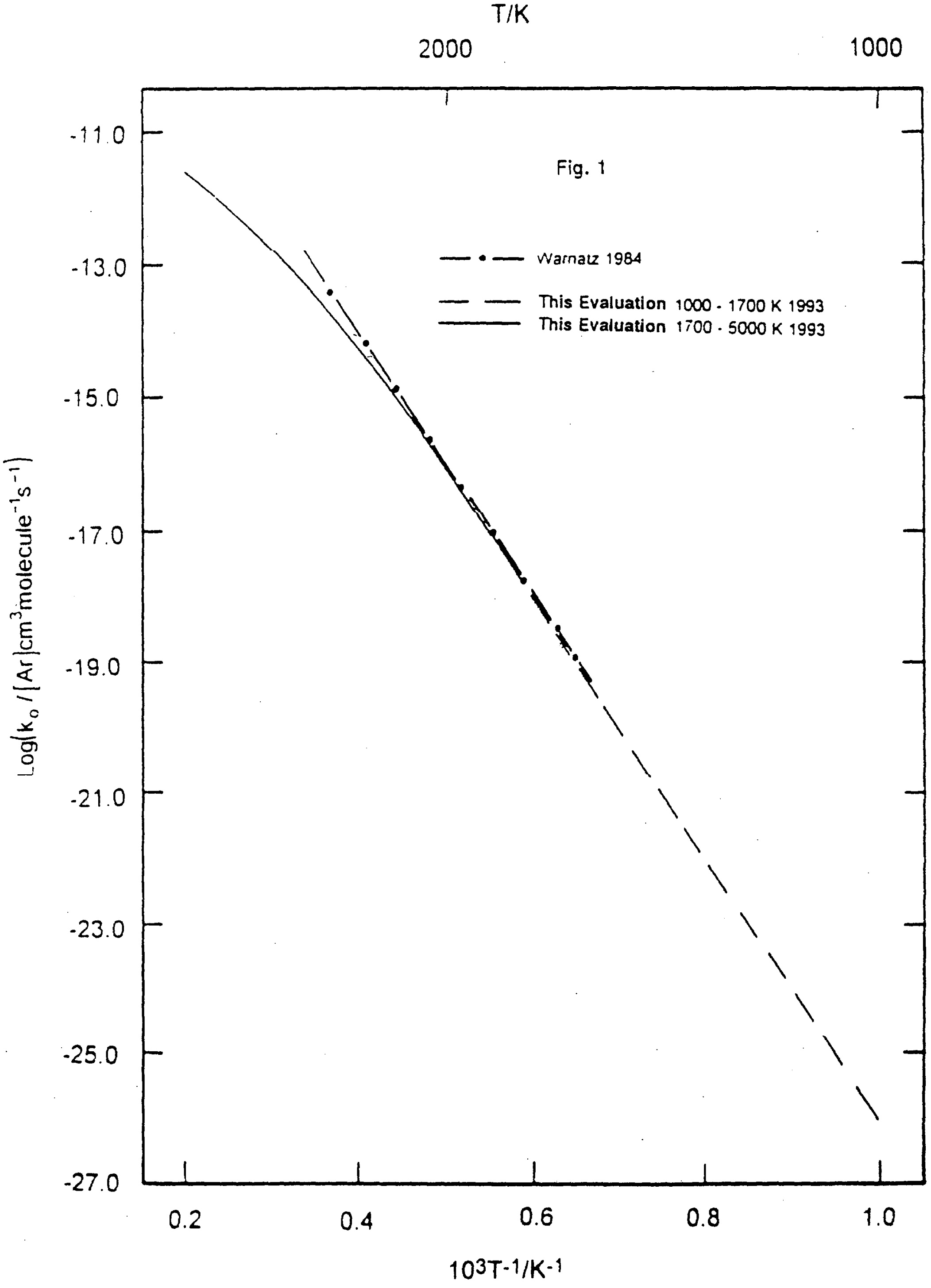
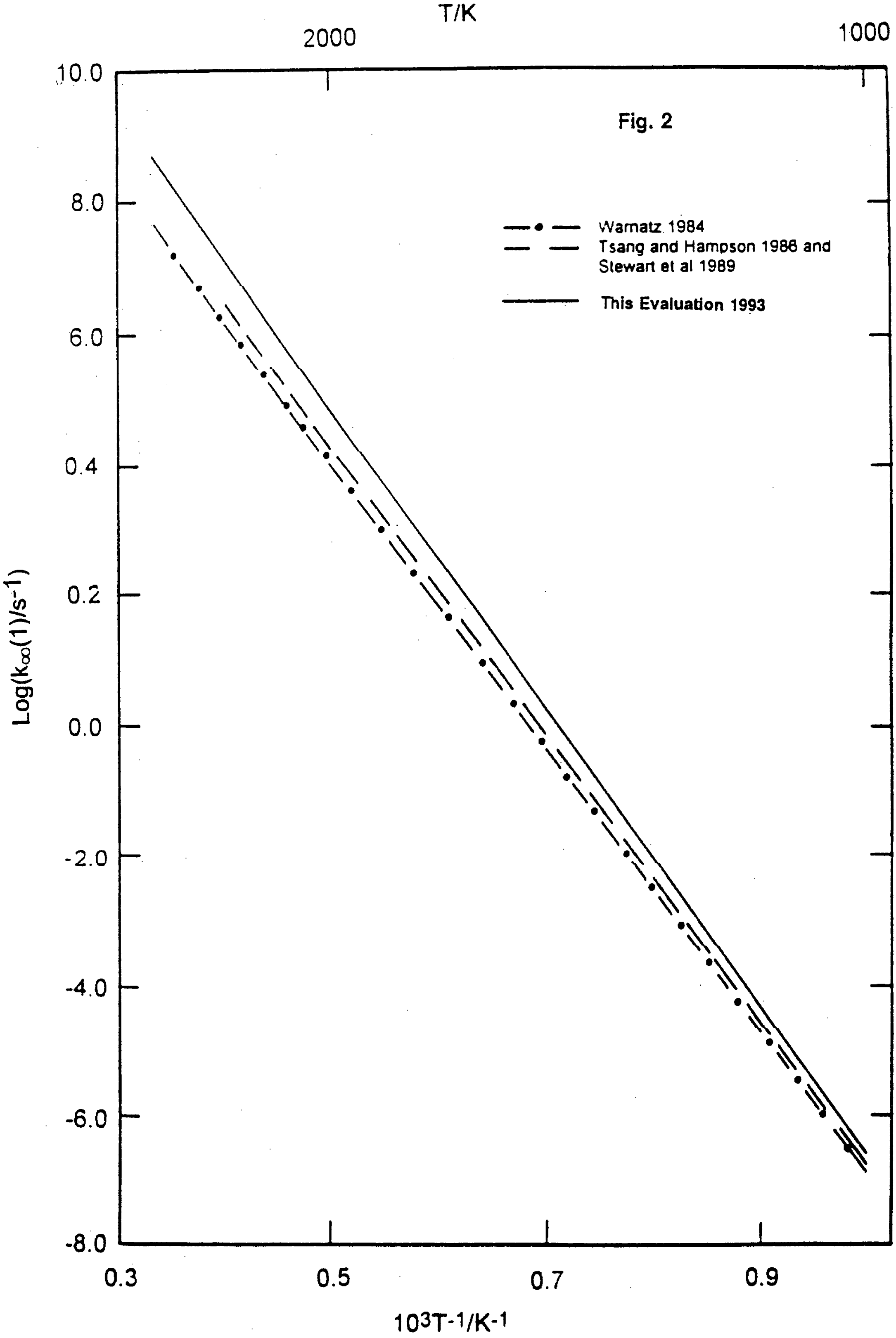
$CH_4 + M \rightarrow H + CH_3 + M$



$CH_4 + M \rightarrow H + CH_3 + M$



$CH_4 + M \rightarrow H - CH_3 + M$

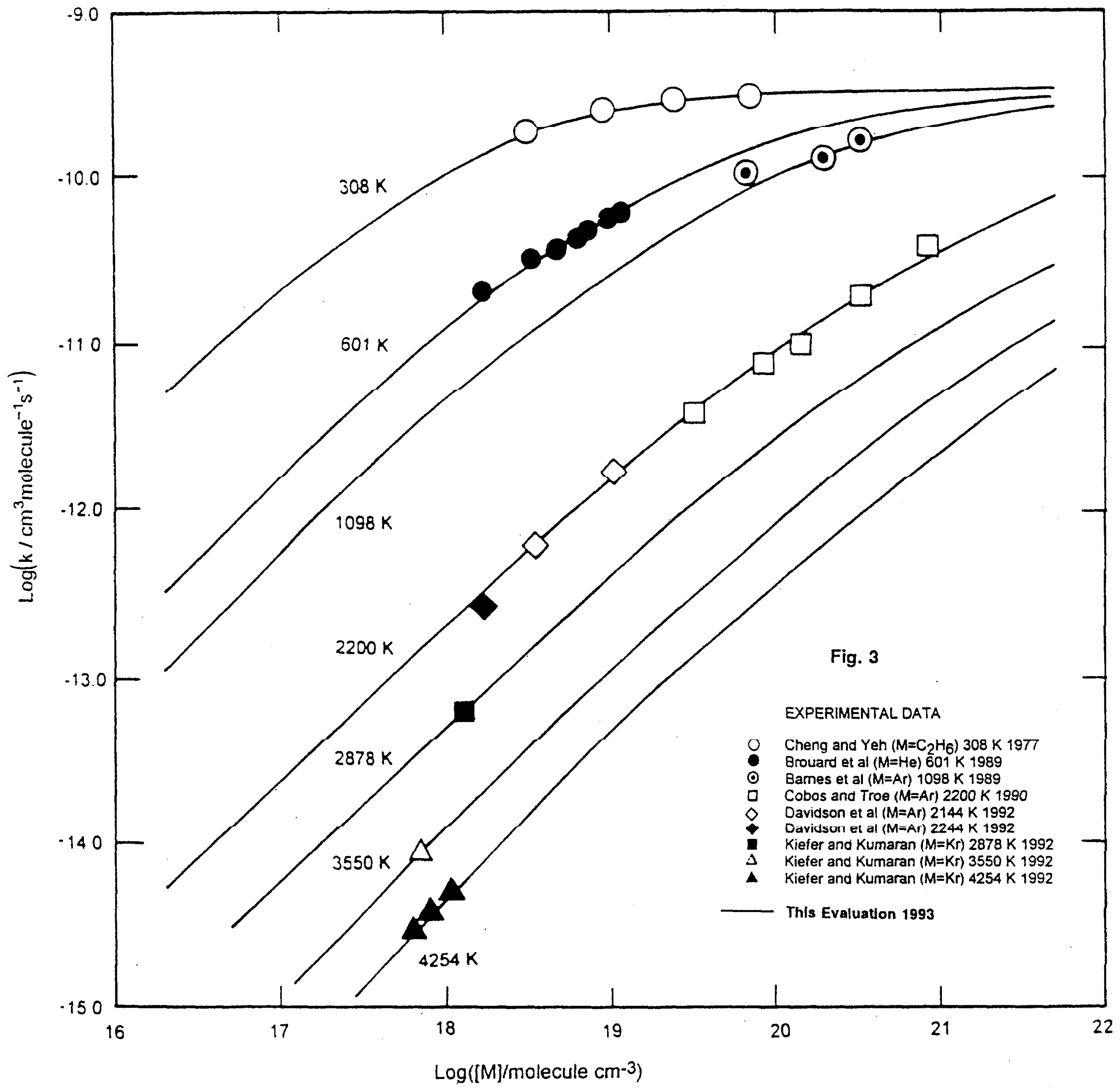
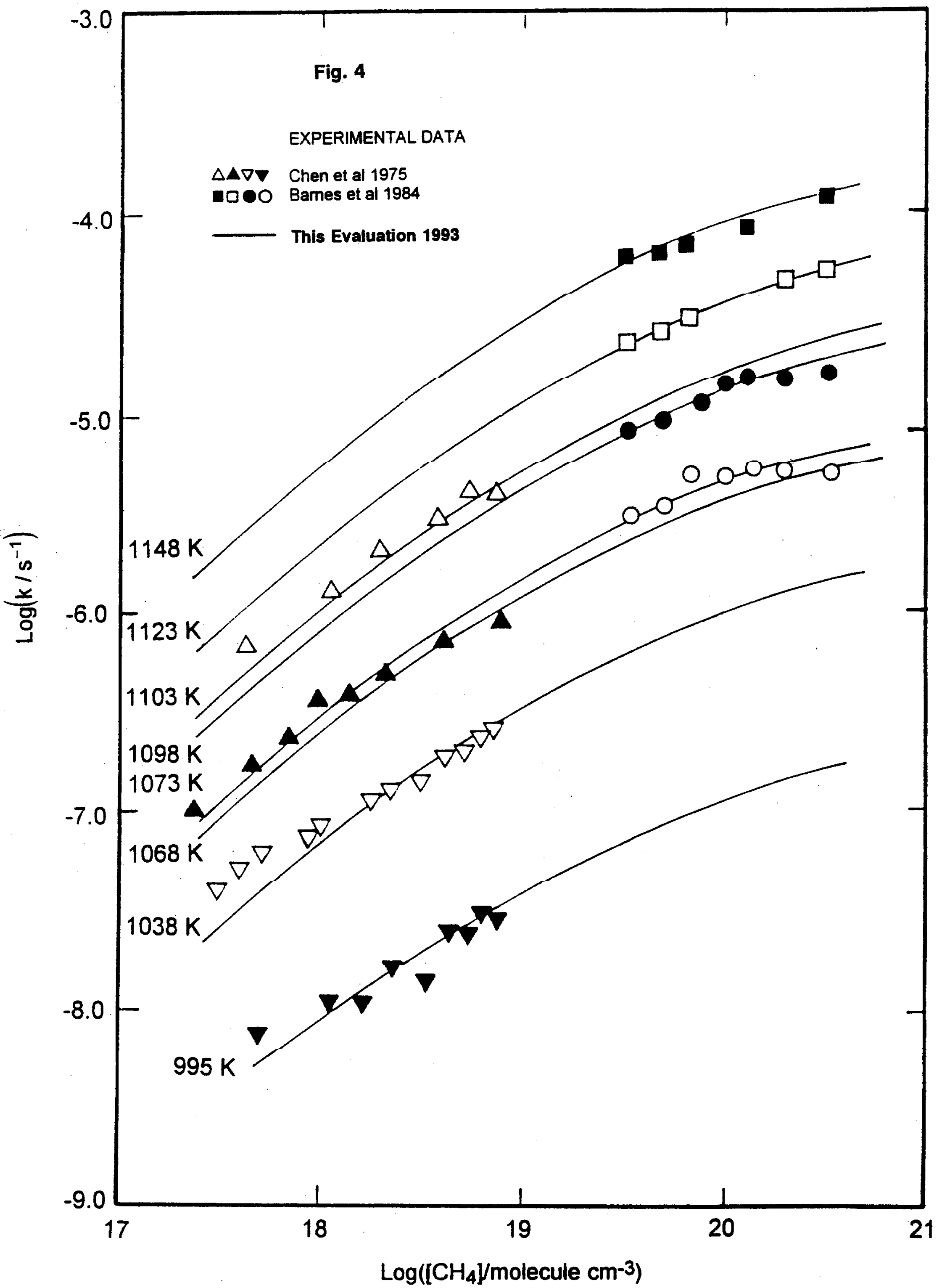


Fig. 3

$CH_4 + M \rightarrow H + CH_3 + M$



$H + HCHO \rightarrow H_2 + HCO$

Thermodynamic data

$\Delta H^\circ_{298} = -58.5$ kJ mol^{-1}
$\Delta S^\circ_{298} = 21.9$ J K^{-1} mol^{-1}
$Kp = 3.8 \cdot 10^2\ T^{-0.40}\exp(+6730/T)$

Rate Coefficient Data

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Comments
Rate Coefficient Measurements			
$3.7 \cdot 10^{-12}$	813	Baldwin and Cowe, 1962[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, Johnson, and Steiner, 1980[5]	(e)
$3.3 \cdot 10^{-11}$	1470–1570	Vandooren *et al.*, 1986[6]	(f)
$4.8 \cdot 10^{-11} \exp(-1879/T)$	1180–1690	Choudhury and Lin, 1989[7]	(g)
Reviews and Evaluations			
$3.8 \cdot 10^{-14}\ T^{1.05}\exp(-1650/T)$	300–2200	CEC, 1992[8]	(h)

Comments

(a) Inhibition of $H_2 + O_2$ reaction at the second limit by HCHO.

(b) Microwave discharge H_2/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/O_2/Ar and HCHO/N_2O/Ar mixtures investigated in reflected shock waves; HCHO detected by IR emission.

(f) Molecular beam mass spectrometric measurements in a lean HCHO-oxygen flame. k derived from kinetic analysis of flame chemistry.

(g) Shock wave pyrolysis of methyl nitrate/1,3,5-trioxane mixtures; CO production by time resolved resonance absorption. k determined by kinetic modelling and was sensitive primarily to the values of $k(H + HCO) = 1.2 \cdot 10^{-10}$ cm^3 molecule^{-1} s^{-1} and $k(HCO + M) = 3.16 \cdot 10^{-7} T^{-1.0}\exp(-8566/T)$ cm^3 molecule^{-1} s^{-1}.

(h) Based on the data of Ridley *et al.*[3], Klemm[4], and Dean *et al.*[5].

Preferred Values

$k = 2.1 \cdot 10^{-16} T^{1.62}\exp(-1090/T)$ cm^3 molecule^{-1} s^{-1} over range 300–1700 K.

Reliability

$\Delta \log k = \pm 0.3$ at 1700 K reducing to ± 0.1 at 300 K.

Comments on Preferred Values

The preferred value is the expression derived by Choudhury and Lin[7] from a non-linear least squares analysis of their recent high temperature data and of the low temperature data of Baldwin and Cowe[1], Westenberg and deHaas[2], Ridley *et al.*[3] and Klemm[4]. The data of Choudhury and Lin appear to be more reliable than the earlier high temperature data of Shecker and Jost[9] and Dean *et al.*[5].

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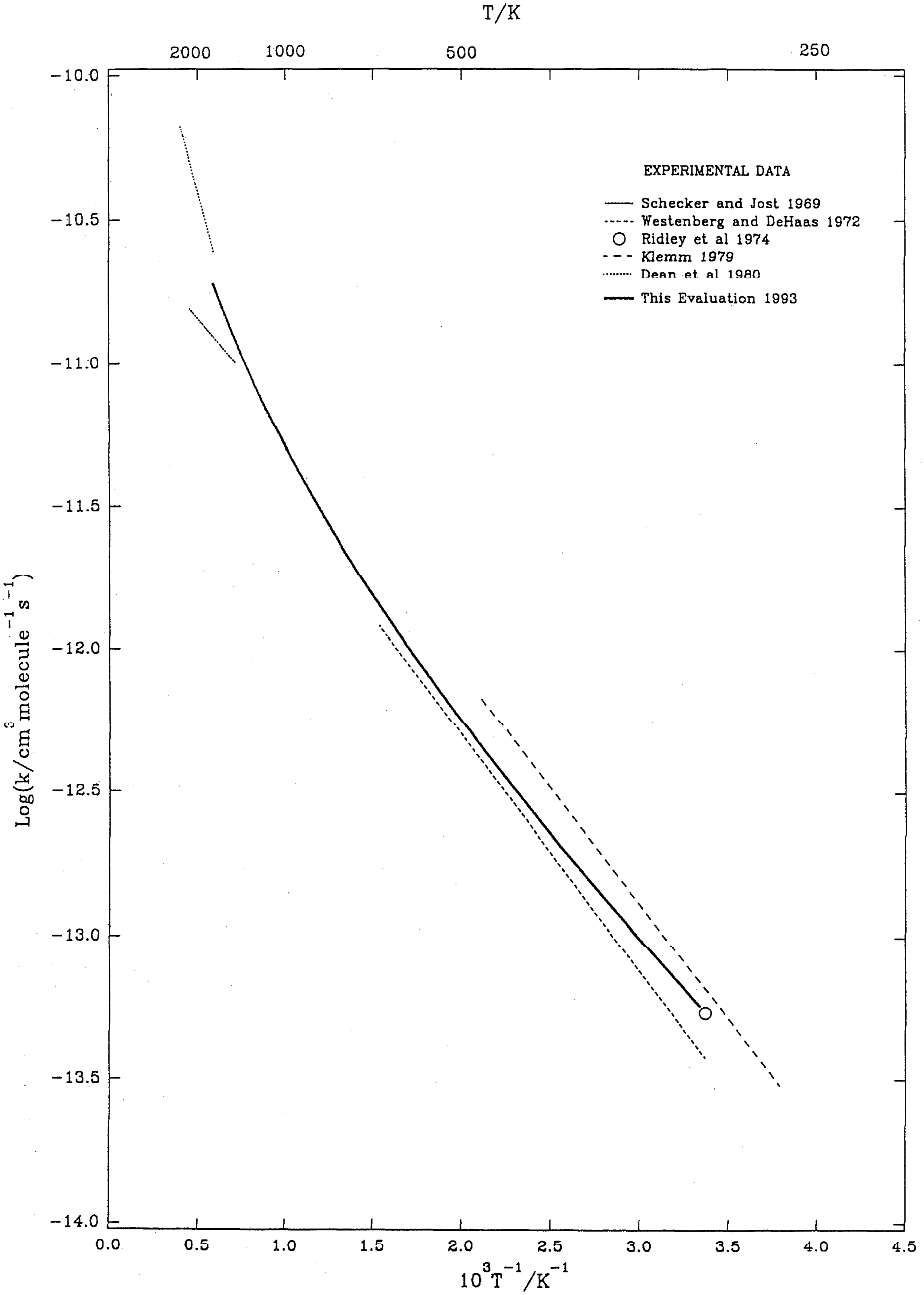
H + HCHO → H_2 + HCO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1000
500
250
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−11.5
−12.0
−12.5
−13.0
−13.5
−14.0
Log(k/cm³ molecule⁻¹ s⁻¹)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
10³T⁻¹/K⁻¹
EXPERIMENTAL DATA
Schecker and Jost 1969
Westenberg and DeHaas 1972
Ridley et al 1974
Klemm 1979
Dean et al 1980
This Evaluation 1993

$H + C_2H_4 (+ M) \rightarrow C_2H_5 (+ M)$

Thermodynamic data

$\Delta H^\circ_{298} = -150$ kJ mol^{-1}

$\Delta S^\circ_{298} = -86.6$ J K^{-1} mol^{-1}

$Kp = 1.8 \cdot 10^{-2} T^{-1.0} \exp(+17830/T)$ atm^{-1}

Rate Coefficient Data

k/cm^3 molecule^{-1} s^{-1}	T/K	[M]/molecule cm^{-3}	References	Comments
Low Pressure Range				
[He] $1.4 \cdot 10^{-29} \exp(-569/T)$	285–604	$(8\text{–}140) \cdot 10^{17}$	Lightfoot and Pilling, 1987[1]	(a)
Intermediate Fall-Off Range				
$3.2 \cdot 10^{-13}$	300	$1.6 \cdot 10^{17}$(He)	Braun and Lenzi, 1967[2]	(b)
$4.3 \cdot 10^{-13}$		$3.2 \cdot 10^{17}$		
$6.7 \cdot 10^{-13}$		$9.3 \cdot 10^{17}$		
$1.9 \cdot 10^{-13}$		$1.6 \cdot 10^{17}$(N_2)		
$4.0 \cdot 10^{-13}$		$4.8 \cdot 10^{17}$		
$8.0 \cdot 10^{-13}$		$24 \cdot 10^{17}$		
$3.3 \cdot 10^{-13}$	300	$1.6 \cdot 10^{17}$(He)	Kurylo, Peterson, and Braun, 1970[3]	(c)
$7.7 \cdot 10^{-13}$		$32 \cdot 10^{17}$		
$1.2 \cdot 10^{-12}$		$162 \cdot 10^{17}$		
$5.6 \cdot 10^{-14}$	300	$1.3 \cdot 10^{16}$(He)	Barker *et al.*, 1970[4]	(d)
$2.5 \cdot 10^{-13}$		$24 \cdot 10^{16}$		
$3.7 \cdot 10^{-13}$		$81 \cdot 10^{16}$		
$1.3 \cdot 10^{-12} \exp(-367/T)$	303–603	$(2.6\text{–}4.3) \cdot 10^{16}$($H_2$)	Teng and Jones, 1972[5]	(e)
$8.7 \cdot 10^{-14}$	300	$0.16 \cdot 10^{17}$(He)	Michael, Osborne, and Suess, 1973[6]	(f)
$6.1 \cdot 10^{-13}$		$24 \cdot 10^{17}$		
$1.1 \cdot 10^{-12}$		$193 \cdot 10^{17}$		
$4.1 \cdot 10^{-13}$	298	$9.7 \cdot 10^{16}$(Ar)	Laupert and von Bünau, 1974[7]	(g)
$3.23 \cdot 10^{-12}$	775	$2.5 \cdot 10^{18}$(He)	Brouard, Lightfoot, and Pilling, 1986[8]	(h)
$2.97 \cdot 10^{-12}$	800	$2.4 \cdot 10^{18}$		
$2.79 \cdot 10^{-12}$	825	$2.3 \cdot 10^{18}$		
$2.0 \cdot 10^{-12}$	800	$1.2 \cdot 10^{18}$(He)	Hanning-Lee *et al.*, 1993[9]	(i)
$3.1 \cdot 10^{-12}$		$3.6 \cdot 10^{18}$		
$4.7 \cdot 10^{-12}$		$7.2 \cdot 10^{18}$		
High Pressure Range				
$1.0 \cdot 10^{-12}$	300	$(1.6\text{–}29) \cdot 10^{17}$($N_2$)	Braun and Lenzi, 1967[2]	(b)
$1.36 \cdot 10^{-12}$	300	$(1.6\text{–}16) \cdot 10^{17}$($N_2$)	Kurylo, Peterson, and Braun, 1970[3]	(c)
$9.1 \cdot 10^{-13}$	298	$(2.4\text{–}5.7) \cdot 10^{19}$($H_2$)	Eyre, Hikida, and Dorfman, 1970[10]	(j)
$9.1 \cdot 10^{-13}$	298	$(2.4\text{–}5.7) \cdot 10^{19}$($H_2$)	Hikida, Eyre, and Dorfman, 1971[11]	(k)
$1.3 \cdot 10^{-11} \exp(-755/T)$	303–478	$5.7 \cdot 10^{19}$(CO_2)	Penzhorn and Darwent, 1971[12]	(l)
$1.6 \cdot 10^{-12}$	300	$(8.8\text{–}12900) \cdot 10^{15}$(He)	Michael, Osborne, and Suess, 1973[6]	(f)
$1.25 \cdot 10^{-12}$	300	$(2.6\text{–}5.3) \cdot 10^{19}$(He)	Mihelcic *et al.*, 1975[13]	(m)
$3.67 \cdot 10^{-11} \exp(-1042/T)$	198–300	$(1.5\text{–}2.3) \cdot 10^{19}$(Ar)	Lee *et al.*, 1978[14]	(n)
$1.1 \cdot 10^{-12}$	298	$(6.5\text{–}39) \cdot 10^{18}$($H_2$)	Ishiwara *et al.*, 1978[15]	(o)
$7.8 \cdot 10^{-13}$	298	$(6.5\text{–}32) \cdot 10^{17}$($H_2$)	Oka and Cvetanović, 1979[16]	(p)
$4.7 \cdot 10^{-11} \exp(-1096/T)$	211–461		Sugawara, Okazaki, and Satu, 1981[17]	(q)
$1.1 \cdot 10^{-12}$	300		Ellul *et al.*, 1981[18]	(r)
$4.39 \cdot 10^{-11} \exp(-1087/T)$	285–604	$(8\text{–}140) \cdot 10^{17}$(He)	Lightfoot and Pilling, 1987[1]	(a)
Reviews and Evaluations				
$k_\infty = 1.6 \cdot 10^{-10} \exp(-1410/T)$	300–800		Kerr and Parsonage, 1972[19]	(s)
$k_\infty = 1.7 \cdot 10^{-11} \exp(-758/T)$	300–2000		Warnatz, 1984[20]	(t)
$k_\infty = 1.42 \cdot 10^{-15} T^{1.49} \exp(-499/T)$	300–900		Tsang and Hampson, 1986[21]	(u)
$k_\infty = 1.795 \cdot 10^{-12} T^{0.454} \exp(-917/T)$	185–1100		Feng *et al.*, 1993[22]	(v)

Comments

(a) Laser flash photolysis–resonance fluorescence study of the reaction H + C_2H_4. H atoms were generated by photolysis of N_2O at 193 nm in the presence of H_2 and monitored by resonance fluorescence.

(b) Flash photolysis of C_2H_4; detection via Lyman-α absorption of H atoms. High pressure extrapolation to gas densities greater than $2.4 \cdot 10^{18}$ molecule cm^{-3}.

(c) Vacuum UV flash photolysis of C_2H_4. Analysis of H atom concentration by resonance fluorescence and absorption of Lyman-α radiation at 121.6 nm. Extrapolation to the high pressure limit via Lindemann plots.

(d) Three different experimental techniques were employed: (a) discharge flow system with Lyman-α absorption detection of H atoms; (b) reactive Lyman-α photometric experiments with H atoms generated from Hg-photosensitized decomposition of H_2; (c) discharge flow system with time-of-flight mass spectrometry.

(e) H atoms generated in a Wood-Bonhoeffer discharge; products C_2H_6, C_3H_8, n-C_4H_{10} and CH_4 determined by GC.

(f) Time-resolved Lyman-α absorption; H produced by Hg photosensitization of H_2.

(g) Discharge flow system; product analysis by MS.

(h) ArF excimer laser flash photolysis of C_2H_4 with detection of H atoms by Lyman-α resonance fluorescence. The approach to the $H + C_2H_4 \rightleftharpoons C_2H_5$ equilibrium was directly observed.

(i) Direct measurements of the approach to the H + C_2H_4 lharohall C_2H_5 equilibrium. H atoms formed by photolysis at 193 nm of C_2H_4-He mixtures and detected by time-resolved resonance fluorescence. Master equation analysis of data.

(j) Pulse radiolysis of H_2 with direct observation of H atoms by Lyman-α absorption spectroscopy.

(k) See comment (i).

(l) Photolysis of HI in the presence of C_2H_4; rate coefficients determined relative to the reaction $H + HI \rightarrow H_2 + I$ for which a value $k = 2.0 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1} was employed.

(m) Pulse radiolysis of H_2 with Lyman-α detection of H atoms.

(n) Flash photolysis–resonance fluorescence measurements. Photolysis of C_2H_4 at $\lambda \geqslant 110$ nm and detection of H atoms by resonance fluorescence in Ar diluent.

(o) Pulse radiolysis of H_2 with detection of H atoms by Lyman-α absorption.

(p) Irradiation of Hg/NO/H_2/C_2H_4 mixtures with modulated light at 253.7 nm in a flow system. Measurements of the luminescence of HNO ($^1A''$).

(q) Pulse radiolysis of H_2; resonance absorption detection of H.

(r) Pulsed Hg-sensitized photolysis of H_2; resonance absorption detection of H.

(s) Review of literature up to 1970.

(t) Review of literature prior to 1980.

(u) The recommended values were obtained by combination of the room temperature rate coefficients with results of the reverse dissociation reaction at higher temperatures. A tabulation of log k/k_∞ over the temperature range 300–2500 K from RRKM calculation is also given.

(v) Expression based on the results of Refs. 1 and 9 and transition state model calculations.

Preferred Values

$k_\infty = 6.6 \cdot 10^{-15} T^{1.28} \exp(-650/T)$ cm^3 molecule^{-1} s^{-1} over range 200–1100 K.

$k_0 = [He] 1.3 \cdot 10^{-29} \exp(-380/T)$ cm^3 molecule^{-1} s^{-1} over range 300–800 K.

$k_0 = [N_2]\ 7.7 \cdot 10^{-30} \exp(-380/T)$ cm^3 molecule^{-1} s^{-1} over range 300–800 K.

$F_c = 0.24\exp(-T/40) + 0.76\exp(-T/1025)$ for M = He and N_2 over range 300–800 K.

Reliability

$\Delta\log k_\infty = \pm 0.3$ over range 200–1100 K.

$\Delta\log k_0 = \pm 0.3$ over range 300–800 K.

$\Delta F_c = \pm 0.1$ over range 300–800 K.

Comments on Preferred Values

This reaction has been extensively studied at low temperatures. The k_∞ value at 300 K is well established. The average of all experimental measurements is $(1.2 \pm 0.3) \cdot 10^{-12}$ cm^3 molecule^{-1} s^{-1}. The analysis of the reaction is based on theoretical fall-off curves[23] and strong collision low pressure rate coefficients[23,24] which were calculated using a reaction threshold of 154.78 kJ mol^{-1} [22]. From this analysis the above recommended limiting rate coefficients were derived. The temperature dependence of k_0 and k_∞ is depicted in Figs. 1 and 2. The resulting collision efficiencies for M = He are approximately independent of temperature, $\beta_c \approx 0.07$, over the range 300–800 K. This finding is consistent with a temperature dependence of $-\langle\Delta E\rangle$ of about $T^{+0.8}$ in good agreement with recent results[22]. Figure 3 shows the room temperature data from Kurylo *et al.*[3] and data at higher temperatures by Pilling and co-workers[1,8,9]. At atmospheric pressure and 300 K the reaction is very close to the high pressure limit, i.e. $k/k_\infty \approx 0.9$, while at 800 K it is in the fall-off regime. The recombination and the dissociation rate coefficients are related via the equilibrium constant given above[22]. The expression for k_0 for M = N_2 is based on the early work of Braun and Lenzi[2] which requires confirmation.

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$H + C_2H_4 + M \rightarrow C_2H_5 + M$

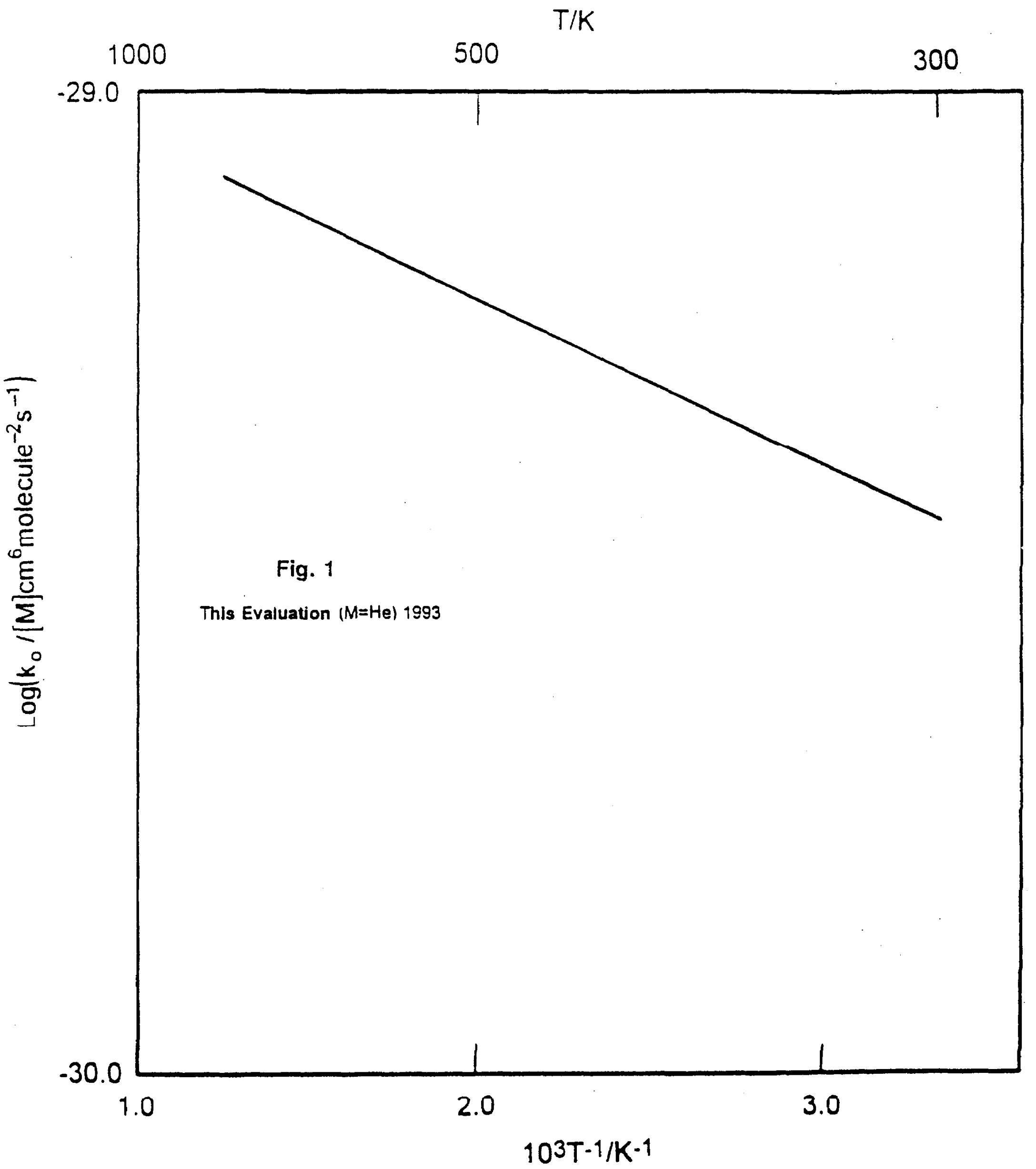
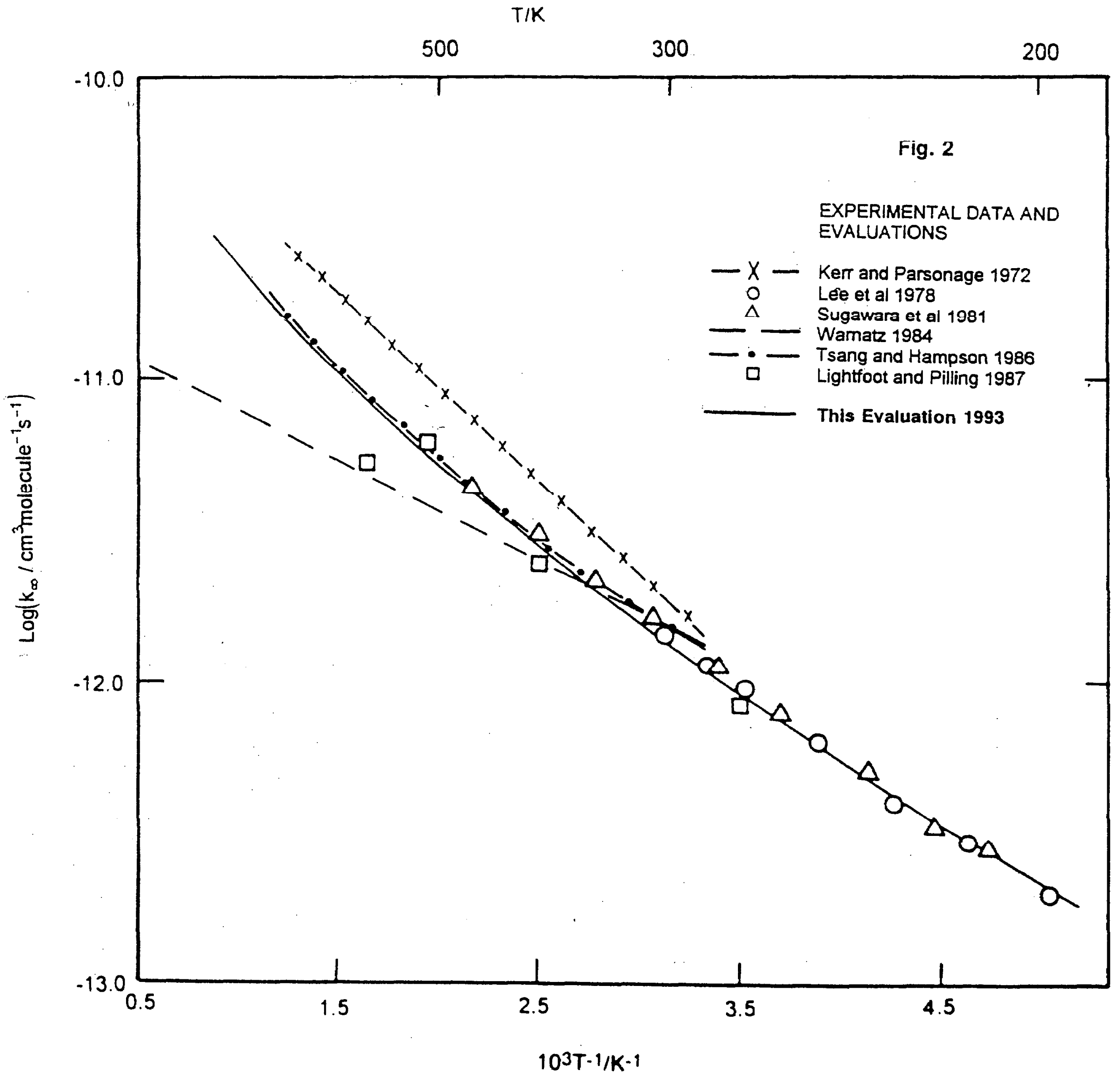


Fig. 1

This Evaluation (M=He) 1993

$H + C_2H_4 + M \rightarrow C_2H_5 + M$



$H + C_2H_4 + M \rightarrow C_2H_5 + M$

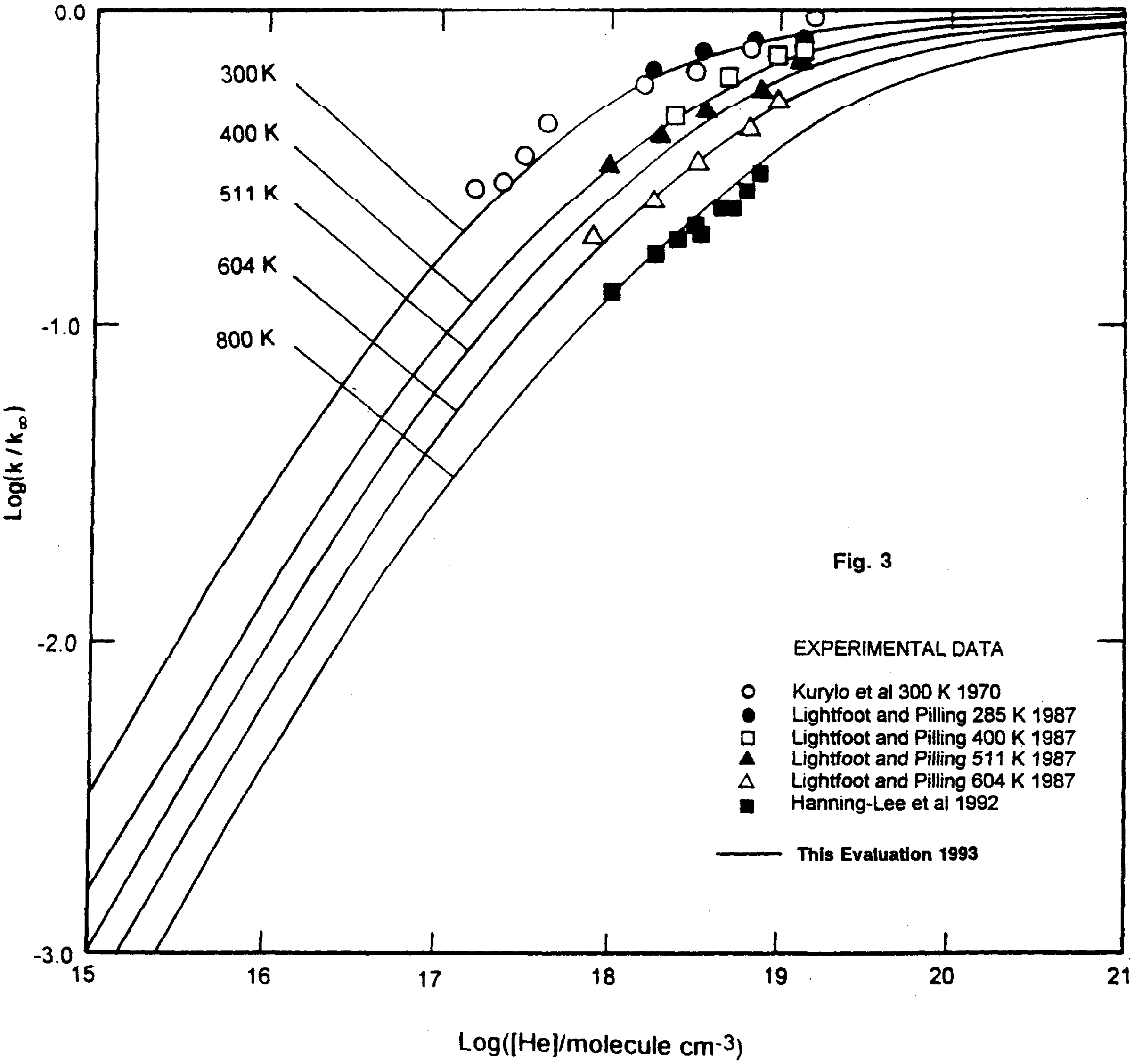


Fig. 3

C_2H_5 (+ M) → C_2H_4 + H (+ M)

Thermodynamic data
$\Delta H^\circ_{298} = 150$ kJ mol^{-1}
$\Delta S^\circ_{298} = 86.6$ J K^{-1} mol^{-1}
$Kp = 5.6\cdot10^{1}T^{1.0}\exp(-17830/T)$ atm.

Rate Coefficient Data

k/s^{-1}	T/K	[M]/molecule cm^{-3}	Reference	Comments
Rate Coefficient Measurements				
Low Pressure Range				
$[C_2H_6]$ $3.0\cdot10^{-6}\exp(-16300/T)$	823–913	$(4.4–68)\cdot10^{17}$	Lin and Back, 1966[1]	(a)
$[C_2H_6]$ $1.1\cdot10^{-6}\exp(-16000/T)$	673–773	$(0.52–120)\cdot10^{17}$	Loucks and Laidler, 1967[4]	(b)
[Ar] $1.7\cdot10^{-8}\exp(-15100/T)$	900–1350	$(2.7–180)\cdot10^{18}$	Glänzer and Troe, 1973[5]	(c)
$[C_2H_6]$ $8.3\cdot10^{-15}$	902	$(1.1–27.2)\cdot10^{17}$	Pacey and Wimalasena, 1984[6]	(d)
$[C_2H_6]$ $3.3\cdot10^{-6}\exp(-17560/T)$	793–813	$(0.12–37)\cdot10^{17}$	Simon, Foucaut and Scacchi, 1988[8]	(e)
Intermediate Fall-Off Range				
$1.4\cdot10^{14}\exp(-19800/T)$	673–773	$7\cdot10^{18}(C_2H_5)$	Bywater and Steacie, 1951[9]	(f)
$4.4\cdot10^{2}$	822.7	$0.78\cdot10^{18}(C_2H_6)$	Lin and Back, 1966[1]	(a)
$9.2\cdot10^{2}$		$1.9\cdot10^{18}$		
$1.6\cdot10^{3}$		$6.9\cdot10^{18}$		
$1.2\cdot10^{3}$	857.7	$0.70\cdot10^{18}$		
$3.0\cdot10^{3}$		$3.1\cdot10^{18}$		
$4.5\cdot10^{3}$		$6.6\cdot10^{18}$		
$2.8\cdot10^{3}$	913	$0.38\cdot10^{18}$		
$4.7\cdot10^{3}$		$0.72\cdot10^{18}$		
$9.2\cdot10^{3}$		$2.1\cdot10^{18}$		
1.3	673	$0.76\cdot10^{17}(C_2H_6)$	Loucks and Laidler, 1967[4]	(b)
3.5		$5.6\cdot10^{17}$		
8.8		$3.2\cdot10^{17}$		
3.1	703	$0.55\cdot10^{17}$		
5.7		$2.7\cdot10^{17}$		
$2.4\cdot10^{1}$		$9.1\cdot10^{17}$		
$2.3\cdot10^{1}$	773	$0.44\cdot10^{17}$		
$6.9\cdot10^{1}$		$3.6\cdot10^{17}$		
$2.7\cdot10^{2}$		$7.7\cdot10^{17}$		
$7.7\cdot10^{2}$	902	$1.1\cdot10^{17}(C_2H_6)$	Pacey and Wimalasena, 1984[6]	(d)
$2.5\cdot10^{3}$		$6.6\cdot10^{17}$		
$5.6\cdot10^{3}$		$27\cdot10^{17}$		
$1.2\cdot10^{3}$	963	$(1.0–25)\cdot10^{17}(C_2H_6)$		
$1.2\cdot10^{12}\exp(-17612/T)$	1200–1700	$1.4\cdot10^{19}$(Ar)	Hidaka *et al.*, 1985[10]	(g)
$1.0\cdot10^{2}$	841	$1.6\cdot10^{17}$ (C_2H_6)	Trenwith, 1986[11]	(h)
$4.7\cdot10^{2}$		$13\cdot10^{17}$		
$1.2\cdot10^{3}$		$110\cdot10^{17}$		
$1.3\cdot10^{2}$	872.5	$0.88\cdot10^{17}$		
$6.9\cdot10^{2}$		$8.3\cdot10^{17}$		
$2.3\cdot10^{3}$		$105\cdot10^{17}$		
$5.7\cdot10^{2}$	913	$1.2\cdot10^{17}$		
$2.3\cdot10^{3}$		$12\cdot10^{17}$		
$5.6\cdot10^{3}$		$99\cdot10^{17}$		
$9.57\cdot10^{1}$	775	$2.5\cdot10^{18}$(He)	Brouard, Lightfoot, and Pilling, 1986[12]	(i)
$1.62\cdot10^{2}$	800	$2.4\cdot10^{18}$		
$3.62\cdot10^{2}$	825	$2.3\cdot10^{18}$		
$2.28\cdot10^{1}$	793	$0.37\cdot10^{17}(C_2H_6)$	Simon, Foucaut, and Scacchi, 1988[8]	(e)
$1.01\cdot10^{2}$		$3.7\cdot10^{17}$		
$2.72\cdot10^{2}$		$37\cdot10^{17}$		
$1.63\cdot10^{1}$	813	$0.12\cdot10^{17}$		
$1.82\cdot10^{2}$		$3.6\cdot10^{17}$		
$5.54\cdot10^{2}$		$36\cdot10^{17}$		
$3.26\cdot10^{2}$	1094	$0.71\cdot10^{16}$	Feng *et al.*, 1992[13]	(j)
$9.27\cdot10^{1}$	901	$4.22\cdot10^{16}$		
$4.49\cdot10^{2}$	927	$15.8\cdot1$[illegible]		

C_2H_5 (+ M) → C_2H_4 + H (+ M) — Continued

Rate Coefficient Data

k/s^{-1}	T/K	[M]/molecule cm^{-3}	Reference	Comments
High Pressure Range				
$1.0 \cdot 10^{13}\exp(-20130/T)$	693–803	$(1.8–21) \cdot 10^{17}$(n-butane)	Purnell and Quinn, 1962[14]	(k)
$3.8 \cdot 10^{13}\exp(-19120/T)$	822.7–913	$(3.8–69) \cdot 10^{17}(C_2H_6)$	Lin and Back, 1966[1]	(a)
$2.7 \cdot 10^{14}\exp(-20580/T)$	673–773	$(0.52–120) \cdot 10^{17}(C_2H_6)$	Loucks and Laidler, 1967[4]	(b)
$1.3 \cdot 10^{13}\exp(-20130/T)$	900–1350	$(2.7–180) \cdot 10^{18}$(Ar)	Glänzer and Troe, 1973[5]	(c)
$3.2 \cdot 10^{13}\exp(-21050/T)$	941–1073	$6.0 \cdot 10^{18}$(Ar)	Pratt and Rogers, 1979[15]	(l)
$2.7 \cdot 10^{4}$	902	$(1.1–27.2) \cdot 10^{17}(C_2H_6)$	Pacey and Wimalasena, 1984[6]	(d)
$8.9 \cdot 10^{12}\exp(-19120/T)$	841–913	$(0.9–110) \cdot 10^{17}(C_2H_6)$	Trenwith, 1986[11]	(h)
$1.6 \cdot 10^{13}\exp(-19120/T)$	793–813	$(0.12–37) \cdot 10^{17}(C_2H_6)$	Simon, Foucaut, and Scacchi, 1988[8]	(e)
Reviews and Evaluations				
k_0 = [M undefined] $1.7 \cdot 10^{-7}\exp(-15640/T)$	700–1500		Warnatz, 1984[16]	(m)
$k_\infty = 2.0 \cdot 10^{13}\exp(-19970/T)$	500–2000			
$k_\infty = 4.9 \cdot 10^{9}T^{1.19}\exp(-18722/T)$			Tsang and Hampson, 1986[17]	(n)
$k_\infty = 1.11 \cdot 10^{10}T^{1.037}$ $\exp(-18504/T)$	200–1100		Feng *et al.*, 1993[13]	(j)
k_0 = [He]$6.63 \cdot 10^{9}T^{-4.99}$ $\exp(-20130/T)$	200–1100			

Comments

(a) Pyrolysis of C_2H_6 in a conventional static system. Measurements of the rate of production of CH_4 and C_4H_{10}. Rate coefficients measured relative to the reaction $C_2H_5 + C_2H_5 \rightarrow C_4H_{10}$ for which a value of $k = 3.3 \cdot 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} was employed[2]. Mechanism with six reactions. Limiting rate coefficients obtained by extrapolation using the method of Ref. 3.

(b) The mercury-photosensitized decomposition of C_2H_6 in a static system was used to generate C_2H_5 radicals. Products measured by volumetry and gas chromatography. Mechanism with four reactions. Rate coefficients measured relative to $C_2H_5 + C_2H_5 \rightarrow C_4H_{10}$ for which a value of $k = 3.3 \cdot 10^{-11}$ cm^3 $molecule^{-1}$ cm^{-1} was used[2]. Extrapolation towards the limiting rate coefficients employing Lindemann plots.

(c) Shock wave study of the thermal decomposition of $C_2H_5NO_2$. From the concentration profiles of $C_2H_5NO_2$ and the product NO_2 the subsequent C_2H_5 decomposition was analysed.

(d) Pyrolysis of C_2H_6 in a flow system. The products CH_4 and C_2H_4 were measured by gas chromatography. Steady-state approximation for a mechanism with nine reactions. Extrapolation based on Ref. 7.

(e) Pyrolysis of C_2H_6 in a static system. The main products were CH_4 and C_2H_4 and were analysed by gas chromatography. Analysis of literature values employing the RRKM and Troe models.

(f) Mercury-photosensitized decomposition of C_2H_6. Analysis of CH_4 and H_2.

(g) Pyrolysis of C_2H_6 behind shock waves. Monitoring of C_2H_4, C_2H_2 and CH_4 concentrations by absorption spectroscopy.

(h) Thermal decomposition of C_2H_6. The concentrations of CH_4 and C_2H_6 determined by gas chromatography. Rate coefficients derived from CH_4 and C_2H_4 yields on the basis of a mechanism with five reactions.

(i) ArF excimer flash photolysis of C_2H_4 with detection of H atoms by Lyman-α resonance fluorescence. The approach to the $H + C_2H_4 \rightleftarrows C_2H_5$ equilibrium was directly observed.

(j) Thermal decomposition of C_2H_5 monitored by using photoionization mass spectrometry. C_2H_5 radicals generated by 193 nm laser photolysis of 3-pentanone. Weak collision effects studied using modified strong collision and master equation analysis.

(k) Pyrolysis of n-butane. The reaction rates were measured by analysing chromatographically the products after short residence times. Extrapolation of the limiting high pressure rate coefficients using the method of Ref. 3.

(l) Pyrolysis of C_2H_6 in a wall-less reactor. Analysis performed by gas chromatography. Mechanism with seven reactions.

(m) Review of literature data.

(n) The recommended values were obtained by combination of the room temperature rate coefficients for the recombination reaction with studies of the dissociation reaction at higher temperatures.

Preferred Values

$k_\infty = 8.2 \cdot 10^{13}\exp(-20070/T)$ s^{-1} over range 700–1100 K.

$k_0 = [C_2H_6]1.7 \cdot 10^{-6}\exp(-16800/T)$ s^{-1} over range 700–900 K.

$F_c = 0.25\exp(-T/97) + 0.75\exp(-T/1379)$ for M = C_2H_6 over range 700–1000 K.

Reliability

$\Delta\log k_\infty = \pm 0.3$ over range 700–1100 K.

$\Delta\log k_0 = \pm 0.3$ over range 700–900 K.

$\Delta F_c = \pm 0.1$ over range 700–1100 K.

Comments on Preferred Values

Several studies of the temperature and the pressure dependencies of this reaction have been published. We have selected the experimental measurements of Refs. 4, 6, 8 and 13 to analyse this reaction. Theoretical fall-off curves[18] were fitted to these data and the resulting k_o values were analysed using the low pressure unimolecular rate theory from Refs. 18 and 19 employing a reaction threshold of 154.78 kJ mol^{-1} [13]. Figures 1 and 2 compare our recommended values of k_o and k_∞ with those reported in previous recommendations. Collisional efficiencies of about 0.14 for M = C_2H_6 between 700 and 800 K were derived, which are consistent with an average energy transferred per collision of $-\langle\Delta E\rangle = 150$ to 210 cm^{-1}. Similarly, from the experiments of Ref. 13 a value of $-\langle\Delta E\rangle = 13\ \text{cm}^{-1}$ for M = Ar was obtained. Figure 3 shows the fall-off curves constructed in this evaluation. The dissociation and recombination rate coefficients are related via the equilibrium constant given above[13].

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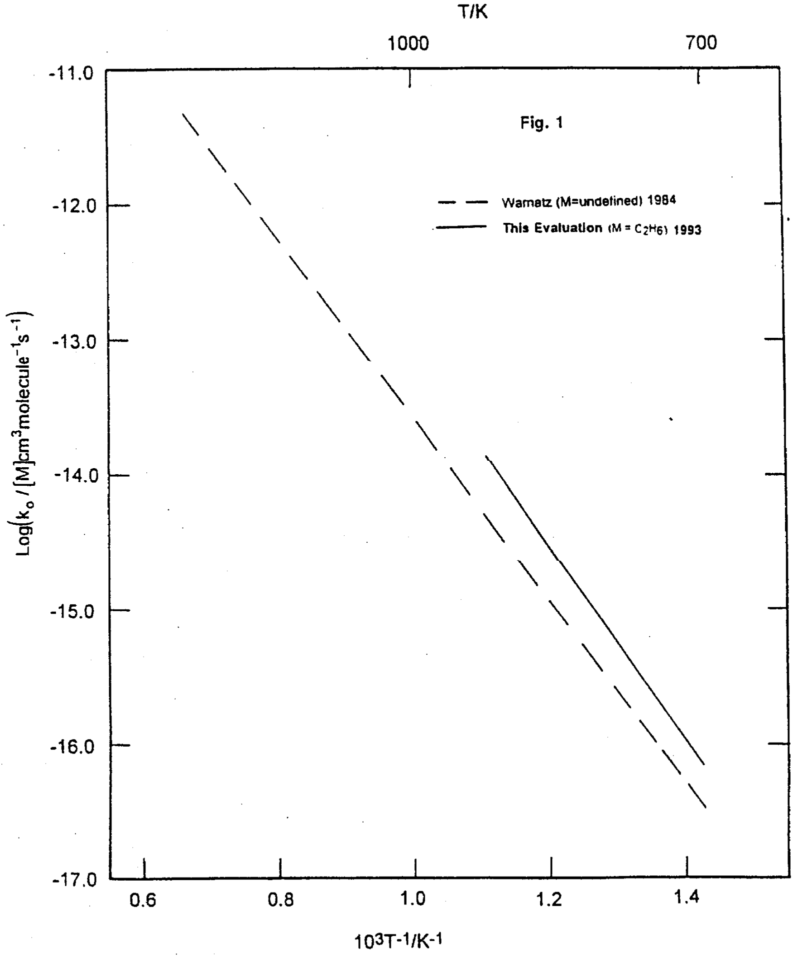
$C_2H_5 + M \rightarrow H + C_2H_4 + M$



$C_2H_5 + M \rightarrow H + C_2H_4 + M$

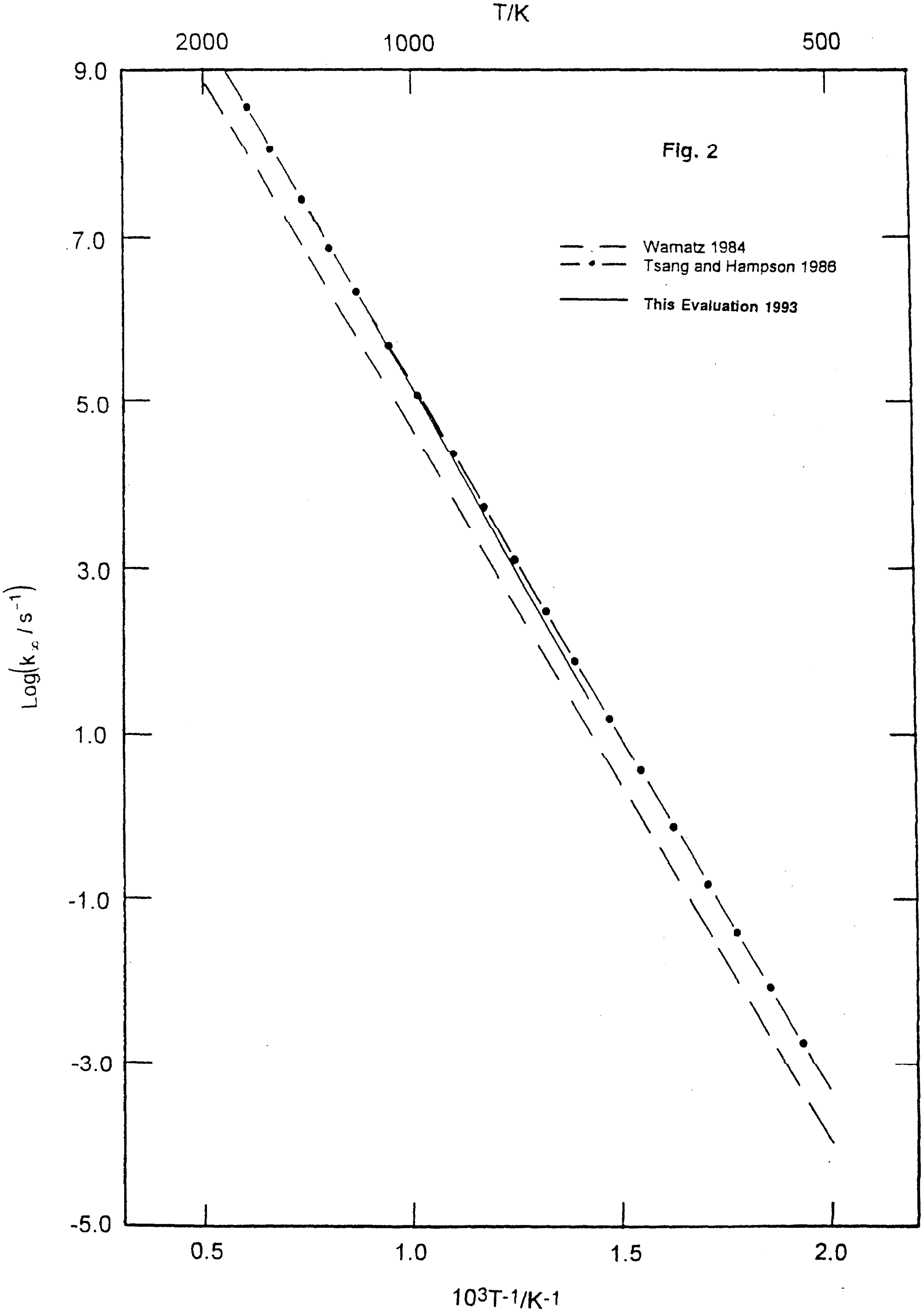
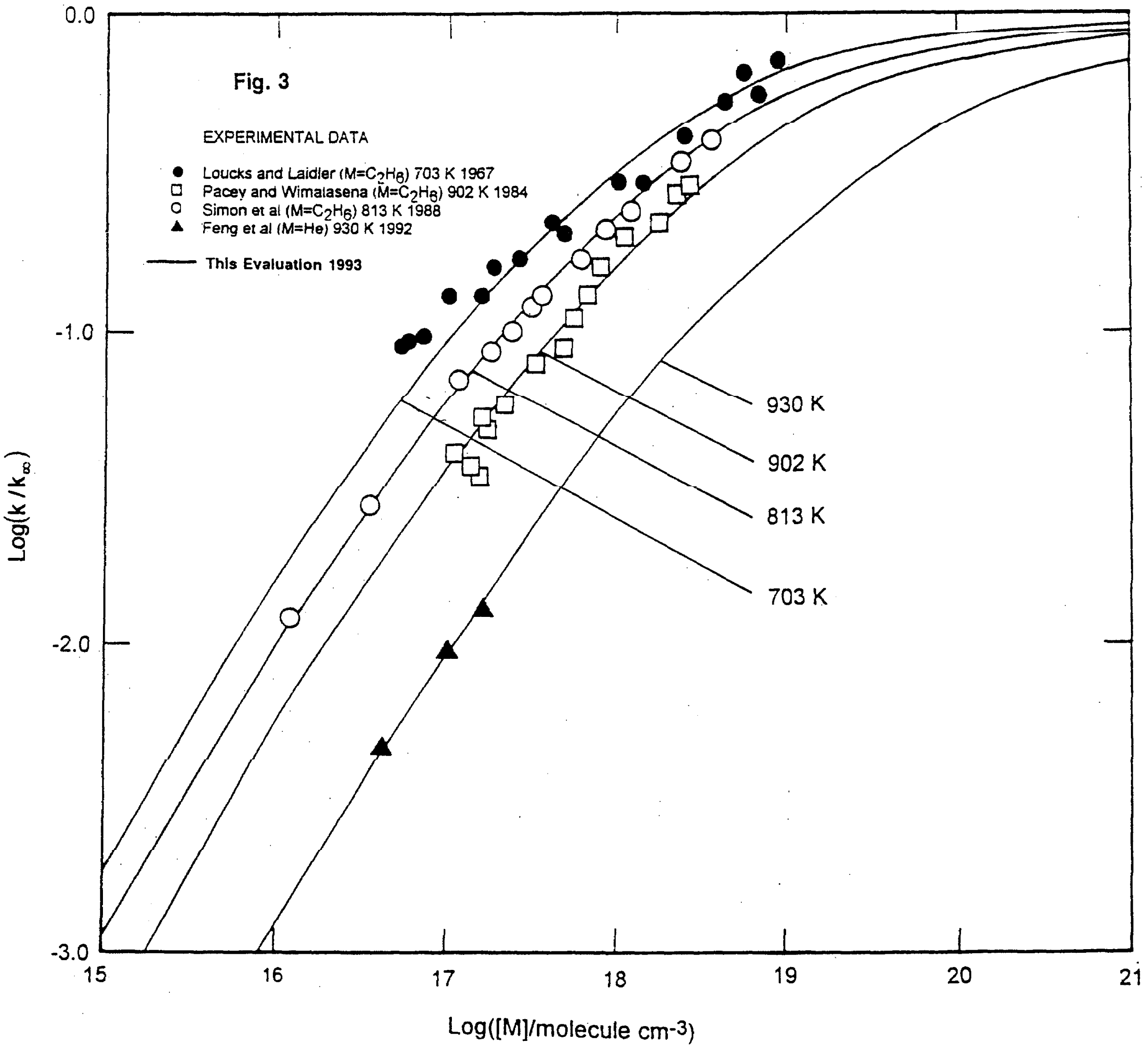


Fig. 2

$C_2H_5 + M \rightarrow H + C_2H_4 + M$



$H + C_6H_5CH_2 (+ M) \rightarrow C_6H_5CH_3 (+ M)$

Thermodynamic Data
$\Delta H^\circ_{298} = -368.0$ kJ mol^{-1}
$\Delta S^\circ_{298} = -110.9$ J K^{-1} mol^{-1}
$Kp = 1.8 \cdot 10^{-2} T^{-1.49} \exp(+44028/T)$ atm^{-1}

Rate Coefficient Data

k/cm^3 molecule^{-1}s^{-1}	T/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)
$4.3 \cdot 10^{-10}$	300	Ackermann *et al.*, 1990[3]	(c)
$4.3 \cdot 10^{-10}$	1300–1650		(d)

Comments

(a) The thermal decomposition of toluene has been reinvestigated 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.

(c) Reaction rate measured using: (1) pulse radiolysis of Ar/toluene mixtures at 1 bar pressure; [$C_6H_5CH_2$] monitored by light absorption at 305.3 nm, (2) flash photolysis and pulsed laser photolysis of Ar/toluene mixtures; [H] monitored by resonance absorption. Results from the different techniques in good agreement.

(d) Shock tube study on Ar/$C_6H_5CH_2I$/C_2H_5I mixtures. [$C_6H_5CH_2$] monitored by light absorption at 260 nm. No temperature dependence of k could be detected.

Preferred Values

$k_\infty = 4.3 \cdot 10^{-10}$ cm^3 molecule^{-1} s^{-1} over the range 300–2000 K.

Reliability

$\Delta \log k_\infty = \pm 0.2$ at room temperature rising to ± 0.5 at 2000 K.

Comments on Preferred Values

The available data at 300 K[2,3] are in good agreement. At higher temperatures the results of Ackermann *et al.*[3] are accepted rather than those from the less direct study of Brouwer *et al.*[1]. As might be expected for such a fast recombination reaction there is no evidence for a significant temperature dependence of the rate constant.

References

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$$\begin{aligned} \mathrm{H + C_6H_5CH_3} &\rightarrow \mathrm{H_2 + C_6H_5CH_2} && (1)\\ &\rightarrow \mathrm{H_2 + C_6H_4CH_3} && (2)\\ &\rightarrow \mathrm{CH_3 + C_6H_6} && (3)\\ \mathrm{H + C_6H_5CH_3\ (+\ M)} &\rightarrow \mathrm{C_6H_6CH_3\ (+\ M)} && (4) \end{aligned}$$

Thermodynamic Data

$\Delta H^\circ_{298}(1) = -68.0\mathrm{Jmol^{-1}}$
$\Delta S^\circ_{298}(1) = 12.3\ \mathrm{J\ K^{-1}\ mol^{-1}}$
$Kp(1) = 2.4\ T^{0.171}\exp(+8060/T)$

$\Delta H^\circ_{298}(2) = 37.5\ \mathrm{kJ\ mol^{-1}}$
$\Delta S^\circ_{298}(2) = 12.1\ \mathrm{J\ K^{-1}\ mol^{-1}}$
$Kp(2) = 2.5\ T^{0.158}\exp(-4630/T)$

$\Delta S^\circ_{298}(3) = -39.4\ \mathrm{J\ K^{-1}\ mol^{-1}}$
$\Delta H^\circ_{298}(3) = 28.9\ \mathrm{kJ\ mol^{-1}}$
$Kp(3) = 2.1\cdot10^4\ T^{-0.940}\exp(+4400/T)$

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			
$k_3 = 3.3\cdot10^{-12}\ \exp(-755/T)$	633	Benson and Shaw, 1967[1]	(a)
$k_4 = 1.7\cdot10^{-13}$	298	Sauer and Ward, 1967[2]	(b)
$k_1 = 1.4\cdot10^{-10}\ \exp(-4630/T)$	863–963	Mkryan, Oganesyan, and Nalbandyan, 1972[3]	(c)
$k_4 = 8.5\cdot10^{-14}$	303	Knutti and Buehler, 1975[4]	(d)
$k_1 = 8.3\cdot10^{-11}\ \exp(-1864/T)$	1500–1800	Astholz, Durant, and Troe, 1981[5]	(e)
$k_1 = 1.3\cdot10^{-28}\ T^{5.5}\ \exp(-171/T)$	600–1700	Rao and Skinner, 1984[6]	(f)
$k_1 = 5.4\cdot10^{-9}\ \exp(-7548/T)$	1600–2150	Pamidimukkala and Kern, 1985[7]	(g)
$k_2 = 5.4\cdot10^{-9}\ \exp(-9561/T)$	1600–2150		
$k_3 = 2.1\cdot10^{-12}\ \exp(-1862/T)$	1600–2150		
$k_1 = 1.8\cdot10^{-20}\ T^{3.0}\ \exp(-1183/T)$	950–1100	Robaugh and Tsang, 1986[8]	(h)
$k_3 = 1.1\cdot10^{-21}\ T^{3.0}\ \exp(+377/T)$	950–1100		
$k_1 = 7.3\cdot10^{-24}\ T^{4.0}\ \exp(-1057/T)$	1300–1800	Kiefer and Mizerka, 1986[9]	(i)
$9.7\cdot10^{-13}$	773	Baldwin, Scott and Walker, 1987[10]	(j)
$k_3 = 5.0\cdot10^{-13}$	773		
$k_2 = 4.2\cdot10^{-10}\ \exp(-8052/T)$	1600–2100	Pamidimukkala *et al.*, 1987[12]	(k)
$k_1 = 8.3\cdot10^{-10}\ \exp(-6290/T)$	1380–1700	Braun-Unkhoff, Frank, and Just, 1989[13]	(l)
$k_1 = 2.1\cdot10^{-9}\ \exp(-7460/T)$	1300–1700	Hippler, Reihs, and Troe, 1990[14]	(m)
Reviews and Evaluations			
$k_1 = 2.1\cdot10^{-10}\ \exp(-4210/T)$	600–1800	Hippler, Reihs, and Troe, 1990[14]	(m)
$k_1 = 6.6\cdot10^{-22}\ T^{3.44}\ \exp(-1570/T)$	600–2500	CEC, 1992[15]	(n)
$k_4 = 1.2\cdot10^{-13}$	298		

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) Pulse radiolysis with product analysis by gas chromatography. Transient species were monitored as function of time by absorption in the wavelength range 260–340 nm. A k-value for 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 reaction (assumed to be 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. 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. 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))re-evaluated using 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.

(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 the competitive process $\mathrm{H + CH_4 \rightarrow CH_3 + H_2}$ with $k = 2.2\text{–}10^{-20}T^{3.0}\exp(-4045/T)$ cm^3 molecule^{-1} s^{-1}. Rate expressions for the formation of benzene and methyl radicals (channel (3)) and of benzyl radicals and hydrogen (channel (1)) were obtained.

(i) Shock tube study on high temperature pyrolysis of ethylbenzene with the laser schlieren technique.

(j) Small amounts of toluene (0.05–0.5%) 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 relative consumption of H_2 and of the additive permits the evaluation of rate constants for the reaction of H, O, and OH with toluene.

(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 constant expression for channel (1) was deduced which is slightly smaller than that of Rao and Skinner[6].

(m) Study using reflected shock waves with the pyrolysis of ethyl iodide as a hydrogen atom source. Toluene and ethyl iodide mole fractions covered range 100–2000 ppm. Temperature range, 1300–1700 K. Absorption signals at 260 nm recorded. At this wavelength the absorption coefficient of benzyl radicals exceeds that of toluene by a factor of 100, allowing very small conversions of toluene to benzyl to be detected. Together with the data of Ref. 8 and unpublished results of Ravishankara and Nicovich, the authors derive an Arrhenius expression for channel (1) for the temperature range 600–1800 K.

(n) See Comments on Preferred Values.

Preferred Values

$k_1 = 6.6\cdot10^{-22}\ T^{3.44} \exp(-1570/T)$ cm^3 molecule^{-1} s^{-1} over range 600–2500 K.

$k_3 = 9.6\cdot10^{-11} \exp(-4070/T)$ cm^3 molecule^{-1} s^{-1} over range 770–1100 K.

$k_4 = 1.2\cdot10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k_1 = \pm0.3$ over range 600–2500 K.
$\Delta\log k_3 = \pm0.3$ over range 770–1100 K.
$\Delta\log k_4 = \pm0.2$ at 298 K.

Comments on Preferred Values

An expression for k_3 has been derived but the other recommendations are unchanged from our previous evaluation.

Most of the available measurements give evidence for the product channel (1) leading to benzyl radicals and molecular hydrogen. Only a few experiments permit a discrimination between the channels at elevated temperatures. Therefore, for the majority of the studies, 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. To reconcile 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]. In the range between room temperature and 1000 K channel (3) appears to be significant. Channel (2) would only be expected to be important at elevated temperatures (> 2560 K) and there are insufficient data available to recommend an expression for k_2. For the addition reaction (4) it is only possible to evaluate a room temperature value. Furthermore the data are insufficient to justify recommendation of a rate expression for the overall H-consuming reaction over the whole temperature range.

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$OH + HO_2 \rightarrow H_2O + O_2$

Thermodynamic Data

$\Delta H^\circ_{298} = -291$ kJ mol^{-1}
$\Delta S^\circ_{298} = -18.8$ J K^{-1} mol^{-1}
$Kp = 0.517\ T^{-0.25}\exp(+35000/T)$

Rate Coefficient Data

k/cm^3 molecule^{-1}s^{-1}	T/K	Reference	Comments
Rate Coefficient Measurements			
$4.8\cdot10^{-11}\exp(+250/T)$	254–382	Keyser, 1988[1]	(a)
$8.0\cdot10^{-11}$	298	Schwab *et al.*, 1989[2]	(b)
$4.98\cdot10^{-11}$	1100	Hippler, Troe and Willner, 1990[3]	(c)
Reviews and Evaluations			
$4.8\cdot10^{-11}\exp(250/T)$	300–2000	CEC, 1992[4]	(d)
$4.8\cdot10^{-11}\exp(250/T)$	250–400	IUPAC, 1992[5]	(e)

Comments

(a) Discharge flow study with [OH] measured by resonance fluorescence and [HO_2] via conversion to OH with 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.

(b) Discharge flow reactor with laser magnetic resonance and resonance fluorescence detection. Decay of [OH] in excess HO_2 under pseudo first order conditions at a pressure of 2 Torr.

(c) Shock wave study in $(CH_3O)_2/O_2/Ar$ mixtures and in H_2O_2/Ar mixtures. [HO_2] and [H_2O_2] monitored by UV absorption in reflected shock waves. [OH] profiles measured behind incident waves. Later reanalysis[6] of the results from this study gives $k = 3.3\cdot10^{-11}$ cm^3 molecule^{-1} s^{-1} over the range 950–1250 K.

(d) See Comments on Preferred Values.

(e) Accepts expression of Keyser[1].

Preferred Values

$k = 4.8\cdot10^{-11}\exp(+250/T)$ cm^3 molecule^{-1} s^{-1} over range 300–2000 K.

Reliability

$\Delta\log k = \pm0.2$ at 300 K rising to ±0.5 at 2000 K.

Comments on Preferred Values

The expression of Keyser[1] was accepted as our previous recommendation which is unchanged here.

The new experimental results of Schwab *et al.*[2] at low temperatures are in good agreement and the higher temperature studies of Hippler and Troe[3] are also compatible with the extrapolation of the Keyser expression. Gonzales *et al.*[7] have carried out a theoretical study of the reaction. By combining their calculated temperature dependence with the mean of the experimental values at 298 K they derive the expression $k = 7.1\cdot10^{-11}\ (T/300)^{-0.21}\exp(113/RT)$ cm^3 molecule^{-1} s^{-1} which agrees closely with our preferred expression.

References

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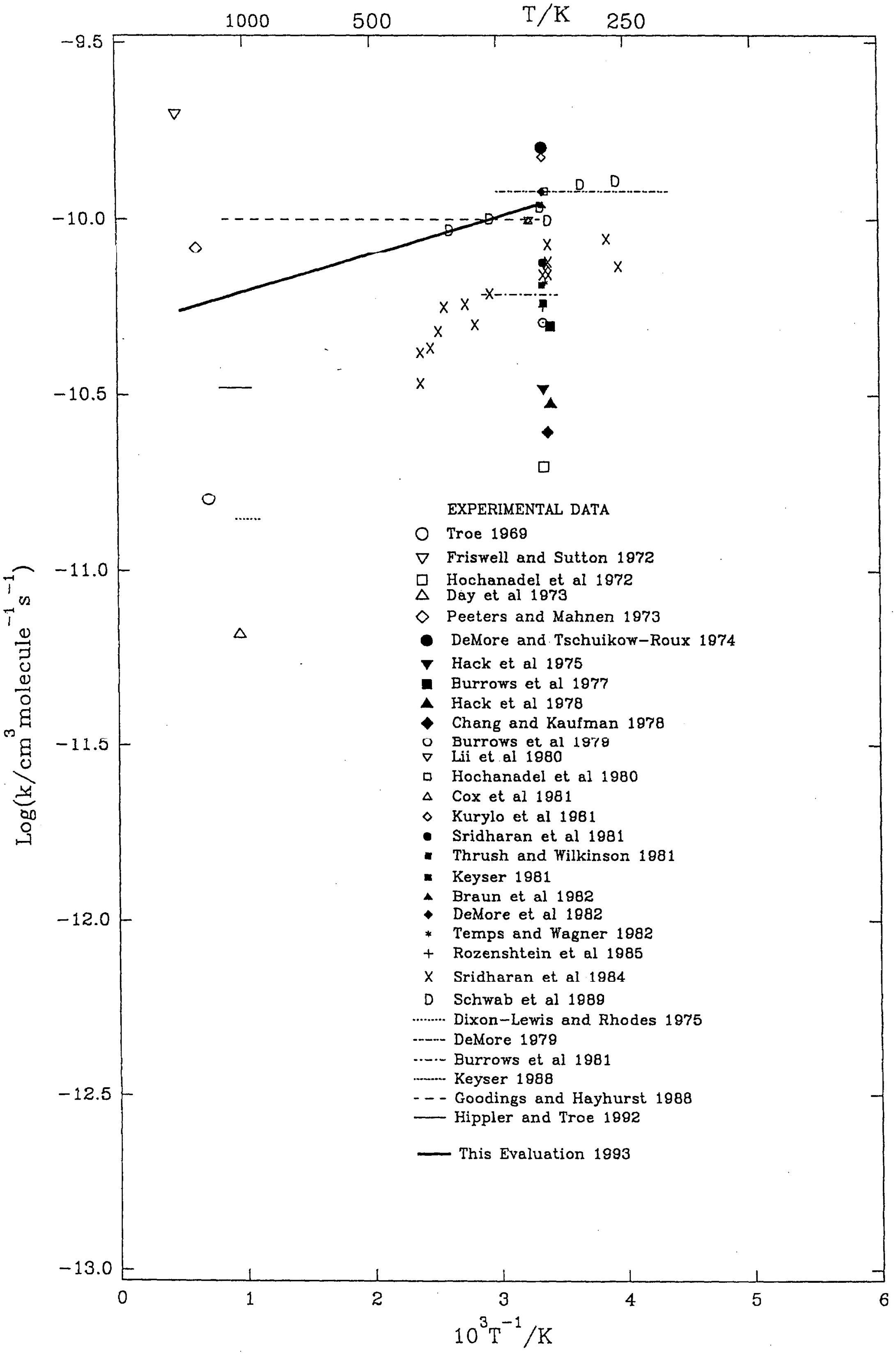
$OH + HO_2 \rightarrow H_2O + O_2$



$OH + H_2O_2 \rightarrow H_2O + HO_2$

Thermodynamic Data

$\Delta H^\circ_{298} = -134$ kJ mol^{-1}

$\Delta S^\circ_{298} = 1.23$ J K^{-1} mol^{-1}

$Kp = 63.7\ T^{-0.61}\exp(+16000/T)$

Rate Coefficient Data

k/cm^3 molecule^{-1}s^{-1}	T/K	Reference	Comments
Rate Coefficient Measurements			
$4.98\cdot10^{-12}$	1100	Hippler, Troe and Willner, 1990[1]	(a)
$1.66\cdot10^{-12} + 9.63\cdot10^{-10}\exp(-4810/T)$	250–1250	Hippler and Troe, 1992[2]	(b)
Reviews and Evaluations			
$1.3\cdot10^{-11}\exp(-670/T)$	300–1100	CEC, 1992[3]	(c)
$2.9\cdot10^{-12}\exp(-160/T)$	240–460	IUPAC, 1992[4]	(d)

Comments

(a) Shock wave study in $(CH_3O)_2/O_2/Ar$ mixtures and in H_2O_2/Ar mixtures. $[HO_2]$ and $[H_2O_2]$ by UV absorption in reflected shock waves. [OH] profiles measured behind incident waves.

(b) Shock tube study in H_2O_2/Ar mixtures. Techniques similar to previous study (comment (a)).

(c) See Comments on Preferred Values.

(d) Accepts the expression obtained by Kurylo *et al.*[5].

Preferred Values

$k = 1.3\cdot10^{-11}\exp(-670/T)$ cm^3 molecule^{-1} s^{-1} over range 300–1000 K.

Reliability

$\Delta\log k = \pm0.2$ at 300 K rising to ±0.5 at 1000 K.

Comments on Preferred Values

The low temperature studies on this reaction indicate a very small temperature coefficient for the rate constant, as reflected in the IUPAC preferred value for the range 240–460 K. Measurements at higher temperatures (>1000 K) show considerable scatter but in general indicate higher values for k than are obtained by extrapolation from the low temperature data. Recent work by Hippler and Troe suggests that this is due to a very rapid increase in the temperature coefficient of k above about 800 K.

Our previous recommendation was a compromise, attempting to represent these differences in behaviour of k at low and high temperatures by a simple expression. Until the behaviour observed by Hippler and Troe is confirmed, we retain this preferred expression but in recognition of its limitations we increase the error limits at high temperatures and continue to limit our recommendations to temperature less than 1000 K.

References

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$$\begin{aligned} OH + CH_3 &\rightarrow H + CH_2OH && (1)\\ &\rightarrow H + CH_3O && (2)\\ &\rightarrow H_2 + HCHO && (3)\\ &\rightarrow H_2O + {}^1CH_2 && (4)\\ OH + CH_3\ (+ M) &\rightarrow CH_3OH\ (+ M) && (5) \end{aligned}$$

Thermodynamic Data

$\Delta H^\circ_{298}(1) = 16.1$ kJ mol^{-1}
$\Delta S^\circ_{298}(1) = -16.7$ J K^{-1} mol^{-1}
$Kp(1) = 1.50\cdot 10^{-4}T^{0.97}\exp(-1570/T)$

$\Delta H^\circ_{298}(2) = 49.6$ kJ mol^{-1}
$\Delta S^\circ_{298}(2) = -34.6$ J K^{-1} mol^{-1}
$Kp(2) = 3.73\cdot 10^{-5}T^{0.78}\exp(-5470/T)$

$\Delta H^\circ_{298}(3) = -300.9$ kJ mol^{-1}
$\Delta S^\circ_{298}(3) = -28.4$ J K^{-1} mol^{-1}
$Kp(3) = 7.94\cdot 10^{-3}T^{0.17}\exp(+36300/T)$

$\Delta H^\circ_{298}(4) = -1.8$ kJ mol^{-1}
$\Delta S^\circ_{298}(4) = -0.2$ J K^{-1} mol^{-1}
$Kp(4) = 26.7T^{-0.48}\exp(+47/T)$

$\Delta H^\circ_{298}(5) = -386.5$ kJ mol^{-1}
$\Delta S^\circ_{298}(5) = -137.9$ J K^{-1} mol^{-1}
$Kp(5) = 1.26\cdot 10^{-7}T^{-0.289}\exp(+46700/T)$ atm^{-1}

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			
$k_2 = 3.3\cdot 10^{-8}\exp(-13800/T)$	1700–2300	Bhaskaran, Frank, and Just, 1979[1]	(a)
k_1 or $k_2 = 1.5\cdot 10^{-9}\exp(-7800/T)$	1850–2500	Roth and Just, 1984[2]	(b)
$k_4 \leq 5\cdot 10^{-12}$	300	Oser *et al.*, 1992[3]	(c)
$k_4 = 1.2\cdot 10^{-10}\exp(-1400/T)$	300–480	Oser *et al.*, 1992[4]	(d)
k_5 (see next data sheet)			
Reviews and Evaluations			
$9\cdot 10^{-11}$	300–2500	Tsang and Hampson, 1986[5]	(e)
$6\cdot 10^{-11}$	300–2000	CEC, 1992[6]	(f)

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_2 derived from a computer simulation of the experimental [H] and [O] profiles. It was suggested that channel (2) proceeds via the sequence $OH + CH_3 \rightarrow H + CH_3O$ and $CH_3O \rightarrow CH_2O + H$, i.e. overall reaction $OH + CH_3 \rightarrow 2H + CH_2O$.

(b) Similar study to that of Bhaskaran *et al.*[1] (see comment (a)) with CH_4/O_2 mixtures.

(c) Fast-flow Teflon reactor; CH_3 from $F + CH_4$ and OH from $H + NO_2$; k_5 data derived for computer modelling of CH_3 and OH profiles measured by mass spectrometry. Data for k_4 derived from measurements of products, H_2O relative to CH_3OH.

(d) Experimental system similar to note (c) but with k_4 derived from measurements of products, HDO relative to CH_3OD, in experiments with OD replacing OH.

(e) Based on data of Bhaskaran *et al.*[1], Roth and Just[2], and Sworski *et al.*[7].

(f) Based on data of Bhaskaran *et al.*[1], and Roth and Just[2].

Preferred Values

$k_4 = 1.2\cdot 10^{-10}(-1400/T)$ cm^3 molecule^{-1} s^{-1} over range 300–1000 K.

Reliability

$\Delta\log k_4 = \pm 0.5$ over range 300–1000 K.

Comments on Preferred Values

We recommend the data of Oser *et al.*[4] for channel (4), based on their product formation study of the yields of H_2O. It should be noted, however, that the recommended value of k_4 is not consistent with the rate coefficient of the reverse reaction, $k_{-4} = (1\text{–}2)\cdot 10^{-10}$ cm^3 molecule^{-1} s^{-1}, based on direct measurements[8] of CH_2 and OH. A reconciliation of these results is possible if $\Delta H^\circ(4)$ is wrong, which seems most likely to be due to an error in the presently accepted value of $\Delta H^\circ_f(CH_2CO)$.

The need remains for more experimental work on the branching ratio of the OH + CH_3 reaction, particularly at higher temperatures.

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$$\begin{array}{rll} OH + CH_3\ (+ M) & \rightarrow CH_3OH\ (+ M) & (1) \\ OH + CH_3 & \rightarrow CH_2OH + H & (2) \\ & \rightarrow CH_3O + H & (3) \\ & \rightarrow HCHO + H_2 & (4) \\ & \rightarrow {}^1CH_2 + H_2O & (5) \end{array}$$

Thermodynamic Data

$\Delta H^\circ_{298}(1) = -386.5\ \mathrm{kJ\ mol^{-1}}$
$\Delta S^\circ_{298}(1) = -137.9\ \mathrm{J\ K^{-1}\ mol^{-1}}$
$Kp(1) = 1.26\cdot 10^{-7} T^{-0.289} \exp(+46700/T)\ \mathrm{atm^{-1}}$

Rate Coefficient Data ($k = k_1$)

k/cm^3 molecule^{-1}s^{-1}	T/K	[M]/molecule cm^{-3}	Reference	Comments
Rate Coefficient Measurements				
Low Pressure Range				
$[He](2.5\pm1)\cdot10^{-27}$	300	$(7.2–150)\cdot10^{15}$	Oser *et al.*, 1992[1]	(a)
$[He](1\pm1)\cdot10^{-27}$	480	$(1.6–14)\cdot10^{16}$	Oser *et al.*, 1992[3]	(b)
Intermediate Fall-off Range				
$1.4\cdot10^{-11}$	1200	$5.7\cdot10^{18}$(Ar)	Bott and Cohen, 1991[4]	(c)
$8.0\cdot10^{-12}$	300	$7.2\cdot10^{15}$(He)	Oser *et al.*, 1992[1]	(a)
$2.2\cdot10^{-11}$		$2.7\cdot10^{16}$		
$6.0\cdot10^{-11}$		$1.5\cdot10^{17}$		
$1.2\cdot10^{-11}$	480	$1.6\cdot10^{16}$(He)	Oser *et al.*, 1992[3]	(b)
$2.2\cdot10^{-11}$		$3.8\cdot10^{16}$		
$4.4\cdot10^{-11}$		$1.4\cdot10^{17}$		
High Pressure Range				
$9.3\cdot10^{-11}$	296	$2.5\cdot10^{19}$(N_2, H_2)	Sworski *et al.*, 1980[2]	(d)
$9.4\cdot10^{-11}$	298	$2.5\cdot10^{19}$(Ar-SF_6)	Anastasi *et al.*, 1991[5]	(e)
$7.6\cdot10^{-11}$	290	$(2.5–230)\cdot10^{17}$(He)	Hughes *et al.*, 1992[6]	(f)
Reviews and Evaluations				
$9.0\cdot10^{-11}$	300–2500	$(2.9–24)\cdot10^{18}$(N_2)	Tsang and Hampson, 1986[7]	(g)
$1.9\cdot10^{-4}(T/298)^{-8.2}\exp(-5874/T)$	600–2500	$(2.9–12)\cdot10^{18}$(N_2)	Dean and Westmoreland, 1987[8]	(h)
$k\infty = 1.7\cdot10^{-10}$	300		Jordan *et al.*, 1991[9]	(i)
$k\infty = 2.9\cdot10^{-10}$	2000			

Comments

(a) Flow system study. CH_3 generated by the reactions $CH_4 + F \rightarrow CH_3 + HF$ and OH by the reaction $H + NO_2 \rightarrow NO + OH$. The CH_3 radicals were calibrated using the reaction $CH_3 + NO_2 \rightarrow CH_3O + NO$, while the OH radicals were calibrated by using an excess of CH_3CHO as scavenger. Both radicals were detected using a time-of-flight mass spectrometer. Mechanism with 15 reactions. Fall-off curves constructed using $k_\infty = 9.3\cdot10^{-11}$ cm^3 molecule^{-1} s^{-1} [2] and $F_c = 0.6$.

(b) See comment (a).

(c) Shock tube study of t-butyl hydroperoxide (generation of OH) and t-butylperoxide (generation of CH_3) mixtures. OH radicals monitored by UV absorption at 309 nm. Mechanism with 6 reactions. A formation yield of CH_3OH of 0.75 was found.

(d) Flash photolysis of H_2O vapour in CH_4. CH_3 radicals generated by reaction of OH with CH_4. The CH_3 concentrations were monitored by absorption at 216 nm. Modelling with 11 reactions. Total rate coefficients given.

(e) Pulse radiolysis of mixtures of CH_4/H_2O in the presence of Ar (940 Torr) and SF_6 (50 Torr). The reactants CH_3 and OH were generated by the reactions of F atoms with CH_4 and with H_2O respectively. CH_3 radicals monitored by UV absorption at 216.4 nm.

(f) CH_3 and OH radicals formed by 193 nm–photolysis of acetone-nitric acid mixtures diluted in He. The CH_3 was monitored by absorption spectroscopy and OH by LIF measurements in a pump/probe mode. In all conditions $[CH_3] \gg [OH]$. The data were modelled together with those of Ref. 3 using a master equation/inverse Laplace transform procedure.

(g) Literature review. The given value is for the total reaction in the pressure independent regime.

(h) Theoretical analysis using the QRRK model.

(I) Variational transition state theory calculations with a sinusoidal rotor model.

Preferred Values

$k_\infty = 1.0\cdot10^{-10}$ cm^3 molecule^{-1} s^{-1} over range 300–2000 K.
$k_\infty = [He]2.3\cdot10^{-27}$ cm^3 molecule^{-1} s^{-1} at 300 K.
$k_0 = [Ar]1.1\cdot10^{-28}\ (T/1000)^{-8.2}$ cm^3 molecule^{-1} s^{-1} over range 1000–2000 K.
$F_c = 0.18\exp(-T/200) + 0.82\exp(-T/1438)$ for M = Ar over range 1000–2000 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ over range 300–2000 K.
$\Delta \log k_0 = \pm 0.3$ for $M = He$ at 300 K.
$\Delta \log k_0 = \pm 0.5$ for $M = Ar$ over range 1000–2000 K.
$\Delta F_c = \pm 0.1$ over range 1000–2000 K.

Comments on Preferred Values

The available database is still limited and more measurements are needed. Figure 1 shows the recent values of Refs. 1–3, 5 and 6 and the high temperature value of Bott and Cohen[9]. The fit to the room temperature values leads to a collisional efficiency $\beta_c = 0.32$[10,11]. The preferred k^∞ is consistent with SACM estimates following Ref. 12. As Fig. 1 shows, the rate coefficients measured at 480 K are notably higher when they are compared with an estimation of the fall-off curve using a temperature independent $-\langle\Delta E\rangle = 160$ cm^{-1} (as determined from the above β_c value at 300 K). More measurements at higher temperatures are necessary. The k_0 values for $M = Ar$ were estimated from the corresponding reverse dissociation process via K_c. The importance of the other reaction channels is still unknown[6]

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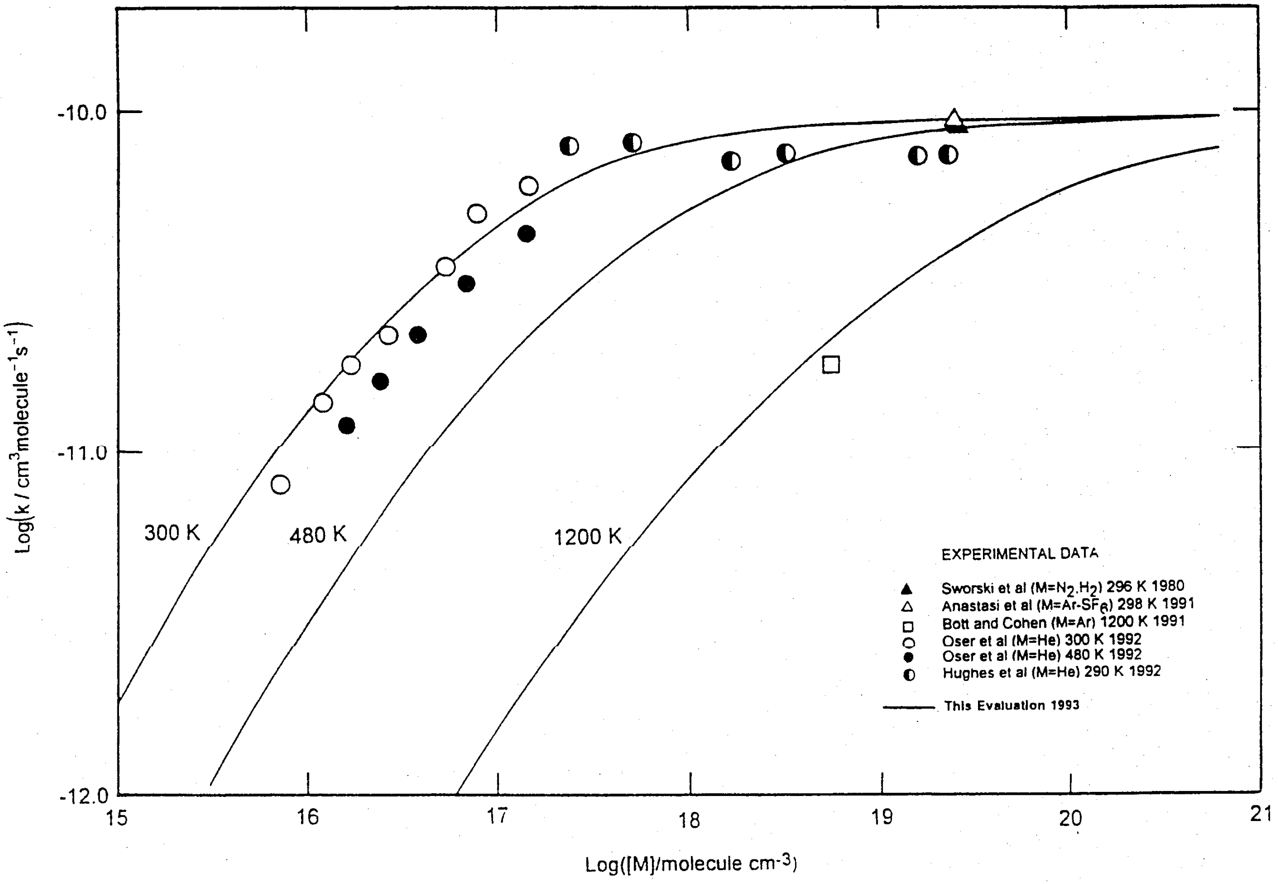
$OH + CH_3 + M \rightarrow CH_3OH + M$



$$
\begin{aligned}
CH_3OH\ (+\ M) &\rightarrow CH_3 + OH\ (+\ M) && (1)\\
&\rightarrow CH_2OH + H\ (+\ M) && (2)\\
&\rightarrow {}^1CH_2 + H_2O + M && (3)
\end{aligned}
$$

Thermodynamic data

$\Delta H^\circ_{298}(1) = 386.5$ kJ mol^{-1}
$\Delta S^\circ_{298}(1) = 137.9$ J K^{-1} mol^{-1}
$Kp(1) = 7.94\cdot10^6 T^{0.29}\exp(-46700/T)$ atm.

$\Delta H^\circ_{298}(2) = 401.9$ kJ mol^{-1}
$\Delta S^\circ_{298}(2) = 121.3$ J K^{-1} mol^{-1}
$Kp(2) = 1.19\cdot10^3 T^{1.26}\exp(-5220/T)$ atm.

$\Delta H^\circ_{298}(3) = 384.7$ kJ mol^{-1}
$\Delta S^\circ_{298}(3) = 137.7$ J K^{-1} mol^{-1}
$Kp(3) = 2.12\cdot10^8 T^{-0.19}\exp(-46700/T)$ atm.

Rate Coefficient Data ($k = k_1$)

k/s^{-1}	T/K	[M]/molecule cm^{-3}	References	Comments
Rate Coefficient Measurements				
Low Pressure Range				
$[Ar]6.6\cdot10^{-9}\exp(-34200/T)$	1545–2180	$(6.0–17)\cdot10^{18}$	Bowman, 1975[1]	(a)
$[Ar]3.3\cdot10^{-7}\exp(-34400/T)$	1600–2100	$(7–230)\cdot10^{17}$	Spindler and Wagner, 1982[2]	(b)
$[Ar]5.5\cdot10^{-8}\exp(-33213/T)$	1372–1842	$(1.1–1.3)\cdot10^{19}$	Hidaka *et al.*, 1989[3]	(c)
Intermediate Fall-Off Range				
$2.1\cdot10^{11}\exp(-45790/T)$	1070–1225	$6.4\cdot10^{18}(N_2)$	Aranowitz, Naegeli, and Glassman, 1977[4]	(d)
$1.9\cdot10^{13}\exp(-40280/T)$	1000–2180	$3.7\cdot10^{18}(N_2)$	Westbrook and Dryer, 1979[5]	(e)
$6.4\cdot10^{11}\exp(-34730/T)$	600–700	$2.8\cdot10^{18}(N_2)$	Cathonnet, Boettner, and James, 1979[6]	(f)
$1.3\cdot10^{12}\exp(-35730/T)$		$5.5\cdot10^{18}$		
$6.0\cdot10^{12}\exp(-37280/T)$	1300–1750	$6.0\cdot10^{18}(Ar)$	Tsubi and Hashimoto, 1981[7]	(g)
$3.5\cdot10^{13}\exp(-37770/T)$		$3.0\cdot10^{19}$		
$8.7\cdot10^{13}\exp(-38250/T)$		$6.0\cdot10^{19}$		
$3.1\cdot10^{1}$	1600	$7.0\cdot10^{17}(Ar)$	Spindler and Wagner, 1982[2]	(b)
$1.4\cdot10^{2}$		$4.0\cdot10^{18}$		
$4.0\cdot10^{2}$	1600	$2.3\cdot10^{19}$		
$3.4\cdot10^{2}$	1800	$7.0\cdot10^{17}(Ar)$		
$1.6\cdot10^{3}$		$4.0\cdot10^{18}$		
$4.9\cdot10^{3}$		$2.3\cdot10^{19}$		
$2.3\cdot10^{3}$	2000	$7.0\cdot10^{17}(Ar)$		
$1.1\cdot10^{4}$		$4.0\cdot10^{18}$		
$3.7\cdot10^{4}$		$2.3\cdot10^{19}$		
$7.9\cdot10^{36}T^{-7.08}\exp(-45290/T)$	1800–2660	$1.2\cdot10^{18}(N_2)$	Cribb, Dove, and Yamazaki, 1985[8]	(h)
$6.6\cdot10^{-2}$	1200	$5.7\cdot10^{18}(Ar)$	Bott and Cohen, 1991[9]	(i)
$1.2\cdot10^{22}T^{-8.0}\exp(-45295/T)$	1800–2700	$1.0\cdot10^{18}(Ne,Ar)$	Cribb, Dove, and Yamazaki, 1992[10]	(j)
High Pressure Range				
$9.4\cdot10^{15}\exp(-45220/T)$	1600–2100	$(7–230)\cdot10^{17}(Ar)$	Spindler and Wagner, 1982[2]	(b)
Reviews and Evaluations				
$k_0 = [Ar]3.3\cdot10^{-7}\exp(-34400/T)$	1000–2500		Warnatz, 1989[11]	(k)
$k_\infty = 9.4\cdot10^{15}\exp(-45220/T)$	1000–2500			
$k_\infty = 1.9\cdot10^{16}\exp(-46192/T)$	300–2500		Tsang, 1987[12]	(l)
$k_\infty = 1.9\cdot10^{16}\exp(-46186/T)$	973–2000		Norton and Dryer, 1990[13]	(m)

Comments

(a) Oxidation of methanol behind shock waves. The concentrations of O, OH, H_2O and CO were measured using spectroscopic techniques. Mechanism with 19 reactions.

(b) Study of the methanol pyrolysis behind reflected shock waves in Ar. The concentration of CH_3 and OH were monitored by absorption at 216 and 308 nm respectively. High and low pressure rate coefficients obtained by extrapolation of the fall-off curves. Channel (1) contributes about 75% and channel (2) about 25% to the total rate.

(c) Thermal decomposition of methanol behind reflected shock waves. IR laser kinetic spectroscopy, and GC analysis of reaction products. Mechanism with 26 reactions.

(d) Pyrolysis of methanol in an adiabatic turbulent flow reactor. Mechanism with 19 steps.

(e) Mechanism for the oxidation of methanol with 89 elementary reactions.

(f) Thermal decomposition of methanol in a static reactor. Measurement of CH_2O by gas chromatography. Mechanism with 10 reactions.

(g) Shock tube study of the thermal oxidation of methanol-oxygen mixtures highly diluted with Ar. Mechanism with 57 steps.

(h) Pyrolysis of methanol studied by the laser schlieren method in incident shock waves and by dynamic spectrometry in reflected shock waves. The reaction occurs by both channels with $k_1/k = 0.8$.

(i) Shock wave study of t-butyl hydroperoxide (generation of HO) and *t*-butylperoxide (generation of CH_3) mixtures. HO concentration monitored by UV absorption at 309 nm. Mechanism with six reactions. In the present work, the resulting recombination rate data have been transformed to dissociation data via the given equilibrium constant.

(j) Pyrolysis of methanol studied by laser schlieren densitometry and dynamic mass spectrometry. Modelling with a mechanism of 28 reactions.

(k) Data evaluation.

(l) Data evaluation and construction of RRKM fall-off curves.

(m) Evaluation of static, flow and shock tube experiments. Mechanism with 66 reactions.

Preferred Values

$k_\infty = 1.7\cdot10^{16}\exp(-45740/T)$ s^{-1} over range 1000–2000 K.

k_0 = [Ar] $1.1\cdot10^{-7}\exp(-33080/T)$ s^{-1} over range 1000–2000 K.

$F_c = 0.18\exp(-T/200) + 0.82\exp(-T/1438)$ for M = Ar over range 1000–2000 K.

Reliability

$\Delta\log k_\infty = \pm0.5$ over range 1000–2000 K.

$\Delta\log k_0 = \pm0.3$ over range 1000–2000 K.

$\Delta F_c = \pm0.1$ over range 1000–2000 K.

Comments on Preferred Values

The recommended values are mainly based on the theoretical analysis of the rate data from Ref. 2 in terms of unimolecular rate theory[14–16]. The modelling leads to the almost temperature independent value k_∞ of $7.0\cdot10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} between 300–2000 K for the reverse recombination reaction in good agreement with recent data by Sworski *et al.*[17] and Anastasi *et al.*[18]. Therefore, because the available experiments are far away from the high pressure regime, we derived the recommended k_∞ using a recombination coefficient of $k_\infty = 1.0\cdot10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} and the given equilibrium constant. Figure 1 shows the temperature dependence of k_0 in comparison with the values recommended by Warnatz[11]. Figure 2 shows that the recommended k_∞ agrees with previous compilations. The value of Tsang[12] and Norton and Dryer[13] are virtually the same as the recommended values and thus, for simplicity, are omitted from Figure 2. Figure 3 shows fall-off curves derived from the preferred k_0 and k_∞ values. The resulting collision efficiencies range from 0.1 to 0.05 over the range 1600–2000 K. The curves also fit the oldest data of Cribb *et al.*[8] very well and are in good agreement with the recombination data measured by Bott and Cohen[9] after conversion to dissociation rates. However, the more recent experiments by Cribb *et al.*[10] yield rate coefficients 2–3 times higher than those reported here at Ar gas density of $1\cdot10^{18}$ molecules cm^{-3}. According to Refs. 2, 8 and 10, the rate coefficient for channel (2) is markedly lower than that of reaction (1). The importance of channel (3) is still unknown.

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$CH_3OH + M \rightarrow CH_3 + OH + M$

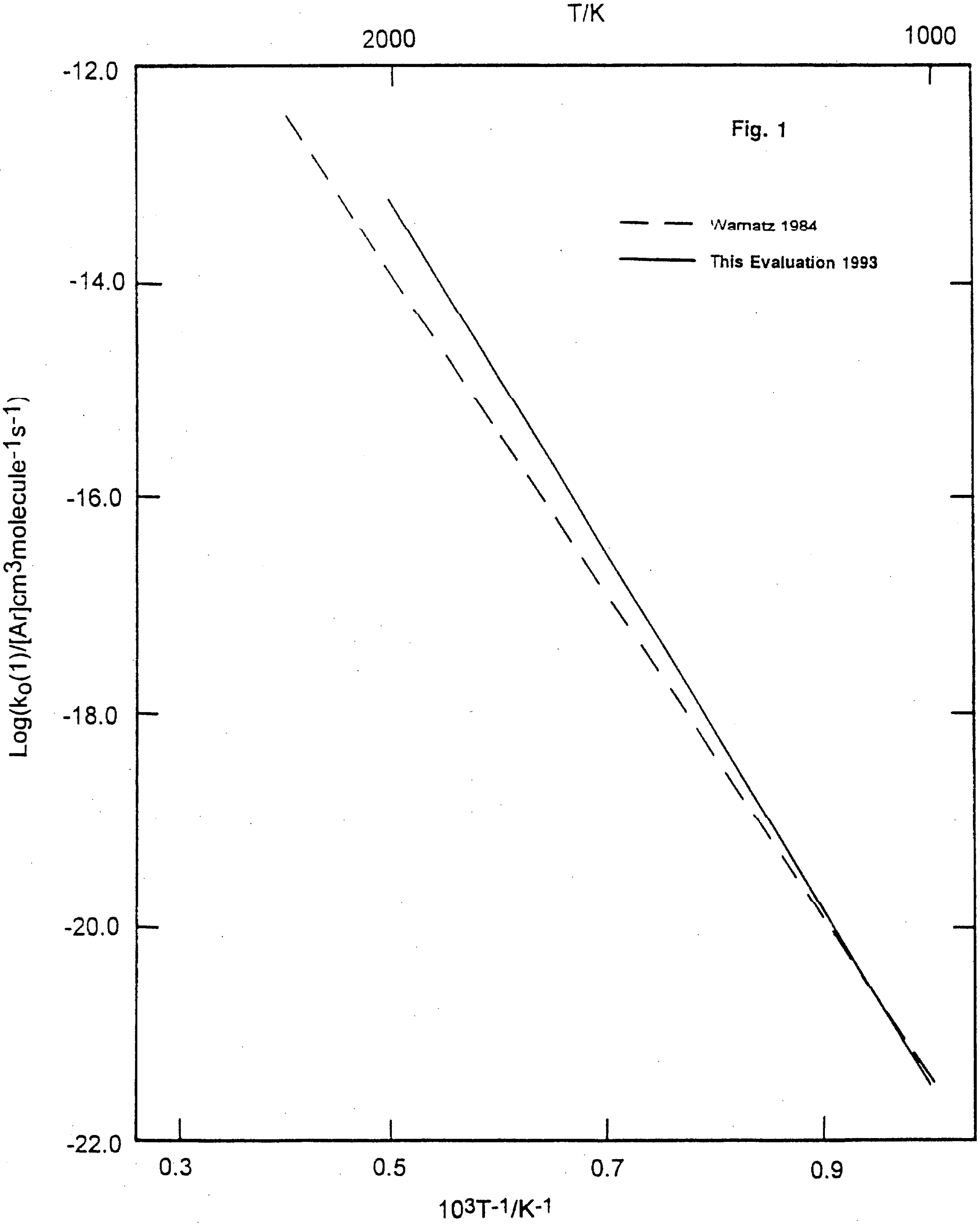
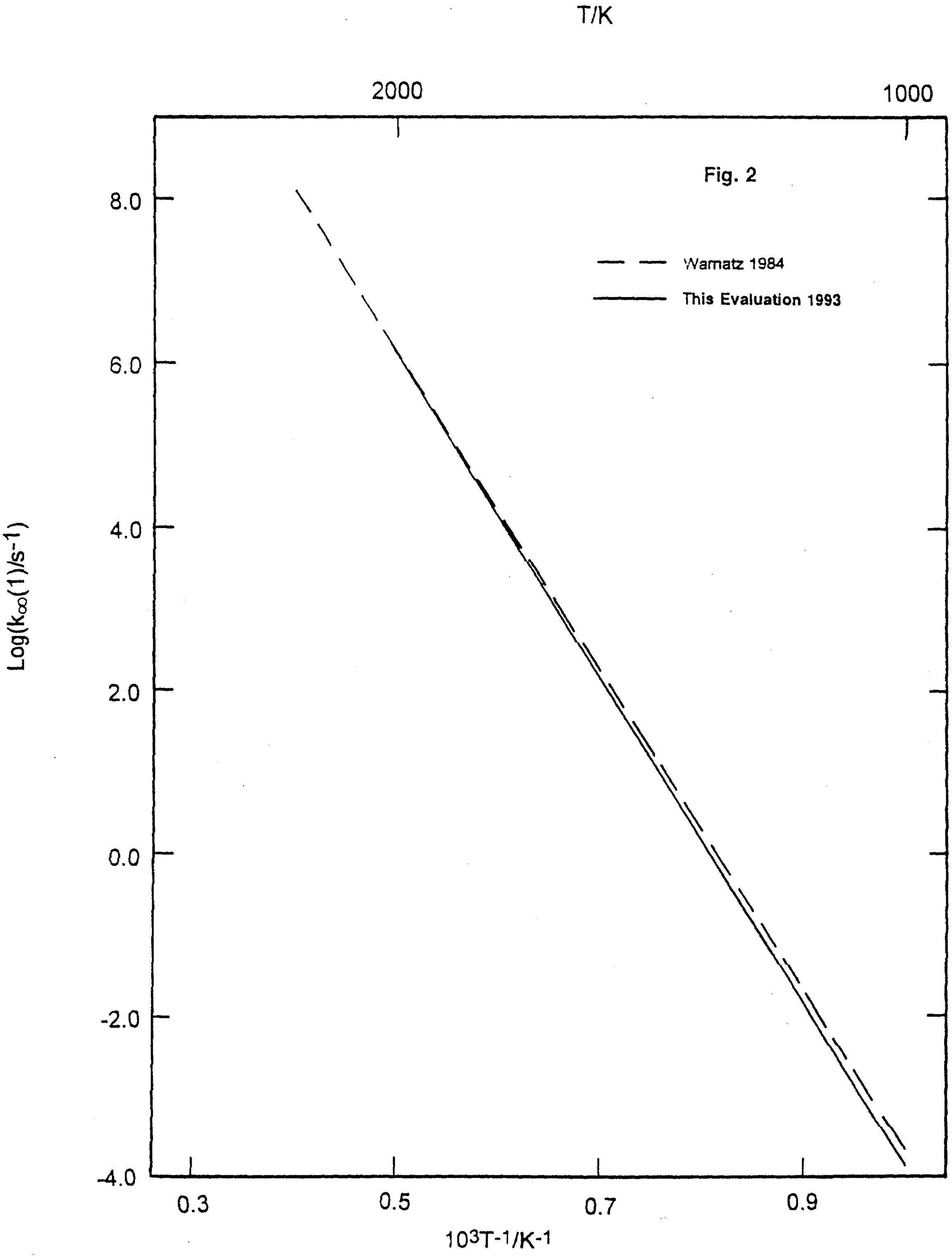


Fig. 1

$CH_3OH + M \rightarrow CH_3 + OH + M$



$CH_3OH + M \rightarrow CH_3 + OH + M$

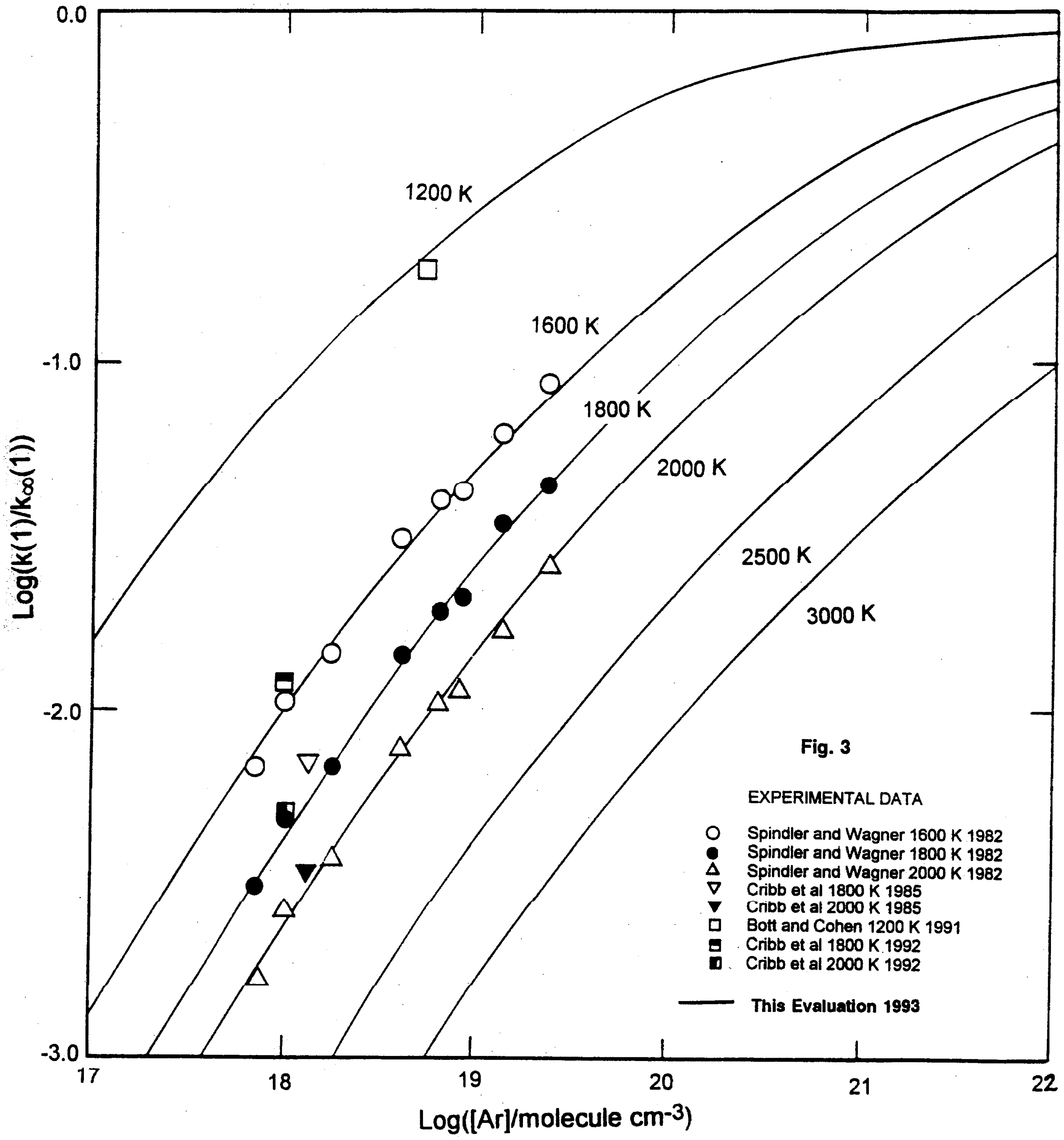


Fig. 3

$$\begin{aligned} OH + C_2H_2 &\rightarrow H_2O + C_2H \quad (1) \\ &\rightarrow CH_2CO + H \quad (2) \\ OH + C_2H_2\ (+ M) &\rightarrow C_2H_2OH\ (+ M) \quad (3) \end{aligned}$$

Thermodynamic Data

$\Delta H^\circ_{298}(1) = 53.1$ kJ mol^{-1}

$\Delta S^\circ_{298}(1) = 11.6$ J K^{-1} mol^{-1}

$Kp(1) = 8.17\cdot10^{2}T^{-0.78}\exp(-6650/T)$

$\Delta H^\circ_{298}(2) = -99.6$ kJ mol^{-1}

$\Delta S^\circ_{298}(2) = -28.1$ J K^{-1} mol^{-1}

$Kp(2) = 5.64\cdot10^{-4}T^{0.57}\exp(+12240/T)$

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

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Comments
Rate Coefficient Measurements			
$1.53\cdot10^{-12}$	1700	Kaiser, 1990[1]	(a)
Reviews and Evaluations			
$k_1 = 4.9\cdot10^{-18}T^2\exp(-3600/T)$	1100–1350	Atkinson, 1989[2]	(b)
$1.0\cdot10^{-10}\exp(-6500/T)$	1000–2000	CEC, 1992[3]	(c)

Comments

(a) Flame study with computer simulation of OH radical profile.

(b) Based on results of Smith *et al.*[4].

(c) See Comments on Preferred Values.

Preferred Values

$k = 1.0\cdot10^{-10}\exp(-6500/T)$ cm^3 molecule^{-1} s^{-1} over range 1000–2000 K.

Reliability

$\Delta\log k = \pm0.1$

Comments on Preferred Values

The recommendations from our previous evaluation[3], which were based on the measurements of Smith *et al.*[4] and Fenimore and Jones[5] are unchanged. The recent study of Kaiser[1] is in good agreement.

At temperatures greater than 1100 K channels (1) and (2) predominate but below 1100 K, at atmospheric pressure, channel (3) becomes significant and the rate constant becomes pressure dependent. Parameters for calculating k_3 are given in Ref. 7. Miller and Melius[6] performed statistical calculations of rate constants based on a BAC-MP4 surface. They concluded that channel (1) is the major high temperature process and is a factor of ≈ 5–10 faster than other channels. They calculate that the second most significant channel leads to formation of $HOC_2H + H$, a process which is ≈ 8 kJ mol^{-1} less endothermic than channel (1). Their calculations could be used as a rough guide of channel efficiencies.

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$OH + C_6H_5CH_3 \rightarrow H_2O + C_6H_5CH_2$ (1)
$\rightarrow H_2O + C_6H_4CH_3$ (2)
$OH + C_6H_5CH_3 (+ M) \rightarrow C_6H_5(OH)CH_3 (+ M)$ (3)

Thermodynamic Data

$\Delta H^\circ_{298}(1) = -130.8$ kJ mol^{-1}
$\Delta S^\circ_{298}(1) = 1.4$ J K^{-1} mol^{-1}
$Kp(1) = 3.2 \cdot 10^{-1} T^{0.23} \exp(+15730/T)$

$\Delta H^\circ_{298}(2) = -17.6$ kJ mol^{-1}
$\Delta S^\circ_{298}(2) = 1.4$ J K^{-1} mol^{-1}
$Kp(2) = 3.7 \cdot 10^{-1} \exp(+2130/T)$

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

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Comments
Rate Coefficient Measurements			
$k_1 = 5.0 \cdot 10^{-12} \exp(-453/T)$	380–473	Perry, Atkinson, and Pitts, 1977[1]	(a)
$k_3 = 3.2 \cdot 10^{-13} \exp(+805/T)$	296–325		
$k_1 = 1.7 \cdot 10^{-11} \exp(-1510/T)$	1700–2800	McLain, Jachimowski, and Wilson, 1979[2]	(b)
$k_1 = 2.1 \cdot 10^{-11} \exp(-1300/T)$	500–1000	Tully *et al.*, 1981[3]	(c)
$k_3 = 3.8 \cdot 10^{-12} \exp(+180/T)$	213–298		
$k_3 = 6.4 \cdot 10^{-12}$	298	Ohta and Ohyama, 1985[4]	(d)
$k_3 = 5.4 \cdot 10^{-12}$	298	Edney, Kleindienst, and Corse, 1986[5]	(e)
$4.8 \cdot 10^{-12}$	773	Baldwin, Scott and Walker, 1987[6]	(f)
$k_3^0 = [He] 5 \cdot 10^{-30} \exp(+1300/T)$	298–353	Bourmada *et al.*, 1988[7]	(g)
$k_3^\infty = 4.6 \cdot 10^{-13} \exp(+760/T)$	298–353		
Reviews and Evaluations			
$1.81 \cdot 10^{-12} \exp(355/T)$	213–324	Atkinson, 1989[8]	(h)
$7.58 \cdot 10^{-18} T^2 \exp(11/T)$	473–1046		
$k_1 = 8.6 \cdot 10^{-15} T \exp(-440/T)$	400–1200	CEC, 1992[9]	(i)

Comments

(a) Flash photolysis–resonance fluorescence technique at total pressures around 10 Torr. The addition channel (2) is the dominant reaction pathway for temperatures below 325 K. The H abstraction reaction (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 concentrations [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 the side-chain hydrogen abstraction channel (1) is the dominant reaction routes at higher temperatures. The rate expression for channel (1) was estimated.

(d) Hexane was used as a reference compound. Photolysis of H_2O_2 was the source of OH. Rate coefficient for OH consumption by (channel (3)) was evaluated at atmospheric pressure.

(e) Rate constant value for reaction (3) derived by using a relative rate technique. Photolysis of methyl nitrite was the source of OH.

(f) Small amounts of toluene (0.05–0.5%) were added to slowly reacting mixtures of $H_2 + O_2$ at 773 K. Under the experimental conditions the hydrogen/oxygen system provides a reproducible source of radicals such as H, O, and OH. Measurement of the relative consumption of the additive and molecular hydrogen permits the evaluation of the rate constants for the reaction of H, O, and OH with the toluene.

(g) Discharge flow study with OH detection by resonance fluorescence. He used as carrier gas. Measurements performed at 298 and 353 K in the fall-off pressure range between 0.5 and 9.8 Torr. Authors derived from their measurements k_0 and k_∞ using Troe's formalism with $F_c = 0.6$. The rate constant expressions are given here in Arrhenius form.

(h) Low temperature recommendations based on data from Refs. 1, 3, and 10. High temperature recommendations based on data from Refs. 1 and 3.

(i) See Comments on Preferred Values.

Preferred Values

$k_1 = 8.6 \cdot 10^{-15} T \exp(-440/T)$ cm^3 molecule^{-1} s^{-1} over range 400–1200 K.

Reliability

$\Delta \log k_1 = \pm 0.5$ at 400 K reducing to ± 0.3 at 1200 K.

Comments on Preferred Values

The recommendations are unchanged from our previous evaluation[9]. The recent study of Bourmada *et al.*[7] is in agreement with the previous studies which indicate that the dominant reaction pathway at and below room temperature is the addition of the OH radical (channel (3)). Side-chain hydrogen abstraction seems to be the main reaction at higher temperatures (channel (1)). The new data are considered reliable, but owing to the pressure dependence of reaction (3) a rate expression is not recommended for that channel. For channel (1) the indirect data of Ref. 2 have not been considered in deriving the rate constant expression and the recommendation for channel (1) is only made for an intermediate temperature range of about 800 degrees.

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$OH + C_6H_5CHO \rightarrow H_2O + C_6H_5CO$ (1)
$\rightarrow H_2O + C_6H_4CHO$ (2)

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

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Comments
Rate Coefficient Measurements			
$1.4 \cdot 10^{-11}$	298	Niki *et al.*, 1978[1]	(a)
$1.18 \cdot 10^{-11}$	298	Kerr and Sheppard. 1981[2]	(b)
Reviews and Evaluations			
$1.29 \cdot 10^{-11}$	298	Atkinson, 1989[3]	(c)

Comments

(a) Photolysis of $C_6H_5CHO/C_2D_4/HONO$ mixtures. Loss of reactants monitored by FTIR. k measured relative to $k(OH + \text{ethylene-}d_4) = 8.78 \cdot 10^{-12}$ cm^3 molecule^{-1} s^{-1}, which was measured relative to $k(OH + C_2H_4)$ in the same study. The value used to calculate the entry in the table is taken from Ref. 3, i.e. $k(OH + C_2H_4) = 8.52 \cdot 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

(b) Photolysis of $C_2H_5CHO/C_2H_4/HONO$ mixtures. Loss of reactants monitored by gas chromatography. k measured relative to $k(OH + C_2H_4) = 8.52 \cdot 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

(c) Based on the data of Niki *et al.*[1] and Kerr and Sheppard[2].

Preferred Value

$k = 1.3 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1} over the range 298–1500 K.

Reliability

$\Delta \log k = \pm 0.5$ at 1500 K reducing to ± 0.1 at 298 K.

Comments on Preferred Values

Only relative rate determinations at room temperature appear to have been carried out for this reaction. The room temperature data agree well and the techniques used have proved reliable for other reactions for which direct measurements are available. The preferred value follows the recommendation of Atkinson[3] which is the simple mean of the two determinations. At room temperature it is apparent that the reaction proceeds entirely (>90%) by abstraction of the benzylic H-atom; this is expected to be the dominant process up to at least 1000 K. Data for reactions of OH with other aldehydes suggest that the temperature coefficient of k will be small.

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$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$

Thermodynamic Data

$\Delta H^\circ_{298} = -165.3$ kJ mol^{-1}
$\Delta S^\circ_{298} = -20.5$ J K^{-1} mol^{-1}
$Kp = 8.1\cdot10^{-3}T^{0.36}\exp(+19800/T)$

Rate Coefficient Data

k/cm^3 molecule^{-1}s^{-1}	T/K	Reference	Comments
Rate Coefficient Measurements			
$7.0\cdot10^{-10}\exp(-6030/T)$ + $2.2\cdot10^{-13}\exp(+820/T)$ (At 1 atmosphere pressure)	300–1100	Hippler, Troe and Willner, 1990[1]	(a)
Reviews and Evaluations			
$3.1\cdot10^{-12}\exp(-775/T)$	550–1250	CEC, 1992[2]	(b)
$2.2\cdot10^{-13}\exp(600/T)$	230–420	IUPAC, 1992[3]	(c)

Comments

(a) Shock tube studies between 750 and 1120 K. Two different HO_2 sources were used, the thermal dissociation of $CH_3O_2CH_3$ in the presence of excess O_2, and the thermal dissociation of H_2O_2. The rate constant expression was obtained by combination with low temperture data which are reviewed fully in the IUPAC compilation[3]. The new data are also in excellent agreement with Troe's[4] original shock tube data point obtained in 1969. However, particularly at the higher temperatures, the data are sensitive to $k(OH + H_2O_2)$ in a relatively complex interpretation.

(b) Based on data obtained by Lightfoot, Veyret and Lesclaux[5] between 298 and 777 K, which showed some evidence of a minimum at about 700 K, and on Troe's[4] single shock tube point at about 1100 K.

(c) Accepts expression of Kircher and Sander[6].

Preferred Values

$k = 7.0\cdot10^{-10}\exp(-6030/T)$ +
$2.2\cdot10^{-13}\exp(+820/T)$ between 550 and 1250 K.
$k = 7.0\cdot10^{-10}\exp(-6030/T)$ between 850 and 1250 K.

Reliability

$\Delta\log k = \pm0.15$ between 550–800 K, rising to ±0.4 at 1250 K.

Comments on Preferred Values

The expression given by Hippler, Troe and Willner[1] is accepted between 550 and 1250 K, over the range where k appears to be independent of pressure[2,3]. The new data confirm the existence of a deep minimum in the range 700–750 K, and are in excellent agreement with Troe's original data point at 1100 K. A theoretical estimate of k by Patrick, Golden and Barker[7] predicts a minimum in the value of k but at the slightly higher temperature of 1000 K. The experimentally observed increase in k above 800 K is unusually marked and, although theoretically possible, confirmation of the observation both for this reaction and related reactions would be helpful. Fortunately at temperatures above 1250 K, the role of HO_2 radicals in combustion becomes less important. Below 550 K, k becomes pressure dependent and is particularly sensitive to polar gases such as H_2O and NH_3. Between 550 and 850 K, use of the bi-exponential expression is necessary. However, between 850 and 1200 K, use of the recommended single exponential expression is sufficiently accurate. Full details of the low temperature data are given in the IUPAC compilation[3].

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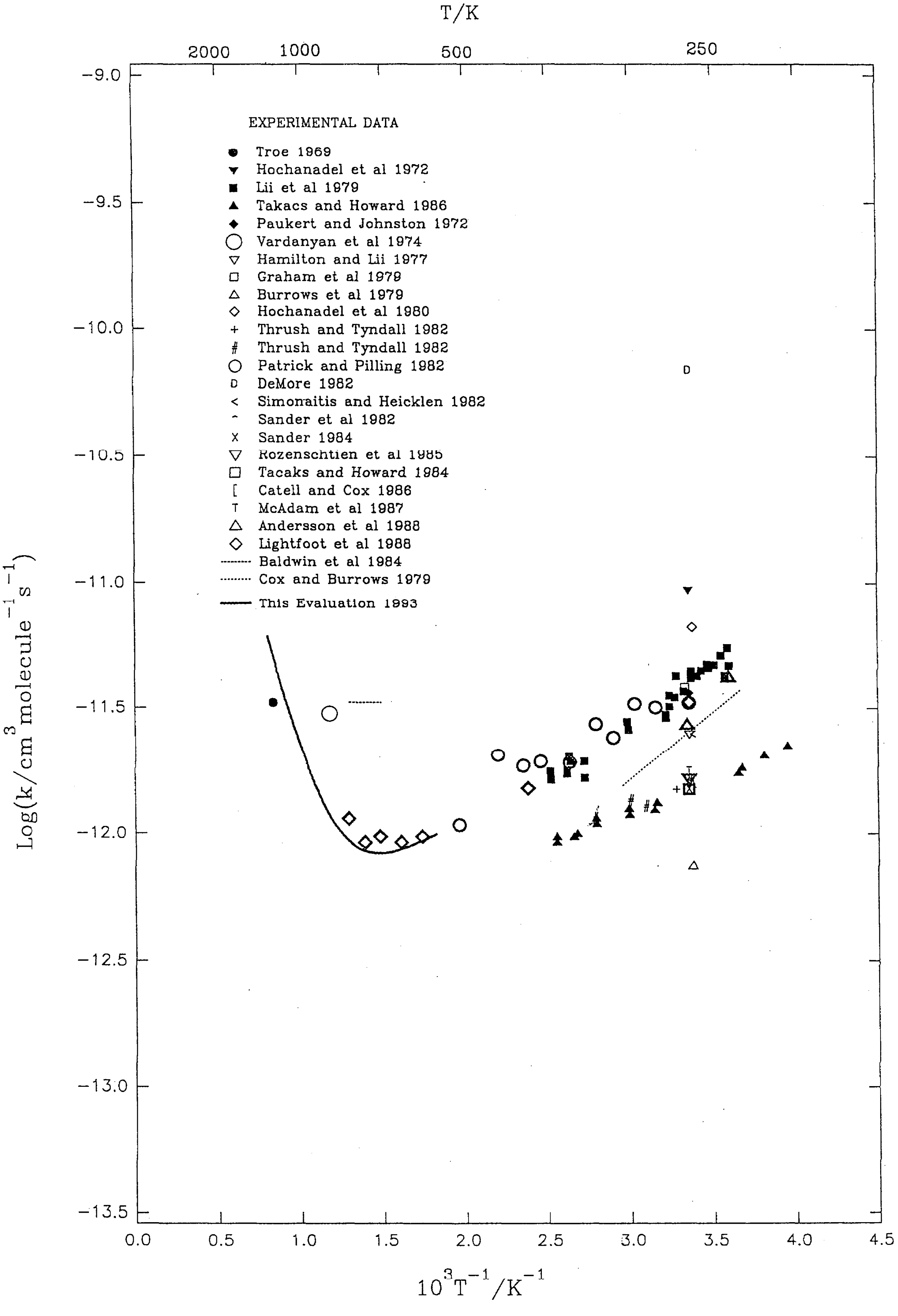
$HO_2 + HO_2 \rightarrow H_2O_2 - O_2$



$HO_2 + CH_3O_2 \rightarrow CH_3OOH + O_2$ (1)
$\rightarrow HCHO + H_2O + O_2$ (2)

Thermodynamic Data

$\Delta H^\circ_{298}(2) = -382.8$ kJ mol^{-1}
$\Delta S^\circ_{298}(2) = 114.3$ J K^{-1} mol^{-1}
$Kp(2) = 1.3 \cdot 10^9 T^{-0.88} \exp(+45140/T)$ atm.

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

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Comments
Rate Coefficient Measurements			(a)
$k = 4.8 \cdot 10^{-12}$	300	Moortgat *et al.*, 1989[1]	(b)
$k_1 = 3.5 \cdot 10^{-12}$			
$k = 4.4 \cdot 10^{-13} \exp(780/T)$	248–573	Lightfoot, Veyret, and Lesclaux, 1990[2]	(c)
$k = 2.9 \cdot 10^{-13} \exp(862/T)$	248–678	Lightfoot *et al.*, 1991[3]	(d)
Branching Ratio Measurements			
$k_1/k = 0.92$ [700 Torr]	295	Wallington and Japar, 1990[4]	(e)
$k_1/k = 0.92$ [15–700 Torr]	295	Wallington, 1991[5]	(e)
Reviews and Evaluations			
$k = 3.8 \cdot 10^{-13} \exp(800/T)$	200–400	NASA, 1992[6]	(f)
$k = 3.8 \cdot 10^{-13} \exp(780/T)$	225–580	IUPAC, 1992[7]	(g)
$k = 5.6 \cdot 10^{-13} \exp(640/T)$	250–600	Wallington, Dagaut, and Kurylo, 1992[8]	(h)
$k = 4.1 \cdot 10^{-13} \exp(790/T)$	230–680	Lightfoot *et al.*, 1992[9]	(i)

Comments

(a) Rate coefficient determinations made prior to 1989 have not been listed explicitly. The measurements can be found in references (10–17) and these have been reviewed in earlier evaluations[6,7].

(b) Modulated photolysis of $CH_3CHO/O_2/N_2$ mixtures at atmospheric pressure with long pathlength UV and FTIR absorption detection. Composite absorptions due to CH_3O_2 and HO_2 recorded at 220 and 250 nm. The waveforms were analysed simultaneously with an assumed reaction scheme. The absorption cross-sections used were for CH_3O, $\sigma_{250}[CH_3O_2] = 4.16 \cdot 10^{-18}$ cm^2 molecule^{-1}, $\sigma_{220}/\sigma_{250} = 0.81$ and for HO_2, $\sigma_{220}[HO_2] = 4.0 \cdot 10^{-18}$ cm^2 molecule^{-1}, $\sigma_{220}[HO_2] = 0.5 \cdot 10^{-18}$ cm^2 molecule^{-1} k_1 was determined by simulating the growth of $[CH_3OOH]$ and the concentration of other products with an assumed reaction scheme.

(c) Flash photolysis of $Cl_2/CH_4/CH_3OH/O_2/N_2$ mixtures with UV absorption detection at 210 and 260 nm. Simultaneous analysis of composite absorption profiles. Cross-sections of CH_3O_2 and HO_2 at the two wavelengths derived from studies on the two self-reactions (with either CH_3OH or CH_4 removed) and NOCl used as an actinometer ($\sigma_{260}[CH_3O_2] = 3.6 \cdot 10^{-18}$, $\sigma_{210}[CH_3O_2] = 2.5 \cdot 10^{-18}$ cm^2 molecule^{-1} and $\sigma_{210}[HO_2] = 5.3 \cdot 10^{-18}$, $\sigma_{260}[HO_2] = 0{\cdot}3 \times 10^{-18}$, $\sigma_{260}[HO_2] = 0.3 \cdot 10^{-18}$ cm^2 molecule^{-1}).

(d) Flash photolysis of $O_2/CH_4/CH_3OH$ mixtures between 600 and 719 K with UV absorption detection. The earlier data of Lightfoot *et al.*[2] were reanalysed using temperature dependent absorption cross-sections[18] and combined with the results of this study.

(e) Growth of CH_3OOH compared to loss of CH_4 following the photolysis of $F_2/CH_4/H_2$/air mixtures using long pathlength FTIR spectroscopy[4]. Conditions arranged so that CH_3O_2 reacted predominantly with HO_2. Complications due to secondary chemistry were mainly avoided by using F_2. The yield of CH_3OOH appeared independent of pressure between 15 and 700 Torr although corrections due to CH_3F formation were made at the lowest pressures[5].

(f) The preferred value at 298 K is a mean of the rate parameters derived by Cox and Tyndall[11], McAdam *et al.*[13], Kurylo and Wallington[14] (as amended in Dāgaut *et al.*[17]), Jenkin *et al.*[16], Moortgat *et al.*[1] and Lightfoot *et al.*[2]. The temperature coefficient was obtained as a rounded-off average of the three temperature-dependent studies[2,11,17] with the A-factor adjusted to give the recommended value of k_{298}.

(g) The recommended rate coefficient at 298 K is the mean of those reported by Dāgaut *et al.*[17], Jenkin *et al.*[16], Moortgat *et al.*[1], Lightfoot *et al.*[2] and Cox and Tyndall[11]. The temperature coefficient is taken from Lightfoot *et al.*[2] and the A-factor adjusted to give the preferred value of k at 298 K.

(h) Based on a single Arrhenius fit of all the available kinetic data excluding the determination by Kan *et al.*[12]. Both values reported by Jenkin *et al.*[16] and Moortgat *et al.*[1] were included. The reaction was assumed to give only CH_3OOH and O_2 as reported by Wallington and Japar[4].

(i) The preferred value at 298 K is a simple mean of the rate parameters derived by Cox and Tyndall[11], Jenkin *et al.*[16], Moortgat *et al.*[1], and Lightfoot *et al.*[2,3], which excludes the low values reported by Kurylo *et al.*[15] and Kan *et al.*[12]. The temperature coefficient was obtained as a rounded-off average of the three latest temperature-dependent studies (Dagaut *et al.*[17], Lightfoot *et al.*[2] and Lightfoot *et al.*[3]), with the *A*-factor adjusted to give the recommended value of k_{298}.

The recent work of Wallington and Japar[4], and Wallington[5] suggests that the only product channel is that leading to the formation of CH_3OOH and O_2.

Preferred Value

$k = 4.1 \cdot 10^{-13} \exp(790/T)$ over the range 298–700 K.
$k_1/k = 1.0 \pm 0.1$ over the range 298–700 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K increasing to ± 0.3 at 700 K.

Comments on Preferred Values

The independent reviews undertaken by Wallington *et al.*[8] and Lightfoot *et al.*[9] have critically evaluated all the kinetic and mechanistic data available on this reaction. The preferred value is that given by Lightfoot *et al.*[9] rather than that determined by Wallington *et al.*[8] due to the incorporation of the more extensive high temperature data from the Bordeaux group[3] in the recommendation made by Lightfoot *et al.*[9]. Wallington *et al.*[8] included the kinetic measurements of Kurylo *et al.*[15] in their Arrhenius analysis which gives a value of the rate constant significantly lower at 298 K than all the other direct measurements. The temperature dependence reported by Kurylo and co-workers (Dagaut *et al.*[17]) is, however, in very good agreement with the other recent temperature dependent studies, suggesting a possible systematic error in their absolute *k* values. The latest IUPAC evaluation[7] does not include the recent study by the Bordeaux group[3], and, for that reason, differs slightly from the present evaluation.

The recent studies of Wallington and Japar[4] and Wallington[5] indicate that channel (1) is the major reaction pathway and this should be assumed for modelling purposes. Further support for this is provided by Lightfoot *et al.*[3] who could only interpret their high temperature data if the reaction was assumed to give mainly CH_3OOH and O_2.

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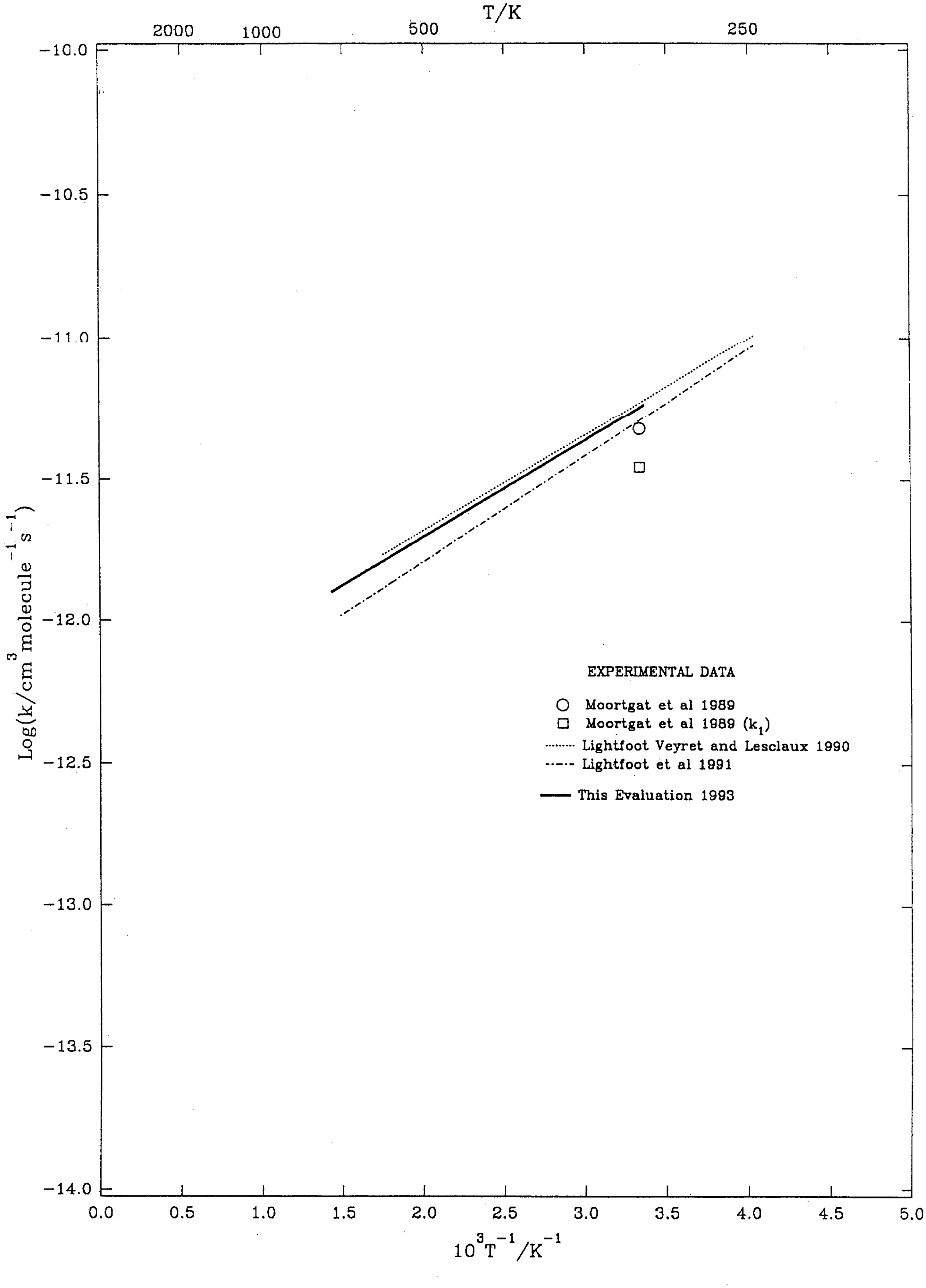
$HO_2 + CH_3O_2 \rightarrow CH_3OOH + O_2$
$\rightarrow HCHO + H_2O + O_2$



$HO_2 + C_6H_5CH_3 \rightarrow H_2O_2 + C_6H_5CH_2$ (1)
$\rightarrow H_2O_2 + C_6H_4CH_3$ (2)

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

k/cm^3 molecule^{-1}s^{-1}	T/K	Reference	Comments
Rate Coefficient Measurements			
$6.9 \cdot 10^{-17}$	773	Baldwin, Scott, and Walker, 1986[1]	(a)

Comments

(a) Studies of the relative rate of consumption of H_2 and toluene when traces of toluene were added to slowly reacting mixtures of $H_2 + O_2$ at 773 K. Interpretation of results gave $(k_1 + k_2)/k_3^{1/2} = 6.5 \cdot 10^{-10}$(cm^3 molecule^{-1} s^{-1})$^{1/2}$; $k_3 = 3.1 \cdot 10^{-12}\exp(-775/T)$cm^3 molecule^{-1} s^{-1} for $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ (see present recommended value).

Preferred Values

$k_1 = 6.6 \cdot 10^{-13}\exp(-7080/T)$ cm^3 molecule^{-1} s^{-1} over range 600–1000 K.

$k_2 = 9 \cdot 10^{-12}\exp(-14500/T)$ cm^3 molecule^{-1} s^{-1} over range 600–1000 K.

Reliability

$\Delta\log k_1 = \pm 0.3$ at 750 K rising to ± 0.5 at 600 K and 1000 K.

$\Delta\log k_2 = \pm 1.0$

Comments on Preferred Values

The value at 773 K is the only experimental determination of $(k_1 + k_2)$. The value of $(k_1 + k_2)/k_3^{1/2}$ is reliable, where k_3 refers to the reaction $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$, and any error in k_3 is reduced by 50% in calculating $(k_1 + k_2)$. On thermochemical grounds $k_2 \leqslant 0.001\, k_1$ at 773 K. The preferred values of k_1 and k_2 are based on the A factor for HO_2 + $(CH_3)_3CC(CH_3)_3$ (per C—H bond)[2] with a reduction in A_1 by a factor of 8 (per C—H bond) due to loss of entropy of activation from increased electron delocalization in the emerging $C_6H_5CH_2$ radical. If k_1 and k_2 obey the non-Arrhenius equation $AT^n\exp(-E/RT)$ with n likely to be between 2 and 3, then extrapolation will lead to low values of k_1 and k_2 above 1000 K.

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$HO_2 + C_6H_5CH_2CH_3 \rightarrow H_2O_2 + C_6H_5CHCH_3$ (1)
$\rightarrow H_2O_2 + C_6H_5CH_2CH_2$ (2)
$\rightarrow H_2O_2 + C_6H_4CH_2CH_3$ (3)

Rate Coefficient Data

k/cm^3 molecule^{-1}s^{-1}	T/K	Reference	Comments
Rate Coefficient Measurements			
$3.0 \cdot 10^{-16}$	773	Baldwin, Scott, and Walker, 1992[1]	(a)

Comments

(a) Studies of the relative rate of consumption of H_2 + ethylbenzene when traces of ethylbenzene were added to slowly reacting mixtures of $H_2 + O_2$ at 773 K. Interpretation of results gave $(k_1 + k_2 + k_3)/k_4^{1/2} = 2.8 \cdot 10^{-9}$ (cm^3 molecule^{-1} s^{-1})$^{1/2}$; $k_4 = 3.1 \cdot 10^{-12}\exp(-775/T)$cm^3 molecule^{-1} s^{-1} for $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ (see present recommended value).

Preferred Values

$k_1 = 4.4 \cdot 10^{-13}\exp(-5680/T)$ cm^3 molecule^{-1} s^{-1} between 600 and 1000 K.

$k_2 = 5.3 \cdot 10^{-12}\exp(-9760/T)$ cm^3 molecule^{-1} s^{-1} between 600 and 1000 K.

$k_3 = 9 \cdot 10^{-12}\exp(-14500/T)$ cm^3 molecule^{-1} s^{-1} between 600 and 1000 K.

Reliability

$\Delta\log k_1 = \pm 0.3$ at 750 K rising to ± 0.5 at 600 K and 1000 K.

$\Delta\log k_2 = \pm 0.5$

$\Delta\log k_3 = \pm 1.0$

Comments on Preferred Values

The value at 773 K is the only experimental determination of $(k_1 + k_2 + k_3)$. The value of $(k_1 + k_2 + k_3)/k_4^{1/2}$ is reliable, where k_4 refers to the reaction $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$, and any error in k_4 is reduced by 50% in calculating $(k_1 + k_2 + k_3)$. On thermochemical grounds $k_3 \approx 0.00025\, k_1$ at 773 K. Assuming $k_2 = 0.5\, k$ ($HO_2 + C_2H_6$), then with $k_1 + k_2 = 3.0 \cdot 10^{-16}$ and

$k(HO_2 + C_2H_6) = 3.5\cdot10^{-17}$ cm^3 molecule^{-1} s^{-1} (Ref. 2), then $k_2 = 1.75\cdot10^{-17}$ and $k_1 = 2.8\cdot10^{-16}$ cm^3 molecule^{-1} s^{-1} at 773 K. The preferred values of k_1, k_2 and k_3 are based on the A factor for $HO_2 + (CH_3)_3CC(CH_3)_3$ (per C—H bond)[3] with a reduction in A_1 by a factor of 8 (per C—H bond) due to loss of entropy of activation from increased electron delocalization in the emerging $C_6H_5CHCH_3$ radical. If k_1, k_2 and k_3 obey the non-Arrhenius equation $k = AT^n \exp(-E/RT)$ with n likely to be between 2 and 3, then extrapolation will lead to low values of k_1 and k_2 above 1000 K.

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$N + O_2 \rightarrow NO + O$

Thermodynamic Data
$\Delta H^\circ_{298} = -133$ kJ mol^{-1}
$\Delta S^\circ_{298} = 13.4$ J K^{-1} mol^{-1}
$Kp = 13.21\ T^{-0.13}\exp(+15930/T)$

Rate Coefficient Data

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Comments
Rate Coefficient Measurements			
$3\cdot10^{-12}\exp(-3100/T)$	390–520	Kistiakowsky and Volpi, 1957[1]	(a)
$3\cdot10^{-12}$	1575	Kaufman and Decker, 1959[2]	(b)
$1.4\cdot10^{-11}\exp(-3600/T)$	412–755	Clyne and Thrush, 1961[3]	(c)
$6.3\cdot10^{-12}\exp(-3500/T)$	453–603	Vlastaras and Winkler, 1967[4]	(d)
$2.34\cdot10^{-11}\exp(-4000/T)$	300–910	Wilson, 1967[5]	(e)
$5.5\cdot10^{-12}\exp(-3200/T)$	280–333	Becker, Groth, and Kley, 1969[6]	(f)
$1.08\cdot10^{-16}$	302	Clarke and Wayne, 1970[7]	(g)
$7.5\cdot10^{-17}$	300	Westenberg, Roscoe, and de Haas, 1970[8]	(h)
$2.6\cdot10^{-11}$	2880	Livesey, Roberts, and Williams, 1971[9]	(i)
$7.2\cdot10^{-17}$	298	Winkler *et al.*, 1986[10]	(j)
$8.8\cdot10^{-17}$	298	Barnett, Marston and Wayne, 1987[11]	(k)
Reviews and Evaluations			
$1.1\cdot10^{-14}T\exp(-3150/T)$	300–3000	Baulch, Drysdale, and Horne, 1973[12]	(l)
$1.5\cdot10^{-11}\exp(-3600/T)$	200–300	NASA, 1990[13]	(m)
$1.5\cdot10^{-14}T\exp(-3270/T)$	298–5000	Cohen, 1991[14]	(n)
$4.4\cdot10^{-12}\exp(-3220/T)$	280–333	IUPAC, 1992[15]	(o)

Comments

(a) N atoms produced in a discharge reacted with O_2 in a low pressure stirred flow reactor. k determined from the reduction in the steady-state concentration of N atoms detected by mass spectrometry upon addition of various amounts of O_2.

(b) Oxygen-sensitized decay of NO observed in static reactor using UV spectrophotometric detection of NO_2. k calculated from the ratio $k(N + O_2)/k(N + NO) = 0.07$ measured at 1575 K and the N + NO rate coefficient at this temperature recommended in this evaluation.

(c) Discharge flow study. k derived directly from the first-order decay of N atoms in the presence of excess O_2. [N] measured along the tube by end-point titration with NO.

(d) Discharge flow study. k determined by measuring [O] and [N] at points along the tube. Total [O], including that produced by reaction was measured by titration with excess NO_2 downstream of conversion of unreacted N atoms to O by end-point titration with NO.

(e) Direct measurement of k using discharge flow method with detection of N atoms by electron spin resonance under pseudo-first-order conditions with O_2 in excess.

(f) Static system with nitrogen discharge at low total pressure (10^{-4} - 10^{-1} Torr) in a stainless steel vessel. k determined from the decay of the intensity of the first positive bands of the N-atom recombination afterglow emission in the presence of O_2.

(g) Discharge flow study with $[O_2] \gg [N]$. k determined by measuring [N] at points along tube by adding excess NO and measuring Δ[NO] from change in photoionization current when discharge turned off.

(h) Direct measurement of k using discharge flow method with $[O_2] \gg [N]$ and detection of N atoms by electron spin resonance.

(i) NO concentration profile measured by probe sampling and chemical analysis in the burned gas of an atmospheric pressure premixed propane-oxygen flame to which N_2 had been added. Single value of k at the mean flame temperature was obtained by fitting to a simple mechanism which was more sensitive to k for O + N_2 reaction than for N + O_2. k is misquoted in abstract of the original reference.

(j) Vibrational state distribution of NO product measured using saturated multi-photon ionization in a discharge flow system. The ratio k/k(N + NO) obtained for NO in specific vibrational states from the slope of the variation of the steady-state [NO(v)] with [O_2]. About 34% of the available exothermicity appears in vibrational levels up to $\upsilon = 7$. Using the recommended 298 K value[13] of k(N + NO) = $3.4 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1} gives the value of $k = \Sigma k(\mathrm{v})$ quoted.

(k) Direct measurement of k using discharge flow method with $[O_2] \gg [N]$. Decay of [N] along tube measured by monitoring intensity of the emission of the first positive band of N_2 resulting from the recombination of N atoms.

(l) Evaluation of data measured up to 1971. Recommended expression gives best fit to high and low temperature data.

(m) Recommendation derived from least squares fit to the data of references (1,5,6,7,8,10 and 11).

(n) Review of measurements of k for forward and reverse reaction. Recommended expression derived by combining low temperature data of references (3,4,6–8) with equilibrium constant and the value of k for reverse reaction at high temperatures recommended by Hanson and Salimian[17], and assuming pre-exponential temperature exponent $n = 1.0$.

(o) Previous CODATA recommendation[16], based on mean of 298 K data in references (3, 5–8) and activation energy of Becker *et al.*[6], unchanged because of good agreement with recent studies of Winkler *et al.*[10], and Barnett *et al.*[11].

Preferred Value

$k = 1.5 \cdot 10^{-14} T \exp(-3270/T)$ cm^3 molecule^{-1} s^{-1} over the range 298–5000 K.

Reliability

$\Delta \log k = \pm 0.12$ over the range 298–1000 K rising to ± 0.3 over the range 1000–5000 K.

Comments on Preferred Values

The recommended expression of Cohen[14] is adopted here, with the same uncertainty limits. This not only gives a good fit to the low temperature data, but also to the less well-determined high temperature measurements and is consistent with the rate of the reverse reaction.

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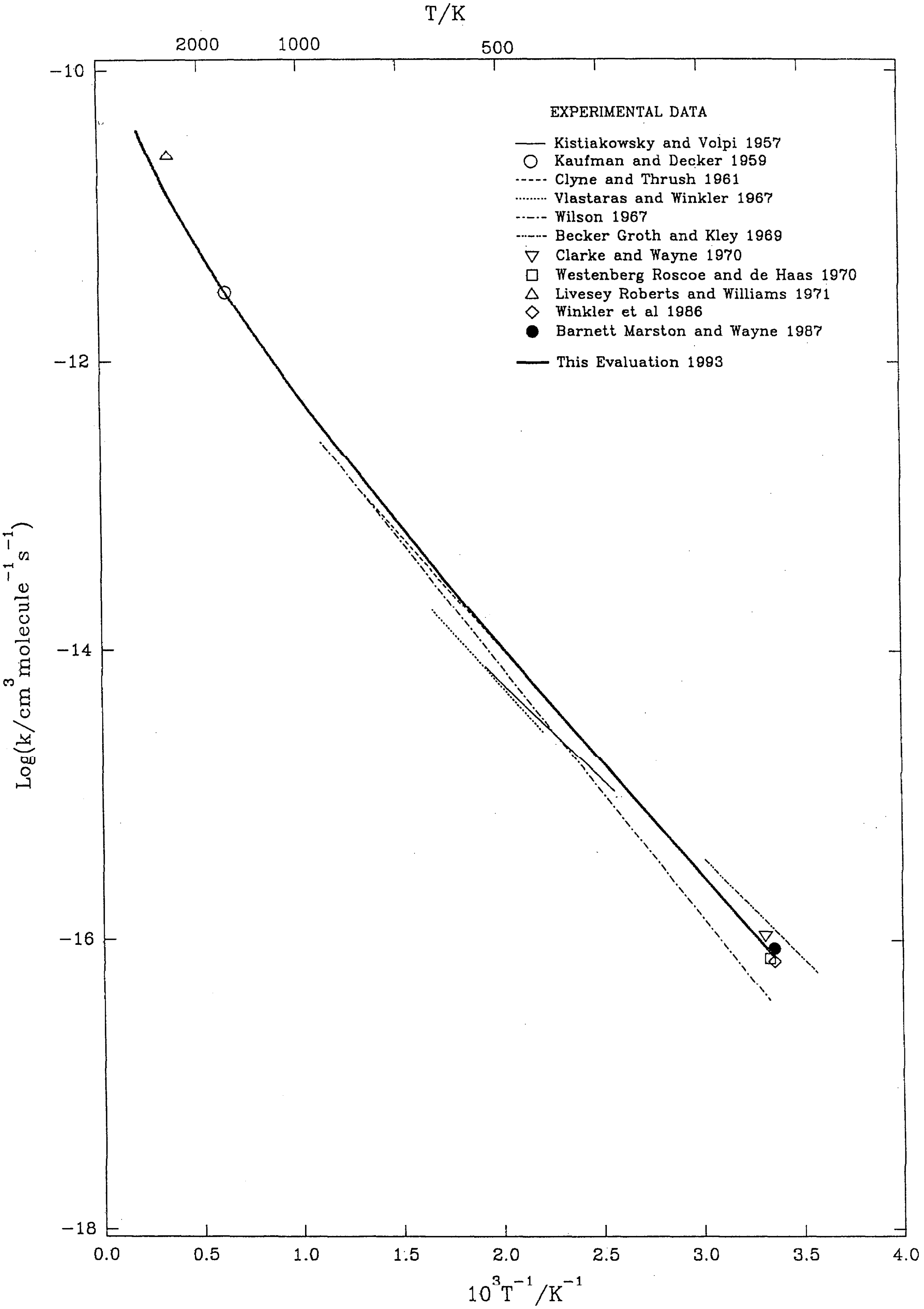
$N + O_2 \rightarrow NO + O$



N + OH → NO + H

Thermodynamic Data

$\Delta H^\circ_{298} = -203.1$ kJ mol^{-1}

$\Delta S^\circ_{298} = -11.6$ J K^{-1} mol^{-1}

$Kp = 4.1\cdot10^{-2}T^{0.26}\exp(+24555/T)$

Rate Coefficient Data

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Comments
Rate Coefficient Measurements			
$4.2\cdot10^{-11}$	320	Campbell and Thrush, 1968[1]	(a)
$7.1\cdot10^{-11}\exp(-790/T)$	1950–2380	Haynes, 1977[2]	(b)
$5\cdot10^{-11}$	298	Howard and Smith, 1980[3]	(c)
$2.21\cdot10^{-10}T^{-0.25}$	250–515	Howard and Smith, 1981[4]	(c)
$7.1\cdot10^{-11}\exp(-790/T)$	1790–2200	Morley, 1981[5]	(d)
$4.2\cdot10^{-11}$	300	Brune, Schwab and Anderson, 1983[6]	(e)
Reviews and Evaluations			
$1.7\cdot10^{-10}$	300–2500	Bowman, 1975[7]	(f)
$6.3\cdot10^{-11}$	300–2500	Miller *et al.*, 1984[8]	(g)
$3.8\cdot10^{-11}\exp(+85/T)$	250–500	IUPAC, 1992[9]	(h)

Comments

(a) The ratio $k/k(\mathrm{O + OH}) = 1.4$ was determined by measuring the catalytic removal of N and O atoms followed photometrically when NO and H_2 were added to a flow of N atoms produced in a discharge. Use of the recommended value[10] for $k(\mathrm{O{+}OH}) = 3.0\cdot10^{-11}$ cm^3 molecule^{-1} s^{-1} leads to the value of k quoted.

(b) Concentration profiles of HCN, NO and total NH_i species (i = 0–3) measured in the burned gases of premixed, fuel-rich ethylene- and acetylene- air flames seeded with NH_3, pyridine or NO, using a probe sampling method. N + OH and N + NO identified as the NO forming and removing reactions. The ratio $k(\mathrm{N + OH})/k(\mathrm{N + NO}) = 1.0$, independent of temperature was determined from analysis of the NO profiles, assuming reactions of the NH_i species to be internally equilibrated. Use of the recommended value for $k(\mathrm{N + NO})$ from this evaluation gives the value of k quoted.

(c) Discharge flow system used to generate steady-state concentration of N atoms; OH radicals formed by flash photolysis of H_2O and their decay monitored by resonance fluorescence under pseudo-first-order conditions with $[\mathrm{N}] \gg [\mathrm{OH}]$. [N] determined by end-point titration with NO.

(d) The ratio $k(\mathrm{N + OH})/k(\mathrm{N + NO}) = 1$ estimated from profiles of NO detected by laser-induced fluorescence in H_2 flames seeded with nitrogen compounds. Use of the recommended value for $k(\mathrm{N + NO})$ from this evaluation gives the value of k quoted.

(e) Direct measurement of k using discharge flow method with $[\mathrm{N}] \gg [\mathrm{OH}]$. OH generated in a movable injector by $F + H_2O$ reaction, with F produced in a CF_4 discharge, and detected by resonance fluorescence or laser magnetic resonance; [N] determined by converting to O atoms with excess NO and measuring calibrated O-atom resonance absorption signal.

(f) Rate coefficient derived by combining the low temperature measurement of Campbell and Thrush[1] with the equilibrium constant and high temperature measurements of k for the reverse reaction[11–13].

(g) Value of k derived for modelling NO formation in combustion systems by combining low temperature measurements of Howard and Smith[4] with shock tube measurements of the reverse rate of Flower *et al.*[14]. The authors point out that extrapolation of the expression of Howard and Smith to high temperatures produced values of k much lower than calculated from the reverse rate data.

(h) Recommendation unchanged from earlier CODATA evaluation[15] which was based on the data of Howard and Smith[3,4].

Preferred Value

$k = 4.7\cdot10^{-11}$ cm^3 molecule^{-1} s^{-1} over the range 300–2500 K.

Reliability

$\Delta\log k = \pm0.1$ at 300 K rising to ±0.3 at 2500 K.

Comments on Preferred Values

The only direct measurements of k are at low temperature (250–500 K). The data are in good agreement, but are sufficiently scattered to make it impossible to discern any temperature dependence of k. The preferred value is the mean of all the low temperature measurements[1,3,4,6] and falls within the range of values of k calculated from the ratio $k/k(\mathrm{N + NO})$ reported in the two flame studies[2,5]. The inconsistency between the measured values of k and the higher value calculated from the equilibrium constant and data for the reverse reaction still needs to be resolved.

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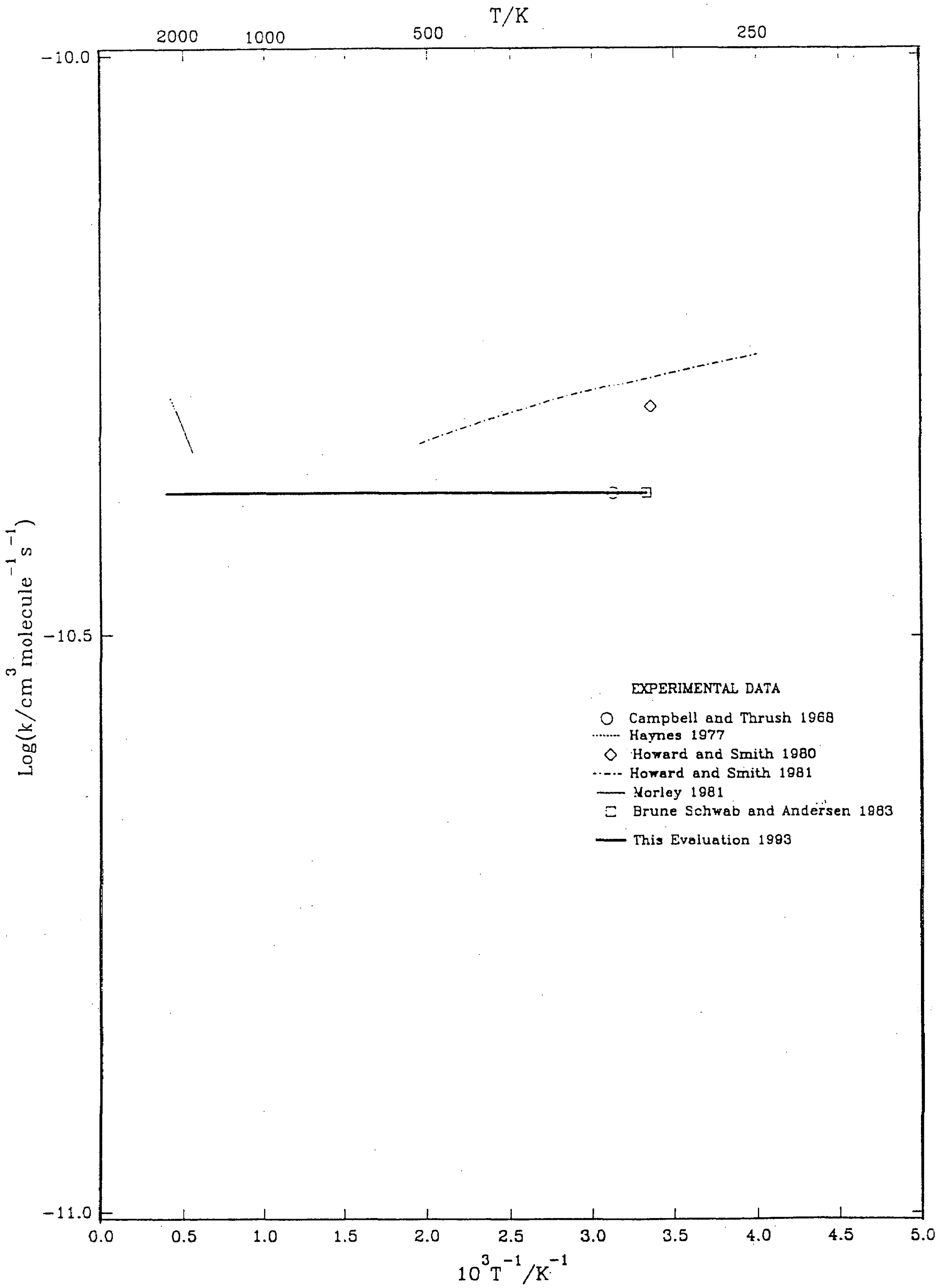
N + OH → NO + H



$N + NO \rightarrow N_2 + O$

Thermodynamic Data

$\Delta H^\circ_{298} = -313.5$ kJ mol^{-1}

$\Delta S^\circ_{298} = -11.3$ J K^{-1} mol^{-1}

$Kp = 0.51T^{-0.10}\exp(+37690/T)$

Rate Coefficient Data

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Comments
Rate Coefficient Measurements			
$5.4\cdot10^{-14}\,T\exp(230/T)$	476–755	Clyne and Thrush, 1961[1]	(a)
$1.7\cdot10^{-11}$	300	Herron, 1961[2]	(b)
$2.2\cdot10^{-11}$	298	Phillips and Schiff, 1962[3]	(c)
$1.8\cdot10^{-11}$	~350	Takezaki and Mori, 1967[4]	(d)
$3\cdot10^{-11}$	298	Lin, Parkes, and Kaufman, 1970[5]	(e)
$8.2\cdot10^{-11}\exp(-410/T)$	298–670	Clyne and McDermid, 1975[6]	(f)
$3.4\cdot10^{-11}$	196–400	Lee, *et al.*, 1978[7]	(g)
$4.5\cdot10^{-11}$	300	Husain and Slater, 1980[8]	(h)
$3.4\cdot10^{-11}$	298	Cheah and Clyne, 1980[9]	(i)
$1.9\cdot10^{-11}$	298	Sugawara, Ishikawa, and Sato, 1980[10]	(j)
$2.2\cdot10^{-11}$	1600–2300	Koshi, *et al.*, 1990[11]	(k)
$7.12\cdot10^{-11}\exp(-787/T)$	1400–3500	Davidson and Hanson, 1990[12]	(l)
$2.4\cdot10^{-11}$	298	Jeoung, Choo, and Benson, 1991[13]	(m)
Reviews and Evaluations			
$2.7\cdot10^{-11}$	300–5000	Baulch, Drysdale, and Horne, 1973[14]	(n)
$5.4\cdot10^{-12}T^{0.3}$	300–4000	Miller, *et al.*, 1984[15]	(o)
$3.1\cdot10^{-11}$	200–400	IUPAC, 1992[16]	(p)
$3.4\cdot10^{-11}$	200–300	NASA, 1990[17]	(q)
$3.2\cdot10^{-11} + 1.3\cdot10^{-14}T\exp(230/T)$	200–4100	Cohen, 1991[18]	(r)

Comments

(a) Discharge flow study. Large excess of O_2 added to flow of N atoms produced residual [NO] in the effluent gas determined by NO + O afterglow intensity. Variation of residual [NO] with [O_2] gave the ratio $k(N + O_2)/k(N + NO) = 0.28\exp(-3500/T)$. Use of the preferred value for $k(N + O_2)$ from this evaluation gives the value of k quoted.

(b) Discharge flow study with mass spectrometric detection of N, and isotopically labelled NO and N_2. k determined from analysis of concentration-time profiles.

(c) Discharge flow study, with mass spectrometric detection of NO. k determined from consumption of NO when added to flow of N atoms.

(d) Pulsed N_2 discharge flow study with time-of-flight mass spectrometric detection of N and NO.

(e) Discharge flow study. N atoms detected by atomic resonance absorption spectroscopy calibrated by chemical titration with NO. Variation of measured absorption with [NO] at fixed reaction time gave k.

(f) Direct measurement of k using the discharge flow method with detection of N atoms by mass spectrometry under pseudo-first-order conditions, $[NO] \gg [N]$.

(g) Direct determination of k using two different techniques, both under pseudo-first-order conditions with $[NO] \gg [N]$ and detection of N atoms by atomic resonance fluorescence. A discharge flow study (p = 1–2 Torr He) gave $k = 2.7\cdot10^{-11}$ cm^3 molecule^{-1} s^{-1}; a flash photolysis study (p = 20–700 Torr N_2) gave $k = 4.0\cdot10^{-11}$ cm^3 molecule^{-1} s^{-1}. No temperature or pressure dependence of k could be claimed with certainty because of scatter in the data nor could any other cause of the discrepancy be identified, so the mean value of the two determinations was reported with 25% error limits.

(h) Direct measurement of k by VUV flash photolysis of N_2O in the presence of N_2 and NO and time-resolved atomic resonance fluorescence detection of N atoms, with $[NO] \gg [N]$.

(i) Direct measurement of k using discharge-flow method with atomic resonance fluorescence detection of N atoms in excess NO.

(j) Direct measurement of k by pulsed radiolysis of N_2 to generate N atoms in the presence of excess NO. Pseudo-first-order decay of [N] followed by time-resolved atomic resonance absorption.

(k) Direct measurement of k using shock tube technique. N atoms generated behind reflected shock waves by 193 nm laser photolysis of NO and first-order decay of [N] followed by atomic resonance absorption spectroscopy. No temperature dependence of k was observed.

(l) Direct measurement of k using shock tube technique. N atoms generated by 193 nm laser photolysis of shock heated NO in Ar and [N] decay followed under first-order conditions by atomic resonance absorption spectroscopy. Uncertainty in k estimated to be ±20% at 1400 K to ±10% at 3500 K.

(m) N atoms produced by a microwave discharge, reacted with NO in a very low pressure reactor and detected by mass spectrometry. k derived from the variation of the steady-state concentration of N with the steady-state concentration of NO in the reactor.

(n) Evaluation of data measured before 1973. Temperature independent value of k recommended based on the mean of the measurements of Phillips and Schiff[3] and Lin *et al.*[5].

(o) Expression derived for the purpose of modelling NO_x chemistry in combustion to obtain consistency between the rate coefficients for the reaction in the forward and reverse directions and the equilibrium constant. The low temperature recommendation of Baulch *et al.*[14] for the forward reaction was combined with the values calculated from the high temperature measurements of the reverse reaction by Monat *et al.*[19] and the equilibrium constant to derive k.

(p) Recommendation unchanged from earlier CODATA[20] evaluation which was based on the mean of the measurements reported in Refs. 6–10. Uncertainty estimated as $\Delta\log k = \pm 0.15$ at 298 K.

(q) Recommendation based on low temperature results of Lee *et al.*[7].

(r) Recommended expression for k is a fit to the combined data sets of Refs. 6, 7, 8 and 12 for the reaction in the forward direction and Monat *et al.*[19] and Thielen and Roth[21] for the reverse reaction.

Preferred Value

$k = 7.1 \cdot 10^{-11} \exp(-790/T)$ cm^3 molecule^{-1} s^{-1} over the range 1400–4000 K.

Reliability

$\Delta\log k = \pm 0.2$ over the range 1400–4000 K.

Comments on Preferred Values

There is quite considerable scatter in the measurements of k even at room temperature, where there are numerous measurements, and uncertainty as to whether or not k is temperature dependent. The only two high temperature studies, which used very similar shock tube methods, have also yielded conflicting results. The data of Koshi *et al.*[11] suggest that the rate constant is temperature independent. The very detailed study of Davidson and Hanson[12] over a large temperature range suggest a small positive temperature dependence in agreement with the low temperature data of Clyne and McDermid[6]. Extrapolation of the Arrhenius expression of Davidson and Hanson[12] cannot accommodate the low temperature data. However, the data of Davidson and Hanson are entirely consistent with the equilibrium constant and the recommended rate of the reverse reaction which is based on measurements made in the same laboratory over the same temperature range. The data of Davidson and Hanson[12] are considered to be the most reliable at high temperatures and their expression is taken for the preferred value of k over the stated temperature range. More data are required at intermediate temperatures to establish the temperature dependence of k down to 300 K.

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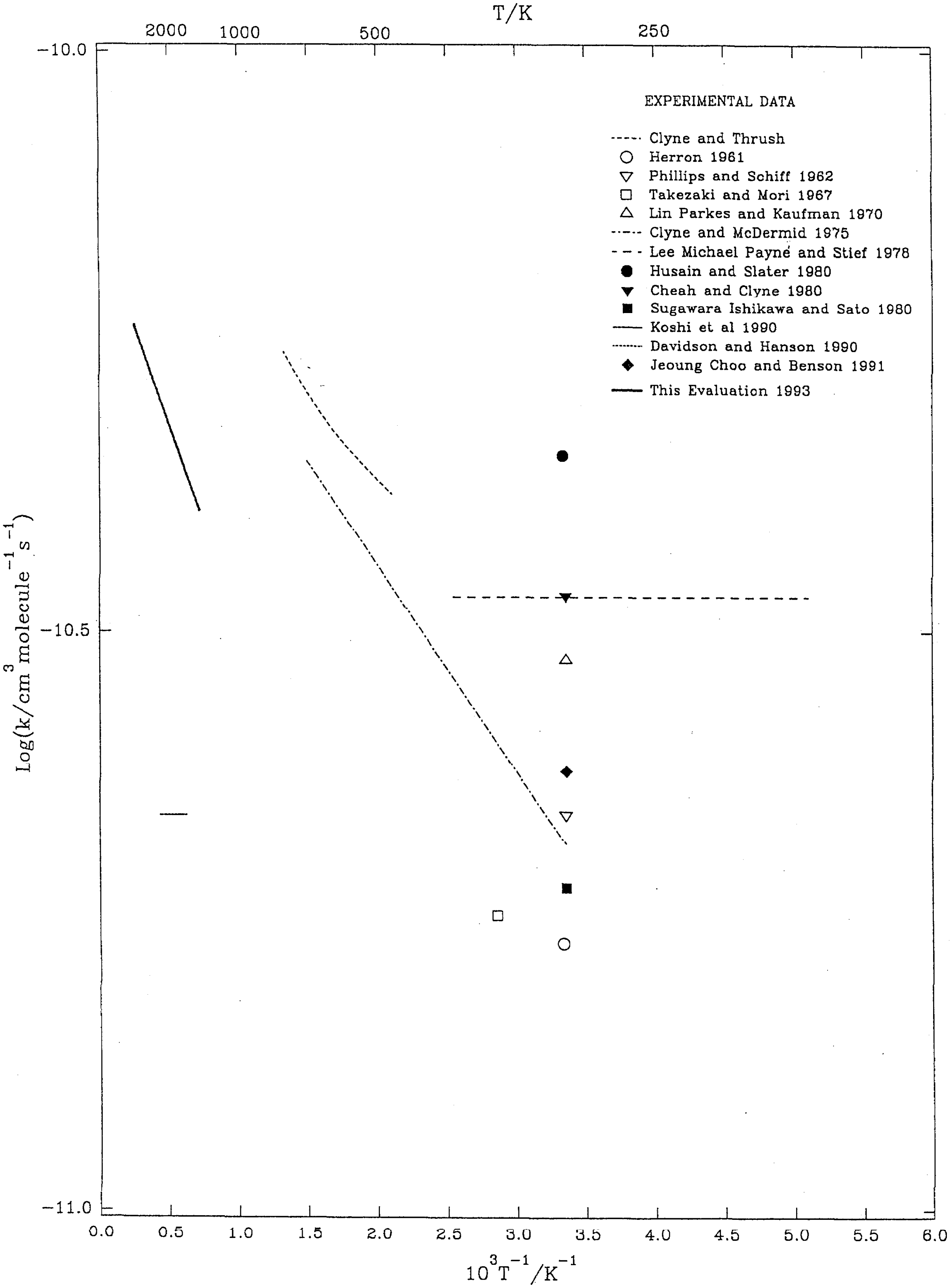
$N + NO \rightarrow N_2 + O$



$$\begin{aligned} \mathbf{NH + O_2} &\rightarrow \mathbf{NO + OH} \quad &\mathbf{(1)} \\ &\rightarrow \mathbf{NO_2 + H} \quad &\mathbf{(2)} \\ &\rightarrow \mathbf{HNO + O} \quad &\mathbf{(3)} \end{aligned}$$

Thermodynamic Data (See Comments on Preferred Values)

$\Delta H^\circ_{298}(1) = -227$ kJ mol^{-1}
$\Delta S^\circ_{298}(1) = 8.05$ J K^{-1} mol^{-1}
$Kp(1) = 8.27\ T^{-0.15} \exp(+27200/T)$

$\Delta H^\circ_{298}(2) = -105$ kJ mol^{-1}
$\Delta S^\circ_{298}(2) = -31.7$ J K^{-1} mol^{-1}
$Kp(2) = 2.22\cdot10^{-4}T^{0.66} \exp(+12900/T)$

$\Delta H^\circ_{298}(3) = -7.73$ kJ mol^{-1}
$\Delta S^\circ_{298}(3) = -4.65$ J K^{-1} mol^{-1}
$Kp(3) = 9.64\cdot10^{-2}T^{0.24} \exp(+1060/T)$

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

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Comments
Rate Coefficient Measurements			
$8.5\cdot10^{-15}$	296	Zetzsch and Hansen, 1978[1]	(a)
$<3.32\cdot10^{-14}$	300	Pagsberg *et al.*, 1979[2]	(b)
$1.26\cdot10^{-13} \exp(-770/T)$	268–543	Hack, Kurzke, and Wagner, 1985[3]	(c)
$k_1 = 7.47\cdot10^{-11} \exp(-5000/T)$	1523–2254	Bain *et al.*, 1986[4]	(d)
$5.81\cdot10^{-11} \exp(-8600/T)$	2200–3270	Mertens *et al.*, 1991[5]	(e)
Reviews and Evaluations			
		Hanson and Salimian, 1984[6]	(f)
$1.26\cdot10^{-13} \exp(-770/T)$	270–550	CEC, 1992[8]	(g)

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) Pulsed radiolysis of NH_3/O_2 mixtures. [NH] monitored by absorption spectroscopy. Decay of [NH] fitted by computer modelling of 23 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; $k \leq (1 \pm 2)\cdot10^{-15}$ cm^3 molecule^{-1} s^{-1} obtained.

(d) Ammonia-oxygen flame study with molecular beam sampling coupled to a mass spectrometer. Results fitted to a complex mechanism, for NO formation, involving numerous assumptions.

(e) Shock tube study. NH produced by the thermal dissociation of HNCO. Time histories of NH ($X^3\Sigma$) and OH($X^2\Pi$) measure behind the shock waves by cw laser absorption at 336 nm and 307 nm, respectively. Results fitted to a large reaction mechanism.

(f) Review of all data to 1984; no expression recommended.

(g) Review of all data to 1991; recommendation based on study of Hack *et al.*[3].

Preferred Values

$(k_1 + k_2) = 1.3\cdot10^{-13} \exp(-770/T)$ cm^3 molecule^{-1} s^{-1} over range 270–550 K.

$k_3 = 6.5\cdot10^{-11} \exp(-9000/T)$ cm^3 molecule^{-1} s^{-1} over range 2200–3500 K.

Reliability

$\Delta\log(k_1 + k_2) = \pm0.25$ over range 270–550 K.
$\Delta\log k_3 = \pm0.5$ over range 2200–3500 K.

Comments on Preferred Values

There are two sets of measurements at high temperatures which differ considerably in their values of k. The more direct study of Mertens *et al.*[4] is preferred but we assign substantial error limits.

At low temperatures the values of Zetzsch and Hansen[1] and Hack *et al.*[3] are in good agreement. These are the basis of our previous recommendations. It was recognized in our previous evaluation that there could be an appreciable increase in E/R at higher temperatures because of changes in the relative importance of the different reaction channels. The results of Mertens *et al.*[4] are in agreement with this expectation.

The measurements of Hack *et al.*[3] indicate that reaction (1) is the predominant channel at low temperatures but at high temperatures the calculations of Melius and Binkley[7] suggest that channel (3) will be more important than (1) and (2). By extrapolating the expression of Hack *et al.*[3] for k ($= k_1 + k_2$) at low temperatures and substracting from the measured high temperature values of k, Mertens *et al.*[4] derived the expression $k_3 = 6.5\cdot10^{-11} \exp(-9000/T)$ cm^3 molecule^{-1} s^{-1}, which is recommended for the range 2200–3500 K. A recent theoretical study by Miller and Melius[9] suggests that channel (3) may be predominant down to 1500 K.

Measurements in the range 300–2000 K are needed to characterize the curvature in the Arrhenius plot.

The thermodynamic data should be used with caution. There are significant uncertainties associated with the data on NH.

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$$\begin{aligned} \mathrm{NH + NO} &\rightarrow \mathrm{H + N_2O} \quad (1)\\ &\rightarrow \mathrm{HN_2 + O} \quad (2)\\ &\rightarrow \mathrm{N_2 + OH} \quad (3) \end{aligned}$$

Thermodynamic Data (See Comments on Preferred Values)

$\Delta H^\circ_{298}(1) = -147$ kJmol^{-1}

$\Delta S^\circ_{298}(1) = -57.3$ J K^{-1} mol^{-1}

$Kp(1) = 4.64\cdot10^{-7}T^{1.10}\exp(+18100/T)$

$\Delta H^\circ_{298}(2) = 47.5$ kJ mol^{-1}

$\Delta S^\circ_{298}(2) = -6.48$ J K^{-1} mol^{-1}

$Kp(2) = 3.58\cdot10^{-2}T^{0.37}\exp(-5530/T)$

$\Delta H^\circ_{298}(3) = -408$ kJ mol^{-1}

$\Delta S^\circ_{298}(3) = -16.7$ J K^{-1} mol^{-1}

$Kp(3) = 0.484\ T^{0.18}\exp(+49000/T)$

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

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Comments
Rate Coefficient Measurements			
$4.8\cdot10^{-11}$	300	Cox, Nelson, and McDonald, 1985[1]	(a)
$5.78\cdot10^{-11}$	269–373	Harrison, Whyte, and Phillips, 1986[2]	(b)
$2.8\cdot10^{-10}\exp(-6400/T)$	2220–3350	Mertens *et al.*, 1991[3]	(c)
$k_1 = 3.3\cdot10^{-12}$	2000	Vandooren *et al.*, 1991[4]	(d)
$k_3 = 2.0\cdot10^{-11}$			
$k_3 = 1.4\cdot10^{-11}$			
Reviews and Evaluations			
—	—	Hanson and Salimian, 1984[5]	(e)
$5.0\cdot10^{-11}$	269–373	CEC, 1992[6]	(f)

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 result.

(c) Shock tube study. NH produced by the thermal dissociation of HNCO. Time histories of NH ($X^3\Sigma$) and OH ($X^2\Pi$) measured behind the shock waves by cw laser absorption at 336 nm and 307 nm, respectively. Results fitted to a large reaction mechanism.

(d) Ammonia oxygen flame study, with fitting to a complex mechanism. Two values of k_3 given corresponding to different values for the rate constant of the NH_2 + NO reaction to which the measurements are sensitive at 2000 K. Our evaluation of the NH_2 + NO rate data favours the value of k_3(NH + NO) = $2.0\cdot10^{-11}$ cm^3 molecule^{-1} s^{-1}.

(e) Review of data to 1985; no recommendation.

(f) Recommendations made for low temperatures only; see Comments on Preferred Values.

Preferred Values

$k = 5.0\cdot10^{-11}$ cm^3 molecule^{-1} s^{-1} over the range 270–380 K.

$k = 2.8\cdot10^{-10}\exp(-6400/T)$ cm^3 molecule^{-1} s^{-1} over range 2220–3350 K.

Reliability

$\Delta\log k = \pm0.2$ over the range 270–380 K.

$\Delta\log k = \pm0.5$ over the range 2220–3350 K.

Comments on Preferred Values

The recent study of Mertens *et al.*[3] is the first direct measurement of k at high temperatures. The previous work of Nip[7], Roose *et al.*[8], Peterson[9] and Morley[10] all involved indirect techniques and gave scattered values much lower than those of Mertens *et al.*[3] which are preferred in this high temperature regime. The single value of Vandooren *et al.*[4] at 2000 K is in agreement with the results of Mertens *et al.*[3].

At low temperatures there is excellent agreement between all of the available studies[1,2,11,12], our preferred value is based on all of them and is unchanged from our previous evaluation[6]. In the only temperature dependent study[2] at low temperatures no variation of k with temperature could be detected over the range 269–373 K. However, the high temperature results give values of k equal to or slightly less than the values found at ambient temperatures. A value of E/R of -520 K is required for the low temperature values to extrapolate to the values obtained by Mertens *et al.*[3] at high temperatures.

By monitoring OH production, Mertens *et al.*[3] were also able to show that over the range 2940–3040 K channel (3) contributes to the extent of (0.19 ± 0.10) of the total k. This is in accord with calculations made by Miller and Melius[13] which suggest that channel (1) is likely to predominate up to 3500 K, and at high temperatures there is a contribution from both channels (2) and (3). It is suggested that the contribution from channel (3), explains the small positive temperature coefficient found by Mertens *et al.*[3].

More work is required, particularly in the 300–2000 K temperature range to establish the temperature dependence. Provisionally, we make separate recommendations for the two temperature ranges with substantial error limits in the case of the high temperature values.

The thermodynamic data should be used with caution. There are significant uncertainties associated with the data on NH.

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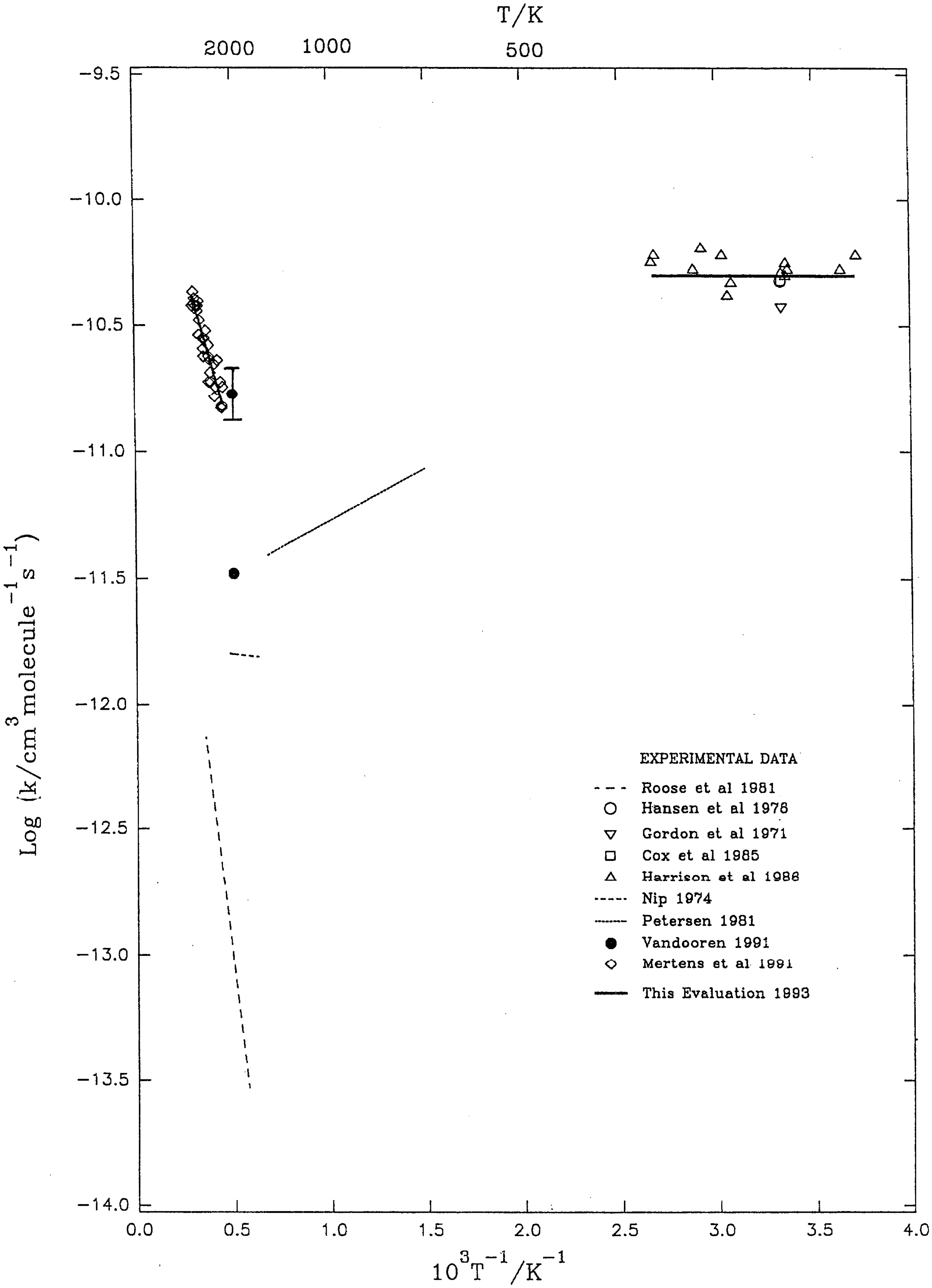
$$\mathrm{NH + NO \rightarrow H + N_2O}$$
$$\mathrm{\rightarrow HN_2 + O}$$
$$\mathrm{\rightarrow N_2 + OH}$$



$NH_3(+M) \rightarrow NH_2 + H(+M)$ (1)
$\rightarrow NH + H_2(+M)$ (2)

Thermoaynamic data

$\Delta H^\circ_{298}(1) = 454.0$ kJ mol^{-1}	$\Delta H^\circ_{298}(2) = 402.2$ kJ mol^{-1}
$\Delta S^\circ_{298}(1) = 116.5$ J K^{-1}	$\Delta S^\circ_{298}(2) = 119.0$ J K^{-1} mol^{-1}
$Kp(1) = 1.5\cdot10^{3}T^{1.0}\exp(-54310/T)$ atm	$Kp(2) = 2.0\cdot10^{3}T^{1.0}\exp(-48090/T)$ atm

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

k/s^{-1}	T/K	[M]/molecule cm^{-3}	References	Comments
Rate Coefficient Measurements				
Low Pressure Range				
$[Ar]7.2\cdot10^{-9}\exp(-40000/T)$	2100–2900	$(7.2\text{–}60)\cdot10^{18}$	Michel and Wagner, 1965[1]	(a)
$[Ar]4.2\cdot10^{-8}\exp(-45800/T)$	2100–2900		Henrici, 1966[2]	(b)
$[Ar]3.8\cdot10^{-9}\exp(-35800/T)$	2500–3000		Takeyama and Miyama, 1966[3]	(c)
$[Ar]6.6\cdot10^{-9}\exp(-41870/T)$	2200–3450	$(1.7\text{–}18)\cdot10^{17}$	Bradley, Butlin, and Lewis, 1967[4]	(d)
$[Ar]9.6\cdot10^{-9}\exp(-38748/T)$	2000–3000	$(2.7\text{–}12)\cdot10^{16}$	Genich, Zhimov, and Manelis, 1975[5]	(e)
$[Kr]2.0\cdot10^{-8}\exp(-45790/T)$	2500–3000	$1.0\cdot10^{18}$	Dove and Nip, 1979[6]	(f)
$[Ar]4.2\cdot10^{-8}\exp(-47200/T)$	2200–3450		Roose, Hanson, and Kruger, 1980[7]	(g)
$[Ar]6.6\cdot10^{-8}\exp(-47270/T)$	2200–3300	$(7.5\text{–}880)\cdot10^{17}$	Holzrichter and Wagner, 1981[8]	(h)
$[Ar]3.0\cdot10^{-8}\exp(-46350/T)$	1740–3050	$(2.7\text{–}108)\cdot10^{17}$	Yumura and Asaba, 1981[9]	(i)
Intermediate Fall-Off Range				
$[Ar]2.3\cdot10^{-8}\exp(-45592/T)$	2050–3070	$(3.0\text{–}5.4)\cdot10^{17}(Ar)$	Yamura *et al.*, 1980[10]	(j)
$2.1\cdot10^{2}$	2400	$1.1\cdot10^{18}$ (Ar)	Holzrichter and Wagner, 1981[8]	(h)
$2.2\cdot10^{3}$		$1.1\cdot10^{19}$		
$1.1\cdot10^{4}$	2400	$8.1\cdot10^{19}$ (Ar)		
$1.6\cdot10^{3}$	2700	$1.1\cdot10^{18}$ (Ar)		
$1.4\cdot10^{4}$		$1.1\cdot10^{19}$		
$7.2\cdot10^{4}$		$8.1\cdot10^{19}$		
$4.4\cdot10^{3}$	2900	$7.5\cdot10^{17}$ (Ar)		
$4.0\cdot10^{4}$		$1.1\cdot10^{19}$		
$1.0\cdot10^{5}$		$2.2\cdot10^{19}$		
High Pressure Range				
$5.5\cdot10^{15}\exp(-54240/T)$	2200–3300		Holzrichter and Wagner, 1981[8]	(h)
Reviews and Evaluations				
$k_0 = [Ar]1.5\cdot10^{-8}\exp(-42400/T)$	2000–3000		Baulch, Drysdale, and Horne, 1973[11]	(k)
$k_0 = [Ar]4.2\cdot10^{-8}\exp(-47200/T)$	1740–3450		Hanson and Salimian, 1984[12]	(l)
$k_0 = [Ar]3.7\cdot10^{-8}\exp(-47040/T)$	1740–3300		Davidson *et al.*, 1990[13]	(m)

Comments

(a) Shock tube study. Decay of [NH_3] monitored by UV absorption at 230–250 nm. Results indicate that the decomposition of NH_3 is unimolecular. No conclusion was given on the mechanism.

(b) Shock tube study of NH_3 dissociation using UV absorption technique to monitor [NH_3] at 230 nm and [NH] at 336 nm. Induction period at lower temperatures.

(c) Shock tube study of 1% NH_3/Ar mixtures. Decay of [NH_3] behind reflected shock monitored at 224.5 nm. Induction period observed at T<2400 K. Rate coefficients derived from the initial decay rates at higher temperatures. Pressures not quoted, probably several atmospheres.

(d) Shock tube study. Decay of NH_3 monitored by IR emission at 3 μm. Rate coefficients obtained from initial decay rates.

(e) Pyrolysis of NH_3 in shock waves. [NH_3] monitored by UV absorption at 220 nm.

(f) Pyrolysis of NH_3 behind reflected shock waves. Mass spectrometric analysis during the reaction. Concentration profiles of NH_3, NH_2, NH, and N_2 measured. Rate coefficient extracted from a computer simulation with 10 reactions.

(g) Shock tube study. Rate coefficients measured behind incident shocks. IR emission of the species NH_3, NH_2 and NH was monitored.

(h) Study of NH_3 decomposition behind incident and reflected shocks in $(7.5\text{–}880)\cdot10^{17}$ molecule cm^{-3} of Ar. The rate coefficients were obtained from the initial slope of the [NH_3] decay as monitored by UV absorption.

(i) Shock tube study. H-atom generation monitored behind incident shocks using atomic resonance absorption at 121.6 nm. Mechanism with correction for boundary layer and wall absorption effects.

(j) Pyrolysis of NH_3 in shock waves. H atoms monitored by Lyman-α absorption at 121.5 nm.

(k) Evaluation of the literature up to 1971.

(l) Evaluation of the literature up to 1981.

(m) Re-evaluation of the data of Refs. 6, 8, 9 and 14 using a value of $1.14 \cdot 10^{-10}\exp(-13216/RT)$ cm^3 molecule^{-1} s^{-1} [15] for the reaction $NH_3 + H \rightarrow NH_2 + H_2$ in the simulation of the pyrolysis of NH_3.

Preferred Values

$k_\infty = 8.3 \cdot 10^{15}\exp(-55170/T)$ s^{-1} over range 2000–3000 K.
$k_0 = [\mathrm{Ar}]\ 7.4 \cdot 10^{-9}\exp(-41560/T)$ s^{-1} over range 2000–3000 K.
$F_c = 0.58\ \exp(-T/4581) + 0.42\ \exp(-T/102)$ for M = Ar over range 2000–3000 K.

Reliability
$\Delta\log k_\infty = \pm 0.4$ over range 2000–3000 K.
$\Delta\log k_0 = \pm 0.3$ over range 2000–3000 K.
$\Delta F_c = \pm 0.1$ for M = Ar over range 2000–3000 K.

Comments on Preferred Values

The available experimental data are far away from the limiting high pressure rate coefficients. The preferred values of k_∞ are based on an SACM analysis for the reverse recombination process[16] and the evaluated equilibrium constant. We have chosen the data from Refs. 2, 6 and 8 to fit theoretical fall-off curves[17]. This procedure leads to collisional efficiencies of about 0.05 when the extrapolated k_0 values are compared with the strong collision limiting low pressure rate coefficients[17,18] evaluated here. In Figs. 1 and 2, the temperature dependence of k_0 and k_∞ is presented. Figure 3 shows the calculated fall-off curves and selected experimental dissociation rate coefficients.

The rate coefficients for the spin-forbidden reaction (2) are about a factor of 40 lower than those of reaction (1)[6,12].

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$$NH_3 + M \rightarrow NH_2 + H + M$$
$$\rightarrow NH + H_2 + M$$

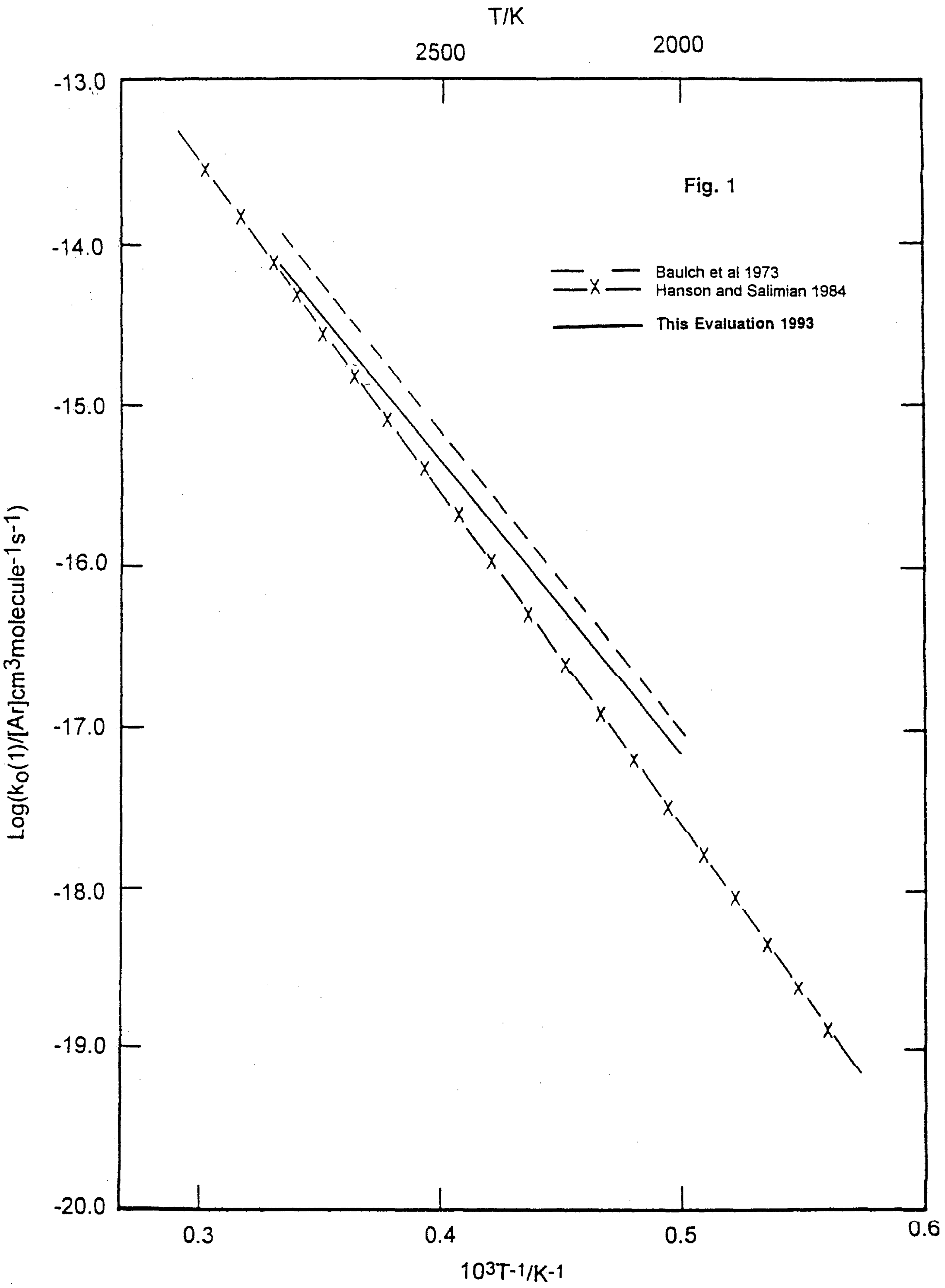
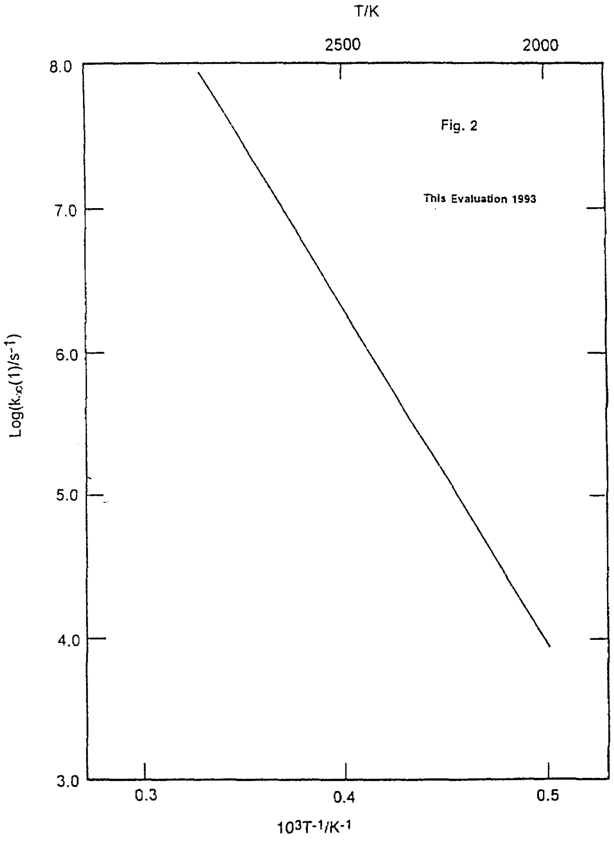
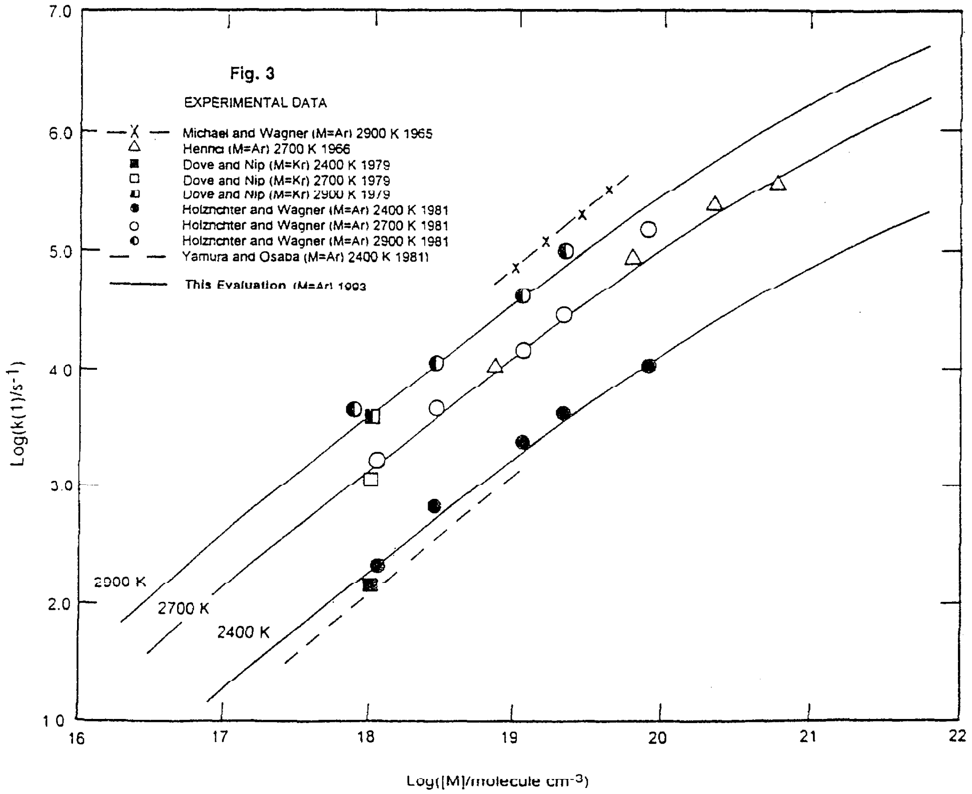


Fig. 1

$$NH_3 + M \rightarrow NH_2 + H + M$$
$$\rightarrow NH + H_2 + M$$





$C + N_2 \rightarrow CN + N$

Thermodynamic Data

$\Delta H^\circ_{298} = 190$ kJ mol^{-1}
$\Delta S^\circ_{298} = 6.2$ J K^{-1} mol^{-1}
$Kp = 0.58\ T^{0.17}\exp(-22890/T)$

Rate Coefficient Data

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Comments
Rate Coefficient Measurements			
$k = 7.5\cdot10^{-11}\exp(-22000/T)$	2350–3290	Lindackers, Burmeister, and Roth, 1990[1]	(a)
$k = 1.0\cdot10^{-10}\exp(-23160/T)$	2660–4660	Dean, Hanson and Bowman, 1990[2]	(b)

Comments

(a) Shock tube study. C atoms generated by pyrolysis of CH_4 or C_2H_6 in Ar and detected behind reflected shock wave by atomic resonance absorption spectroscopy (ARAS). Analysis of perturbations to [C] on addition of N_2 gave k. N atoms also detected by atomic resonance absorption spectroscopy. The A-factor is misquoted in abstract of original reference.

(b) Shock tube study. C atoms generated by pyrolysis of C_3O_2 in Ar and N_2 and decay of [C] followed behind reflected shock wave under first-order conditions by atomic resonance absorption spectroscopy.

Preferred Value

$k = 8.7\cdot10^{-11}\exp(-22600/T)$ cm^3 molecule^{-1} s^{-1} over the range 2000–5000 K.

Reliability

$\Delta\log k = \pm0.2$ over the range 2000–5000 K.

Comments on Preferred Values

The two direct measurements of k using very similar shock tube techniques, are in excellent agreement. The preferred value is derived from averaging the Arrhenius parameters of each expression. It lies well within the broad range of values calculated from the equilibrium constant and indirect measurements of the reverse rate coefficient, which differ by over an order of magnitude.

References

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$$\begin{aligned} \mathrm{C + NO} &\rightarrow \mathrm{CN + O} \quad (1)\\ &\rightarrow \mathrm{CO + N} \quad (2) \end{aligned}$$

Thermodynaic Data

$\Delta H^\circ_{298}(1) = -122.6$ kJ mol^{-1}
$\Delta S^\circ_{298}(1) = -5.1$ J K^{-1} mol^{-1}
$Kp(1) = 19.4\ T^{-0.41}\exp(+13940/T)$

$\Delta H^\circ_{298}(2) = -444.8$ kJ mol
$\Delta S^\circ_{298}(2) = -17.9$ J K^{-1} mol^{-1}
$Kp(2) = 1.5\cdot10^{-1}T^{-0.05}\exp(+53500/T)$

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

k/cm^3 molecule^{-1} s^{-1}	T/K	References	Comments
Rate Coefficient Measurements			
$1.1\cdot10^{-10}$	300	Braun *et al.*, 1968[1]	(a)
$7.3\cdot10^{-11}$	300	Husain and Kirsch, 1971[2]	(b)
$4.8\cdot10^{-11}$	300	Husain and Young, 1975[3]	(c)
$1.6\cdot10^{-11}$	300	Becker, Brockmann, and Wiesen, 1988[4]	(d)
$8.0\cdot10^{-11}$	1550–4050	Dean, Hanson, and Bowman, 1991[5]	(e)
$k_1/k = 0.42\pm0.18$	2430–4040		
$2.7\cdot10^{-11}$	300	Dorthe *et al.*, 1991[6]	(f)

Comments

(a) Single shot flash photolysis of C_3O_2. [C] monitored by light absorption in the 166 nm region and photographic plate photometry. Total pressure 150 Torr.

(b) Single shot flash photolysis of C_3O_2. [C] monitored by resonance absorption at 166 nm. Total pressure 53 Torr and 527 Torr. No pressure dependence of k observed.

(c) Repetitive flash photolysis of C_3O_2. [C] monitored by resonance absorption at 166 nm with signal averaging. Total pressure 27 Torr.

(d) Pulsed laser photolysis at 248 nm of slowly flowing CH_2Br_2/He mixtures. [C] monitored by two-photon LIF at 143.5 nm. Total pressure 2 Torr.

(e) Shock tube study. C atoms produced by pyrolysis of C_3O_2 in C_3O_2/Ar mixtures at temperatures 2435–3737 K, and by laser photolysis at 193 nm of C_3O_2/Ar mixtures in temperature range 1576–1940 K. [C] monitored by ARAS at 156.1 nm. Possible reaction products, CN, N, O, were studied using laser absorption or ARAS. Computer modelling of large reaction scheme shows [CN] profile particularly sensitive to branching ratio.

(f) Fast flow reactor; C atoms produced by discharge in CO/He mixtures. [C] monitored by detection of chemiluminescence from C + OCS reaction.

Preferred Values

$k = 2.5\cdot10^{-11}$ cm^3 molecule^{-1} s^{-1} at 300 K.

$k = 8.0\cdot10^{-11}$ cm^3 molecule^{-1} s^{-1} over the range 1500–4050 K.

$k_1/k = 0.40$; $k_2/k = 0.60$ over the range 2400–4050 K.

Reliability

$\Delta\log k = \pm0.3$ at 300 K.
$\Delta\log k = \pm0.3$ over the range 1500–4050 K.
$\Delta k_1/k = \Delta k_2/k = \pm0.25$.

Comments on Preferred Values

The measured values of k at low temperatures range over a factor of 7. It has been suggested[4] that in the earlier studies, by flash photolysis, this scatter might be due to the high photolysis flash intensities used. The trend in values of k with time as detection methods improved and lower flash intensities could be employed is in accord with this. The most recent study, employing pulsed laser photolysis[4], has produced the lowest value of k yet obtained.

The alternative explanation involves pressure dependence of k but in the sole investigation of pressure effects Braun *et al.*[1] found no evidence for them. In a recent discharge flow study Dorthe *et al.*[6] also obtain a low value of k, identical with that of Becker *et al.*[4], if the usual plug flow assumptions were made, but 65% higher on making corrections for the flow pattern in their flow tube. Our recommendations at 300 K are based on the work of Becker *et al.*[4] and Dorthe *et al.*[6].

At high temperatures (1550–4050 K) there is only one study, by Dean *et al.*[5]. The work seems sound and their results are accepted with slightly enhanced error limits until confirmed by other studies. More studies are required to establish the temperature dependence of k between 300 and 1500 K.

The only investigation of the branching ratio is in the high temperature work of Dean *et al.*[5] which is accepted as the basis of our recommendations.

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$CH + N_2 \rightarrow HCN + N$ (1)
$CH + N_2 (+ M) \rightarrow CHN_2 (+ M)$ (2)

Thermodynamic Data
$\Delta H^\circ_{298}(1) = 13.6$ kJ mol^{-1}
$\Delta S^\circ_{298}(1) = 19.5$ J K^{-1} mol^{-1}
$Kp(1) = 5.0\cdot 10^2 T^{-0.55}\exp(-1420/T)$

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

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Comments
Rate Coefficient Measurements			
$7.14\cdot 10^{-14}$	300	Braun, McNesby, and Bass, 1967[1]	(a)
$1.01\cdot 10^{-12}$	300	Bosnali and Perner, 1971[2]	(b)
$1.3\cdot 10^{-12}\exp(-5540/T)$	1530–1900	Blauwens, Smets, and Peeters, 1977[3]	(c)
$9.3\cdot 10^{-13}$	300	Butler *et al.*, 1980[4]	(d)
$k_\infty = 6.3\cdot 10^{-13}$	300	Wagal *et al.*, 1982[5]	(e)
$k_0 = 2.6\cdot 10^{-31}$ cm^6 molecule^{-2} s^{-1}			
$1.7\cdot 10^{-14}\exp(975/T)$ at 100 Torr Ar	297–675	Berman and Lin, 1983[6]	(f)
$k_\infty = 2\cdot 10^{-11}$			
$k_0 = 2.8\cdot 10^{-31}$ cm^6 molecule^{-2} s^{-1}			
$7.1\cdot 10^{-14}$	300	Duncanson and Guillory, 1983[7]	(g)
$2.0\cdot 10^{-12}\exp(-6840/T)$	1700–2200	Matsui and Yuuki, 1985[8]	(h)
$8.0\cdot 10^{-14}$	300	Becker, Engelhardt, and Wiesen, 1989[9]	(i)
$1.0\cdot 10^{-12}\exp(-7000/T)$	2632–2859	Lindackers, Burmeister, and Roth, 1990[10]	(j)
$7.3\cdot 10^{-12}\exp(-11060/T)$	2500–3820	Dean, Hanson, and Bowman, 1990[11]	(k)
$2.58\cdot 10^{-15}\exp(1150/T)$ at 20 Torr Ar	301–894	Becker *et al.*, 1992[12]	(l)

Comments

(a) Flash photolysis of CH_4. [CH] monitored by flash absorption using photographic recording. Pressures 1–40 Torr.

(b) Pulse radiolysis of CH_4. [CH] monitored by absorption spectroscopy. Pressure not given but likely to be approximately 1 atm.

(c) Flat, nitrogen diluted, flames of C_2H_4, C_2H_6, or CH_4 burning in O_2 studied at pressures in range 18–43 Torr. Concentration profiles of NO, O, OH, H, CH, CH_2, C_2, C_2H and C measured by molecular beam sampling and mass spectrometry. Concentration of both CH and CH_2 shown to correlate with prompt NO. Results can be interpreted in terms of $CH + N_2$ reaction or $CH_2 + N_2$ reaction.

(d) Pulsed laser photolysis at 193 nm of slowly flowing mixtures of $CHBr_3/Ar/N_2$. CH produced by multiphoton absorption by $CHBr_3$ and [CH] monitored by LIF near 430 nm. Total pressure 30–100 Torr.

(e) CH produced by pulsed CO_2 laser multiphoton dissociation of CH_3NH_2, CH_3CN, or c-C_3H_6. [CH] monitored by LIF. Slowly flowing mixtures of source gas and N_2 in Ar buffer gas used at total pressures over range 1–80 Torr. Limiting k_0 and k_{infinity} values obtained using simple Lindemann model.

(f) Pulsed laser photolysis at 266 nm of slowly flowing mixtures of $CHBr_3/Ar/N_2$. [CH] monitored by LIF at 429.8 nm. Total pressure varied over range 25–787 Torr at 297 K, and temperature varied over range 297–675 K at 100 Torr total pressure.

(g) CH produced by pulsed CO_2 laser multiphoton dissociation of CH_3OH. [CH] monitored by LIF at 430.0 nm. Ar (10 Torr) used as buffer gas.

(h) Study of premixed, flat CH_4/air flames by light absorption, by saturation ion current measurements, and by microprobe sample extraction and analysis for total hydrocarbons and NO_x. Total pressure, 760 Torr.

(i) Pulsed laser photolysis at 248 nm of slowly flowing $CH_2Br_2/Ar/N_2$ and $CHClBr_2/Ar/N_2$ mixtures. [CH] monitored by LIF at 430 nm. Total pressure, 2 Torr.

(j) Technique as in (i) but total pressure 20 Torr.

(k) Reflected shock waves in $C_2H_6/N_2/Ar$ mixtures at pressures 1.5–1.79 bar. [N] profiles monitored by atomic resonance absorption. [N] profiles fitted by computer simulation of reaction scheme. Fitting shown to be sensitive to k.

(l) Shock tube studies on $CH_4/N_2/Ar$ and $C_2H_6/N_2/Ar$ mixtures at pressures 0.62–1.02 atm. [CH] profile monitored by laser absorption at 431.131 nm. [N] profile monitored in some experiments by atomic resonance absorption. [CH] profiles fitted using computer simulation of reaction scheme; fitting shown to be sensitive to k.

Preferred Value

$k = 2.6\cdot 10^{-12}\exp(-9030/T)$ cm^3 molecule^{-1} s^{-1} over the range 2000–4000 K at $p < 760$ Torr.

Reliability

$\Delta\log k = \pm 0.3$ over range 2000–4000 K at $p < 760$ Torr.

Comments on Preferred Values

Since this reaction was first suggested as a source of 'prompt' NO in flames its kinetics have been the subject of a number of studies. At low temperatures the rate constant has been shown to be pressure dependent and to have a negative temperature coefficient[6]. When the effects of pressure are allowed for the measured values of the rate constant are in good agreement.

The pressure dependence of k has been investigated by Wagal *et al.*[5] and by Berman and Lin[6]. The mechanism proposed for the reaction is

$$\begin{array}{ll} \mathrm{CH + N_2 \xleftrightarrow{a} CHN_2^*} & \mathrm{\xrightarrow{b} HCN + N} \\ & \mathrm{\xrightarrow[M]{c} CHN_2} \end{array}$$

The effects of pressure on k and the negative temperature coefficient at low temperatures are accounted for by competition between collisional stabilization of the energized CHN_2^* adduct and decomposition back to $CH + N_2$. This competition has been modelled by Wagal *et al.*[5] using a simple Lindemann treatment and by Berman and Lin[6] who used RRKM theory. The experimental results were obtained under conditions far removed from the high pressure limit of k and much closer to the low pressure limit. Not surprisingly, therefore, the two different treatments give values of k_0 in good agreement but there are very large differences in the values of k_∞

At sufficiently high temperatures the rate constant has a positive temperature coefficient and appears to be independent of pressure[3,8]. Path b is included in the above mechanism to account for this. At high temperatures, path b becomes more important than the decomposition of the adduct back to $CH + N_2$ and any pressure effect would be due to competition between b and c until, at sufficiently high temperatures, b dominates completely and k becomes pressure independent. From the modelling studies of Berman and Lin[6] and Lindackers *et al.*[10] it seems that adduct formation will dominate at low temperatures and will contribute to the overall rate constant at $T<2000$ K and $p<760$ Torr. This transition temperature region will move to higher values of T at higher pressures.

There are high temperature values of k based on both flame[3,8] and shock tube studies[10,11]. They exhibit considerable differences both in the absolute values of k and its temperature coefficient. The flame studies were performed at lower temperatures and hence may have some contribution from adduct stabilization, channel 2. The slightly lower values of E/R obtained in these studies may be evidence of this. Our recommendations, therefore, are based on the shock tube work of Lindackers *et al.*[10] and Dean *et al.*[11]. These give significantly different values of E/R, probably more than can be explained by contributions from adduct formation at the temperatures and pressures employed. For the temperature coefficient, we take a mean value of E/R from these two studies and the pre-exponential factor is based on this value of E/R and the virtually identical value of k at 2000 K given by the expression of Dean *et al.*[11] and Lindackers *et al.*[10]. Our recommendations are limited to high temperatures and pressures where channel 1 is expected to be dominant. Some direct confirmation that the products of the reaction at high temperatures are HCN + N comes from the work of Dean *et al.*[11] where the [N] profile was measured and modelled satisfactorily.

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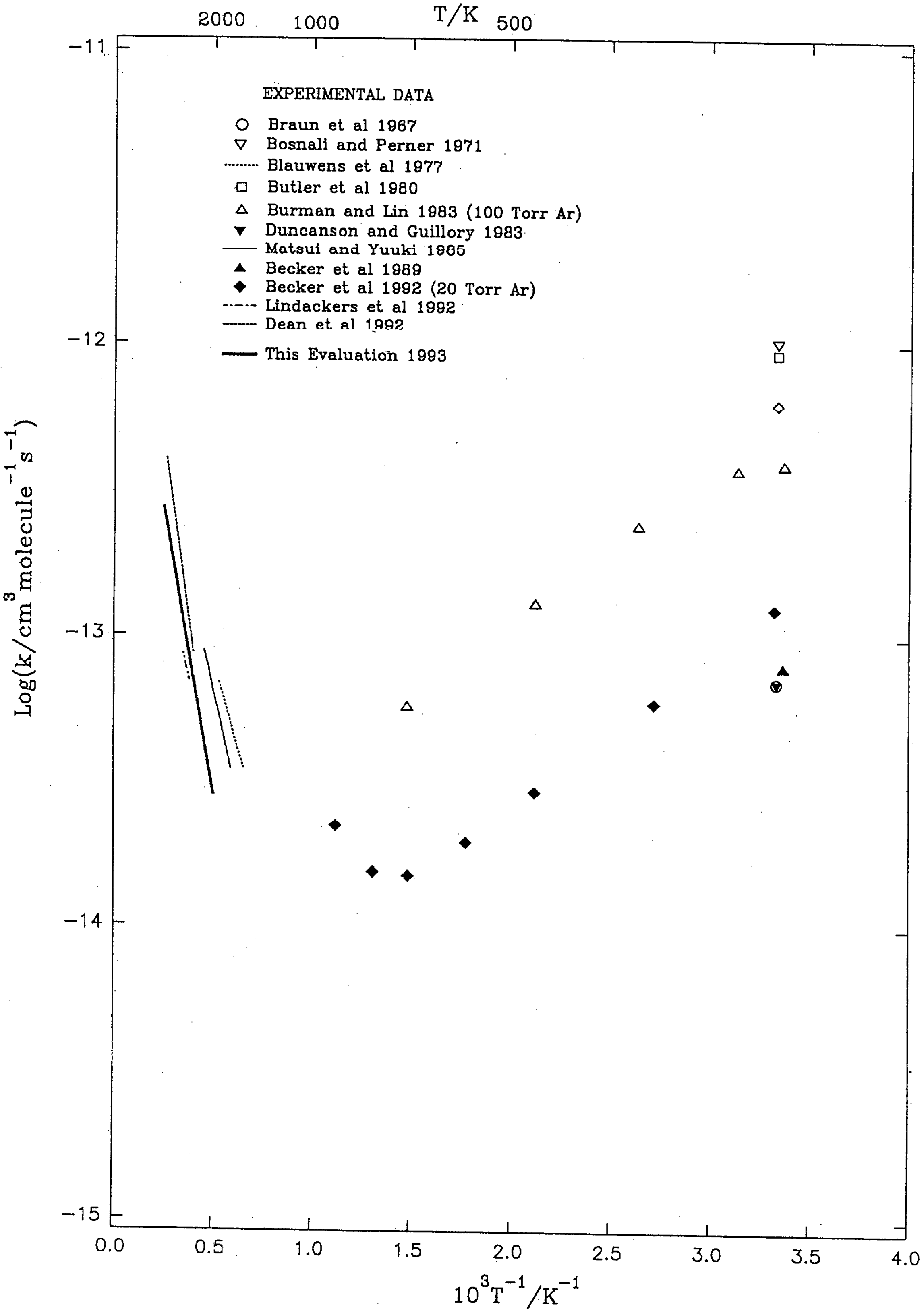
$CH + N_2 \rightarrow HCN + N$
$CH + N_2 (+M) \rightarrow CHN_2 (+M)$



$$\begin{aligned} CH + NO &\rightarrow CO + NH \quad (1)\\ &\rightarrow CN + OH \quad (2)\\ &\rightarrow HCN + O \quad (3) \end{aligned}$$

Thermodynamic Data

$\Delta H^\circ_{298}(1) = -438.5$ kJ mol^{-1}
$\Delta S^\circ_{298}(1) = -3.6$ J K^{-1} mol^{-1}
$Kp(1) = 1.2\ T^{-0.28}\exp(+52620/T)$

$\Delta H^\circ_{298}(2) = -210.3$ kJ mol^{-1}
$\Delta S^\circ_{298}(2) = -7.5$ J K^{-1} mol^{-1}
$Kp(2) = 3.0\ T^{-0.27}\exp(+25160/T)$

$\Delta H^\circ_{298}(3) = -300.1$ kJ mol^{-1}
$\Delta S^\circ_{298}(3) = -30.9$ J K^{-1} mol^{-1}
$Kp(3) = 6.9\cdot10^{-2}\ T^{0.03}\exp(+35400/T)$

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

k/cm^3 molecule^{-1} s^{-1}	T/K	References	Comments
Rate Coefficient Measurements			
$2.9\cdot10^{-10}$	300	Butler *et al.*, 1980[1]; 1981[2]	(a)
$1.9\cdot10^{-10}$	297–676	Berman *et al.*, 1982[3]	(b)
$2.0\cdot10^{-10}$	300	Wagal *et al.*, 1982[4]	(c)
$2.5\cdot10^{-10}$	300	Lichtin *et al.*, 1983[5]; 1984[6]	(d)
$1.66\cdot10^{-10}$	2570–3790	Dean *et al.*, 1991[7]	(e)

Comments

(a) Pulsed laser photolysis at 193 nm of slowly flowing mixtures of $CHBr_3$/Ar/NO at pressures of 100 Torr. CH produced by multiphoton absorption by $CHBr_3$ and [CH] monitored by LIF near 430 nm.

(b) Pulsed laser photolysis at 266 nm of slowly flowing mixtures of $CHBr_3$/Ar/NO at pressures of 100 Torr. [CH] monitored by LIF in 430 nm region.

(c) CH produced by multiphoton pulsed laser dissociation (CO_2 laser) of CH_3NH_2, CH_3CN or c-C_3H_6. [CH] monitored by LIF. Slowly flowing mixtures of source gas with Ar and NO at total pressures of approximately 5 Torr.

(d) Pulsed laser photolysis at 266 nm of slowly flowing mixtures of $CHBr_3$/Ar/NO at 21 Torr. Emissions from excited states of CH and from NH observed. NH emission monitored at 336.2 nm used to obtain k.

(e) Shock tube study. Pyrolysis of C_2H_6/NO/Ar or CH_4/NO/Ar mixtures. CH, NH and OH detected by narrow-linewidth laser absorption. [CH] profile in presence and absence of NO compared. k derived by fitting [CH] profiles using large reaction mechanism. Checks carried out to show [CH] profile sensitive to k.

Preferred Values

$k = 2.0\cdot10^{-10}$ cm^3 molecule^{-1} s^{-1} over the range 300–4000 K.

Reliability

$\Delta\log k = \pm0.25$ over the range 300–4000 K.

Comments on Preferred Values

The studies at low temperatures[1–6] are in good agreement. All of them have used the pulsed laser photolysis of slowly flowing gas mixtures but with a variety of CH sources. There is agreement between results whether obtained by monitoring NH production or from measuring [CH] decay.

In the only high temperature study[7], the value of k obtained agrees well with the low temperature measurements. There are no published measurements in the intermediate temperature range but unpublished results of Casleton and Morgantown are quoted in Ref. 7 as giving $k = 1.5\cdot10^{-10}$ cm^3 molecule^{-1} s^{-1} over the range 300–1500 K. As might be expected from such a fast reaction there is no evidence for an appreciable temperature coefficient for k.

As well as the three listed, there are a number of other possible exothermic reaction channels leading to H + NCO, N + HCO, H + CNO. Objections to all of these have been raised[8] and the only experimental study[7] has been aimed at seeking products from channels 1, 2 or 3. From the yield of NH it was concluded that channel 1 contributes less than 10% to k and measurements of the OH yield suggested that channel 2 was also a minor contributor (certainly less than 30% and likely to be less than 10%). Attempts to confirm the predominence of channel 3 by measuring O atom profiles was hindered by interfering reactions and experimental difficulties in the detection method. The assumption that reaction 3 is the main pathway therefore requires confirmation and no recommendation is made for the branching ratios.

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$^1CH_2 + NO \rightarrow$ Products

Rate Coefficient Data

k/cm^3 molecule^{-1} s^{-1}	T/K	References	Comments
Rate Coefficient Measurements			
$<4 \cdot 10^{-11}$	300	Laufer and Bass, 1974[1]	(a)
$1.6 \cdot 10^{-10}$	300	Langford, Petek, and Moore, 1983[2]	(b)
$1.65 \cdot 10^{-10}$	295–431	Biggs *et al.*, 1991[3]	(c)
$1.63 \cdot 10^{-10}$	296–645	Hancock and Heal, 1992[4]	(d)

Comments

(a) Flash photolysis of ketene with product analysis by G.C. Rate constants obtained from the decrease in yield of C_2H_2 with increasing amounts of NO.

(b) $^1CH_2$ produced from the photolysis of ketene at 308 nm. $[^1CH_2]$ monitored in absorption between 590 and 610 nm.

(c) Laser flash photolysis of ketene at 308 nm. $[^1CH_2]$ monitored using cw resonance absorption at 590.5 nm.

(d) As in (c) but quartz cell used instead of stainless steel.

Preferred Values

$k = 1.6 \cdot 10^{-10}$cm^3 molecule^{-1} s^{-1} over range 290–650 K.

Reliability

$\Delta \log k = \pm 0.2$ over range 290–650 K.

Comments on Preferred Values

All of the available data are in good agreement. By comparing the temperature coefficient of physical quenching (e.g. with Ar) with the lack of any such effect on k of varying [NO], Hancock and Heal[4] conclude that reactive quenching must be important and perhaps be the predominant means of $^1CH_2$ removal.

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$^1CH_2 + C_2H_4 (+ M) \rightarrow C_3H_6 (+ M)$ (1)
$\rightarrow {}^3CH_2 + C_2H_4$ (2)

Thermodynamic Data

$\Delta H^\circ_{298}(1) = -457$ kJ mol^{-1}
$\Delta S^\circ_{298}(1) = 150$ J K^{-1} mol^{-1}
$Kp(1) = 25.7\ T^{0.57}\exp(+55400/T)$ atm.$^{-1}$

$\Delta H^\circ_{298}(2) = -37.7$ kJ mol^{-1}
$\Delta S^\circ_{298}(2) = 6.8$ J K^{-1} mol^{-1}
$Kp(2) = 2.17\ T^{0.016}\exp(+4520/T)$

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

k/cm^3 molecule^{-1} s^{-1}	T/K	References	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)
$k_2/k = 0.13$	295	Bohland, Temps, and Wagner, 1985[3]	(c)
$2.3 \cdot 10^{-10}$	298	Hack *et al.*, 1989[4]	(d)
$k_2/k = 0.2$	298		
Reviews and Evaluations			
$1.5 \cdot 10^{-10}$ $k_2/k = 0.13$	300–1000	CEC, 1992[5]	(e)

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 zero triplet quantum yield at 308 nm. The k_2/k value represents an upper limit.
(d) Pulsed laser photolysis of ketene, with LIF monitoring of $^1CH_2$ and LMR monitoring of $^3CH_2$.
(e) Value of Langford *et al.*[1] accepted.

Preferred Values

$k = 2.0\cdot10^{-10}$ cm^3 molecule^{-1} s^{-1} over range 300–1000 K.
$k_2/k = 0.2$.

Reliability

$\Delta\log k = \pm0.5$ at 1000 K reducing to ±0.2 at 300 K.
$\Delta(k_2/k) = \pm0.1$.

Comments on Preferred Values

There is excellent agreement between the two direct determinations of $k^{1,4}$; the recommendation is a rounded mean of these two values. Hack *et al.*[4] used a similar technique to Bohland *et al.*[3] to determine k_2/k_1, but with an improved method of data analysis; the value of Hack *et al.*[4] has been adopted. At higher temperatures the fall-off effects will cause the rate constant to decrease.

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$$\begin{aligned} {}^3CH_2 + O_2 &\rightarrow CO + OH + H && (1)\\ &\rightarrow CO_2 + H_2 && (2)\\ &\rightarrow CO + H_2O && (3)\\ &\rightarrow CH_2O + O && (4)\\ &\rightarrow CO_2 + 2H && (5) \end{aligned}$$

Thermodynamic Data

ΔH°_{298} (1) = -241 kJ mol^{-1}
ΔS°_{298} (1) = 95.2 J K^{-1} mol^{-1}
$Kp(1) = 1.15\cdot10^3T^{0.74}\exp(+29000/T)$ atm.

ΔH°_{298} (3) = -739 kJ mol^{-1}
ΔS°_{298} (3) = -14.3 J K^{-1} mol^{-1}
$Kp(3) = 4.14\ T^{-0.456}\exp(+88880/T)$

ΔH°_{298} (5) = -345 kJ mol^{-1}
ΔS°_{298} (5) = 42.4 J K^{-1} mol^{-1}
$Kp(5) = 4.87\cdot10^{-4}\ T^{1.92}\exp(+42000/T)$ atm.

ΔH°_{298} (2) = -781 kJ mol^{-1}
ΔS°_{298} (2) = -56.2 J K^{-1} mol^{-1}
$Kp\ (2) = 1.55\cdot10^{-5}T^{0.637}\exp(+94100/T)$

ΔH°_{298} (4) = -254 kJ mol^{-1}
ΔS°_{298} (4) = -21.0 J K^{-1} mol^{-1}
$Kp\ (4) = 4.66\cdot10^{-3}T^{0.34}\exp(+30800/T)$

Rate Coefficient Data ($k = k_1 + k_2 + k_3 + k_4 + k_5$)

k/cm^3 molecule^{-1} s^{-1}	T/K	References	Comments
Rate Coefficient Measurements			
$3.24\cdot10^{-12}$	293	Darwin *et al.*, 1989[1]	(a)
Reviews and Evaluations			
$4.1\cdot10^{-11}\exp(-750/T)$	300–1000	CEC, 1992[2]	(b)

Comments

(a) Laser flash kinetic spectrometric study with photolysis of ketene at 351 nm used as the source of $^3CH_2$ which was detected at 883.3 cm^{-1} by cw diode laser absorption.
(b) Review of all studies up to 1989. Recommended E/R based on Ref. 3 and combined with the room temperature measurement of Bohland *et al.*[4] to give A factor.

Preferred Values

$k = 4.1\cdot10^{-11}\exp(-750/T)$ cm^3 molecule^{-1} s^{-1} over range 300–1000 K.

Reliability

$\Delta\log k = \pm0.5$ at 1000 K reducing to ±0.1 at 300 K.

Comments on Preferred Values

The direct measurement of Darwin *et al.*[1] confirms that of Bohland *et al.*[4]. This value has been adopted together with the temperature dependence of Vinckier and Debruyn[3]. The limited information on the channel efficiencies was discussed in the previous evaluation[2].

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$CH_3 + CO (+ M) \rightarrow CH_3CO (+ M)$

Thermodynamic data

$\Delta H^\circ_{298} = -45.1$ kJ mol^{-1}

$\Delta S^\circ_{298} = -125.4$ J K^{-1} mol^{-1}

$Kp = 2.2 \cdot 10^{-4}\, T^{-1.0} \exp(+5170/T)$ atm^{-1}

Rate Coefficient Data

k/cm^3 molecule^{-1} s^{-1}	T/K	[M]/molecule cm^{-3}	References	Comments
Rate Coefficient Measurements				
Low Pressure Range				
[CO]$5.7 \cdot 10^{-36}$	303	$(3\text{–}24) \cdot 10^{18}$	Anastasi and Maw, 1982[1]	(a)
[CO]$10.7 \cdot 10^{-36}$	343			
Intermediate Fall-Off Range				
$6.8 \cdot 10^{-15} \exp(-1964/T)$	300	$(2.4\text{–}7.2) \cdot 10^{18}$ $((CH_3)_2N_2, CO, (CH_3)_4C)$	Kerr and Calvert, 1965[2]	(b)
$1.0 \cdot 10^{-18}$	273	$2.9 \cdot 10^{18}$ $((CH_3)_2N_2, CO, SF_6)$	Watkins and Word, 1979[3]	(c)
$1.8 \cdot 10^{-18}$		$12 \cdot 10^{18}$		
$3.6 \cdot 10^{-18}$		$96 \cdot 10^{18}$		
$1.8 \cdot 10^{-18}$	298	$3.2 \cdot 10^{18}$(CO)	Parkes, 1981[4]	(d)
$6 \cdot 10^{-18}$		$24 \cdot 10^{18}$		
$3.6 \cdot 10^{-18}$	303	$3.0 \cdot 10^{18}$(CO)	Anastasi and Maw, 1982[1]	(a)
$5.6 \cdot 10^{-18}$		$1.6 \cdot 10^{19}$		
$7.9 \cdot 10^{-18}$		$2.4 \cdot 10^{19}$		
$6.1 \cdot 10^{-18}$	343	$3.0 \cdot 10^{18}$		
$1.6 \cdot 10^{-17}$		$1.6 \cdot 10^{19}$		
$1.7 \cdot 10^{-17}$		$2.1 \cdot 10^{19}$		
High Pressure Range				
$2.64 \cdot 10^{-13} \exp(-3010/T)$	260–413	$(1.8\text{–}10) \cdot 10^{19}$ $((CH_3)_2N_2$, CO, $SF_6)$	Watkins and Word, 1974[3]	(c)
$>1 \cdot 10^{-17}$	298		Parkes, 1981[4]	(d)
$1.6 \cdot 10^{-17}$	303	$(3\text{–}24) \cdot 10^{18}$(CO)	Anastasi and Maw, 1982[1]	(a)
$5.7 \cdot 10^{-17}$	343			
Reviews and Evaluations				
$k_0 = [N_2] 4.0 \cdot 10^{-10} T^{-7.56} \exp(-5490/T)$	300–1700		Tsang and Hampson, 1986[5]	(c)
$k_\infty = 7.64 \cdot 10^{-13} \exp(-3073/T)$	260–507		Bencsura *et al.*, 1992[6]	(f)

Comments

(a) Molecular modulation technique; photolysis of azomethane/CO mixtures. UV absorption detection of CH_3 and CH_3CO.

(b) Photolysis of azomethane at 366 nm in the presence of CO and CH_3CHO.

(c) Photolysis of azomethane in the presence of CO and SF_6. Product analysis by gas chromotography. Rate coefficients determined relative to the rate coefficient of the reaction $CH_3 + CH_3$ for which a value of $3.65 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature was used. Lindemann-Hinselwood extrapolation used to obtain k_∞.

(d) Molecular modulation technique; photolysis of azomethane/CO mixtures. UV absorption detection of CH_3 and CH_3CO at 214 and 223 nm respectively. $\sigma(CH_3CO) = 1.0 \cdot 10^{-17}$ *cm*^{3} *molecule*$^{-1}$ at 223 *nm* was used.

(e) Based on data of references 1, 3 and 4 and an RRKM treatment.

(f) Study of the pyrolysis of CH_3CO. CH_3CO generated by photolysis of 2-butanone and detected by mass spectrometry. k_∞ was theoretically estimated.

Preferred Values

$k_\infty = 8.4 \cdot 10^{-13} \exp(-3455/T)$ s^{-1} over range 300–500 K.

k_o = [He]$3.0 \cdot 10^{-34} \exp(-1910/T)$ s^{-1} over range 400–500 K.

k_o = [N_2]$4.2 \cdot 10^{-36}$ s^{-1}over range 300–350 K.

$F_c = 0.5$ for M = He over range 400–500 K.

$F_c = 0.6$ for M = N_2 over range 300–350 K.

Reliability

$\Delta \log k_\infty = \pm 0.5$ over range 300–500 K.

$\Delta \log k_o = \pm 0.2$ for M = He over range 400–500 K.

$\Delta \log k_o = \pm 0.5$ for M = N_2 over range 300–350 K.

$\Delta F_c = \pm 0.1$ for M = He over range 400–500 K.

$\Delta F_c = \pm 0.1$ for M = N_2 over range 300–350 K.

Comments on Preferred Values

The preferred rate coefficients k_∞ and k_o were derived from the preferred dissociation rate coefficients and K_c. The value of K_c of Bencsura *et al.*[6] was adopted. In deriving the expressions for k_o the values of k_o(M = N_2) were assumed to be equal to k_o (M = CO). Figures 1 and 2 show the temperature dependence of the limiting rate coefficients. The analysis of the k_o values with the theory of Ref. 7 yields a $\beta_c = 0.11$ at 420 K and 0.093 at 500 K for M = He. Experimental and fitted fall-off curves[8] are depicted in Fig. 3. More direct determinations of the kinetics of this reaction are required.

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$CH_3 + CO + M \rightarrow CH_3CO + M$

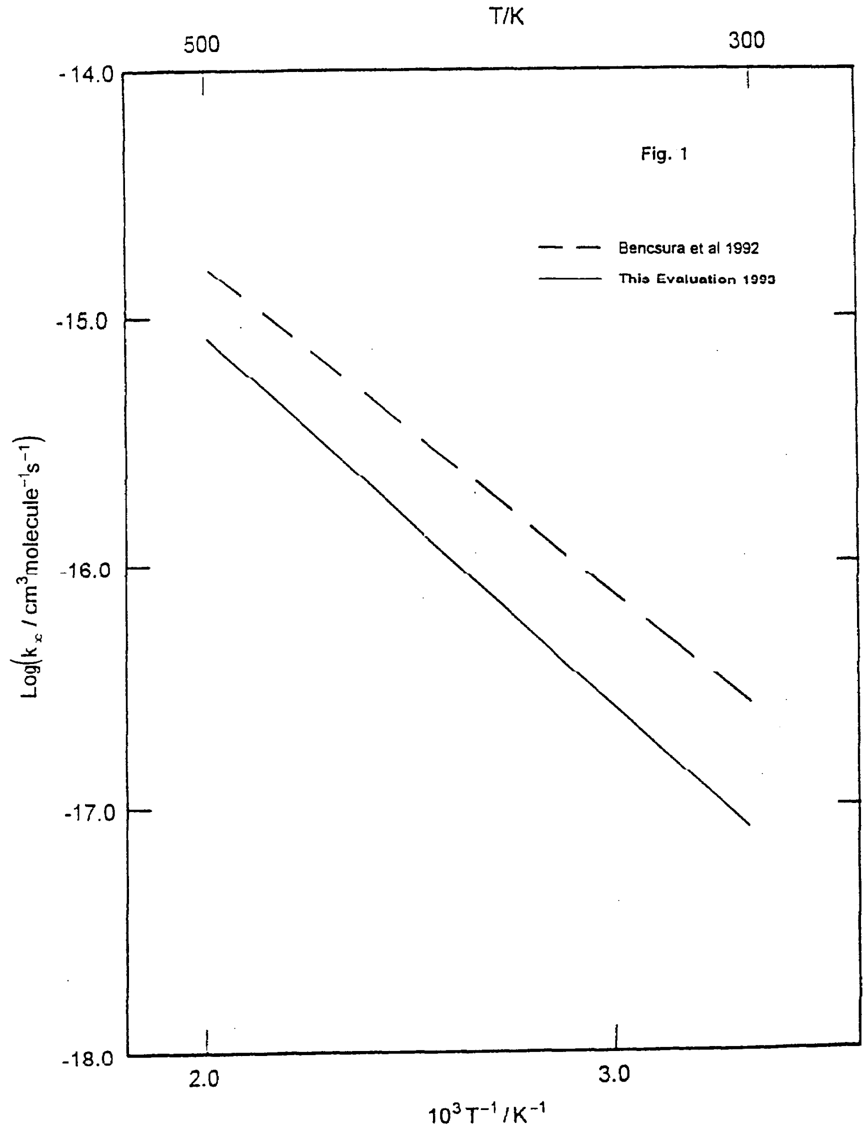

Fig. 1

$CH_3 + CO + M \rightarrow CH_3CO + M$

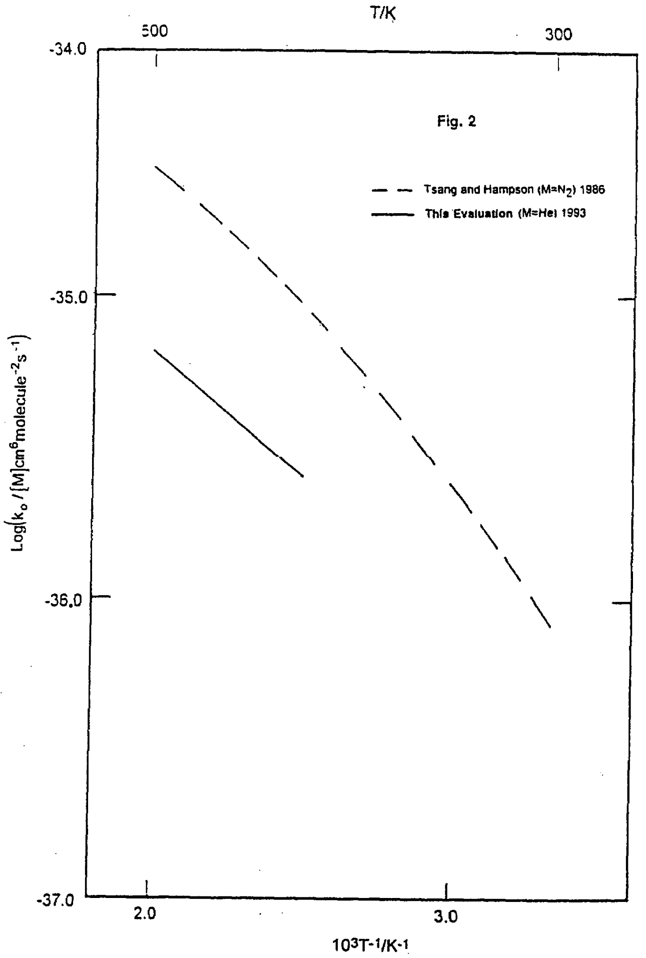

Fig. 2

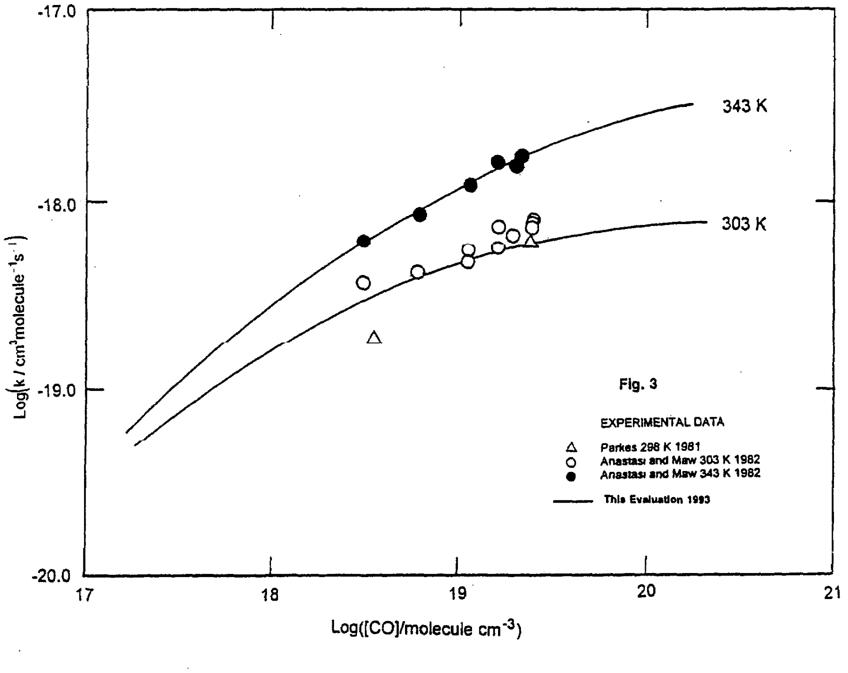

Fig. 3

CH_3CO (+ M) → CH_3 + CO (+ M)

Thermodynamic data
ΔH°_{298} = 45.1 kJ mol^{-1}
ΔS°_{298} = 125.4 J K^{-1} mol^{-1}
$Kp = 4.5\cdot10^{3}T^{1.0}\exp(-5170/T)$ atm.

Rate Coefficient Data

k/s^{-1}	T/K	[M]/molecule cm^{-3}	References	Comments
Rate Coefficient Measurements				
Low Pressure Range				
$[CO]3.1\cdot10^{-17}$	343	$(3–21)\cdot10^{18}$	Anastasi and Maw, 1982[1]	(a)
$[He]6.7\cdot10^{-9}\exp(-6921/T)$	420–500	$(3–18)\cdot10^{16}$	Bencsura *et al.*, 1992[2]	(b)
Intermediate Fall-Off Range				
1.71	325.7	$1.8\cdot10^{17}$	Frey and Vinall, 1973[3]	(c)
5.17		$6.0\cdot10^{17}$		
7.36		$10.3\cdot10^{17}$		
$5.0\cdot10^{2}$	506.7	$6.6\cdot10^{17}$	Szirovicza and Walsh, 1979[4]	(d)
$31\cdot10^{2}$		$67.1\cdot10^{17}$		
$51\cdot10^{2}$		$136\cdot10^{17}$		
13	323	$1.1\cdot10^{19}$ (CO)	Anastasi and Maw, 1982[1]	(a)
16		$1.7\cdot10^{19}$		
30		$2.2\cdot10^{19}$		
31	343	$0.3\cdot10^{19}$		
40		$1.1\cdot10^{19}$		
52		$2.1\cdot10^{19}$		
23	353	$6.8\cdot10^{18}$(Ar)	Baldwin *et al.*, 1987[5]	(e)
52		$20\cdot10^{18}$		
100		$49\cdot10^{18}$		
$6.06\cdot10^{1}$	440	$6.0\cdot10^{16}$(He)	Bencsura *et al.*, 1992[2]	(b)
$1.62\cdot10^{2}$		$18\cdot10^{16}$		
$1.31\cdot10^{2}$	460	$6.0\cdot10^{16}$(He)		
$3.55\cdot10^{2}$		$18\cdot10^{16}$		
$1.98\cdot10^{2}$	500	$3.0\cdot10^{16}$(He)		
$3.88\cdot10^{2}$		$6.0\cdot10^{16}$		
High Pressure Range				
$1.6\cdot10^{13}\exp(-8660/T)$	260–413	$(1.8–8)\cdot10^{19}$	Watkins and Word, 1974[6]	(f)
186	343	$(3–21)\cdot10^{18}$	Anastasi and Maw, 1982[1]	(a)
$2.0\cdot10^{13}\exp(-8806/T)$	332–478	$(6.8–49)\cdot10^{18}$	Baldwin *et al.*, 1987[5]	(e)
Reviews and Evaluations				
$k_o = [CO]\ 2.0\cdot10^{-9}\exp(-6302/T)$	300–500		Warnatz, 1984[7]	(g)
$k_\infty = 3.0\cdot10^{12}\exp(-8420/T)$	300–500			
$k_o = [N_2]1.4\cdot10^{19}T^{-8.62}\exp(-11284/T)$	300–2000		Tsang and Hampson, 1986[8]	(h)
$k_\infty = 2.5\cdot10^{13}\exp(-8244/T)$	260–507		Bencsura *et al.*, 1992[2]	(b)

Comments

(a) Modulated photolysis of azomethane in the presence of excess of CO; CH_3 and CH_3CO detected by molecular modulation-UV absorption at 216 and 223 nm respectively. An empirical procedure based on Kassel integrals was used to evaluate k_∞ from the measurements at 343 K.

(b) Laser photolysis of 2-butanone at 248 nm was used to generate CH_3CO radicals. Decay monitored by time-resolved mass spectrometry. Theoretical analysis using a master equation formalism. The experiments were fitted using a threshold energy of 65.3 kJ mol^{-1}. k_∞ was theoretically evaluated.

(c) Photolysis of 3,3-dimethylbutan-2-one at 313 nm. Analysis of the products by gas chromotography. Mechanism with 15 reactions. Rate coefficients determined relative to the reaction $CH_3CO + CH_3CO \rightarrow CH_3COCOCH_3$ for which a value $3.7\cdot10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} was assumed.

(d) CH_3CO formed as secondary product of the reactions of HI with ketene at 498–525 K. Products detected by chromatography. RRKM analysis of the thermal decomposition of CH_3CO.

(e) Photolysis of methyl cyclobutyl ketone at 313 nm (steady state) and 308 nm (laser photolysis) in Ar. Product analysis by gas chromatography. k_∞ obtained by modelling of the mechanism and RRKM theory using step sizes for deactivation of 250 cm^{-1}. Rate coefficients depend on $k(CH_3 + CH_3)$ and also $k(CH_3CO + CH_3CO)$ for which values from Ref. 1 were used.

(f) Photolysis of azomethane in the presence of CO diluted in SF_6; product analysis by gas chromatography. The value of k depends on the values of the rate coefficients for the reactions $CH_3 + CH_3$ and $CH_3 + CH_3CO$. Short Lindemann-Hinshelwood extrapolation used to obtain k_∞.
(g) Review of literature prior to 1980.
(h) RRKM treatment of data in Refs. 1 and 5 using a step size of 450 cm^{-1}.

Preferred Values

$k_\infty = 2.8 \cdot 10^{13} \exp(-8630/T)$ s^{-1} over range 300–500 K.
$k_0 = [He]1.0 \cdot 10^{-8} \exp(-7080/T)$ s^{-1} over range 400–500 K.
$k_0 = [Ar]7.0 \cdot 10^{-18}$ s^{-1} at 353 K.
$F_c = 0.5$ for M = He over range 400–500 K.

Reliability
$\Delta \log k_\infty = \pm 0.5$ over range 300–500 K.
$\Delta \log k_0 = \pm 0.2$ for M = He over range 400–500 K.
$\Delta \log k_0 = \pm 0.4$ for M = Ar at 353 K.
$\Delta F_c = \pm 0.1$ over range 400–500 K.

Comments on Preferred Values

The k_∞ value adopted is based on the results of Refs. 1, 5 and 6. In order to reconcile the dissociation and the recombination results we have taken for k_∞ a value two times greater than the average value of the results from these references. The preferred k_0 values for M = He were derived from the fit to the data of Bencsura *et al.*[2]. Figures 1 and 2 show the temperature dependence of the k_∞ and k_0 together with values from previous compilations. The equilibrium constant given above was evaluated using recent thermodynamic values for the CH_3CO radical[2,9]. Figure 3 shows the fall-off curves constructed[10] with the recommended k_∞ and k_0 values and the experimental data. An analysis of the k_0 values in terms of the unimolecular rate theory from Ref. 11 and a threshold energy of $E_0 = 65.3$ kJ mol^{-1} [2] leads to collisional efficiencies for M = He of 0.11 and 0.093 at 420 K and 500 K respectively. These values are consistent with an average energy transferred per collision of 60 cm^{-1}.

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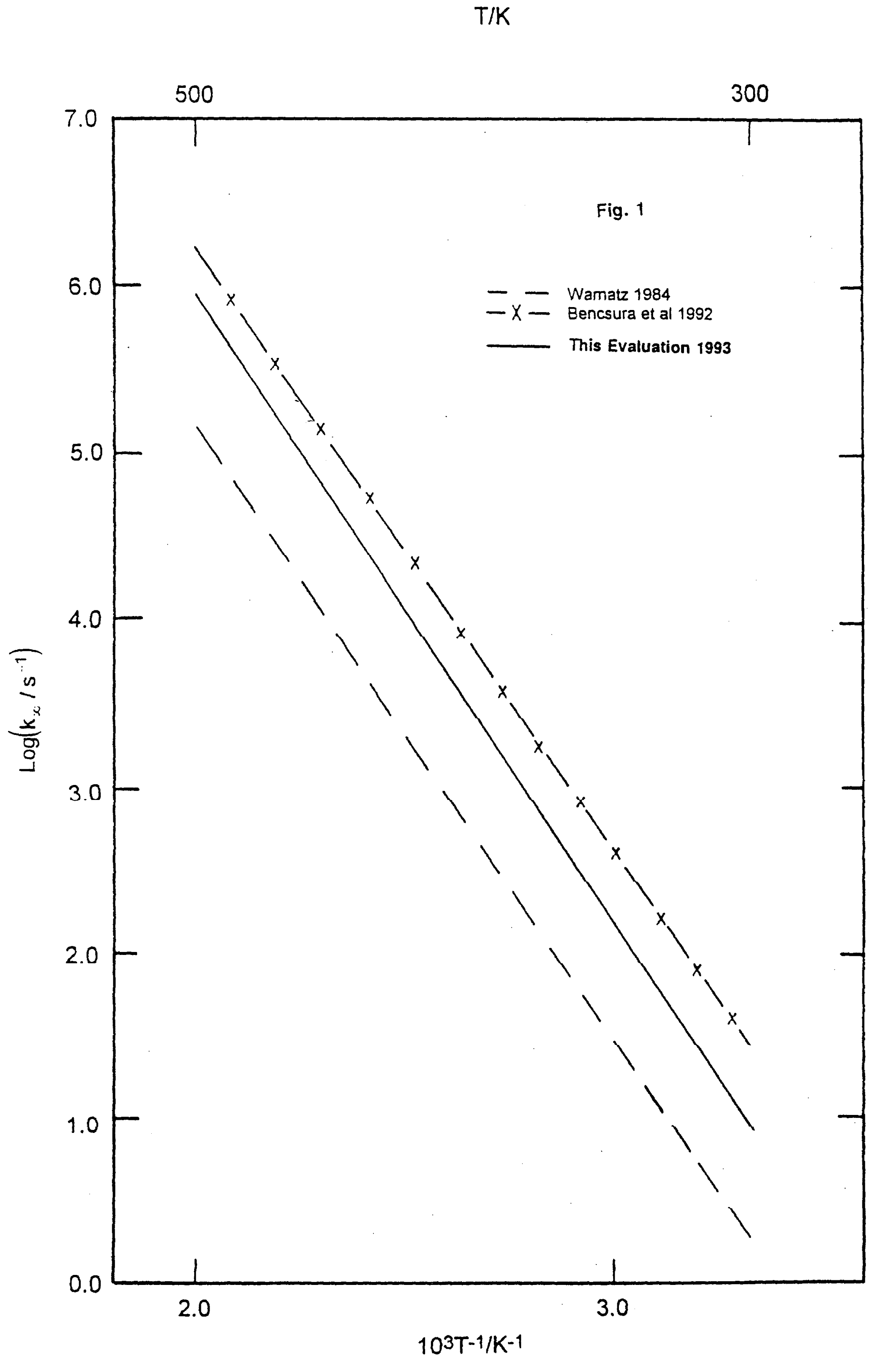
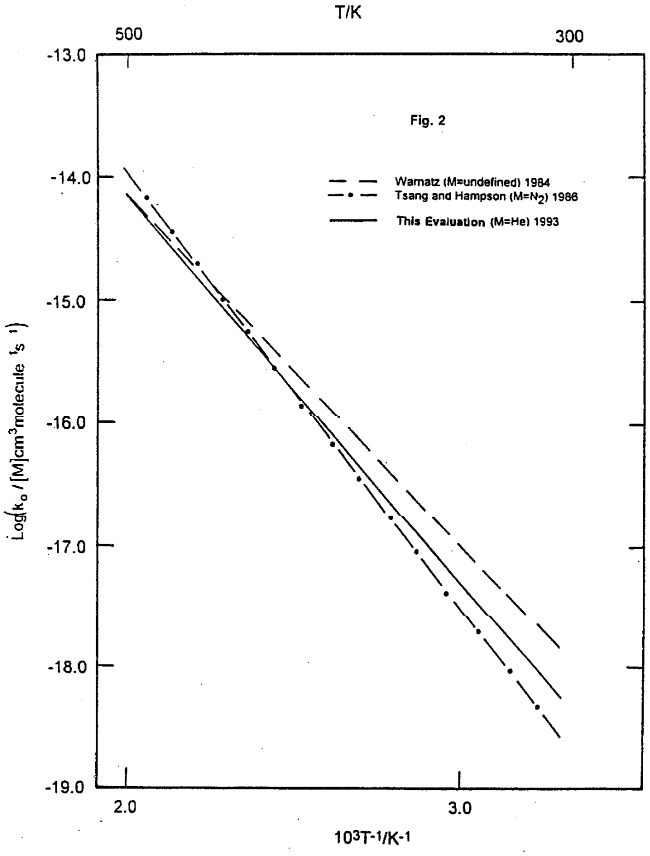
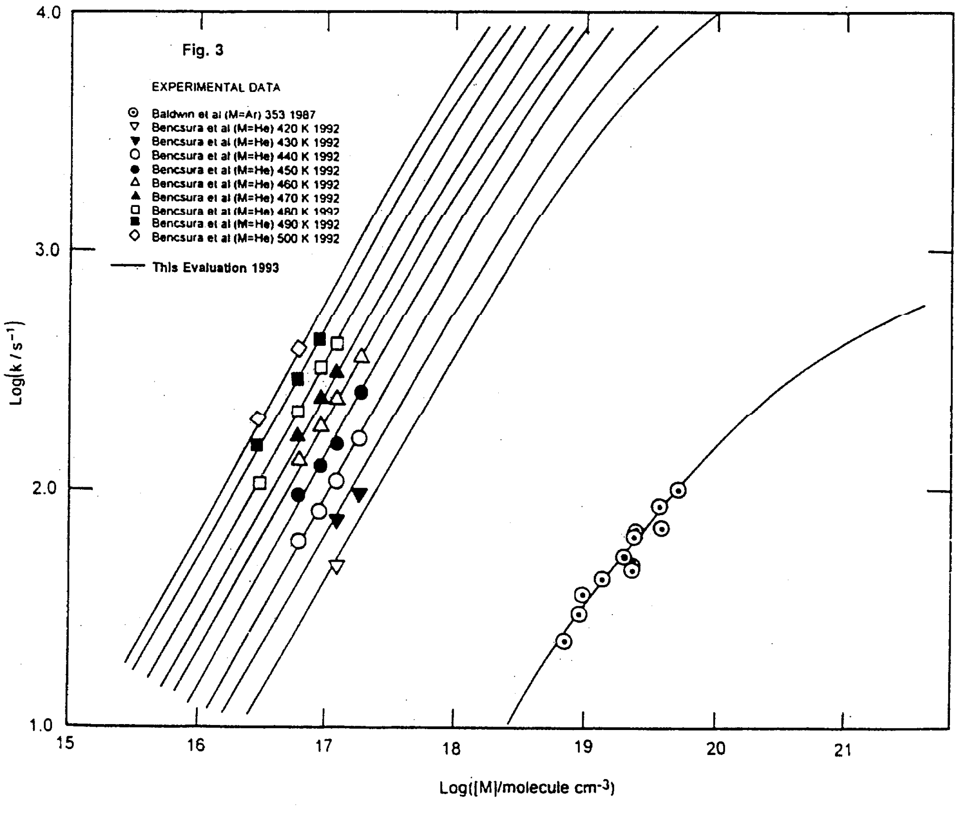
$CH_3CO + M \rightarrow CH_3 + CO + M$



$CH_3CO + M \rightarrow CH_3 + CO + M$





$CH_3 + CH_3 (+ M) \rightarrow C_2H_6 (+ M)$

Thermodynamic data
$\Delta H^\circ_{298} = -375$ kJ mol^{-1}
$\Delta S^\circ_{298} = -159$ J K^{-1} mol^{-1}
$Kp = 2.41\cdot10^{-10}T^{0.236}\exp(+45700/T)$ 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				
$4.0\cdot10^{-11}$	250–450	$(3.2–29.4)\cdot10^{18}(N_2)$	Parkes *et al.*, 1976[1]	(a)
$5.5\cdot10^{11}$	295	$1.6\cdot10^{18}(N_2)$	Callear and Metcalfe, 1976[2]	(b)
$2.0\cdot10^{-11}$	450	$6.4\cdot10^{16}$(He)	Van den Berg, 1976[3]	(c)
$4.0\cdot10^{-11}$		$6.4\cdot10^{17}$		
$3.2\cdot10^{-12}$	1350	$1.2\cdot10^{18}$(Ar)	Glänzer *et al.*, 1976, 1977[4]	(d)
$1.3\cdot10^{-11}$		$1.5\cdot10^{19}$		
$1.8\cdot10^{-11}$		$6.0\cdot10^{19}$		
$1.6\cdot10^{-11}$		$1.2\cdot10^{20}$		
$5.2\cdot10^{-11}$	295	$2.5\cdot10^{19}(N_2)$	Hochanadel *et al.*, 1977[5]	(e)
$7.0\cdot10^{-12}$	640–818	$1.0\cdot10^{17}$(Ar)	Sepehrad *et al.*, 1979[6]	(f)
$8.0\cdot10^{-12}$		$1.9\cdot10^{17}$		
$2.4\cdot10^{-12}$	1700–1800	$1.4\cdot10^{18}$(Ar)	Zaslonko and Smirnov, 1979[7]	(g)
$5.3\cdot10^{-11}$	295	$1.6\cdot10^{18}$(*n*-pentane)	Adachi *et al.*, 1980[8]	(h)
$1.1\cdot10^{-11}$	823	$4.7\cdot10^{16}$(*n*-pentane)	Pacey and Wimalasena, 1980[9]	(i)
$2.6\cdot10^{-11}$		$5.4\cdot10^{17}$		
$6.0\cdot10^{-11}$		$3.9\cdot10^{18}$		
$5.5\cdot10^{-11}$	296	$2.5\cdot10^{19}$(Ar)	Hippler *et al.*, 1984[10]	(j)
$6.3\cdot10^{-11}$		$2.5\cdot10^{20}$		
$5.0\cdot10^{-11}$		$5.2\cdot10^{21}$		
$5.0\cdot10^{-11}$		$2.8\cdot10^{19}(N_2)$		
$4.6\cdot10^{-11}$		$2.5\cdot10^{20}$		
$2.6\cdot10^{-11}$		$2.5\cdot10^{21}$		
$1.8\cdot10^{-11}$		$5.0\cdot10^{21}$		
$5.2\cdot10^{-11}$	296	$1.6\cdot10^{17}$(Ar)	Macpherson *et al.*, 1985[11]	(k)
$5.7\cdot10^{-11}$		$1.3\cdot10^{18}$		
$6.0\cdot10^{-11}$		$1.6\cdot10^{19}$		
$1.9\cdot10^{-11}$	577	$8.4\cdot10^{16}$(Ar)		
$3.5\cdot10^{-11}$		$1.1\cdot10^{18}$		
$4.1\cdot10^{-11}$		$6.6\cdot10^{18}$		
$3.8\cdot10^{-11}$	302	$1.3\cdot10^{17}(N_2)$	Arthur, 1986[12]	(l)
$4.0\cdot10^{-11}$		$2.7\cdot10^{18}$		
$4.0\cdot10^{-11}$		$1.8\cdot10^{19}$		
$4.7\cdot10^{-11}$	373–463	$6.3\cdot10^{17}(N_2)$	Arthur and Biordi, 1986[13]	(m)
$4.4\cdot10^{-11}$	296	$3.8\cdot10^{16}$(Ar)	Slagle *et al.*, 1988[14]	(n)
$5.2\cdot10^{-11}$		$3.4\cdot10^{17}$		
$3.4\cdot10^{-12}$	906	$4.0\cdot10^{16}$(Ar)		
$1.5\cdot10^{-12}$		$7.9\cdot10^{17}$		
$2.9\cdot10^{-11}$		$6.4\cdot10^{18}$		
$6.65\cdot10^{-11}$	200	$4.15\cdot10^{17}$(Ar)	Walter *et al.*, 1990[15]	(o)
$6.86\cdot10^{-11}$		$4.79\cdot10^{18}$		
$7.30\cdot10^{-11}$		$1.94\cdot10^{19}$		
$1.70\cdot10^{-11}$	300	$4.7\cdot10^{15}$(Ar)		
$3.3\cdot10^{-11}$		$2.4\cdot10^{16}$		
$4.1\cdot10^{-11}$		$6.95\cdot10^{16}$		
$1.1\cdot10^{-11}$	408	$6.9\cdot10^{15}$(Ar)		
$2.1\cdot10^{-11}$		$3.69\cdot10^{16}$		
$2.9\cdot10^{-11}$		$7.46\cdot10^{16}$		
$1.3\cdot10^{-11}$	1200	$6.2\cdot10^{19}$(Ar)	Hwang *et al.*, 1990[16]	(p)
$1.3\cdot10^{-11}$	1400	$2.0\cdot10^{20}$(Ar)		
$1.2\cdot10^{-11}$		$3.3\cdot10^{20}$		
$1.4\cdot10^{-11}$		$6.4\cdot10^{20}$		
$6.1\cdot10^{-12}$	1500	$5.0\cdot10^{19}$(Ar)		
$8.6\cdot10^{-12}$		$4.1\cdot10^{20}$		
$9.3\cdot10^{-12}$		$6.5\cdot10^{20}$		
$6.0\cdot10^{-12}$	1600	$2.0\cdot10^{20}$(Ar)		
$1.2\cdot10^{-11}$		$1.0\cdot10^{21}$		

$CH_3 + CH_3 (+ M) \rightarrow C_2H_6 (+ M)$ — Continued

Rate Coefficient Data

k/cm^3 molecule^{-1} s^{-1}	T/K	[M]/molecule cm^{-3}	Reference	Comments
High Pressure Range				
$5.8\cdot10^{-11}$	296	$(2.5–523)\cdot10^{19}$(Ar)	Hippler *et al.*, 1984[10]	(j)
Reviews and Evaluations				
$k_\infty = 5.1\cdot10^{-11}$	300		Quack and Troe, 1977[17]	(q)
$k_\infty = 4.8\cdot10^{-11}$	1300			
$k_\infty = 4\cdot10^{-11}$	250–420		Baulch and Duxbury, 1980[19]	(r)
$k_\infty = 4\cdot10^{-10}T^{-0.4}$	300–1200		Warnatz, 1984[20]	(s)
$k_\infty = 1.7\cdot10^{-9}T^{-0.64}$	250–1400		Tsang and Hampson, 1986[21]	(t)
$k_\infty = 1.5\cdot10^{-7}T^{-1.18}\exp(-329/T)$	300–2000		Wagner and Wardlaw, 1988[22]	(u)
$k_0 = [Ar]8.8\cdot10^{-7}T^{-7}\exp(-1390/T)$				
$F_c = 0.38\exp(-T/73) + 0.62\exp(-T/1180)$				
$k_\infty = 6\cdot10^{-11}$	300–1400		Troe, 1989[23]	(v)
$k_\infty = 1.7\cdot10^{-9}T^{-0.64}$	250–1400		Tsang, 1989[24]	(w)
$k_0 = [Ar]0.313\cdot10^{-11}T^{-5.246}\exp(-858/T)$	200–2000		Walter *et al.*, 1990[15]	(o)
$k_\infty = 0.153\cdot10^{-6}T^{-1.174}\exp(-320/T)$	200–2000			
$F_c = 0.595\exp(-T/1120) + 0.405\exp(-T/69.6)$	200–2000			
$k_\infty = 1.91\cdot10^{-9}T^{-0.6}$	1200–1600		Hwang *et al.*, 1990[16]	(p)
$k_\infty = 6.0\cdot10^{-11}$	300–2000		CEC, 1992[25]	(x)
$k_0 = [Ar]3.5\cdot10^{-7}T^{-7}\exp(-1390/T)$	300–2000			
$F_c = 0.38\exp(-T/73) + 0.62\exp(-T/1180)$	300–2000			

Comments

(a) Molecular modulation spectroscopy, CH_3 detection at 216 nm.

(b) Flash photolysis of $HgMe_2$, $k = 4.9\cdot10^{-11}$ 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) The CH_3 radicals were generated by 193 nm laser photolysis of acetone at 200 K and by the reaction $F + CH_4 \rightarrow HF + CH_3$ at 300 and 408 K. At lower temperatures the CH_3 radicals were monitored by their UV absorption at 216.36 nm, while at 300 K and 408 K they were detected via the reaction $CH_3 + NO_2 \rightarrow CH_3O + NO$. NO concentrations were determined by measuring the NO signal at m/e = 30 amu. These and previous measurements from Ref. 14 were interpreted, between 200–2000 K, using a variational RRKM theory.

(p) Reflected shock wave study. CH_3 absorption coefficients calibrated via dissociation of azomethane and monitored at 216.5 nm by UV absorption spectroscopy. Computer simulation of a mechanism with seven reactions. The values given for the intermediate fall-off range are average values taken from Table 1 of this work.

(q) 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. 18.

(r) Systemic evaluation of earlier work.

(s) Data evaluation and simplified fall-off construction.
(t) Construction of fall-off curves over the range 300–2500 K.
(u) Modelling with variational transition state theory, RRKM theory, and including weak collision effects. Based on experimental data from Refs. 4, 10, 11, and 14.
(v) Modelling of experimental data from Refs. 4, 10, 11, and 14 with constant $k_{rec,\infty}$ as suggested by the statistical adiabatic channel model from Ref. 15.
(w) See comment (t).
(x) See Comments on Preferred Values.

Preferred Values

$k_\infty = 6.0 \cdot 10^{-11} \mathrm{cm}^3$ molecule^{-1} s^{-1} over range 300–2000 K.

$k_0 = [\mathrm{Ar}] 3.5 \cdot 10^{-7} T^{-7} \exp(-1390/T)$ 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

$\Delta \log k_\infty = \pm 0.3$ over range 300–2000 K.
$\Delta \log k_0 = \pm 0.3$ for M = Ar over range 300–2000 K.
$\Delta F_c = \pm 0.1$ for M = Ar over range 300–2000 K.

Comments on Preferred Values

The recommended values are based mainly in the extensive sets of data from Refs. 4, 10, 11 and 14 up to 1000 K and the new experiments over the range 200–400 K from Ref. 15 which essentially agree with previous measurements. Recent experiments[16] over the range 1200–1400 K again suggest a negative temperature coefficient of k_∞ which is of the order $k_\infty \propto T^{-0.6}$. However, these new data are inconsistent with the results from Ref. 4 although the same technique was applied. The difference of the rate coefficients (about a factor of 2) is due to different CH_3 absorption coefficients. Because the uncertainty of the high pressure shock wave experiments is probably larger than that of the low pressure shock wave experiments, we prefer the data of Ref. 4 and retain the interpretation of Ref. 25 based on the analysis of Ref. 22. Nevertheless, the question of the temperature coefficient of k_∞ at high temperatures remains open ($k_\infty \propto T^n$ with about $0 \leqslant n \leqslant 0.6$). Figure 1 shows fall-off curves between 200–1600 K. The recommended values are consistent with those of the dissociation reaction via the equilibrium constant given above. For M = N_2 expressions identical with those for M = Ar may be assumed.

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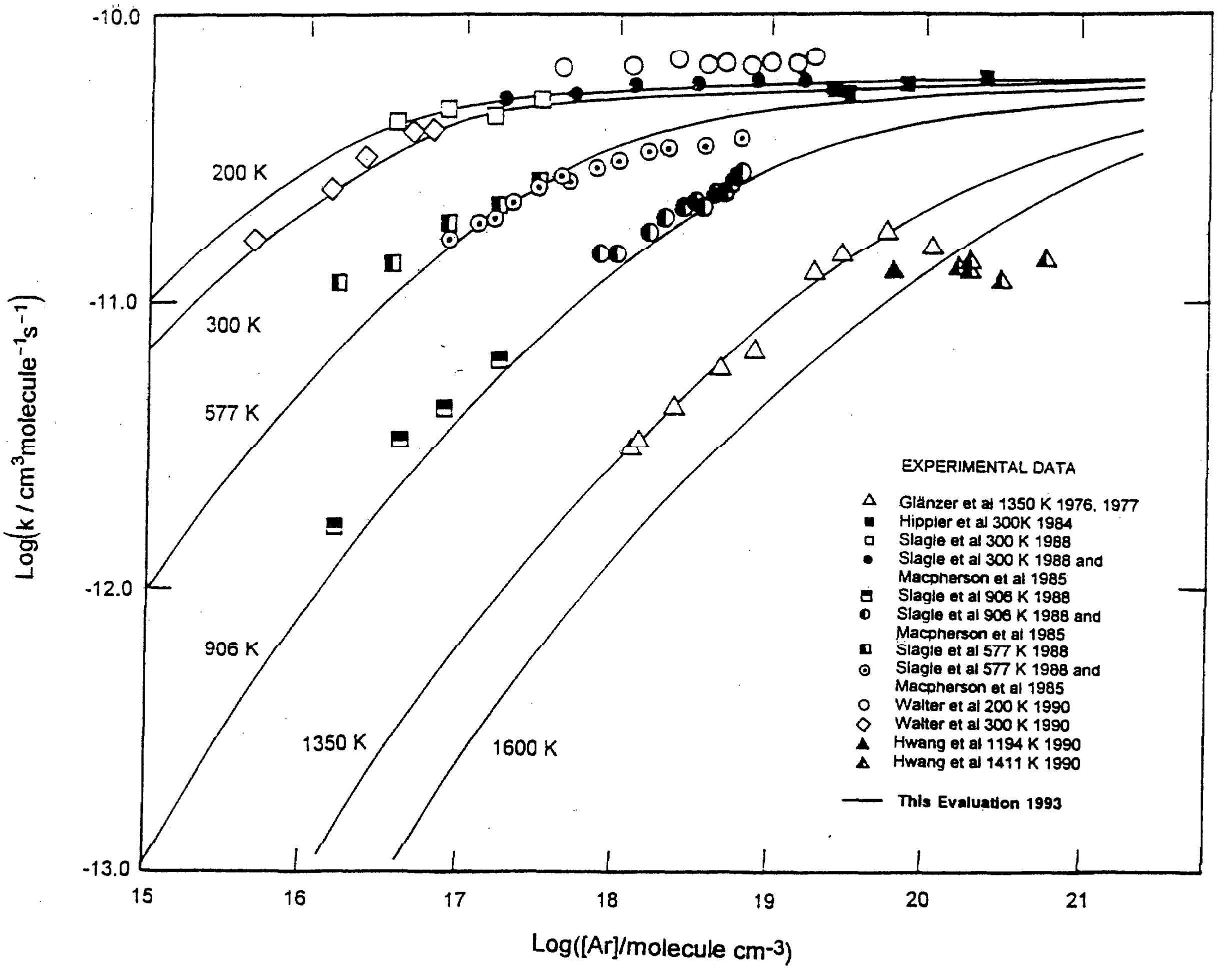
$CH_3 + CH_3 + M \rightarrow C_2H_6 + M$



C_2H_6 (+ M) → CH_3 + CH_3 (+ M)

Thermodynamic data
$\Delta H^\circ_{298} = 375$ kJ mol^{-1}
$\Delta S^\circ_{298} = 159$ J K^{-1} mol^{-1}
$Kp = 4.15\cdot10^{9}T^{-0.236}\exp(-45700/T)$ atm.

Rate Coefficient Data

k/s^{-1}	T/K	[M]/molecule cm^{-3}	Reference	Comments
Rate Coefficient Measurements				
Intermediate Fall-Off Range				
$1.2\cdot10^{-7}$	823	$7.9\cdot10^{16}(C_2H_6)$	Lin and Back, 1966[1]	(a)
$1.3\cdot10^{-7}$		$1.9\cdot10^{17}$		
$1.4\cdot10^{-7}$		$7.0\cdot10^{17}$		
$6.7\cdot10^{-6}$	893	$4.4\cdot10^{17}$		
$8.4\cdot10^{-6}$		$2.3\cdot10^{18}$		
$8.9\cdot10^{-6}$		$4.9\cdot10^{18}$		
$1.7\cdot10^{-4}$	999	$9.7\cdot10^{15}$		
$5.7\cdot10^{-4}$		$1.1\cdot10^{17}$		
$1.0\cdot10^{-3}$		$8.2\cdot10^{17}$		
$4.1\cdot10^{-7}$	839	$7.6\cdot10^{15}(C_2H_6)$	Trenwith, 1966, 1967, 1979[2]	(b)
$1.5\cdot10^{-7}$		$1.3\cdot10^{17}$		
$2.5\cdot10^{-7}$		$3.2\cdot10^{18}$		
$2.3\cdot10^{-3}$	873	$5.1\cdot10^{15}$		
$1.2\cdot10^{-6}$		$1.1\cdot10^{17}$		
$1.9\cdot10^{-6}$		$1.6\cdot10^{18}$		
$4.8\cdot10^{-16}$	913	$3.4\cdot10^{16}$		
$1.7\cdot10^{-5}$		$8.8\cdot10^{17}$		
$2.4\cdot10^{-5}$		$7.0\cdot10^{18}$		
$3.5\cdot10^{-8}$	813	$1.2\cdot10^{17}(C_2H_6)$	Scacchi *et al.*, 1971[3]	(c)
$5.8\cdot10^{-8}$		$6.2\cdot10^{17}$		
$7.7\cdot10^{-8}$		$2.5\cdot10^{18}$		
$2.0\cdot10^{15}\exp(-44280/T)$	1400–2200	$5.0\cdot10^{17}(Ar)$	Izod *et al.*, 1971[4]	(d)
$2.1\cdot10^{-7}$	838	$3.0\cdot10^{17}(C_2H_6)$	Clark and Quinn, 1976[5]	(e)
$4.2\cdot10^{-7}$		$7.6\cdot10^{18}$		
$4.8\cdot10^{-7}$		$2.1\cdot10^{19}$		
	1300–2500	$(6.6–26.5)\cdot10^{17}(Ar)$	Olson *et al.*, 1979[6]	(f)
$2.8\cdot10^{15}\exp(-42400/T)$	1240–1500	$1.3\cdot10^{16}(Ar)$	Chiang and Skinner, 1981[7]	(g)
$2.0\cdot10^{-7}$	841	$1.1\cdot10^{17}(C_2H_6)$	Kanan *et al.*, 1983[8]	(h)
$2.5\cdot10^{-7}$		$2.1\cdot10^{17}$		
$7.6\cdot10^{-7}$	871	$5.4\cdot10^{16}$		
$1.1\cdot10^{-6}$		$1.6\cdot10^{17}$		
$2.0\cdot10^{-6}$		$4.2\cdot10^{18}$		
$5.7\cdot10^{-6}$	913	$5.2\cdot10^{16}$		
$1.3\cdot10^{-5}$		$2.0\cdot10^{17}$		
$6.2\cdot10^{-6}$	902	$1.1\cdot10^{17}(C_2H_6)$	Pacey and Wimalasena, 1984[9]	(i)
$7.0\cdot10^{-6}$		$3.2\cdot10^{17}$		
$1.1\cdot10^{-5}$		$1.1\cdot10^{18}$		
$3.4\cdot10^{-5}$	938	$5.4\cdot10^{17}(H_2)$	Cao and Back, 1984[10]	(j)
$4.6\cdot10^{-5}$		$1.8\cdot10^{18}$		
$5.2\cdot10^{-5}$		$3.4\cdot10^{18}$		
$2.6\cdot10^{-4}$	998	$5.1\cdot10^{17}$		
$4.2\cdot10^{-4}$		$2.0\cdot10^{18}$		
$3.6\cdot10^{-4}$		$3.2\cdot10^{18}$		
$8.0\cdot10^{-4}$	1038	$5.0\cdot10^{17}$		
$1.1\cdot10^{-3}$		$1.1\cdot10^{18}$		
$2.4\cdot10^{-3}$		$2.8\cdot10^{18}$		
High Pressure Range				
$7.9\cdot10^{16}\exp(-45040/T)$	1200–1430	$(9–33)\cdot10^{18}$	Burcat *et al.*, 197.	(k)
$5.2\cdot10^{16}\exp(-44700/T)$	840–913	$(3.4–77.6)\cdot10^{17}(C_2H_6)$	Trenwith, 1979[2]	(b)

C_2H_6 (+ M) → CH_3 + CH_3 (+ M)

Rate Coefficient Data

k/s^{-1}	T/K	[M]/molecule cm^{-3}	Reference	Comments
Reviews and Evaluations				
$k_\infty = 2.4\cdot10^{16}\exp(-44010/T)$	750–1500		Baulch and Duxbury, 1980[12]	(l)
$k_0 = [Ar]1.7\cdot10^{-5}\exp(-34280/T)$	800–2500		Warnatz, 1984[13]	(m)
$k_\infty = 2.4\cdot10^{16}\exp(-44020/T)$	750–2000			
$k_\infty = 3.2\cdot10^{22}T^{-1.79}\exp(-45834/T)$	300–1400		Tsang and Hampson, 1986[14]	(n)
$k_\infty = 3.0\cdot10^{22}T^{-1.79}\exp(-45834/T)$	300–1400		Tsang, 1989[15]	(o)
$k_\infty = 1.8\cdot10^{21}T^{-1.24}\exp(-45700/T)$	300–2000		CEC, 1992[16]	(p)
$k_0 = [Ar]1.1\cdot10^{25}T^{-8.24}\exp(-47090/T)$	300–2000			
$k_0 = [C_2H_6]4.5\cdot10^{-2}\exp(-41930/T)$	800–1000			
$F_c(Ar) = 0.38\exp(-T/73) + 0.62\exp(-T/1180)$	300–2000			
$F_c(C_2H_6) = 0.54\exp(-T/1250)$	800–1000			

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 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.

(k) 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).

(p) Critical evaluation of gas phase chemical reactions for use in modelling combustion processes.

Preferred Values

$k_\infty = 1.8\cdot10^{21}T^{-1.24}\exp(-45700/T)$ s^{-1} over range 300–2000 K.

$k_0 = [Ar]1.1\cdot10^{25}T^{-8.24}\exp(-47090/T)$ s^{-1} over range 300–2000 K.

$k_0 = [N_2]1.1\cdot10^{25}T^{-8.24}\exp(-47090/T)$ s^{-1} over range 300–2000 K.

$k_0 = [C_2H_6]4.5\cdot10^{-2}\exp(-41930/T)$ s^{-1} over range 800–1000 K.

$F_c = 0.38\exp(-T/73) + 0.62\exp(-T/1180)$ for M = Ar and for M = N_2 over range 300–2000 K.

$F_c = 0.54\exp(-T/1250)$ for $M = C_2H_6$ over range 800–1000 K.

Reliability

$\Delta\log k_\infty = \pm0.3$ over range 300–2000 K.

$\Delta\log k_0 = \pm0.5$ for M = Ar and $M = N_2$ over range 300–2000 K.

$\Delta\log k_0 = \pm0.5$ for $M = C_2H_6$ over range 800–1000 K.

$\Delta F_c = \pm0.1$ for M = Ar over range 300–2000 K.

$\Delta F_c = \pm0.1$ 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 $2CH_3 + M \rightarrow C_2H_6 + M$ from this evaluation and the expression given for the equilibrium constant. They are based on the combined evaluation of dissociation and recombination data given in the review of Ref. 17 which assumes a nearly temperature independent rate coefficient k_∞ for the reverse recombination over the range 300–2000 K. For M = N_2 an expression for k_0 identical with that for M = Ar is assumed. In Figs. 1 and 2 the dependence on temperature of the recommended k_0 and k_∞ is shown together with the values recommended in previous compilations. Figure 3 shows fall-off curves for experiments performed near 1000 K. Theoretical fall-off curves based on the preferred values are depicted in Fig. 4. The expressions for k_0 and F_c also follow from the combination of experimental and theoretical data analysed in Ref. 17. The preferred values obtained in this way are in good agreement with the available dissociation experiments and measurements performed at lower temperatures for the reverse association of CH_3 radicals. They are not influenced by the numerous mechanistic complications of the high temperature shock tube studies of this dissociation.

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[17] J. Troe, Comb. Flame **78**, 59 (1989).

$C_2H_6 + M \rightarrow CH_3 + CH_3 + M$

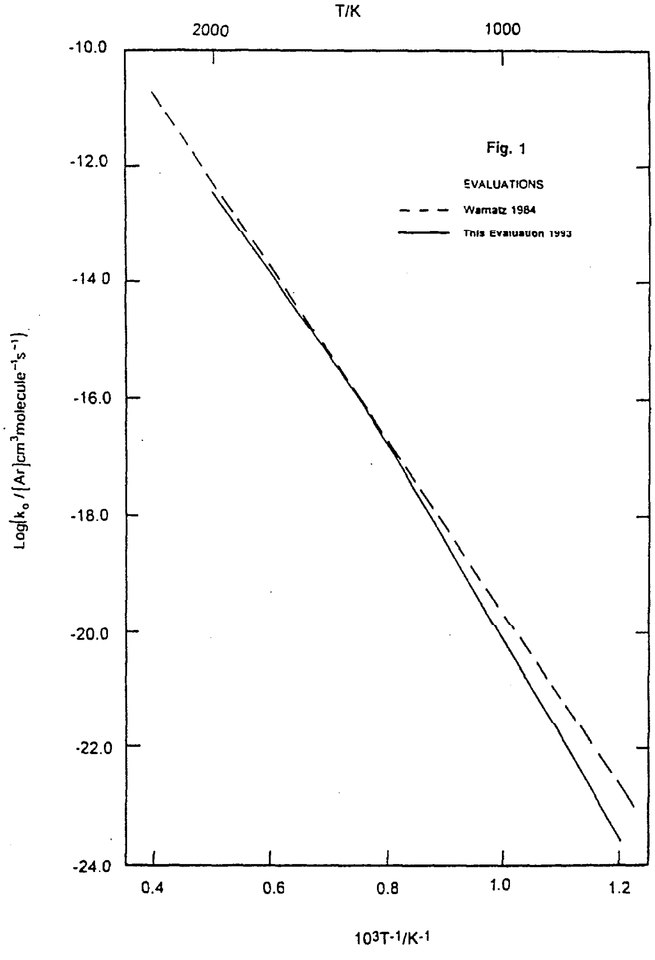


Fig. 1

$C_2H_6 + M \rightarrow CH_3 + CH_3 + M$

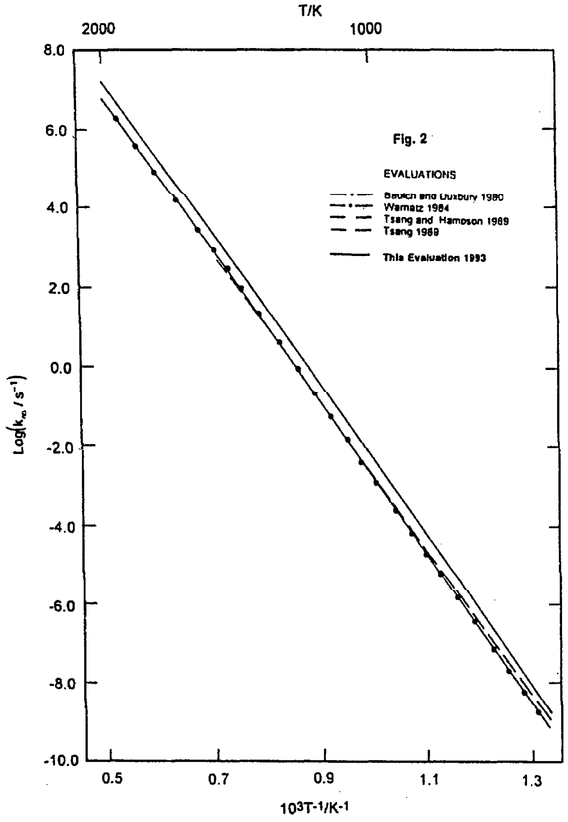


Fig. 2

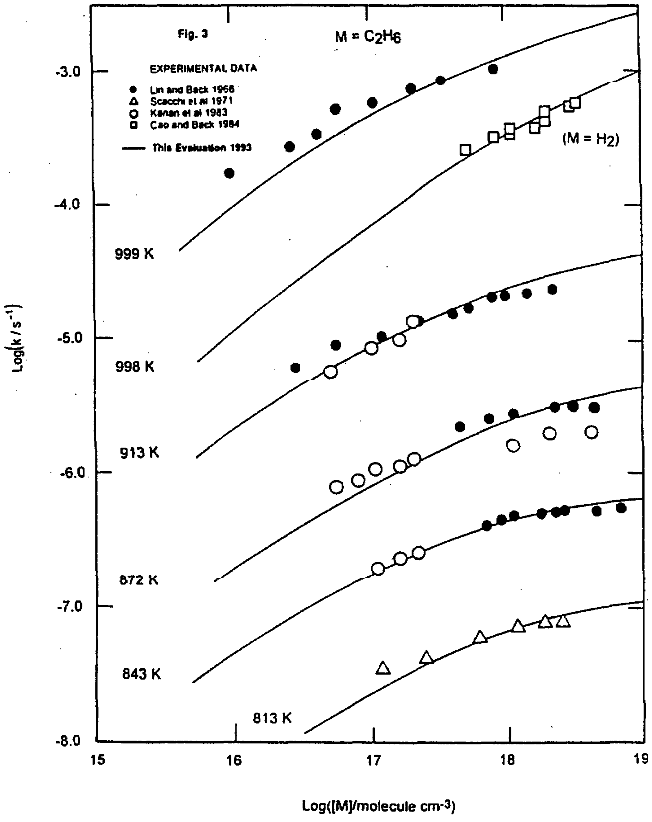
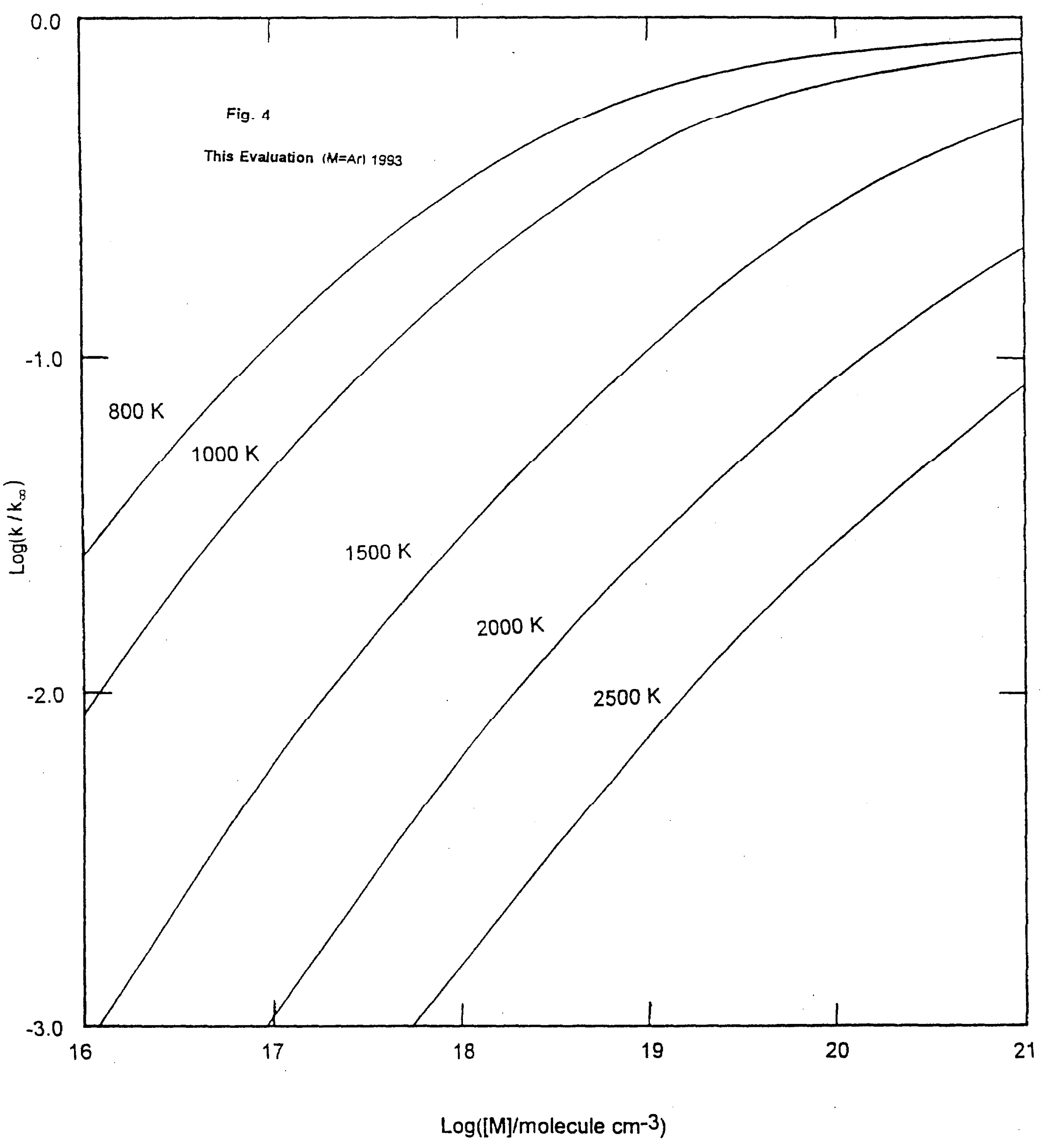


Fig. 3

$C_2H_6 + M \rightarrow CH_3 + CH_3 + M$



$CH_3 + HCHO \rightarrow CH_4 + HCO$

Thermodynamic data
$\Delta H^\circ_{298} = -61.2$ kJ mol^{-1}
$\Delta S^\circ_{298} = -20.7$ J K^{-1} mol^{-1}
$Kp = 2.1\ T^{-0.18}\exp(+7360/T)$

Rate Coefficient Data

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Comments
Rate Coefficient Measurements			
$4.2\cdot10^{-9}\exp(-11600/T)$	1170–1630	Choudhury, Sanders, and Lin, 1989[1]	(a)
Reviews and Evaluations			
$9.2\cdot10^{-21}T^{2.81}\exp(-2950/T)$	300–2500	Tsang and Hampson, 1986[2]	(b)
$3.0\cdot10^{-12}\exp(-3610/T)$	300–1000	CEC, 1992[3]	(c)

Comments

(a) Shock tube study of decomposition of *t*-butyl hydroperoxide/trioxane mixtures to generate CH_3 and HCHO, with kinetic modelling of observed CO formation. The expression: $1.48\cdot10^{-36}T^{7.4}\exp(-483/T)$ cm^3 molecule^{-1} s^{-1} was calculated using transition state theory with quantum mechanical tunnelling correction, which gave a good description of all reliable data in the temperature range 300–2000 K.

(b) Based on data of Held *et al.*[4], Manthorne and Pacey[5], Anastasi[6] and the low temperature data evaluation of Kerr and Parsonage[7].

(c) Based on data in Refs. 4,5,6,7 and in Selby[8].

Preferred Values

$k = 1.29\cdot10^{-31}T^{6.1}\exp(-990/T)$ cm^3 molecule^{-1} s^{-1} over range 300–2000 K.

Reliability
$\Delta\log k = \pm0.2$ over range.

Comments on Preferred Values

The new results provide a significant extension in the temperature range and confirm earlier indications that this reaction exhibits non-Arrhenius behaviour. Curvature in the Arrhenius plot is not so dramatic as suggested by the high temperature data of Aronowitz and Naegeli[9] and Hsu and Lin[10], which was not included in previous evaluations due to the uncertainty arising from the complex chemistry of the reaction systems employed. Reference to the Arrhenius plot shows that the new data are consistent with the lower temperature data of Held *et al.*[4], Manthorne and Pacey[5] and the evaluation of Kerr and Parsonage[7], but not the data reported by Anastasi[6]. Choudhury *et al.*[11] have re-analysed the data of Anastasi, which was obtained using the direct molecular modulation technique, taking account of additional CH_3 radical loss processes. The reworked rate constants are much more consistent with the data at higher and lower temperatures. The recommended expression is a best fit to the data of Choudhury *et al.*[1], the reworked data from Anastasi, together with those at lower temperatures from Refs. 4, 5, and 7.

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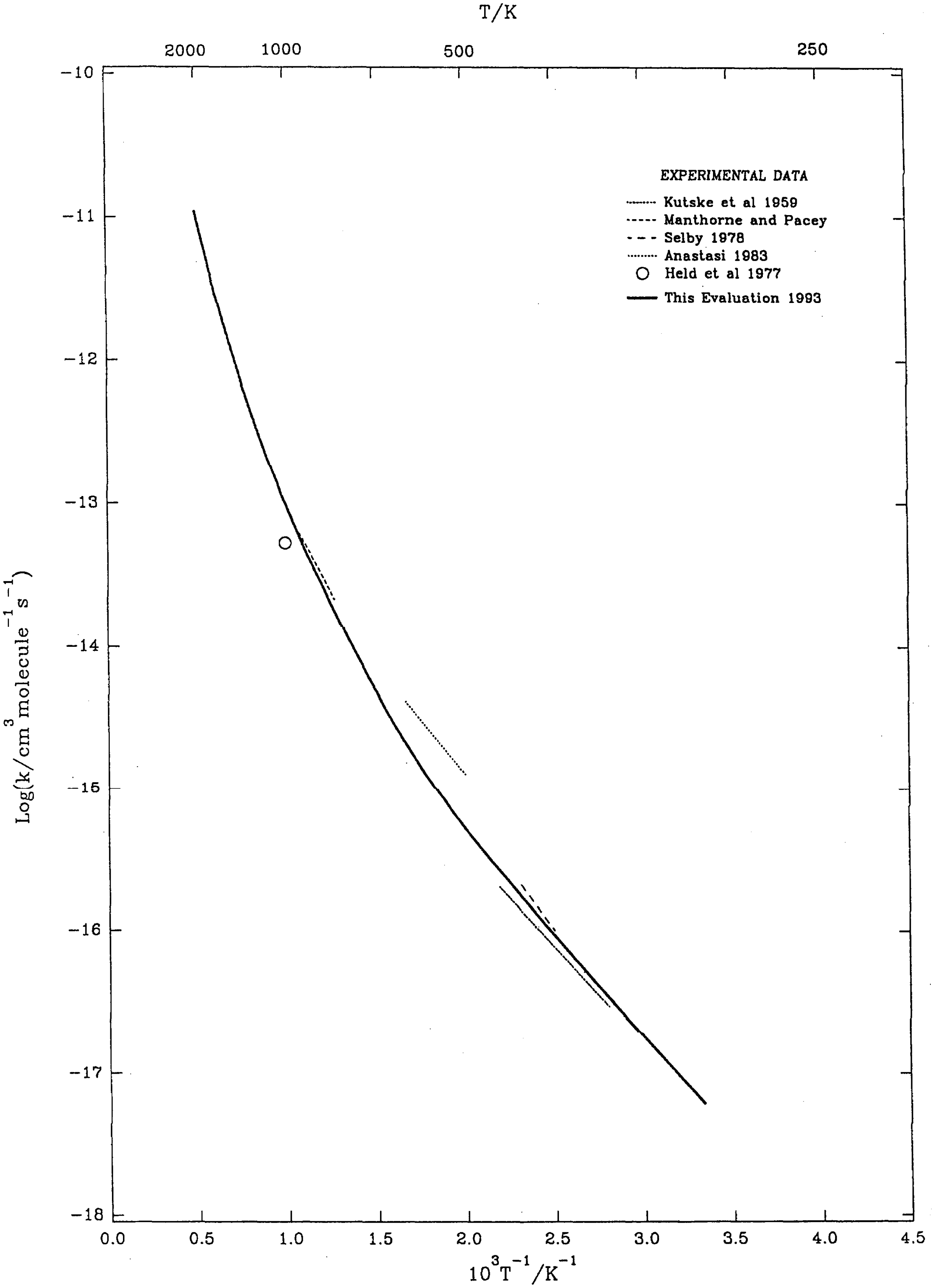
$CH_3 + HCHO \rightarrow CH_4 + HCO$



$CH_3 + C_2H_5 (+ M) \rightarrow C_3H_8 (+ M)$ (1)
$CH_3 + C_2H_5 \rightarrow CH_4 + C_2H_4$ (2)

Thermodynamic Data

$\Delta H^\circ_{298}(1) = -367$ kJ mol^{-1}
$\Delta S^\circ_{298}(1) = -175$ J K^{-1} mol^{-1}
$Kp(1) = 4.4\text{–}10^{-13}T^{+0.96}\exp(+44700/T)$ atm^{-1}

$\Delta H^\circ_{298}(2) = -285$ kJ mol^{-1}
$\Delta S^\circ_{298}(2) = -40.5$ J K^{-1} mol^{-1}
$Kp(2) = 3.0\cdot10^{-3}T^{0.078}\exp(+34500/T)$ 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				
$3.3\cdot10^{-10}$	298	$4.3\cdot10^{18}(H_2)$	Pagsberg, Ratajczak, and Sillesen, 1992[1]	(a)
High Pressure Range				
$(9.3 \pm 4.2)\cdot10^{-11}$	300	$1.2\cdot10^{17}$(Ar)	Garland and Bayes, 1990[2]	(b)
Reviews and Evaluations				
$k_\infty = 1.2\cdot10^{-11}$	300–2000		Warnatz, 1984[3]	(c)
$k_\infty = 4.7\cdot10^{-11}(T/300)^{-0.5}$	300–2500		Tsang and Hampson, 1986[5]	(d)
$k_\infty = 3.2\cdot10^{-10}T^{-0.32}$	300–2500		Tsang, 1989[6]	(e)
$k_\infty = 4.7\cdot10^{-11}$	300–800		CEC, 1992[8]	(f)
$k_2/k_1 = 0.04$				

Comments

(a) Pulse radiolysis of H_2/C_2H_4 mixtures. CH_3 monitored by IR absorption at the Q(3,3) line of the $v_2 = 0 \rightarrow 1$ vibrational transition at 606.12 cm^{-1}. A value $k_2/(k_1 + k_2) = 0.5$ was estimated by gas chromatographic analysis.

(b) Co-photolysis of acetone (1–35 mTorr.) and 3-pentanone (5 mTorr.). $[CH_3]$ and $[C_2H_5]$ decays monitored by photoionization mass spectrometry using the resonance lines of 121.6 nm and 147 nm. Computer modelling of the concentration profiles of the two radicals. Rate coefficient assumed in the high pressure limit.

(c) Review of literature data. Recommended value based on results of Ref. 4.

(d) Evaluated from the rate coefficients of CH_3 and C_2H_5 self-recombination reactions and the cross combination ratio.

(e) Derived from results of Parkes and Quinn[7] for C_2H_5 self-recombination over the range 300–800 K and the geometrical mean rule of cross combination ratios.

(f) Accepts the recent value of k_∞ of Anastasi and Arthur[9] at 308 K.

Preferred Values

$k_\infty(1) = 5.6\cdot10^{-11}$ cm^3 molecule^{-1} s^{-1} over range 300–2000 K.

Reliability

$\Delta\log k_\infty(1) = \pm0.3$ over the range 300–2000 K.

Comments on Preferred Values

The recommended value for $k_\infty(1)$ is a weighted average of earlier experiments[2,5,6,9] in agreement with SACM calculations following Ref. 10. A temperature independent value of $k_\infty(1)$ is assumed until more definitive experimental information is available.

Reduced fall-off curves of this recombination are identical to those for the dissociation $C_3H_8 + M \rightarrow CH_3 + C_2H_5 + M$ and are represented on the corresponding data sheet. A branching ratio $k_2/(k_1 + k_2) = 0.04$ for 300 K follows from Refs. 5 and 8. Nevertheless, a value of 0.5 has been recently estimated in Ref. 1. A confirmation of this last value is necessary.

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C_3H_8 (+ M) → CH_3 + C_2H_5 (+ M)

Thermodynamic data
ΔH°_{298} = 367 kJ mol^{-1}
ΔS°_{298} = 175 J K^{-1} mol^{-1}
$Kp = 2.3 \cdot 10^{12} T^{-0.96} \exp(-44700/T)$ atm.

Rate Coefficient Data

k/s^{-1}	T/K	[M]/molecule cm^{-3}	Reference	Comments
Rate Coefficient Measurements				
Intermediate Fall-Off Range				
$1.3 \cdot 10^{16} \exp(-41800/T)$	1050–1250	$1 \cdot 10^{19}$(Ar)	Lifshitz and Frenklach, 1975[1]	(a)
$4.0 \cdot 10^{16} \exp(-42520/T)$	817	$1.2 \cdot 10^{18}$(C_3H_8)	Allara and Edelson, 1975[2]	(b)
$5.0 \cdot 10^{16} \exp(-42723/T)$	748–793		Jezequel, Baronnet, and Niclause, 1978[4]	(c)
12.5	1250	$(2.6–6.0) \cdot 10^{18}$(Ar)	Bradley, 1979[5]	(d)
37.6	1350			
82.6	1450			
153	1550			
$3 \cdot 10^{-3}$	1008	$5.7 \cdot 10^{18}$(Ar)	Pratt and Rogers, 1979[6]	(e)
$2.5 \cdot 10^{16} \exp(-41400/T)$	1300–1700	$5 \cdot 10^{18}$(Ar)	Koike and Gardiner, 1980[7]	(f)
$6.7 \cdot 10^{16} \exp(-45390/T)$	1200–1450	$1.5 \cdot 10^{19}$(Ar)	Chiang and Skinner, 1981[8]	(g)
$4.5 \cdot 10^{16} \exp(-42623/T)$	873–1053	$2.0 \cdot 10^{18}$(N_2)	Juste, Scacchi and Niclause, 1981[9]	(h)
$4.0 \cdot 10^{16} \exp(-42800/T)$	1110–1235	$6.0 \cdot 10^{18}$(N_2)	Hautman *et al.*, 1981[10]	(i)
$3.6 \cdot 10^{14} \exp(-37600/T)$	1300–1700	$9.0 \cdot 10^{18}$(Ar,N_2)	Simmie, Gardiner, and Eubank, 1982[11]	(j)
$5.1 \cdot 10^{16} \exp(-41969/T)$	773–793	$2.5 \cdot 10^{18}$(C_3H_8)	Kanan, Purnell, and Smith, 1983[12]	(k)
$7.74 \cdot 10^{11} \exp(-28030/T)$	1400–1800	$(0.9–3.6) \cdot 10^{18}$(Kr)	Al-Alami and Kiefer, 1983[13]	(l)
$4.5 \cdot 10^{-7} \exp(-28030/T)$[Kr]	1800–2300	$(0.5–1.0) \cdot 10^{18}$(Kr)		
$1.1 \cdot 10^{16} \exp(-42270/T)$	1100–1450	$1 \cdot 10^{19}$(Ar)	Hidaha, Oki, and Kawano, 1989[14]	(m)
Reviews and Evaluations				
$k_\infty = 1.5 \cdot 10^{16} \exp(-41300/T)$	1100		Tsang, 1969[15]	(n)
$k_\infty = 5.6 \cdot 10^{16} \exp(-42600/T)$	1100		Tsang, 1981[16]	(o)
$k_\infty = 5.0 \cdot 10^{15} \exp(-42095/T)$	800–2000		Warnatz, 1984[17]	(p)
$k_\infty = 7.9 \cdot 10^{22} T^{-1.8} \exp(-44637/T)$	300–1200		Tsang, 1988[18]	(q)
$k_\infty = 6.9 \cdot 10^{22} T^{-1.79} \exp(-44637/T)$	300–1200		Tsang, 1989[20]	(r)

Comments

(a) Shock wave study using mixtures of 0.4–1.6% C_3H_8 in Ar. Mechanism with reactions discussed.

(b) Modelling of the C_3H_8 pyrolysis based on results of Leathard and Purnell[3].

(c) Pyrolysis of C_3H_8 with chromatographic analysis of products. The major primary products are methane, ethylene, hydrogen and propene. Modelling of reaction.

(d) Pyrolysis of C_3H_8 in Ar studied in a single-pulse shock tube. Analysis of products by gas chromatography.

(e) Early stages of the pyrolysis of C_3H_8 studied by a wall-less reactor technique. Measurements of the rates of formation of methane, ethene and propene.

(f) Thermal decomposition of C_3H_8 in a shock tube coupled to IR laser absorption spectroscopy. Modelling with a 44-reaction mechanism.

(g) Pyrolysis of C_3H_8-Ar mixtures behind reflected shock waves. H atoms monitoring by atomic resonance absorption spectroscopy.

(h) Thermal decomposition of C_3H_8 in a continuous jet-stirred reactor. Reaction products measured by gas chromatography.

(i) Turbulent flow reactor study of C_3H_8 pyrolysis. The kinetics are described by a 34-reaction mechanism.

(j) Shock wave study using mixtures of 5% C_3H_8 in Ar and N_2. Analysis by IR laser absorption kinetic spectroscopy.

(k) Pyrolysis of C_3H_8 in a static reactor. Products analysed by GC.

(l) Pyrolysis of C_3H_8 studied in incident shock waves with the laser-schlieren technique. Mechanism with 30 reactions.

(m) Thermal decomposition of C_3H_8 studied in reflected shock waves monitoring absorption-time profiles at 3.39 μm due to C_3H_8, C_2H_4, C_2H_2 and CH_4.

(n) Estimation based on the geometrical mean rule and thermochemical parameters.

(o) Review of literature.

(p) Review of literature data.

(q) Review of literature data. The recommended value is based on the high pressure limiting rate coefficient for the recombination $CH_3 + C_2H_5 \rightarrow C_3H_8$ ($4.7 \cdot 10^{-44} (T/300)^{-0.5}$ cm^3 $molecule^{-1}$ s^{-1} [19]) and the equilibrium constant tabulated here.

(r) Based on the results of Parkes and Quinn[21] for the reaction $C_2H_5 + C_2H_5 \rightarrow n\text{-}C_4H_{10}$ and the geometrical mean rule.

Preferred Values

$k_\infty = 1.1 \cdot 10^{17} \exp(-42470/T)$ s^{-1} over range 700–2000 K.

$k_0 = [Ar]1.3 \cdot 10^{-5} \exp(-32700/T)$ s^{-1} over range 700–2000 K.

$F_c = 0.24\exp(-T/1946) + 0.76\exp(-T/38)$ for M = Ar over range 700–2000 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ over range 700–2000 K.

$\Delta \log k_0 = \pm 0.5$ for M = Ar over range 700–2000 K.

$\Delta F_c = \pm 0.2$ over range 700–2000 K.

Comments on Preferred Values

The preferred values are based on theoretical modelling[22–24] which is required to reconcile the largely scattered data. These calculations predict for the high pressure rate coefficient of the reverse recombination process a value $5.6 \cdot 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} over the range 300–2000 K. The value at 300 K is in good agreement with recent direct determinations[25,26]. The preferred dissociation rate coefficient k_∞ is obtained via detailed balance. The recommended k_0 was estimated using an average energy transferred per collision of 120 cm^{-1} which leads to collisional efficiencies of 0.12–0.18 between 700–2000 K. In Figs. 1 and 2 the temperature dependence of k_0 and k_∞ is shown. Figure 3 shows theoretical falloff curves and selected experimental rate coefficients. At 1250 K there is considerable scatter in the results.

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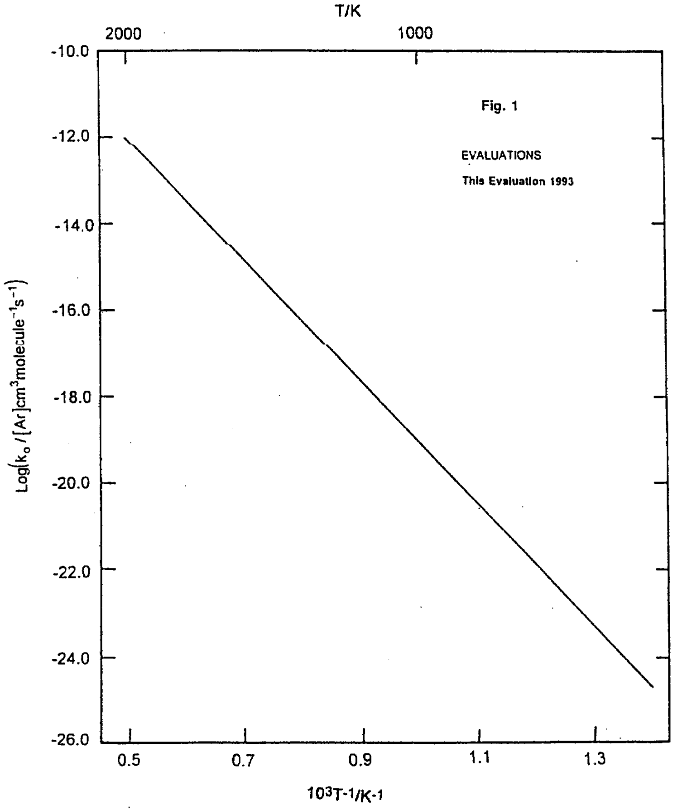
$C_3H_8 + M \rightarrow CH_3 + C_2H_5 + M$



$C_3H_8 + M \rightarrow CH_3 + C_2H_5 + M$

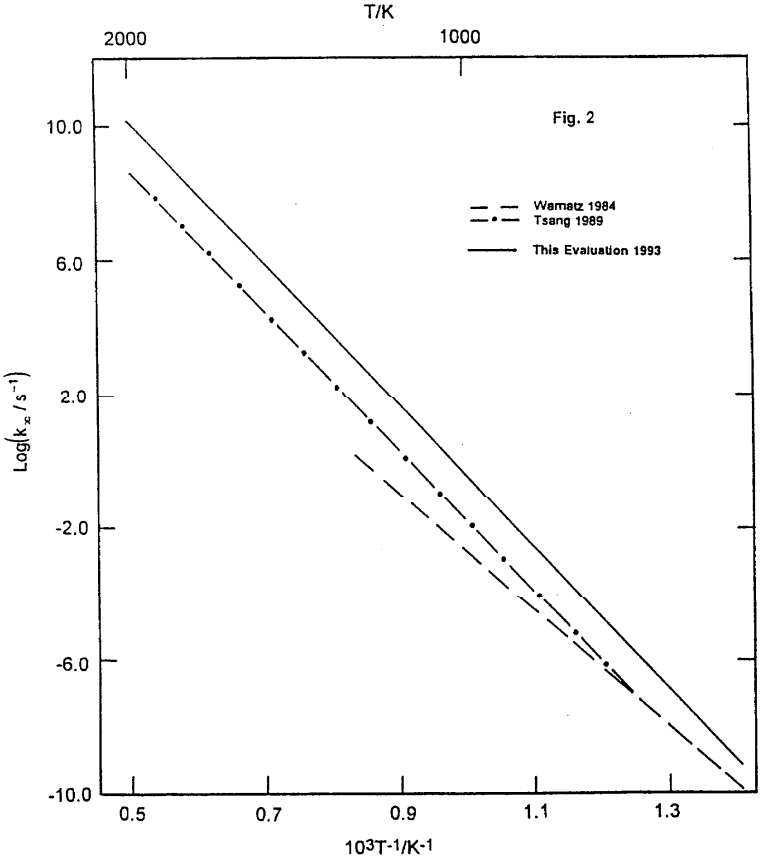


Fig. 2

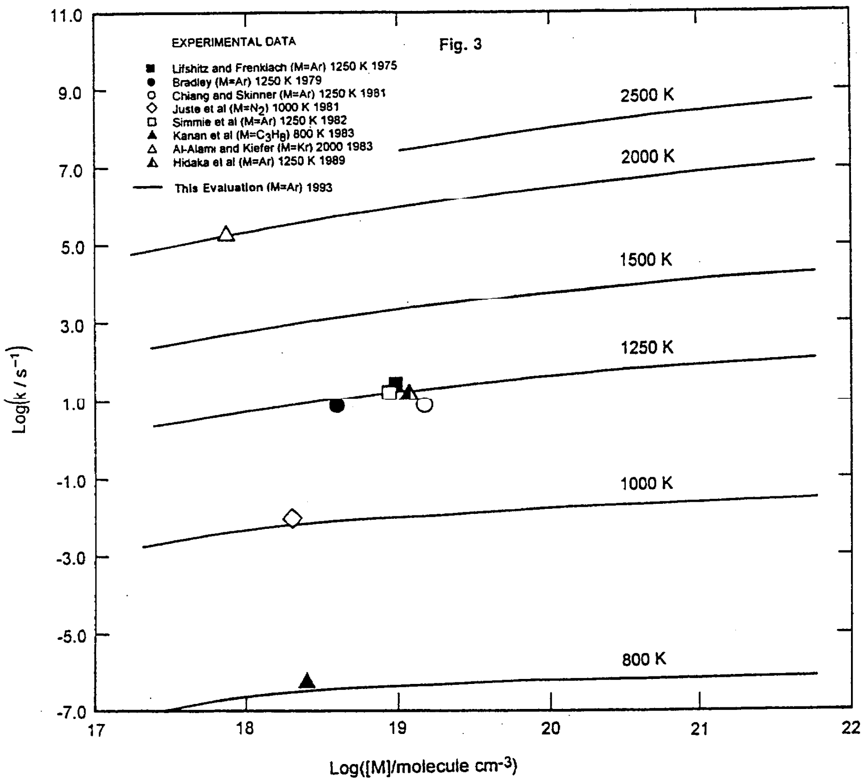


Fig. 3

$HCHO (+ M) \rightarrow CHO + H (+ M)$ (1)
$\rightarrow CO + H_2 (+ M)$ (2)

Thermodynamic Data

$\Delta H^\circ_{298}(1) = 377$ kJ mol^{-1}
$\Delta S^\circ_{298}(1) = 121$ J K^{-1} mol^{-1}
$Kp(1) = 1.19 \cdot 10^4 T^{0.879} \exp(-45400/T)$ atm.

$\Delta H^\circ_{298}(2) = 5.3$ kJ mol^{-1}
$\Delta S^\circ_{298}(2) = 109.3$ J K^{-1} mol^{-1}
$Kp(2) = 1.36 \cdot 10^5 T^{0.37} \exp(-895/T)$ atm.

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

k/cm^3 molecule^{-1}s^{-1}	T/K	Reference	Comments
Rate Coefficient Measurements			
Low Pressure Range			
$[M]8.0 \cdot 10^{-8} \exp(-36300/T)$	1400–2200	Schecker and Jost, 1969[1]	(a)
$[M]3.5 \cdot 10^{-8} \exp(-17700/T)$	1350–2900	Peeters and Mahnen, 1973[2]	(b)
$[M]1.7 \cdot 10^{-10} \exp(-43800/T)$	1070–1225	Aronowitz *et al.*, 1977[3]	(c)
$[M]2.2 \cdot 10^{-8} \exp(-35600/T)$	1700–2300	Bhaskaran *et al.*, 1979[4]	(d)
$[M]6.0 \cdot 10^{-7} \exp(-43800/T)$	1800–2500	Dean *et al.*, 1979[5]	(e)
$[M]5.5 \cdot 10^{-8} \exp(-40800/T)$	1600–3000	Dean *et al.*, 1980[6]	(f)
$[M]4.2 \cdot 10^{-10} \exp(-14600/T)$	1400–2000	Vandooren and Van Tiggelen, 1981[7]	(g)
$[M]5.25 \cdot 10^{-9} \exp(-37700/T)$	2200–2650	Saito *et al.*, 1985[8]	(h)
$[M]k_o(2) = [Ar]3.89 \cdot 10^{-15}$	1915	Buxton and Simpson, 1986[9]	(i)
$= [Ar]1.74 \cdot 10^{-14}$	2107		
$= [Ar]2.34 \cdot 10^{-14}$	2218		
$[M]k_o(1) = 2.08 \cdot 10^{-8} \exp(-39171/T)$	1650–2200	Rimpel and Just, 1988[10]	(j)
$[M]k_o(2) = 5.18 \cdot 10^{-10} \exp(-28100/T)$	1900–2400		
$k_o(1) = [Ar]2.7 \cdot 10^{12} T^{-5.54} \exp(-48660/T)$	1700–3200	Irdam *et al.*, 1992[11]	(k)
Reviews and Evaluations			
$[M]k_o(1) = 8.3 \cdot 10^{-8} \exp(-38500/T)$	1000–3000	Warnatz, 1984[12]	(l)
$[M]k_o(1) = 2.0 \cdot 10^{17} T^{-6.9} \exp(-48590/T)$	1000–3000	Tsang and Hampson, 1986[13]	(m)
$[M]k_o(1) = [Ar]2.1 \cdot 10^{-8} \exp(-39200/T)$	1500–2500	CEC, 1992[14]	(n)

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) Shock tube study of thermal decomposition of HCHO. Analysis by cwCO laser absorption to follow HCHO decay and CO production. Measurements performed between 1750–2220 K and total gas density from $1.28 \cdot 10^{18}$ to $1.32 \cdot 10^{19}$ molecule cm^{-3} (0.05–2% of H_2CO).

(j) Thermal decomposition of HCHO behind reflected shock wave. H atom production measured by ARAS. M = Ar.

(k) Shock tube study of the pyrolysis of HCHO. The HCHO was generated by the thermal dissociation of its cyclic trimer, 1,3,5-trioxane. RRKM analysis based on *ab initio* potential energy surface. The simulations shows that reaction (2) is 2–3 times faster than reaction (1) between 2000–3000 K.

(l) Based on the shock tube data of Schecker and Jost[1], Bhaskaran *et al.*[4], and Dean *et al.*[5,6].

(m) Theoretical calculation of k_1 in Ar using RRKM theory.

(n) Critical evaluation of gas phase chemical reactions for use in modelling combustion processes.

Preferred Values

$k_o(1) = [Ar]2.7 \cdot 10^{12} T^{-5.54} \exp(-48660/T)$s^{-1} over range 1700–3200 K.

$k_o(2)/k_o(1) \approx 2.5$ over range 2000–3000 K.

Reliability

$\Delta[k_o(2)/k_o(1)] = \pm 0.5$ over range 2000–3000 K.

Comments on Preferred Values

The reaction in second order under all conditions relevant to combustion. Recent shock waves studies are in conflict. the results of Buxton and Simpson[9] are in good agreement with those of Dean *et al.*[6] and Saito *et al.*[8] indicating that channel (2) is unimportant near 2000 K. However, Rimpel and Just[10] and more recently Irdam *et al.*[11] suggest that reaction (2) predominates over reaction (1). In fact, from Ref. 11 a $k_o(2) \approx (2\text{–}3)k_o(1)$ has been found. We have revised the preferred values for $k_o(1)$, and the recommended value corresponds to Ref. 11. On the other hand, even though the value of the branching ratio is unclear, we have selected a $k_o(2)/k_o(1)$ value similar to that given in Ref. 11.

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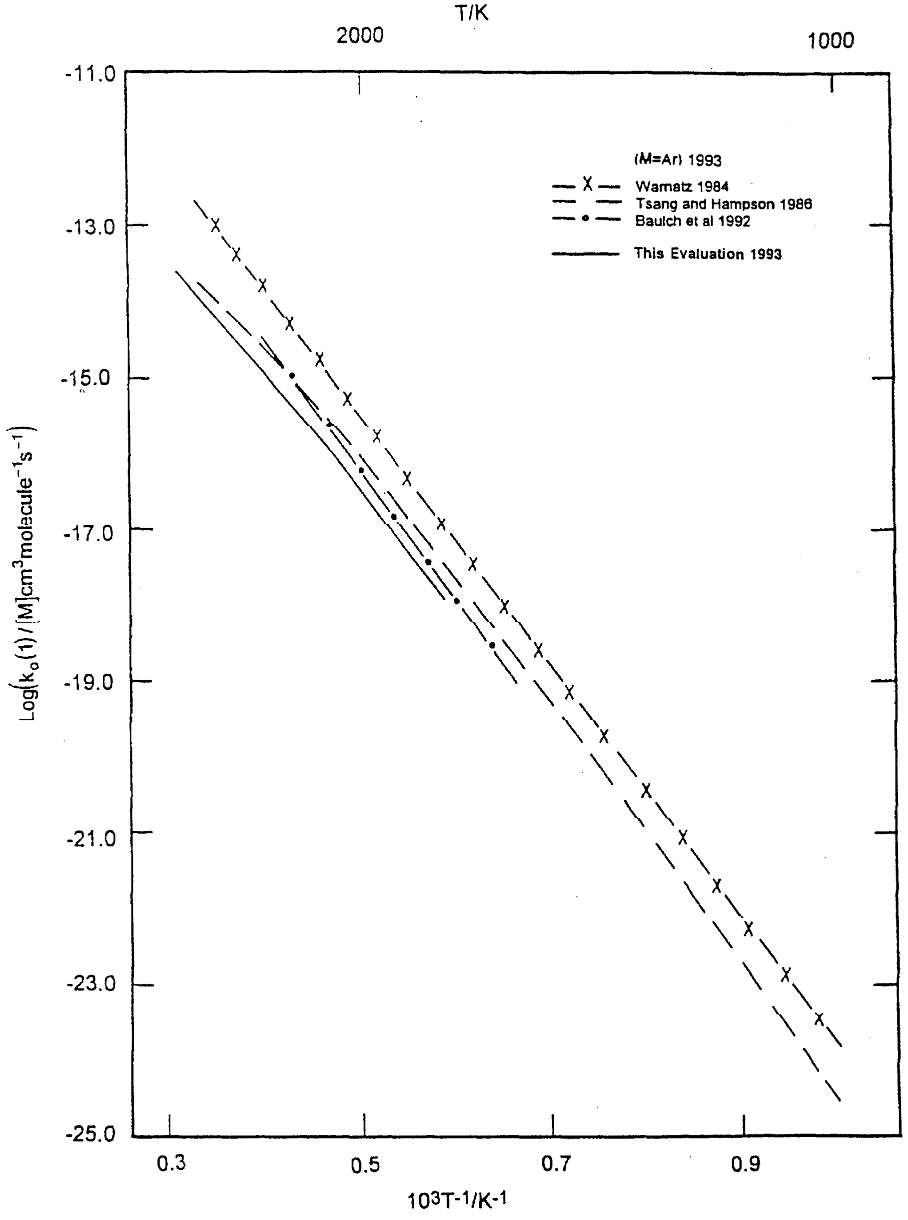
HCHO + M → CHO + H + M



CH_3O (+ M) → HCHO + H (+ M)

Thermodynamic Data
$\Delta H^\circ_{298} = 85.8$ kJ mol^{-1}
$\Delta S^\circ_{298} = 105$ J K^{-1} mol^{-1}
$Kp = 6.67\cdot 10^4 T^{0.67} \exp(-10300/T)$ atm.

Rate Coefficient Data

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Comments
Rate Coefficient Measurements			
$9.05\cdot 10^{-11} \exp(-6794/T)$ (M = Ar or He)	550–1660	Choudhury *et al.*, 1990[1]	(a)
Reviews and Evaluations			
$3.16\cdot 10^2\ T^{-2.7} \exp(-15400/T)$	300–1000	CEC, 1992[2]	(b)

Comments

(a) Pyrolysis of CH_3ONO in static system (550–770 K) with product analysis (CO, HCHO and CH_3OH) by FTIR spectroscopy, and in shock tube (1000–1660 K) with product analysis (CO and NO) by laser absorption spectroscopy. Rate constants obtained from kinetic modelling of the product yields, and compared with theoretical RRKM calculations.

(b) Based on k_∞ from Batt[3] and RRKM calculations carried out by Tsang and Hampson[4].

Preferred Value

$k_0 = 9.0\cdot 10^{-11} \exp(-6790/T)$ cm^3 molecule^{-1} s^{-1} over the range 300–1700 K.

Reliability
$\Delta \log k_0 = \pm 0.3$ over the range 300–1700 K.

Comments on Preferred Values

Under practically all conditions in combustion systems, the reaction is in the second-order region. The recent experimental measurements of k_0 are the first reported for this reaction. The values are substantially higher than the previous theoretical estimates of Greenhill *et al.*[5] and Tsang and Hampson[4] (e.g. a factor of 150 at 555 K and a factor of 2 at 1250 K). The experimental data provide the basis for the recommended values.

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$CH_3O + O_2$ → HCHO + HO_2 (1)
→ $CH_2OH + O_2$ (2)
→ HCHO + H + O_2 (3)

Thermodynamic data
ΔH°_{298} (1) = −122.0 kJ mol^{-1}
ΔS°_{298} (1) = 14.1 J K^{-1} mol^{-1}
Kp (1) = $4.63 T^{-0.28} \exp(+14500/T)$

ΔH°_{298} (2) = −33.4 kJ mol^{-1}
ΔS°_{298} (2) = 17.9 J K^{-1} mol^{-1}
Kp (2) = $4.02 T^{0.19} \exp(+3900/T)$

ΔH°_{298} (3) = 85.8 kJ mol^{-1}
ΔS°_{298} (3) = 104.7 J K^{-1} mol^{-1}
Kp (3) = $6.67\cdot 10^4 T^{0.67} \exp(-10300/T)$ 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			
$7.28\cdot 10^{-43} T^{9.5} \exp(2768/T)$	298–973	Wantuck *et al.*, 1987[1]	(a)
Reviews and Evaluations			
$7.2\cdot 10^{-14} \exp(-1080/T)$	298–610	IUPAC, 1992[2]	(b)
$3.9\cdot 10^{-14} \exp(-900/T)$	200–300	NASA, 1992[3]	(c)
$6.7\cdot 10^{-14} \exp(-1070/T)$	300–1000	CEC, 1992[4]	(d)

Comments

(a) Laser photolysis of CN_3ONO or CH_3OH at 193 nm; CH_3O monitored by LIF. Pseudo first order conditions with excess O_2. Non Arrhenius behaviour observed over the whole temperature range. Their own data together with those of Gutman *et al.*[5] and Lorenz *et al.*[6] were well described by a bi-exponential expression: $k = 1.5 \cdot 10^{-10}\exp(-6028/T) + 3.6 \cdot 10^{-14}\exp(-880/T)$ cm^3 molecule^{-1} s^{-1}.

(b) Based on data of Gutman *et al.*[5], Lorenz *et al.*[6] and Wantuck *et al.*[1].

(c) Based on data of Lorenz *et al.*[6].

(d) Based on data of Gutman *et al.*[5], Lorenz *et al.*[6].

Preferred Values

$k_1 = 3.6 \cdot 10^{-14} \exp(-880/T)$ cm^3 molecule^{-1} s^{-1} over range 300–1000 K.

Reliability

$\Delta \log k_1 = \pm 0.1$ at 500 K rising to ± 0.3 at 300 K and 1000 K.

Comments on Preferred Values

The new data from Wantuck *et al.*[1] extend the temperature range for which direct measurements of k are available up to 1000 K. The agreement with earlier direct rate measurements in the overlapping temperature range is good. The temperature dependence in the new study is non-Arrhenius over the whole range covered and suggests an increasing contribution, at the higher temperatures, of additional channels: $CH_3O + O_2 \rightarrow CH_2OH + O_2$ (2) and $CH_3O + O_2 \rightarrow HCHO + H + O_2$ (3) for methoxy radical removal by O_2. The double exponential expression given by Wantuck *et al.*[1], was obtained by fitting the data from the three direct studies[1,5,6], and is applicable for the overall reaction up to 1000 K. The component with the larger E/R of 6028 K is remarkably similar to the expression recommended in this evaluation for the decomposition reaction: $CH_3O + M \rightarrow HCHO + H + M$ (M = Ar or He, $k = 9.0 \cdot 10^{-11}\exp(-6790/T)$ cm^3 molecule^{-1} s^{-1}), and therefore may be provisionally assigned to channel (3).

The recommendation for channel (1) is the low E/R component of the bi-exponential expression of Wantuck *et al.*[1]; it is not significantly different from that recommended by NASA[3] for this reaction in the low temperature range.

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$CH_2OH + O_2 \rightarrow CH_2O + HO_2$

Thermodynamic Data

$\Delta H^\circ_{298} = -88.3$ kJ mol^{-1}

$\Delta S^\circ_{298} = -3.8$ J K^{-1} mol^{-1}

$Kp = 11.5T^{-0.47}\exp(+10570/T)$

Rate Coefficient Data

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Comments
Rate Coefficient Measurements			
$1.7 \cdot 10^{-11}$	296	Miyoshi, Matsui, and Washida, 1990[1]	(a)
Reviews and Evaluations			
$1.7 \cdot 10^{-11}\exp(-3600/T)$	300–2000	Warnatz, 1984[2]	(b)
$9.1 \cdot 10^{-12}$	298	NASA, 1992[3]	(c)
$2.6 \cdot 10^{-9}T^{-1} + 1.2 \cdot 10^{-10}\exp(-1800/T)$	300–1200	CEC, 1992[4]	(d)
$9.4 \cdot 10^{-12}$	298	IUPAC, 1992[5]	(e)

Comments

(a) Laser flash photolysis of CH_3COCH_2OH with decay of CH_2OH monitored by photoionization MS.
(b) Based on high-temperature data from shock-tube and other studies.
(c) Average of data of Grotheer *et al.*[6], Dōbē *et al.*[7], and Payne *et al.*[8].
(d) See Comments on Preferred Values.
(e) Average of room temperature data of Grotheer *et al.*[6], Nesbitt *et al.*[9], Pagsberg *et al.*[10], Miyoshi *et al.*[1], Grotheer *et al.*[11], Dōbē *et al.*[7], and Payne *et al.*[8].

Preferred Value

$k = 2.6 \cdot 10^{-9} T^{-1} + 1.2 \cdot 10^{-10} \exp(-1800/T)$ cm^3 molecule^{-1} s^{-1} over range 300–1200 K.

Reliability

$\Delta \log k = \pm 0.1$ at 300 K increasing to ± 0.3 at 1200 K.

Comments on Preferred Values

The results of Miyoshi *et al.*[1] have become available since our previous evaluation[4], and are in good agreement with the other most recent room temperature measurements[6–11]. Our previous recommendation[4], based on an average room temperature rate coefficient[6–11], and the temperature dependences observed by Vandooren and van Tiggelen[12] and by Grotheer *et al.*[6], remains unaltered.

As previously pointed out[4], it is difficult to reconcile the data of Nesbitt *et al.*[9], over the temperature range 215–250 K, with the recommended high temperature data. More work is needed to confirm the temperature dependence of this reaction.

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$$\begin{aligned} CH_3O_2 + CH_3O_2 &\rightarrow CH_3O + CH_3O + O_2 \quad (1)\\ &\rightarrow CH_3OH + HCHO + O_2 \quad (2)\\ &\rightarrow CH_3OOCH_3 + O_2 \quad (3) \end{aligned}$$

Thermodynamic Data

$\Delta H^\circ_{298}(1) = 19.8$ kJ mol^{-1}

$\Delta S^\circ_{298}(1) = 124.8$ J K^{-1} mol^{-1}

$Kp(1) = 8.0\cdot10^{11}T^{-1.65}\exp(-2080/T)$ atm

$\Delta H^\circ_{298}(2) = -337.7$ kJ mol^{-1}

$\Delta S^\circ_{298}(2) = 126.0$ J K^{-1} mol^{-1}

$Kp(2) = 1.2\cdot10^{18}T^{-3.38}\exp(+38800/T)$ 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			(a)
$k = 3.6\cdot10^{-13}$	298	Simon, Schneider, and Moortgat, 1990[1]	(b)
$k = 1.3\cdot10^{-13}\exp(365/T)$	248–573	Lightfoot, Veyret, and Lesclaux, 1990[2]	(c)
$k = 1.3\cdot10^{-13}\exp(297/T)$ at 11 Torr	268–350	Jenkin and Cox, 1991[3]	(d)
$k = 8.9\cdot10^{-14}\exp(424/T)$ at 760 Torr			
$k = 1.0\cdot10^{-13}\exp(416/T)$	248–650	Lightfoot *et al.*, 1991[4]	(e)
Branching Ratio Measurements			(a)
$k_1/k_2 = 7.5\exp(-760/T)$	376–430	Ballod *et al.*, 1989[5]	(f)
$k_1/(k_2 + k_3) = 45\exp(-1470/T)$	388–573	Lightfoot, Veyret, and Lesclaux, 1990[2]	(c)
$k_1/(k_2 + k_3) = 19\exp(-1131/T)$	223–333	Horie, Crowley, and Moortgat, 1990[6]	(g)
Reviews and Evaluations			
$k = 2.5\cdot10^{-13}\exp(190/T)$	200–400	NASA, 1992[7]	(h)
$k_1/k = 0.35$; $k_2/k = 0.55$; $k_3/k = 0.10$	298		
$k = 1.1\cdot10^{-13}\exp(365/T)$	200–400	IUPAC, 1992[8]	(i)
$k = 9.2\cdot10^{-14}\exp(390/T)$	250–600	Wallington, Dagaut, and Kurylo, 1992[9]	(j)
$k_1/(k_2 + k_3) = 37.3\exp(-1350/T)$			
$k = 9.1\cdot10^{-14}\exp(416/T)$	248–650	Lightfoot *et al.*, 1992[10]	(k)
$k_1/(k_2 + k_3) = 25\exp(-1165/T)$	228–573		

Comments

(a) Studies on this reaction undertaken prior to 1989 (references 11–26) are not listed explicitly but have been discussed previously in the NASA[7] and IUPAC[8] evaluations and in the recent reviews of peroxy radical chemistry[9,10].

(b) Molecular modulation study of the broad-band photolysis (280–370 nm) of $Cl_2/CH_4/O_2$ mixtures. The UV absorption spectrum of CH_3O_2 was recorded between 220 and 270 nm and calibrated by determining the rate of loss of Cl_2. Numerical analysis of individual waveforms between 230 and 260 nm was undertaken with an assumed mechanism, and the branching ratios taken from the study of Niki *et al.*[19].

(c) Flash photolysis of $Cl_2/CH_4/O_2/N_2$ mixtures with UV absorption detection between 210 and 260 nm. Composite transient absorption profiles due to CH_3O_2 and HO_2 analysed using UV absorption cross-sections taken from McAdam *et al.*[23]. Absorption cross-sections used (in units of 10^{-18} cm^2 molecule^{-1})–CH_3O_2, $\sigma_{210} = 2.5$, $\sigma_{240} = 4.8$, $\sigma_{260} = 3.6$; HO_2, $\sigma_{210} = 5.3$, $\sigma_{240} = 1.8$; $\sigma_{260} = 0.3$. At higher temperatures, pairs of composite waveforms were analysed simultaneously.

(d) Molecular modulation study of the 254 nm photolysis of $CH_3I/O_2/N_2$ mixture with UV absorption detection. UV absorption spectrum of CH_3O_2 recorded between 210 and 320 nm but presence of a second absorber, tentatively assigned to CH_3OOI, observed at longer wavelengths. MM waveforms recorded between 210 and 240 were consistent with those obtained from $Cl_2/CH_4/O_2$ system. Difficulties were apparent in using photolysis rate of CH_3I to calibrate absorption spectrum of CH_3O_2. Only the ratio k/σ given but rate parameters have been derived using the UV absorption spectrum and temperature branching ratios recommended by Lightfoot *et al.*[10].

(e) Flash photolysis of $O_2/CH_4/CH_3OH$ mixtures between 600 and 719 K with UV absorption detection. The earlier data of Lightfoot *et al.*[2] were reanalysed using temperature dependent absorption cross-sections[28] and combined with the results of this study.

(f) Thermal decomposition of static mixtures of di-*t*-butylperoxide and O_2 used to study branching ratios of CH_3O_2 over the temperature range 376–430 K. Chromatographic analysis used for acetone and methanol. HCHO converted into a complex with chromotropic acid and detected spectrophotometrically. Iodometric analysis used for CH_3OOH. Arrhenius fit to experimental data undertaken with their preferred value of the branching ratio, ($k_1/k_2 = 0.6$) at 298 K.

(g) Continuous photolysis of $Cl_2/CH_4/O_2$ mixtures with molecular beam sampling. Molecular beam deposited onto a cold finger at 50 K before cooling to 5 K. FTIR spectroscopy used to identify products and quantify yields.

(h) The NASA evaluation used an averaged value of the cross-section at 250 nm of $4.0\cdot10^{-18}$ cm^2 molecule^{-1}. This cross-section was used to obtain k from a weighted average of values of k/σ from the studies of Cox and Tyndall[16], Jenkin *et al.*[24], Sander and Watson[20], McAdam *et al.*[23], Kurylo and Wallington[22] and Lightfoot *et al.*[2], The temperature dependence was based on the studies of Sander and Watson[20], Kurylo and Wallington[22], Lightfoot *et al.*[2], and Jenkin and Cox[3]. Branching ratios $k_1/k = 0.35$; $k_2/k = 0.55$; and, $k_3/k = 0.1$, are recommended at 298 K based on the FT-IR studies of Kan *et al.*[15], Niki *et al.*[19], and the study of Lightfoot *et al.*[2]. No evidence is found for the occurrence of a channel leading to the products $CH_3OOH + CH_2O_2$.

(i) The IUPAC evaluation noted that the studies of Simon *et al.*[1], Lightfoot *et al.*[2] and Jenkin and Cox[3] gave values of k/σ (250 nm) which were in excellent agreement. The branching ratio was taken from the low temperature study of Horie *et al.*[6] as the experimental conditions were the most relevant for atmospheric modelling purposes. This branching ratio was used to give the overall elementary rate constant. The E/R value was taken from the study of Lightfoot *et al.*[2] because of the wide temperature range covered in that work.

(j) Wallington *et al.*[9] have used their recommended spectrum for CH_3O_2 (σ_{240}=$4.42\cdot10^{-18}$ cm^2 molecule^{-1}) to deduce rate parameters from the observed k/σ values. They derived $k_{obs} = 4.6\cdot10^{-13}$ cm^3 molecule^{-1} s^{-1} (omitting the Sander and Watson kinetic data obtained at 270 nm[18]). A single unweighted Arrhenius fit of the kinetic data obtained by Sander and Watson[20], Kurylo and Wallington[22], Jenkin and Cox[3], Lightfoot *et al.*[2] and the unpublished work of Anastasi *et al.*[25] gave $k_{obs} = 2.5\cdot10^{-13}\exp(180/T)$.

Wallington *et al.*[9] noted the good agreement between the different studies of the branching ratios at room temperature and recommend $k_1/k = 0.35$, $k_2/k = 0.58$ and $k_3/k = 0.07$ which is based on an average of the studies of Parkes[12], Weaver *et al.*[11], Kan *et al.*[18], Niki *et al.*[19] and Horie *et al.*[6]. A linear regression analysis of all the data except the 388 K data point of Lightfoot *et al.*[2] was undertaken in which either α (= k_1/k) or $\log_e \beta$ [$\beta = k_1/(k_2 + k_3)$] was plotted against the inverse of the absolute temperature. The expressions derived were

$$\alpha = 1.24 - \frac{280}{T} \text{ and } \beta = 37.3\exp(-1350/T)$$

(k) Lightfoot *et al.*[10] have recommended a UV absorption spectrum for CH_3O_2 based on an average of the measurements of Jenkin *et al.*[24], Moortgat *et al.*[26], Simon *et al.*[1], Jenkin and Cox[3], Dagaut and Kurylo[27], and Lightfoot and Jemi-Alade[28]. The spectrum was normalised to a value of $4.58\cdot10^{-18}$ cm^2 molecule^{-1} at 240 nm based on the above studies but excluding the relative spectra reported by Jenkin and Cox[3], and Lightfoot and Jemi-Alade[28]. The spectrum was used to scale the k/σ values reported in the different kinetics studies to give $k_{obs} = 4.9\cdot10^{-13}$ cm^3 molecule^{-1} s^{-1}. The branching ratio data were analysed simultaneously to give the temperature dependent expression $\beta = 25\exp(-1165/T)$ which was used to derive k_{298} as $3.7\cdot10^{-13}$ cm^3 molecule^{-1} s^{-1}. The temperature dependent branching ratio was used to convert the observed rate constant into the elementary rate constant. The studies of Sander and Watson[20], Kurylo and Wallington[22], Lightfoot *et al.*[2], Jenkin and Cox[3], all gave E/R values which lay between −365 and −481 K. The low pressure study of Jenkin and Cox[3] gave a slightly lower value of −297 for E/R which was significant at the 1σ level. Lightfoot *et al.*[10] took the E/R value derived by Lightfoot *et al.*[4] and combined this with the value $k_{298} = 3.7\cdot10^{-13}$ cm^3 molecules^{-1} s^{-1} to give their recommended expression.

Preferred Values

$k = 9.1\cdot10^{-14}\exp(420/T)$ over the range 298–700 K.
$k_1/k_2 = 25\exp(-1170/T)$; $k_3 = 0$ over the range 298–700 K.

Reliability

$\Delta\log k = \pm0.1$ at 298 K increasing to ±0.3 at 700 K.

Comments on Preferred Values

Experimental determinations of the rate constants for the $CH_3O_2 + CH_3O_2$ reaction are usually carried out by monitoring the decrease in concentration of CH_3O_2, leading to the rate law

$$\frac{d[CH_3O_2]}{dt} = -2k_{obs}[CH_3O_2]^2$$

The rate constant, k_{obs}, defined by this equation is only identical with $k(= k_1 + k_2 + k_3)$ when the experiments are carried out in the absence of O_2. For experiments performed in the presence of O_2, k_{obs} is related to k by $k_{obs} = k(1 + \alpha)$ where α is the branching ratio for channel 1 i.e. $\alpha = k_1/k$. This arises because the CH_3O formed via channel 1 reacts rapidly with O_2 to form HO_2. The reaction of HO_2 with CH_3O_2 is about 20 times faster at room temperature than the self-reaction of CH_3O_2 so that a second CH_3O_2 is rapidly lost on the time scale of the CH_3O_2 decay. Under such experimental conditions it is therefore necessary to have values of α to derive values of k.

Most studies have monitored CH_3O_2 by UV absorption and the derivation of accurate values of k is critically dependent on the quality of the data on the UV absorption cross-sections.

Wallington *et al.*[9] and Lightfoot *et al.*[10] have independently undertaken a critical appraisal of the available literature on the UV absorption spectrum of CH_3O_2 and the kinetic and mechanistic data on the self-reaction of CH_3O_2. The kinetic parameters are very dependent on the absorption cross-sections chosen for CH_3O_2 and differences in rate parameters between studies reflect, in part, the different values used for the absorption cross-sections. The two reviews recommend cross-sections at 240 nm of $4.42\cdot10^{-18}$ cm^2 molecule^{-1} (Wallington *et al.*[9]) and $4.58\cdot10^{-18}$ cm^2 molecule^{-1} (Lightfoot *et al.*[10]). The recommended rate expressions in the two reviews give similar values over the temperature range of the experimental data. The expression of Lightfoot *et al.*[10] utilizes new data generated by the Bordeaux group[4] which extends the temperature range of the kinetic measurements to higher temperatures (up to 650 K). The expressions derived by Lightfoot *et al.*[10] for the overall rate constant and for the branching ratios are the preferred choice of this recommendation due to the inclusion of rate parameters measured at the higher temperatures. The most recent IUPAC evaluation does not include the new measurements of Lightfoot *et al.*[4] and, for that reason, differs slightly from the present evaluation.

There is some disagreement over the exact magnitude of the value for the branching ratio for channel (3). The latest studies suggest that the channel is minor ($k_3/k = <0.05$) and for practical applications can be set to zero.

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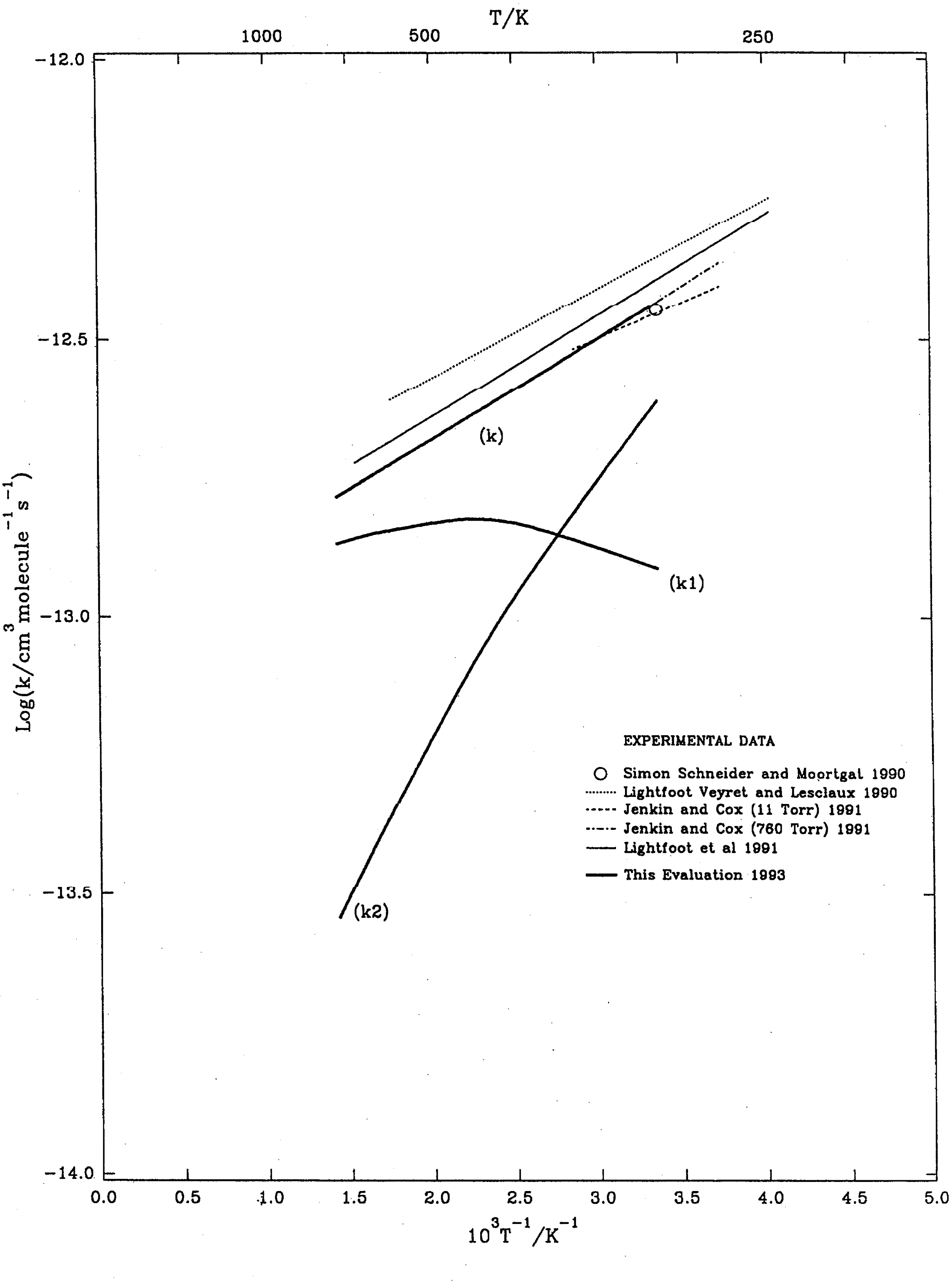
$$CH_3O_2 + CH_3O_2 \rightarrow CH_3O + CH_3O + O_2$$
$$\rightarrow CH_3OH + HCHO + O_2$$
$$\rightarrow CH_3OOCH_3 + O_2$$



CH_3OOH (+ M) → CH_3O + OH (+ M)

Thermodynamic data
$\Delta H^\circ_{298} = 195$ kJ mol^{-1}

Rate Coefficient Data

k/s^{-1}	T/K	Reference	Comments
Rate Coefficient Measurements			
$6.3 \cdot 10^{14}\exp(-21300/T)$	600–719	Lightfoot, Roussel, and Lesclaux, 1991[1]	(a)
Reviews and Evaluations			
$k_\infty = 4.0 \cdot 10^{15}\exp(-21600/T)$	450–1000	CEC,1992[2]	(b)

Comments

(a) UV absorption measurements of the kinetics of CH_3O_2 and HO_2 in the flash photolysis of O_2-CH_4-CH_3OH mixtures. CH_3OOH formed *in situ* by reaction of CH_3O_2 and HO_2 with decay by thermal decomposition, reforming the precursor radicals by subsequent reactions of CH_3O and OH. k_3 obtained by fitting time dependent absorption at 210 nm and 240 nm up to 1000 ms. Pressure = 1 atm.

(b) Based on thermochemistry together with an assumed temperature independent value for the rate constant of the reverse reaction.

Preferred Values

$k = 6 \cdot 10^{14} \exp(-21300/T)$ s^{-1} over range 500–800 K and 1 atm. pressure.

Reliability

$\Delta \log k = \pm 0.2$ at 600 K increasing to ± 0.5 at ends of range.

Comments on Preferred Values

The new measurements of the kinetics of this reaction overcome the main difficulties encountered in all the previous experimental measurements of the rate constants, i.e. interference by heterogeneous decomposition on the reactor walls. Thus both Kirk[3] and Kaiser *et al.*[4] measured much higher values, particularly at low temperatures, which gave unreasonably low Arrhenius parameters, incompatible with the thermochemistry.

The most recent thermochemical data[5] for D(CH_3-OOH) gives $\Delta H^\circ = 195$ kJ mol^{-1}, which is approximately 12 kJ mol^{-1} greater than the value obtained by group methods. The new values are consistent with the new experimental values only if the reaction was in the fall-off region. A good fit to the experimental data was obtained by Lightfoot *et al.*[1] by RRKM analysis using $k_\infty = 3 \cdot 10^{16}\exp(-22900/T)$ s^{-1}, and a collision efficiency of 0.35. However, the derived A factor corresponds to an unreasonably high rate for the reverse association reaction. Alternatively, if the measured values are at the high pressure limit at 1 atm., they can be modelled with a reasonable A factor, but only with a lower ΔH°. Until the degree of fall-off is established, this problem cannot be resolved and a recommendation cannot be given for k_∞. The preferred expression for k is that given by Lightfoot *et al.*[1], and applies to 1 atm pressure and a limited temperature range.

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$CN + O_2 \rightarrow NCO + O$

Thermodynamic Data
$\Delta H^\circ_{298} = -26.6$ kJ mol^{-1}
$\Delta S^\circ_{298} = -14.5$ J K^{-1} mol^{-1}
$Kp = 3.44 \cdot 10^{-4} T^{-0.92} \exp(+3500/T)$

Rate Coefficient Data

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Comments
Rate Coefficient Measurements			
$1.16 \cdot 10^{-11}$	1928–3100	Burmeister *et al.*, 1988[1]	(a)
$1.24 \cdot 10^{-11} \exp(200/T)$	295–775	Durant and Tully, 1989[2]	(b)
$1.4 \cdot 10^{-11} \exp(220/T)$	294–1000	Atakan *et al.*, 1989[3]	(c)
$2.2 \cdot 10^{-11}$	298	Jensen *et al.*, 1990[4]	(d)
$1.0 \cdot 10^{-11} \exp(220/T)$	292–1565	Balla and Casleton, 1991[5]	(e)
$1.66 \cdot 10^{-11}$	1550–4500	Davidson *et al.*, 1991[6]	(f)
Reviews and Evaluations			
$1.1 \cdot 10^{-11} \exp(205/T)$	290–760	IUPAC, 1992[7]	(g)
$1.1 \cdot 10^{-11} \exp(205/T)$	298–2500	CEC, 1992[8]	(h)

Comments

(a) Shock tube study. CN generated from $C_2N_2/O_2/Ar$ and $BrCN/O_2/Ar$ mixtures. [N] and [O] in post shock zone monitored by ARAS. [N] and [O] temporal profiles fitted to complex reaction mechanism; fit shown to be sensitive to k.

(b) Pulsed laser photolysis at 193 nm of flowing $C_2N_2/O_2/He$ or $ClCN/O_2/He$ mixtures. Pressures 100–400 Torr. [CN] and [NCO] monitored by LIF.

(c) Pulsed laser photolysis at 193 nm of flowing $C_2N_2/O_2/N_2$ mixtures. Pressures 3–50 Torr. [CN] monitored by LIF. CN ($\upsilon = 1$) also studied.

(d) Pulsed laser photolysis at 193 nm of flowing $C_2N_2/O_2/Ar$ mixtures at $p = 3$ Torr. [CN] monitored by LIF.

(e) As in (d). Pressures 5–50 Torr.

(f) Shock tube study. In one series of experiments $C_2N_2/O_2/Ar$ mixture were shock heated in temperature range 2700–3800 K at pressures 0.62–1.05 atm. In other experiments $C_2N_2/O_2/Ar$ mixtures were shock heated in range 1550–1950 K and pressures 1.19–1.57 atm. with CN generated by 193 nm photolysis pulse. In all cases [CN] monitored by laser absorption spectroscopy.

(g) Based on the temperature coefficient of Sims and Smith[9] and data close to 298 K.

(h) See Comments on Preferred Value.

Preferred Value

$k = 1.2 \cdot 10^{-11} \exp(210/T)$ cm^3 molecule^{-1} s^{-1} over range 290–4500 K.

Reliability
$\Delta \log k = \pm 0.15$ over range 290–4500 K.

Comments on Preferred Values

The recent measurements are all in excellent agreement with the recommendations in our previous evaluation[8] which are changed only slightly. Only measurements since 1988 are tabulated. Earlier results[9–13] are in good agreement on the temperature coefficient of k over a wide temperature range. Our recommended value of E/R is the mean of the values of Sims and Smith[9], Durant and Tully[2], Atakan *et al.*[3], Balla and Casleton[5] and Davidson *et al.*[6]. The pre-exponential factor is based on this value of E/R and the mean value of k at 700 K from these five studies.

The graph shows only the results of the recent studies listed in the Table. For earlier studies see Ref. 8.

The reaction has an alternative, highly exothermic channel, giving CO + NO ($\Delta H^\circ_{298} = -455$ kJ mol^{-1}). There is experimental evidence to suggest that it is unimportant both at high and low temperatures[14,15].

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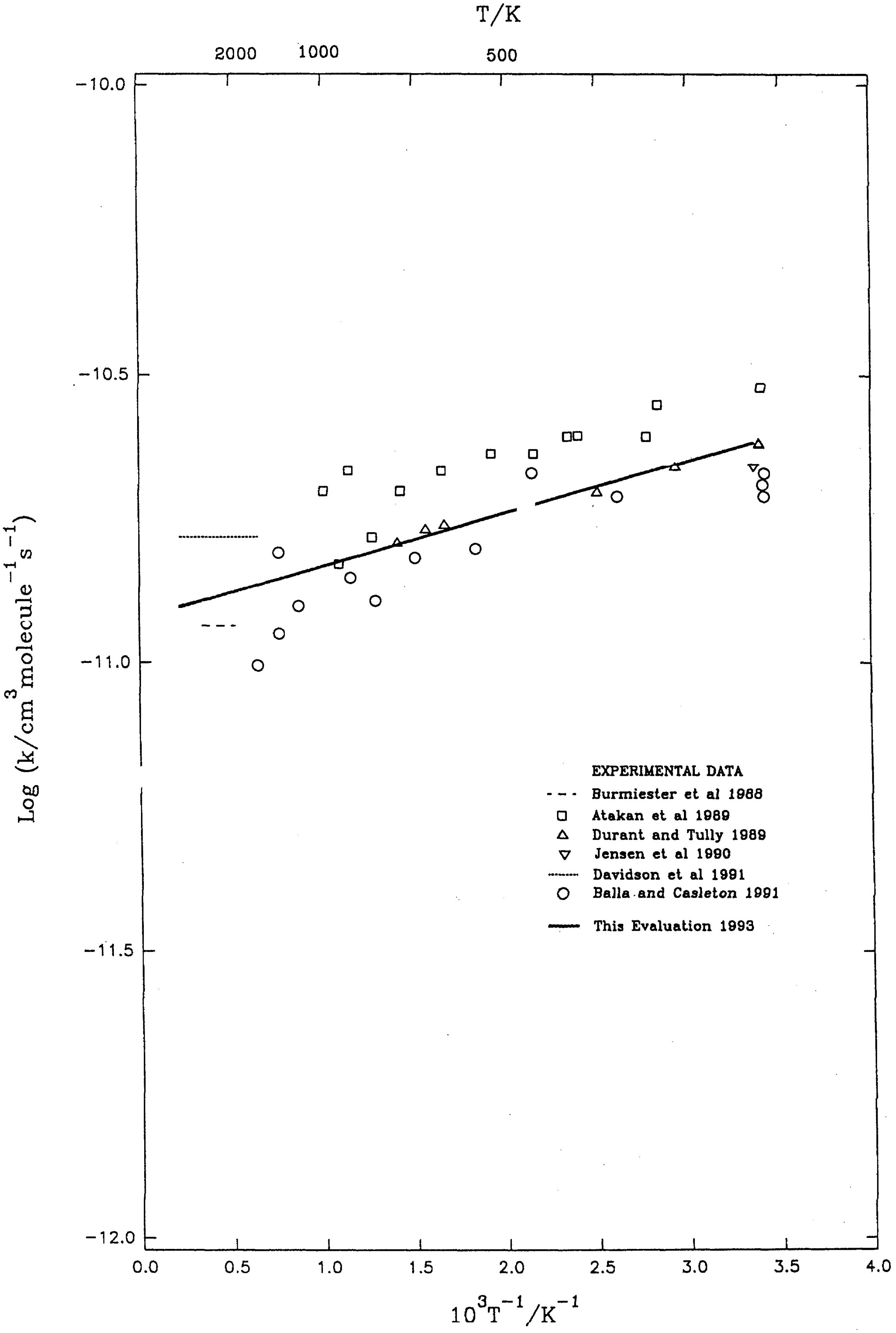
$CN + O_2 \rightarrow NCO + O$



$CN + H_2 \rightarrow HCN + H$

Thermodynamic Data

$\Delta H^\circ_{298} = -82.0$ kJ mol^{-1}
$\Delta S^\circ_{298} = -16.7$ J K^{-1} mol^{-1}
$Kp = 7.5 \cdot 10^{-4} T^{0.73} \exp(+10170/T)$

Rate Coefficient Data

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Comments
Rate Coefficient Measurements			
$<3.3 \cdot 10^{-13}$	687	Boden and Thrush, 1967[1]	(a)
$1.0 \cdot 10^{-10} \exp(-2670/T)$	275–398	Albers *et al.*, 1974[2]	(b)
$1.0 \cdot 10^{-10} \exp(-2670/T)$	259–396	Schacke, Wagner, and Wolfrum, 1977[3]	(c)
$1.4 \cdot 10^{-14}$	300	Li, Sayah, and Jackson, 1984[4]	(d)
$4.9 \cdot 10^{-14}$	294	Lichtin and Lin, 1985[5]	(e)
$1.25 \cdot 10^{-10}$	2700–3500	Szekely, Hanson, and Bowman, 1983[6]	(f)
$3.0 \cdot 10^{-10} \exp(-4000/T)$	2050–3160	Natarajan and Roth, 1986[7]	(g)
$2.45 \cdot 10^{-14}$	298	de Juan *et al.*, 1987[8]	(h)
$2.6 \cdot 10^{-14}$	298	Balla and Pasternack, 1987[9]	(i)
$2.4 \cdot 10^{-12} (T/298)^{1.6} \exp(-1340/T)$	295–768	Sims and Smith, 1988[10]	(j)
$5.1 \cdot 10^{-19} T^{2.45} \exp(-1119/T)$	294–1000	Atakan *et al.*, 1989[11]	(k)
$2.23 \cdot 10^{-21} T^{3.31} \exp(-756/T)$	209–740	Sun *et al.*, 1990[12]	(l)
Reviews and Evaluations			
$1.1 \cdot 10^{-10} \exp(-2700/T)$	300–1000	Baulch *et al.*, 1981[13]	(m)

Comments

(a) Discharge flow study. CN produced by reaction of O atoms with cyanogen. [CN] monitored by absorption between 387.6 and 388.6 nm.

(b) Flash photolysis, discharge flow study with photolysis of C_2N_2 ($\geqslant$ 165 nm). CN detected in absorption at 388.3 nm.

(c) Flash photolysis of C_2N_2/H_2 mixtures. [CN] monitored by kinetic absorption spectroscopy.

(d) Pulsed laser photolysis of $C_2N_2/Ar/H_2$ mixtures at 193 nm. [CN] monitored by LIF.

(e) CN generated by pulsed laser photolysis of ICN at 266 nm. [CN] monitored by LIF of CN ($A \leftarrow X$) and CN ($B \leftarrow X$) transitions.

(f) Shock tube study on mixtures of $C_2N_2/H_2/Ar$. [CN] monitored by broad-band absorption spectroscopy.

(g) Shock tube study of $C_2N_2/H_2/Ar$ mixtures, with ARAS monitoring of H atom concentrations.

(h) Pulsed laser photolysis of NCNO at 572 nm. [CN] monitored by LIF at 388 nm.

(i) Pulsed laser photolysis of C_2N_2 at 193 nm. [CN] and [HCN] monitored by diode laser absorption.

(j) Pulsed laser photolysis of NCNO at 532 nm; LIF monitoring of [CN].

(k) Pulsed laser photolysis of C_2N_2 at 193 nm. LIF monitoring of [CN] at 386.871 nm and 386.887 nm.

(l) Pulsed laser photolysis of ICN at 248 nm; LIF monitoring of [CN] at 388 nm.

(m) Evaluation of data to 1980.

Preferred Value

$k = 3.2 \cdot 10^{-20} T^{2.87} \exp(-820/T)$ over the range 200–3500 K.

Reliability

$\Delta \log k = \pm 0.2$ at 300 K rising to ± 0.5 at 3500 K.

Comments on Preferred Values

There is very good agreement among the most recent studies of this reaction over a wide temperature range. The older, discharge flow studies[1,2], in general give low values for k and are not used in deriving the recommended expression, which is based on the data of Refs. 3–12.

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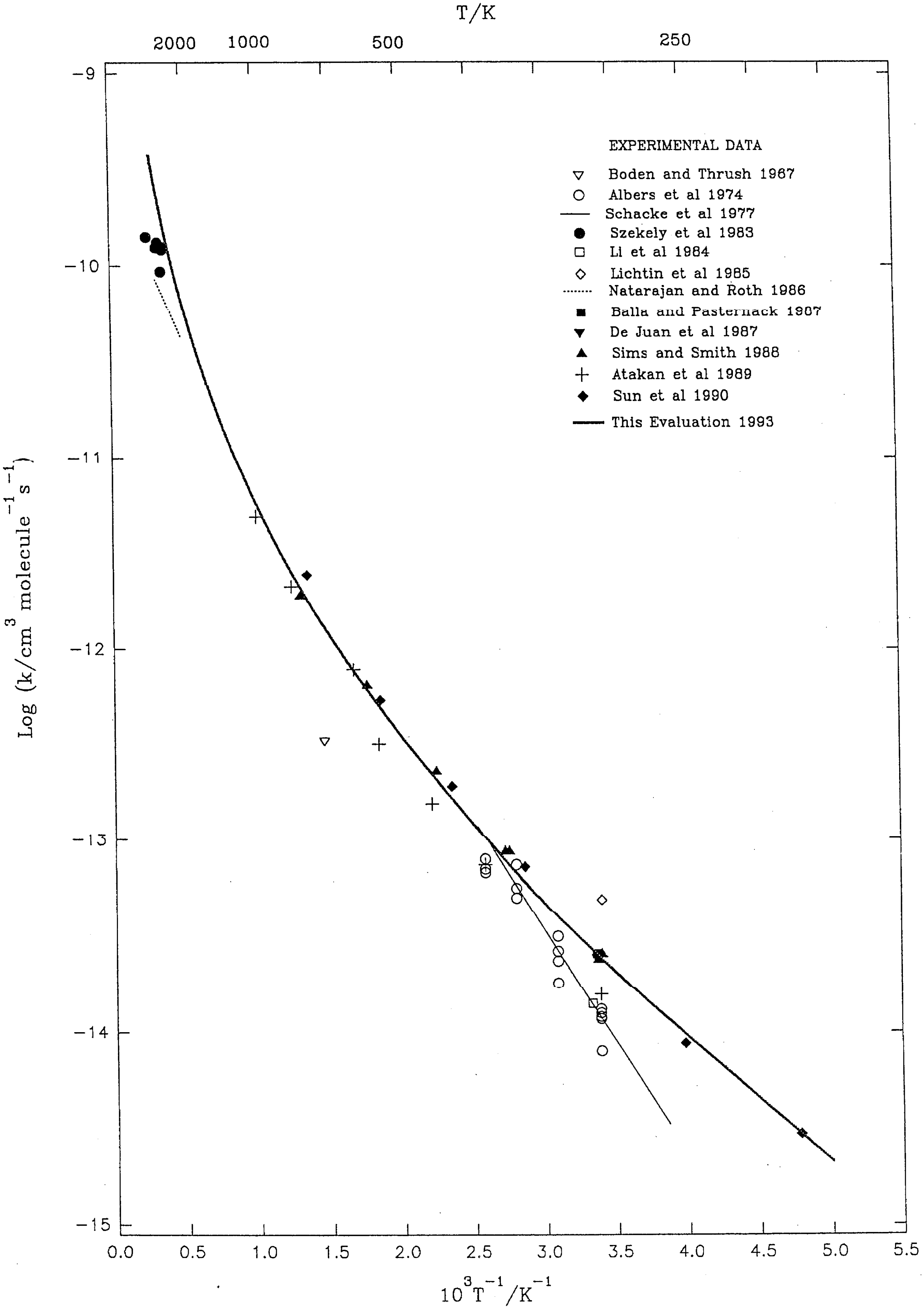
CN + H_2 → HCN + H


T/K
2000
1000
500
250
-9
-10
-11
-12
-13
-14
-15
Log (k/cm^3 molecule^-1 s^-1)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
10^3 T^-1/K^-1
EXPERIMENTAL DATA
▽ Boden and Thrush 1967
○ Albers et al 1974
— Schacke et al 1977
● Szekely et al 1983
□ Li et al 1984
◇ Lichtin et al 1985
······ Natarajan and Roth 1986
■ Balla and Pasternack 1987
▼ De Juan et al 1987
▲ Sims and Smith 1988
+ Atakan et al 1989
◆ Sun et al 1990
— This Evaluation 1993

$CN + CH_4 \rightarrow HCN + CH_3$

Thermodynamic Data
$\Delta H^\circ_{298} = -79.4$ kJ mol^{-1}
$\Delta S^\circ_{298} = -7.18$ J K^{-1} mol^{-1}
$K_p = 9.79 \cdot 10^{-2} T^{0.55} \exp(+9570/T)$

Rate Coefficient Data

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Comments
Coefficient Measurements			
$5.0 \cdot 10^{-13}$	293	Schacke, Wagner, and Wolfrum, 1977[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)
$1.14 \cdot 10^{-12}$	300	Anastasi and Hancock, 1988[5]	(e)
$5.6 \cdot 10^{-13}$	294	Sayah *et al.*, 1988[6]	(f)
$8.4 \cdot 10^{-13}$, CN($v = 1$)			
$2.07 \cdot 10^{-19} T^{2.64} \exp(78/T)$	294–1260	Atakan and Wolfrum, 1991[7]	(g)
$1.0 \cdot 10^{-19} T^{2.64} \exp(220/T)$	292–1500	Balla *et al.*, 1991[8]	(h)
Reviews and Evaluations			
$1.5 \cdot 10^{-11} \exp(-940/T)$	260–400	CEC, 1992[9]	(i)

Comments

(a) Flash photolysis of CH_4(0.037–0.4 Torr)/C_2N_2(0.05–0.2 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, $\upsilon = 0$, $\upsilon = 1$] 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 Torr)/CH_4(0–0.15 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) Flash photolysis of flowing mixtures of C_2N_2/Ar/CH_4. [CN] monitored by LIF. Total pressure, 20 Torr.
(f) Pulsed laser photolysis at 193 nm of flowing mixtures of C_2N_2/Ar/CH_4. [CN] monitored by LIF. Total pressure, 5–30 Torr.
(g) Method as in (f). No pressure dependence of rate constant in range 2–38 Torr.
(h) Method as in (f). Pressure range 5–60 Torr.

Preferred Value

$k = 1.5 \cdot 10^{-19} T^{2.64} \exp(150/T)$ cm^3 molecule^{-1} s^{-1} over range 290–1500 K.

Reliability

$\Delta \log k = \pm 0.3$ over range 290 to 1500 K.

Comments on Preferred Values

Until the two recent studies of Balla *et al.*[8] and Atakan and Wolfrum[7] the available data had been restricted to low temperatures (<400 K). These studies have extended the data to 1500 K and are in good agreement over the whole temperature range. The preferred values are based on the two expressions for k derived by Balla *et al.*[8] and Atakan and Wolfrum[7].

Other exothermic reaction channels are possible but a search by Balla *et al.*[8] for alternative products found none; the formation of HCN + CH_3 appears to be the only pathway. The reaction is believed to occur by initial addition rather than by direct abstraction but no evidence has been found for any pressure dependence of k.

The rate of the reaction is increased by vibrational excitation of the CN and there have been a number of measurements of $k(\upsilon = 1)$ which are in good agreement[1,2,6].

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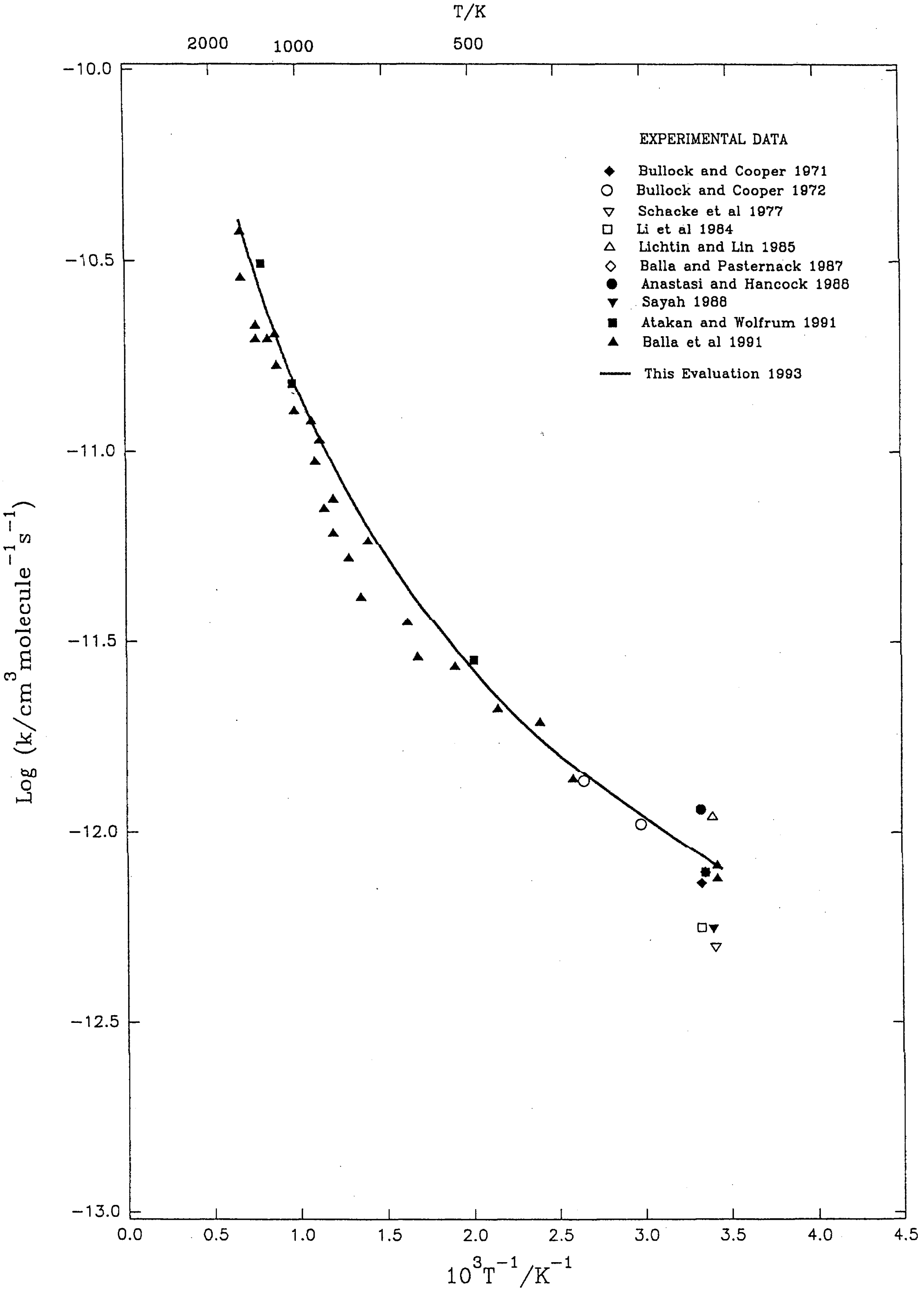
CN + CH_4 → HCN + CH_3



$NCO + NO \rightarrow N_2O + CO$ (1)
$\rightarrow N_2 + CO_2$ (2)
$\rightarrow N_2 + CO + O$ (3)

Thermodynamic Data

$\Delta H^\circ_{298}(1) = -278$ kJ mol^{-1}
$\Delta S^\circ_{298}(1) = -25.4$ J K^{-1} mol^{-1}
$Kp(1) = 0.164\ T^{-0.19}\exp(+33400/T)$

$\Delta H^\circ_{298}(2) = -643$ kJ mol^{-1}
$\Delta S^\circ_{298}(2) = -37.5$ J K^{-1} mol^{-1}
$Kp(2) = 7.22\cdot10^{-2}T^{0.30}\exp(+77300/T)$

$\Delta H^\circ_{298}(3) = -111$ kJ mol^{-1}
$\Delta S^\circ_{298}(3) = 107$ J K^{-1} mol^{-1}
$Kp(3) = 2.96\cdot10^{6}T^{0.22}\exp(+13100/T)$ 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			
$1.66\cdot10^{-12}$	1329–1846	Fifer and Holmes, 1982[1]	(a)
$1.69\cdot10^{-11}\exp(197/T)$	294–538	Perry, 1985[2]	(b)
$3.4\cdot10^{-11}$	295	Hancock and McKendrick, 1986[3]	(c)
$5.0\cdot10^{-7}T^{-1.53}\exp(-260/T)$	294–1260	Atakan and Wolfrum, 1991[4]	(d)
$2.9\cdot10^{-12}$	2380–2660	Mertens *et al.*, 1992[5]	(e)
Reviews and Evaluations			
$1.7\cdot10^{-11}\exp(200/T)$	300–600	CEC, 1992[6]	(f)

Comments

(a) Shock tube study of $HCN/NO_2/Ar$ mixtures. $[NO_2]$ monitored by absorption at 450 nm. $[NO^*]$, $[OH^*]$, and $[NO^*_2]$ monitored by emission at 237, 307, and 427.5 nm respectively. Value of k obtained is only an estimate from computer modelling of a 23 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 infra-red 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 in which vibrational excitation of NCO may have influenced results.

(d) Pulsed laser photolysis of $(CN)_2/O_2/NO$ mixtures at 193 nm. NCO produced by rapid reaction of photolytically generated CN with O_2. [NCO] monitored by LIF.

(e) Shock tube study of $HNCO/N_2O/Ar$ mixtures. [NCO] monitored by absorption at 440.79 nm. k derived by fitting [NCO] profile to reaction scheme. Profile shown to be sensitive to value of k.

(f) Based on data of Perry[2] and of Hancock and McKendrick[3].

Preferred Values

$k = 2.3\cdot10^{-6}T^{-1.73}\exp(-380/T)$ over the range 290–3000 K.

Reliability

$\Delta\log k = \pm0.25$ over the range 290–3000 K.

Comments on Preferred Values

The studies of Atakan and Wolfrum[4] and Mertens *et al.*[5] considerably extend the temperature range over which data are available. At low temperatures Atakan and Wolfrum[4] obtain values in good agreement with those of Perry[2] and Hancock and McKendrick[3]. An extrapolation of the expression for k given by Atakan and Wolfrum[4] to higher temperatures allows comparison with the high temperature data of Fifer and Homes[1] and of Mertens *et al.*[4]. The agreement with the results of Mertens *et al.*[4] is excellent. Fifer and Homes[1] obtained only an approximate value of k from their shock tube study; their data are a factor of 3–4 lower than obtained from Atakan and Wolfrum's expression.

Mertens *et al.*[5] have combined the results in Refs. 2–5 to derive the expression which is recommended in the present evaluation.

The only information about branching ratios is indirect and limited to low temperatures. Hancock and McKendrick[3] observe no NO + O chemiluminescence in their experiments suggesting an absence of channel (3). Atakan and Wolfrum[4] quote unpublished work of Hancock *et al.* in which infra-red chemiluminescence from the reaction products were studied. Vibrationally excited CO and N_2O were observed but not CO_2. Mertens *et al.*[5] report results of Cooper and Herschberger, in press, which indicate that at room temperatures both channels (1) and (2) are important. The substantial curvature in the Arrhenius plot may indicate a change in mechanism as the temperature is increased and further studies at high temperature to investigate this possibility are clearly desirable.

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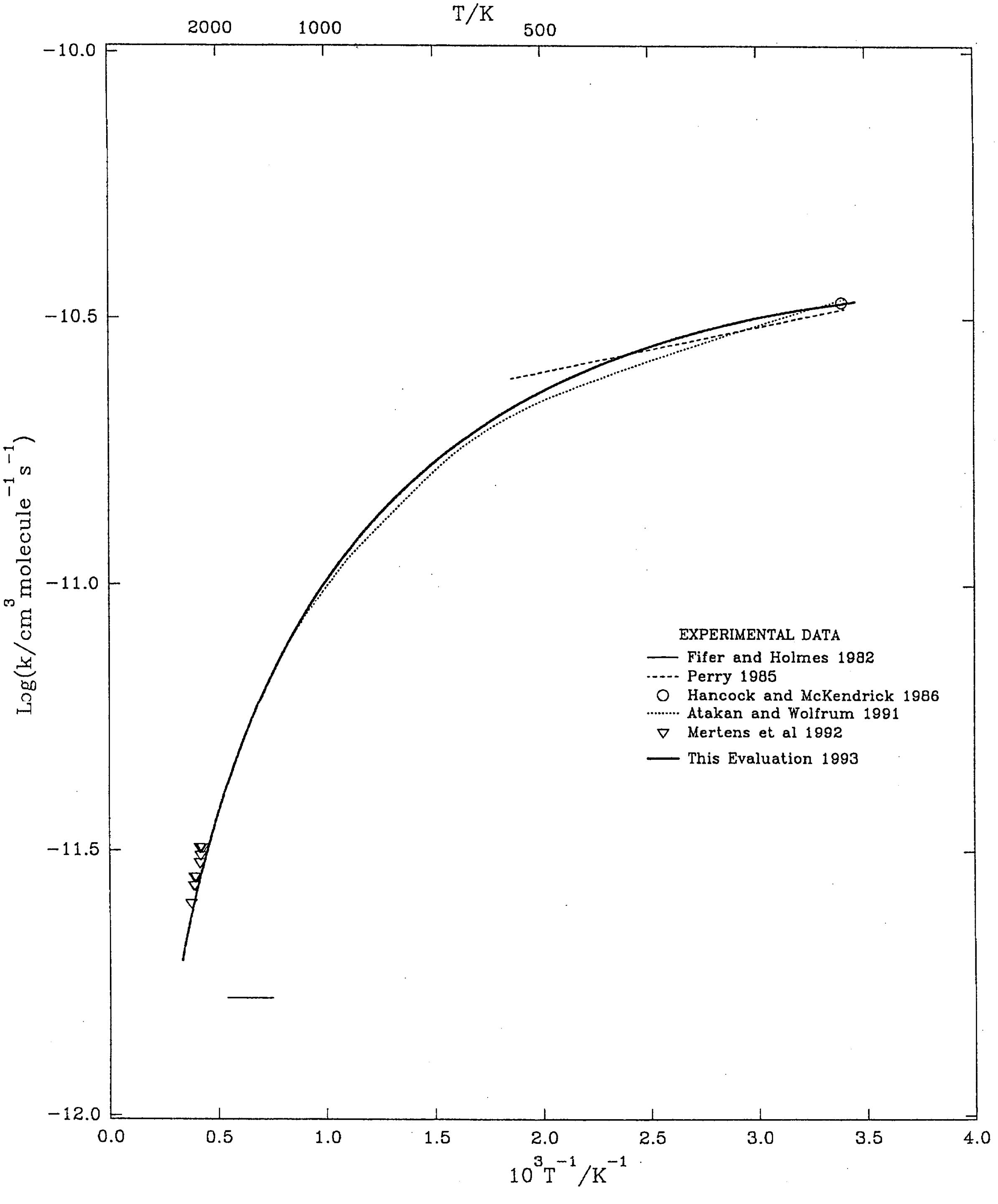
$NCO + NO \rightarrow N_2O + CO$
$\rightarrow N_2 + CO_2$
$\rightarrow N_2 + CO + O$



$C_2H + H_2 \rightarrow C_2H_2 + H$

Thermodynamic Data
$\Delta H^\circ_{298} = -116$ kJ mol^{-1}
$\Delta S^\circ_{298} = -22.5$ J K^{-1} mol^{-1}
$Kp = 1.38 \cdot 10^{-4} T^{0.87} \exp(+14300/T)$

Rate Coefficient Data

k/cm^3 molecule^{-1}s^{-1}	T/K	Reference	Comments
Rate Coefficient Measurements			
$4.4 \cdot 10^{-13}$	298	Lander *et al.*, 1990[1]	(a)
$1.8 \cdot 10^{-11} \exp(-1090/T)$	298–438	Koshi *et al.*, 1992[2]	(b)
$7.1 \cdot 10^{-13}$ $5.1 \cdot 10^{-13}$	293	Koshi, Nishida, and Matsui, 1992[3]	(c)
Reviews and Evaluations			
$2.5 \cdot 10^{-11} \exp(-1564/T)$	300–3000	Warnatz, 1984[4]	(d)
$1.9 \cdot 10^{-11} \exp(-1443/T)$	300–2800	Gardiner *et al.*, 1985[5]	(e)
$1.8 \cdot 10^{-11} \exp(-1455/T)$	300–2500	Tsang and Hampson, 1986[6]	(f)
$2.5 \cdot 10^{-11} \exp(-1564/T)$	300–2500	CEC, 1992[7]	(g)

Comments

(a) Pulsed laser photolysis of CF_3C_2H at 193 nm. Transient [C_2H] monitored by diode IR laser absorption in presence of a large excess of H_2. No pressure dependence of the decay rate found.

(b) Relative rate measurement. Pulsed ArF laser photolysis of C_2H_2/H_2 mixtures to generate C_2H and H. Formation of C_4H_2 by the reaction $C_2H + C_2H_2 \rightarrow C_4H_2 + H$ monitored by time-resolved mass spectrometry. Yield of C_4H_2 as a function of [H_2] gives k/k_1 where k_1 refers to the reaction of C_2H with C_2H_2 to give C_4H_2. Value of $k_1 = 1.5 \cdot 10^{-10}$ cm^3 molecule^{-1} s^{-1} used, obtained from a shock tube study in the same laboratory[2].

(c) Pulsed ArF laser photolysis of C_2H_2/H_2 mixtures. Reaction monitored by LIF detection of H and by time-resolved mass spectrometric detection of C_4H_2 in separate experiments. The former gives $k = (7.1 \pm 1.1) \cdot 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

(d) Review of literature to 1986.

(e) Re-analysis of data from shock tube studies of Koike and Morinaga[8] and of Tanzawa and Gardiner[9].

(f) Accepts expression of Brown and Laufer[10] derived from value of k at 300 K from Laufer and Bass[11] together with BEBO calculation of temperature coefficient.

(g) Expression derived by Warnatz[4] accepted.

Preferred Values

$k = 1.8 \cdot 10^{-11} \exp(-1090/T)$ cm^3 molecule^{-1} s^{-1} over range 300–2500 K.

Reliability

$\Delta \log k = \pm 0.3$ at 300 K rising to ± 0.5 at 2500 K.

Comments on Preferred Values

The expression obtained by Koshi *et al.*,[2] is adopted. This is significantly different from our previously recommended expression at low temperatures. Although the expression is based on low temperature results, when extrapolated it agrees well with the existing high temperature studies.

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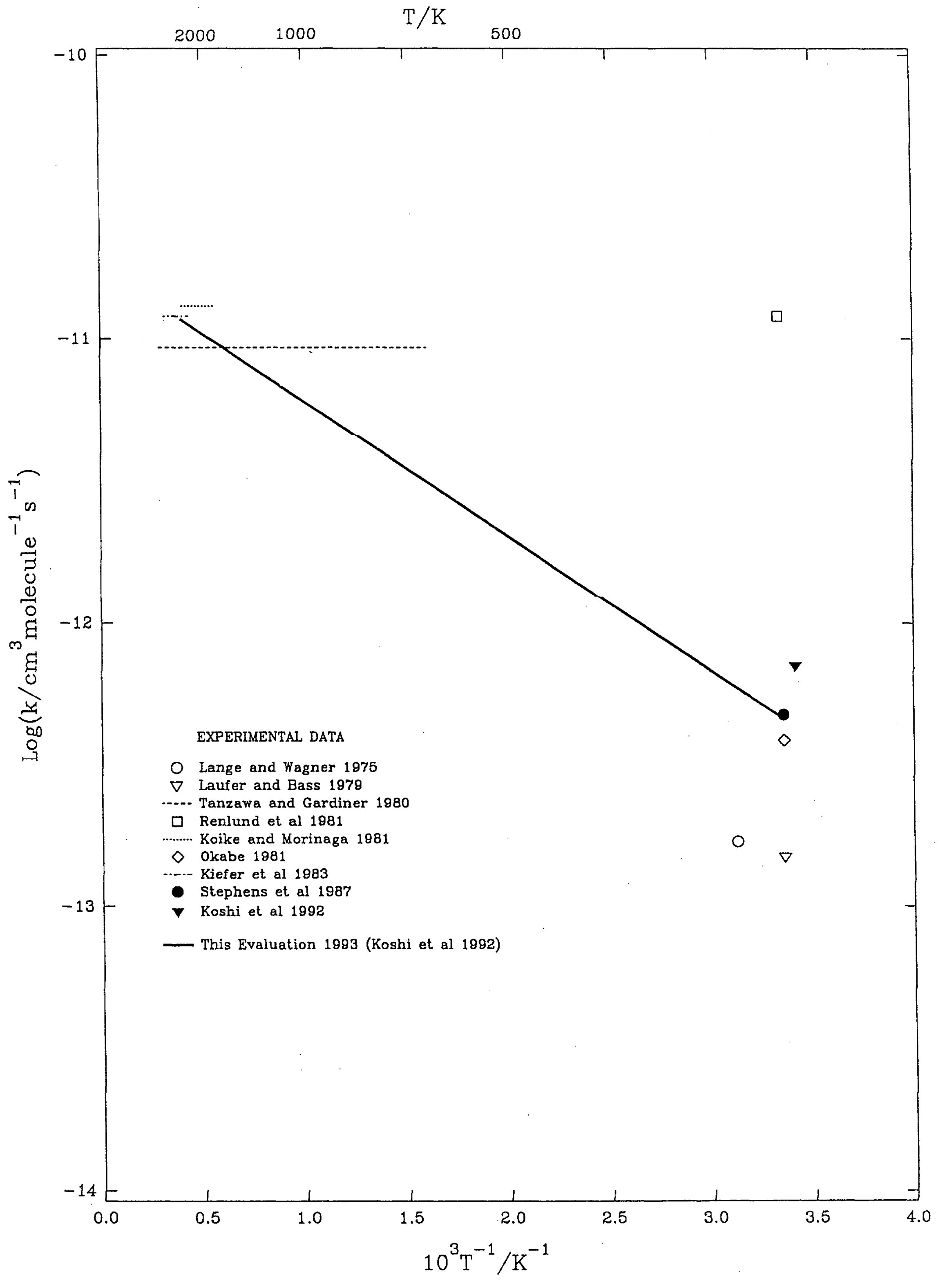
$C_2H + H_2 \rightarrow C_2H_2 + H$



$C_2H + CH_4 \rightarrow$ Products

Rate Coefficient Data

k/cm^3 molecule^{-1}s^{-1}	T/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)
$3.2 \cdot 10^{-12}$	298	Okabe, 1981[3]	(c)
$3.0 \cdot 10^{-12}$	298	Lander *et al.*, 1990[4]	(d)
Reviews and Evaluations			
$3.0 \cdot 10^{-12}\exp(-250/T)$	300–2500	Tsang and Hampson, 1986[5]	(e)
$2.0 \cdot 10^{-12}$	298	CEC, 1992[6]	(f)

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 m Torr Ar or He.

(b) VUV flash photolysis of C_2HCF_3. Gas chromatographic sampling of products $[C_2H_2]$ monitored by absorption spectroscopy at 152 nm. k independent of pressure between 20 and 700 Torr.

(c) Relative rate study photolysis of C_2H_2/CH_4 mixtures at 147 nm. $[C_4H_2]$, $[C_2H_4]$, and $[C_2H_2]$ measured by absorption spectroscopy at $\approx$ 165 nm, 174.4 nm, and 151.9 nm, respectively. Relative rates $k_{C_2H+CH_4}/k_{C_2H+C_2H_2} = 0.032$. k given in Table based on $k_{C_2H+C_2H_2} = 1.0 \cdot 10^{-10}$ cm^3 molecule^{-1} s^{-1} (this review).

(d) Pulsed laser photolysis at 193 nm of CF_3C_2H to produce C_2H. $[C_2H]$ monitored by IR diode laser absorption in presence of large excess of CH_4. No pressure dependence of k found (8–70 Torr He).

(e) Accepts expression of Brown and Laufer[7] derived from value of k at 300 K from Laufer[8] together with BEBO calculation of temperature coefficient.

(f) Based on Refs. 1–3.

Preferred Values

$k = 3.0 \cdot 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

The recent measurements of Lander *et al.*[4] are the most direct to date and given a value of k in good agreement with the relative rate measurement of Okabe[3]. Our recommendations are based on these results but with fairly wide error limits.

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$C_2H + C_2H_6 \rightarrow C_2H_2 + C_2H_5$

Thermodynamic Data

$\Delta H^\circ_{298} = -99.1$ kJ mol^{-1}

$\Delta S^\circ_{298} = -61.1$ J K^{-1} mol^{-1}

$Kp = 4.73 \cdot 10^{-9} T^{1.64} \exp(+12640/T)$

Rate Coefficient Data

k/cm^3 molecule^{-1}s^{-1}	T/K	Reference	Comments
Rate Coefficient Measurements			
$6.5 \cdot 10^{-12}$	297	Laufer, 1981[1]	(a)
$2.4 \cdot 10^{-11}$	298	Okabe, 1983[2]	(b)
$3.6 \cdot 10^{-11}$	298	Lander *et al.*, 1990[3]	(c)
Reviews and Evaluations			
$6.5 \cdot 10^{-12}$	300–2500	Tsang and Hampson, 1986[4]	(d)
—	—	CEC, 1992[5]	(e)

Comments

(a) VUV flash photolysis of CF_3C_2H. Gas chromatographic sampling of products. $[C_2H_2]$ monitored by absorption spectroscopy at 152 nm. No pressure dependence of k found (20–700 Torr He).

(b) Relative rate study. Photolysis of C_2H_2/C_2H_6 mixtures at 147 nm. $[C_4H_2]$, $[C_2H_4]$ and $[C_2H_2]$ measured by sampling and absorption spectroscopy at 165 nm, 174.4 nm, and 151.9 nm respectively. $k(C_2H + C_2H_6)/k(C_2H + C_2H_2) = 0.240$ obtained. $k(C_2H + C_2H_2) = 1.0 \cdot 10^{-10}$ cm^3 molecule^{-1} s^{-1} (this review) used to obtain tabulated value of k.

(c) Pulsed laser photolysis at 193 nm of CF_3C_2H to produce C_2H. $[C_2H]$ monitored by IR diode laser absorption in presence of large excess of C_2H_6. Small pressure dependence of k observed over range 8–70 Torr He.

(d) Accepts analysis of Brown and Laufer[6] who derived their result from the value of k at 300 K from Laufer[1] together with a BEBO calculation indicating a negligible temperature coefficient for k.

(e) No recommendation made.

Preferred Values

No recommendation.

Comments on Preferred Values

The recent measurements of Lander *et al.*[3] are the most direct study of this reaction but, although a value of k in reasonable agreement with the relative rate values of Okabe[2], is obtained, Lander *et al.*[3] also observed a significant pressure effect which could indicate complexities in the mechanism. The reaction requires more detailed study before recommendations for k can be made.

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$C_2H + C_2H_2 \rightarrow C_4H_2 + H$

Thermodynamic Data
$\Delta H^\circ_{298} = -102$ kJ mol^{-1}
$\Delta S^\circ_{298} = -43.5$ J K^{-1} mol^{-1}
$Kp = 4.46\cdot10^{-7}T^{1.43}\exp(+12600/T)$

Rate Coefficient Data

k/cm^3 molecule^{-1}s^{-1}	T/K	Reference	Comments
Rate Coefficient Measurements			
$1.3\cdot10^{-10}$	298	Shin and Michael, 1991[1]	(a)
$2.5\cdot10^{-10}$	1236–1475		
$1.6\cdot10^{-10}$	293	Koshi, Nishida and Matsui, 1992[2]	(b)
$1.4\cdot10^{-10}$			
$1.4\cdot10^{-10}$	298	Koshi *et al.*, 1992[3]	(c)
$1.4\cdot10^{-10}$	409		
$1.3\cdot10^{-10}$	438		
$1.5\cdot10^{-10}$	1600		
$1.8\cdot10^{-10}$	1613		
$1.5\cdot10^{-10}$	1638		
$1.5\cdot10^{-10}$	2010		
$1.9\cdot10^{-10}$	2177		
Reviews and Evaluations			
$4.0\cdot10^{-11}$	300–2500	Tsang and Hampson, 1986[4]	(d)
$5\cdot10^{-11}$	300–2700	CEC, 1992[5]	(e)

Comments

(a) Pulsed laser (193 nm) photolysis of C_2H_2/He mixtures. [H] monitored by atomic resonance absorption. High temperature experiments carried out by pulsed photolysis of shock heated C_2H_2/He mixtures. Scatter on results is such that they can be interpreted as k temperature independent over temperature range or represented by the expression

$k = 3.02\cdot10^{-10}\exp(-235/T)$ cm^3 molecule^{-1} s^{-1}.

(b) Pulsed ArF laser photolysis of C_2H_2. Reaction monitored by LIF detection of H and by time-resolved mass spectrometric detection of C_4H_2 in separate experiments. The former gives $k = (1.6\pm0.1)\cdot10^{-10}$ cm^3 molecule^{-1} s^{-1} and the latter, $k = (1.4\pm0.1)\cdot10^{-10}$ cm^3 molecule^{-1} s^{-1}.

(c) Measurements in the range 298–438 were carried out by pulsed laser photolysis with time-resolved mass spectrometric detection of C_4H_2 (see comment (b)). For experiments at higher temperatures shock heating of C_2H_2/Ar mixtures was employed with pulsed ArF laser photolysis of the heated mixture behind the reflected shock wave. [H] was monitored by ARAS.

(d) Mean of the values of Refs. 8 and 9.

(e) Based on Refs. 6–9.

Preferred Values

$k = 1.5\cdot10^{-10}$ cm^3 molecule^{-1} s^{-1} over the range 300–2700 K.

Reliability

$\Delta\log k = \pm0.2$ at 298 K rising to ±0.5 at 2700 K.

Comments on Preferred Values

There are now several low temperature studies of this reaction which are in very good agreement[1,2,3,6]. The measurements at high temperature are more scattered[1,3,7] but together with the low temperature data they indicate a very small temperature coefficient for the rate constant, as would be expected for such a fast reaction. The recommendations are based on the low temperature results of Stephens *et al.*[6], Shin and Michael[1], and Koshi *et al.*[2,3] and the rate constant is taken to be temperature independent but substantial error limits are assigned at high temperatures.

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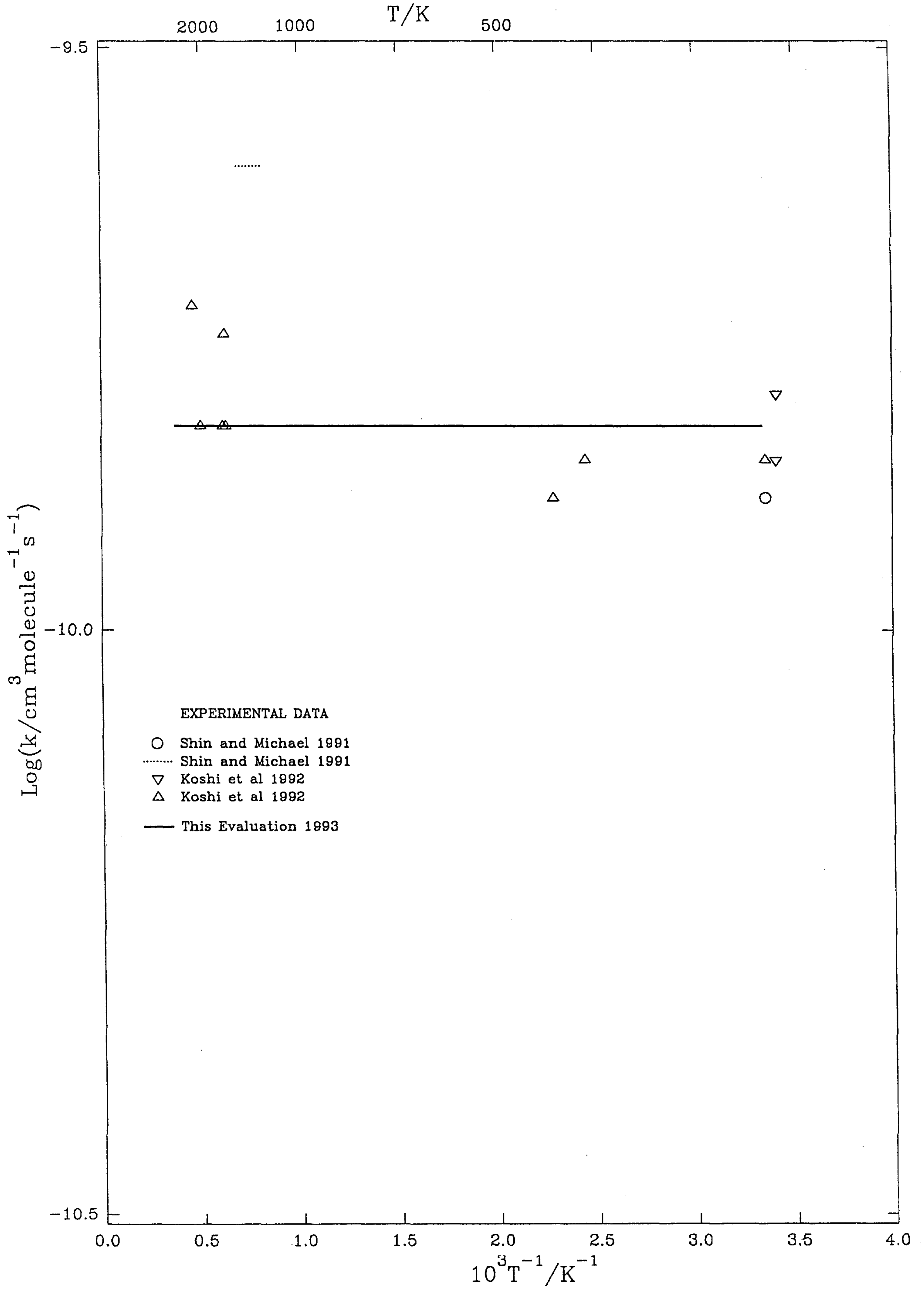
$C_2H + C_2H_2 \rightarrow C_4H_2 + H$



$$\begin{aligned} C_2H_3 + O_2 &\rightarrow C_2H_2 + HO_2 && (1)\\ &\rightarrow H_2CO + CHO && (2)\\ &\rightarrow C_2H_3O + O && (3)\\ &\rightarrow C_2H_3O_2 && (4)\end{aligned}$$

Thermodynamic Data

$\Delta H^\circ_{298}(1) = -49.0$ kJ mol^{-1}
$\Delta S^\circ_{298}(1) = -6.9$ J K^{-1} mol^{-1}
$Kp(1) = 1.69 \cdot 10^{-2} T^{0.55} \exp(+5940/T)$

$\Delta H^\circ_{298}(2) = -358.6$ kJ mol^{-1}
$\Delta S^\circ_{298}(2) = 6.6$ J K^{-1} mol^{-1}
$Kp(2) = 23.1 T^{-0.33} \exp(+43000/T)$

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			
$k_1 = 1.7 \cdot 10^{-12}$	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)
$k_2 = 1.0 \cdot 10^{-11}$	296	Park, Heaven, and Gutman, 1984[3]	(c)
$k_2 = 1.0 \cdot 10^{-11}$	298	Krueger and Weitz, 1988[4]	(d)
$k_3 = 2.5 \cdot 10^{-12}$	298	Munk *et al.*, 1987[5]	(e)
$k = 6.7 \cdot 10^{-12}$	298	Fahr and Laufer, 1988[6]	(f)
Reviews and Evaluations			
$9.0 \cdot 10^{-12}$	300–2000	CEC, 1992[7]	(g)

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)–photoionization 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[8].

(c) Excimer laser flash photolysis (193 nm)–photoionization mass spectrometry at 0.4–4.0 Torr.

(d) Excimer laser flash photolysis (248 nm), diode laser spectroscopy on C_2H_4 in $C_2H_3I/HCl/O_2$ mixtures at ≈7 Torr. The effect of O_2 on the rate of growth of C_2H_4, generated in the C_2H_3 + HCl reaction, was used to determine k.

(e) Pulse radiolysis with a variety of 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.

(f) Spectroscopic study with vacuum UV photolysis of $Sn(C_2H_3)_4$ or $Hg(C_2H_3)_2$, monitoring the decay of C_2H_3 at 164.7 and 168.3 nm by absorption spectroscopy. Total pressure 400 Torr.

(g) Based on Park *et al.*[3].

Preferred Values

$k = 9.0–10^{-12}$ cm^3 molecule^{-1} s^{-1} over range 300–2000 K.

Reliability

$\Delta \log k = \pm 0.3$ over range 300–600 K; ±0.5 over range 600–2000 K.

Comments on Preferred Values

There is excellent agreement between the low pressure studies of Slagle *et al.*[2] and Krueger and Weitz[4]. The higher pressure measurements of Fahr and Laufer[6] are in reasonable agreement and clearly do not confirm the significant decrease in k with pressure suggested by the measurements of Munk *et al.*[5] who obtained their data by observing the rate of growth of an absorption feature attributed to $C_2H_3O_2$.

The available experimental data are in agreement that channel (2) dominates, at $T < 1000$ K. Flame modelling, however, suggests that channel (1) becomes more significant at higher temperatures[9].

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C_2H_4 (+ M) → C_2H_2 + H_2 (+ M) (1)
→ C_2H_3 + H (+ M) (2)

Thermodynamic data

$\Delta H^\circ_{298}(1) = 174.2$ kJ mol^{-1}
$S^\circ_{298}(1) = 112.3$ J K^{-1} mol^{-1}
$Kp(1) = 1.13\cdot10^4T^{-0.83}\exp(-2115/T)$ atm.

$\Delta H^\circ_{298}(2) = 451.5$ kJ mol^{-1}
$\Delta S^\circ_{298}(2) = 126.9$ J K^{-1} mol^{-1}
$Kp(2) = 1.46\cdot10^5T^{0.608}\exp(-54400/T)$ atm.

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

k/s^{-1}	T/K	[M]/molecule cm^{-3}	Reference	Comments
Rate Coefficient Measurements				
Low Pressure Range				
[Ar]$2.95\cdot10^{-7}\exp(-39000/T)$	1675–2210	$(2.5\text{–}32)\cdot10^{18}$	Roth and Just, 1973[1]	(a)
[Ar]$4.3\cdot10^{-7}\exp(-39900/T)$	1700–2200	$(6\text{–}16)\cdot10^{18}$	Just, Roth and Damm, 1976[2]	(b)
[Ar]$4.9\cdot10^{-7}\exp(-40887/T)$	2000–2540	$(1.1\text{–}3.3)\cdot10^{18}$	Tanzawa and Gardiner, 1980[3]	(c)
[Kr]$2.5\cdot10^{-9}\exp(-27900/T)$	2300–3200	$(7\text{–}32)\cdot10^{18}$	Kiefer *et al.*, 1983[4]	(d)
Intermediate Fall-Off Range				
0.44	1168	$1.2\cdot10^{20}$(Ar)	Skinner and Sokoloski, 1960[6]	(e)
$8.2\cdot10^1$	1423			
$1.52\cdot10^3$	1788			
$8.6\cdot10^{-1}$	2100	$2.5\cdot10^{19}$(M)	Leroux and Mathieu, 1961[7]	(f)
4.2	2450			
$6.4\cdot10^{-2}$	1176	$2.5\cdot10^{19}$(C_2H_4)	Towell and Martin, 1961[8]	(g)
$1.5\cdot10^1$	1374			
$6.5\cdot10^1$	1470			
$1.0\cdot10^2$	1330	$(1.6\text{–}2.3)\cdot10^{19}$(Ar)	Kozlov and Knorre, 1962, 1963[9]	(h)
$3.1\cdot10^2$	1460			
$2.9\cdot10^3$	1830			
$1.4\cdot10^3$	1712	$(7.3\text{–}52)\cdot10^{18}$(Ne)	Gay *et al.*, 1966[10]	(i)
$6.9\cdot10^3$	2020			
$1.1\cdot10^4$	2170			
$3.3\cdot10^3$	1950	$8.3\cdot10^{17}$(Ar)	Homer and Kistiakowsky, 1967[11]	(j)
$4.8\cdot10^3$	2060			
$2.0\cdot10^4$	2260			
Reviews and Evaluations				
$k_0(1) =$ [Ar]$4.3\cdot10^{-7}\exp(-39930/T)$	1500–2500		Warnatz, 1989[12]	(k)
$k_0(2) =$ [Ar]$4.3\cdot10^{-7}\exp(-48590/T)$				
$k_\infty(1) = 7.9\cdot10^{12}T^{0.44}\exp(-44670/T)$	1100–2500		Tsang and Hampson, 1986[13]	(l)

Comments

(a) Shock tube study of C_2H_4 (0.1–1%)/Ar mixtures in reflected shocks. [C_2H_4] and [C_2H_2] followed simultaneously by IR emissions at 3.0 and 3.35 μm respectively. Emission profiles corrected for interference between emission bands. C_2H_4 decay found to proceed in two distinct phases: an initial phase of second order for which the rate coefficient was given as indicated above, and a later phase for which the best interpretation was given by an order of 0.6 in [Ar] with rate coefficient $k = 2.85\cdot10^{-2}\exp(-26570/T)$ cm$^{1.8}$ molecule$^{-0.6}$ s^{-1}.

(b) Shock tube study C_2H_4 (20–800 ppm)/Ar mixtures in reflected shocks. [H] followed by atomic resonance absorption at 121.5 nm calibrated by H_2 dissociation in H_2/Ar mixtures. [C_2H_4] followed by absorption at 100.8 nm. H absorption corrected for C_2H_4 and C_2H_2 contribution. The results of this work and those of Ref. 1 led the authors to conclude that there were two pathways for C_2H_4 dissociation. Both sets of data were analysed to give k_1 (which was used in the analysis to obtain k_2). The analysis of C_2H_4 decomposition showed a strong influence of diluent on channel (2) but only weak effects on channel (1). The expression $k_2 = 6.3\cdot10^{-7}\exp(-49400/T)$cm^3 molecule^{-1} s^{-1} was obtained for reaction 2.

(c) Shock tube study of incident shock waves in C_2H_4 (2.5, 5 and 10%)/Ar mixtures. Analysis by laser schlieren technique. Data analysis by computer modelling of a 14 reaction mechanism. k_1 was obtained by optimization of the model to fit initial deflection of laser beam. k_2 taken from Ref. 2 multiplied by 1.2 to improve fit to laser schlieren data.

(d) Shock tube study of 3% C_2H_4/Kr mixtures. Laser schlieren technique. Initial dissociation of C_2H_4 was clearly resolved over the range 2300–3200 K. Rate coefficients for both dissociation channels were derived from the initial gradients and the location of the C_2H_2 gradient maximum. For reaction 2 the following value was obtained: $k_2 = 2.3\cdot10^{-9}\exp(-41180/T)$cm^3 molecule^{-1} s^{-1}. AnRRKM calculation[5] using $E_0 - \Delta H^\circ_0 = 355.6\pm8.4$ kJ

mol^{-1} for channel (1) give a good fit to the data of Refs. 1, 3 and 4.

(e) Shock tube study of C_2H_4 (0.466–6%) in Ar. Analysis for H_2, C_2H_6, C_2H_4 and C_2H_2 by gas chromatography.

(f) Flame study. C_2H_4/O_2 flames at 1 atm with $[CH_4]/[O_2]$ ratios from 1.75 to 2.07. Products quenched and analyzed for CH_4, C_2H_2, C_2H_4, C, CO and higher hydrocarbons.

(g) Flow system, C_2H_4 passed through ceramic reactor tube; products analyzed by mass spectrometry. Production of C_2H_2 and C_4 hydrocarbons found to be first and second order respectively.

(h) Shock tube study of C_2H_4 (0.2% and 5%)/Ar mixtures in reflected shocks. Reaction products sampled and analyzed for H_2, CH_4, C_2H_6, C_2H_4 and C_2H_2 by gas chromatography. C_2H_4 decomposition rate found to be independent of pressure. Conversion to C_2H_2 increases with increasing temperature.

(i) Shock tube study of C_2H_4 (0.5–3%)/Ne mixtures in reflected shocks; products sampled by mass spectrometry of C_2H_2 and H_2 which were the only products observed. C_2H_4 decay is first order in $[C_2H_4]$ and of order 1/2 in [Ne].

(j) Flow system study of C_2H_4 (8.13–14.9%)/H_2 mixtures. Products CH_4, C_2H_6, C_2H_2, C_3H_6 monitored by gas chromatography.

(k) Data evaluation.

(l) Data evaluation and construction of RRKM fall-off curves.

Preferred Values

$k_o(1) = [Ar,Kr]5.8\cdot10^{-8}\exp(-36000/T)$ s^{-1} over range 1500–3200 K.

$k_o(2) = [Ar]4.3\cdot10^{-7}\exp(-48600/T)$ s^{-1} over range 1500–3200 K.

Reliability

$\Delta\log k_o$ (1) = ±0.3 over range 1500–3200 K.
$\Delta\log k_o$ (2) = ±0.5 over range 1500–3200 K.

Comments on Preferred Values

The thermal decomposition of C_2H_4 apparently is dominated by the 1,1 elimination channel to form singlet vinylidene (:C=CH_2) which immediately isomerizes to acetylene. All experiments reported are in the fall-off region close to the low pressure limit. Figure 1 gives Arrhenius plots of k_o from Refs. 1–4. The agreement among the rate coefficients is quite satisfactory, thus, we have chosen an average k_o as the preferred value. A theoretical analysis[14] of these rate coefficients using a recent determination of the reaction barrier by Kiefer *et al.*[15], 355.6 kJ mol^{-1}, leads to collisional efficiencies β_c ranging from 0.002 to 0.004 between 1700 to 3200 K. However, employing a value of $\Delta H^\circ_o = 368.2$ kJ mol^{-1} an almost constant $\beta_c \approx 0.006$ is obtained over the same temperature range. The experiments provide no information about the high pressure rate coefficient. The second channel (2) is expected to depend strongly on the bath gas[16].

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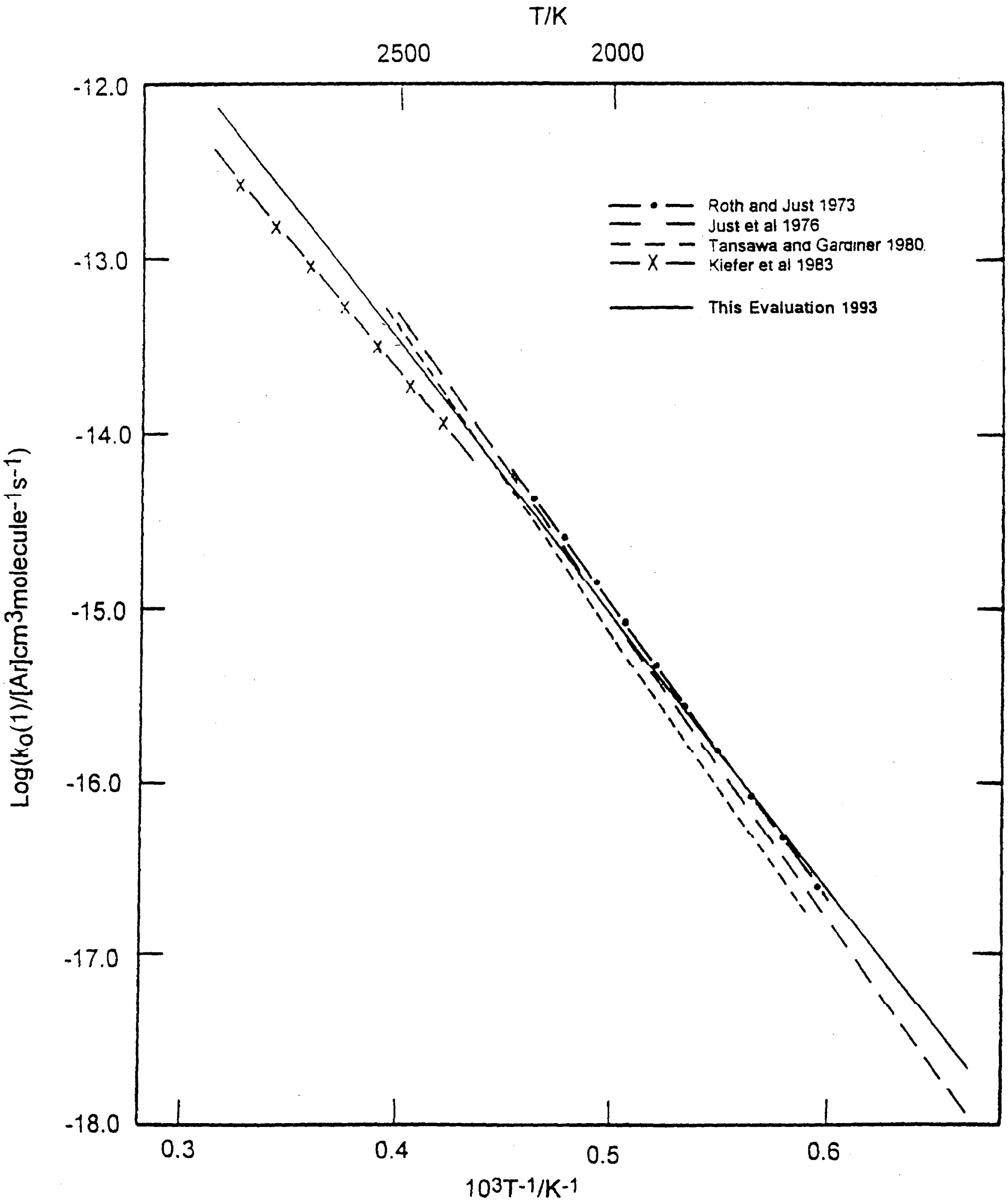
$C_2H_4 + M \rightarrow C_2H_2 + H_2 + M$
$\rightarrow C_2H_3 + H + M$



C_2H_5OOH (+ M) → C_2H_5O + 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			
$2.5\cdot10^{13}\exp(-19000/T)$ (M = C_6H_6)	553–653	Kirk and Knox, 1960[1]	(a)
Reviews and Evaluations			
$2.2\cdot10^{15}\exp(-21600/T)$	—	Benson and O'Neal, 1970[2]	(b)
$4.0\cdot10^{15}\exp(-21600/T)$	400–1000	CEC,1992[3]	(c)

Comments

(a) Pyrolysis of C_2H_5OOH in benzene carrier gas flow system (553–653 K) at total pressure of 10–20 Torr. Analysis of the amount of peroxide consumed and phenyl product allowed distinction between homogeneous and heterogeneous components; expression given is for homogeneous reaction.

(b) Based on data of Kirk and Knox[1] and transition state calculation.

(c) Based on analogy with the estimated high pressure limit for decomposition of methyl hydroperoxide.

Preferred Values

$k_\infty = 4.0\cdot10^{15}\exp(-21600/T)$ s^{-1} over range 400–800 K.

eliability
$\Delta\log k = \pm0.3$

Comments on Preferred Values

The cited experimental measurements are the only reported for this reaction, and were overlooked in the previous CEC evaluation[3]. The Arrhenius parameters are substantially lower than measured recently for CH_3OOH decomposition[4], although the rate coefficient values at 650 K are comparable. There is a strong possibility that the reaction is in the fall-off region at the low pressures used which would account for the low *A* factor. The uncertainties do not allow a firm recommendation but the expression recommended previously for k_∞ is consistent with the data.

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$$C_6H_5CH_3\ (+\ M) \rightarrow H + C_6H_5CH_2\ (+\ M) \qquad (1)$$
$$\rightarrow CH_3 + C_6H_5\ (+\ M) \qquad (2)$$

Thermodynamic Data

$\Delta H^\circ_{298}(1) = 367.9$ kJ mol^{-1}	$\Delta H^\circ_{298}(2) = 424.1$ kJ mol^{-1}
$\Delta S^\circ_{298}(1) = 110.9$ J K^{-1} mol^{-1}	$\Delta S^\circ_{298}(2) = 162.5$ J K^{-1} mol^{-1}
$Kp(1) = 5.6\text{–}10^{1} T^{1.49} \exp(-44030/T)$ atm	$Kp(2) = 2.1\text{–}10^{10}\ T^{-0.50} \exp(-51450/T)$ atm

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

k/s^{-1}	T/K	Reference	Comments
Rate Coefficient Measurements			
$k_1 = 2.0\text{–}10^{13} \exp(-38900/T)$	1011–1138	Swarc, 1948[1]	(a)
$k_1 = 2.5\text{–}10^{12} \exp(-37091/T)$	1011–1122	Takahashi, 1960[2]	(b)
$k_1 = 1.3\text{–}10^{18} \exp(-52340/T)$	1185–1206		
$k_1 = 6.3\text{–}10^{14} \exp(-42778/T)$	913–1143	Price, 1962[3]	(c)
$k_2 = 3.4\text{–}10^{14} \exp(-40262/T)$	1073–1373	Errede and DeMaria, 1964[4]	(d)
$k_1 = 9.2\text{–}10^{15} \exp(-44737/T)$	920–970	Brooks, Cummings, and Peacock, 1971[5]	(e)
$k_1 = 1.7\text{–}10^{14} \exp(-41268/T)$	1410–1730	Rao and Skinner, 1984[6]	(f)
$k_1 = 2.0\text{–}10^{15} \exp(-44393/T)$	1500–1900	Mueller-Markgraf and Troe, 1986[7]	(g)
$k_1 = 8.1\text{–}10^{12} \exp(-36534/T)$	1300–1800	Mizerka and Kiefer, 1986[8]	(h)
$k_2 = 4.0\text{–}10^{11} \exp(-45291/T)$	1300–1800		
$k_2 = 8.9\text{–}10^{12} \exp(-36534/T)$	1600–2100	Pamidimukkala *et al.*, 1987[9]	(i)
$k_1 = 2.8\text{–}10^{15} \exp(-44730/T)$	1450–1900	Brouwer, Mueller-Markgraf, and Troe, 1988[10]	(j)
$k_1 = 3.6\text{–}10^{15} \exp(-45000/T)$	1380–1700	Braun-Unkhoff, Frank, and Just, 1989[13]	(k)
$k^\infty = 1\text{–}10^{15} \exp(-43300/T)$ $k_1^\infty = 6.3\text{–}10^{15} \exp(-45465/T)$	1250–1500	Hippler, Reihs, and Troe, 1990[14]	(l)
Reviews and Evaluations			
$k_1 = 3.2\text{–}10^{15} \exp(-44439/T)$	920–1140	Benson and O'Neal, 1970[11]	(m)
$k_1 = 2.7\text{–}10^{14} \exp(-41722/T)$	1050–1600	Rao and Skinner, 1984[6]	(n)
$k_1 = 3.1\text{–}10^{15} \exp(-44890/T)$	920–2200	CEC, 1992[15]	(o)

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 decomposition 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[11] who suggested that the pre-exponential factor and the activation energy obtained seem unlikely for this reaction.

(e) Pyrolysis of toluene/nitrogen mixtures in a static system at total pressures below 300 mbar ($P_{\text{toluene}} \leq 30$ mbar). Stable compounds analysed 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 pressures 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 by toluene and benzyl in the 200–350 nm range[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[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 in 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 spectroscopy 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 $1.2–10^{16} \exp(-47505/T)$ 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 toluene dissociation predominantly 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) 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 separate 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 $0.2–k_1$. The rate expression for channel (1) is in excellent agreement with the results of Brouwer *et al.*[10]

(l) Thermal dissociation of high concentrations of toluene studied in reflected shock waves. Absorption signals mostly at 260 nm, were recorded (see also Ref. 10). At this wavelength the absorption coefficient of the benzyl radical exceeds that of toluene by a factor of 100, and very small conversions of toluene to benzyl can be detected. Density range $3–10^{-6}–2–10^{-4}$ mol cm^{-3}. No dependence of the measured rate constant on total pressure observed. Allowing for the presence of some fall off in the data of Ref. 13, the authors evaluate from the present work and that of Ref. 13 a high pressure limiting rate constant for channel (1).

(m) Re-evaluation 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.

(n) See comment (f). The limiting high pressure rate constant for toluene decomposition (channel (1)) is derived from RRKM calculations and $k_H = 1.5–k_D$.

(o) See Comments on Preferred Values.

Preferred Values

$k_1 = 3.1–10^{15} \exp(-44890/T)$ 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

The recommendations are unchanged from our previous evaluation.[15] A large variety of studies on toluene pyrolysis exist in the lower temperature range, up to approximately 1000 K, but most of these studies were conducted under experimental conditions in which bimolecular reactions of toluene leading to dibenzyl and other compounds dominate. The investigation of unimolecular 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, covering a density range of about $(1–3)–10^{-5}$ mol cm^{-3}, is 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 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 $T \leqslant 2000$ K.

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TABLE 1. Evaluated rate data for some reactions of ethyl, i-propyl, and t-butyl radicals

Reaction	k/cm^3 molecule^{-1} s^{-1}	T/K	$\pm\,\Delta \log k$	Note
	Ethyl Radicals			
$C_2H_5 + M \rightarrow C_2H_4 + H + M$	$k^\infty = 8.2\cdot10^{13}\exp(-20070/T)s^{-1}$	700–1100	0.3	A1
	$k^\circ = [C_2H_5]1.71\cdot10^{-6}\exp(-16800/T)s^{-1}$	700–900	0.3	A1
	$F_c\,(C_2H_6) = 0.25\exp(-T/97){+}0.75\exp(-T/1379)$	700–1000	$\Delta F_c = \pm0.1$	A1
$C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$	$1.7\cdot10^{-14}\exp(+1100/T)$	600–1200	0.3	A2
$C_2H_5 + H_2 \rightarrow C_2H_6 + H$	$5.1\cdot10^{-24}T^{3.6}\exp(-4250/T)$	700–1200	0.2 at 700 K rising to 0.6 at 1200 K	A3
$C_2H_5 + CH_3 \rightarrow C_2H_4 + CH_4$	$1.9\cdot10^{-12}$	300–800	0.4	A4
$\rightarrow C_3H_8$	$k^\infty = 5.6\cdot10^{-11}$	300–800	0.3	A4
$C_2H_5 + C_2H_2 \rightarrow C_2H_5CH{=}CH$	$5.6\cdot10^{-14}\exp(-3520/T)$	300–600	0.5	A5
$C_2H_5 + C_2H_4 \rightarrow n\text{-}C_4H_9$	$1.8\cdot10^{-13}\exp(-3670/T)$	300–600	0.5	A6
$C_2H_5 + C_2H_5 \rightarrow n\text{-}C_4H_{10}$	$k^\infty = 1.9\cdot10^{-11}$	300–1200	0.3	A7
$\rightarrow C_2H_6 + C_2H_4$	$2.4\cdot10^{-12}$	300–1200	0.4	A7
$C_2H_5 + C_2H_5CHO \rightarrow C_2H_6 + C_2H_5CO$	$2.9\cdot10^{-13}\exp(-3660/T)$	300–700	0.3	A8
$C_2H_5 + C_3H_5 \rightarrow CH_2{=}C{=}H_2 + C_2H_6$	$1.6\cdot10^{-12}\exp(66/T)$	500–1200	0.3	A9
$\rightarrow C_3H_6 + C_2H_4$	$4.3\cdot10^{-12}\exp(66/T)$	500–1200	0.4	
$\rightarrow CH_3CH_2CH_2CHCH_2$	$k^\infty = 3.3\cdot10^{-10}\exp(66/T)$	500–1200	0.4	
	i-Propyl Radicals			
$i\text{-}C_3H_7 + M \rightarrow C_3H_6 + H + M$	$k^\infty = 8.76\cdot10^{7}T^{1.76}\exp(-17870/T)s^{-1}$	170–1000	0.3	B1
	$k^\circ = [He]3.56\cdot10^{-7}\exp(-14200/T)s^{-1}$	750–830	0.3	B1
	$F_c(He) = 0.35$	750–830	$\Delta F_c = \pm0.1$	B1
$i\text{-}C_3H_7 + O_2 \rightarrow C_3H_6 + HO_2$	$3.3\cdot10^{-14}\exp(+1290/T)$	600–800	0.5	B2
$i\text{-}C_3H_7 + H_2 \rightarrow C_3H_8 + H$	$1.3\cdot10^{-23}T^{3.28}\exp(-4360/T)$	300–1200	0.5	B3
$i\text{-}C_3H_7 + C_2H_2 \rightarrow (CH_3)_2CHCH{=}CH$	$5.3\cdot10^{-14}\exp(-3470/T)$	300–600	0.5	B4
$i\text{-}C_3H_7 + C_2H_4 \rightarrow (CH_3)_2CHCH_2CH_2$	$7.5\cdot10^{-14}\exp(-3470/T)$	300–600	0.5	B5
$i\text{-}C_3H_7 + i\text{-}C_3H_7 \rightarrow C_6H_{14}$	$k^\infty = 6.8\cdot10^{-12}$	300–1000	0.1 at 300 K rising to 0.3 at 1000 K	B6
$\rightarrow C_3H_8 + C_3H_6$	$4.2\cdot10^{-12}$	300–1000	0.1 at 300 K rising to 0.5 at 1000 K	B6
$i\text{-}C_3H_7 + i\text{-}C_3H_7CHO \rightarrow C_3H_8 + (CH_3)_2CHCO$] $\rightarrow C_3H_8 + (CH_3)_2CCHO$]	$6.6\cdot10^{-14}\exp(-3170/T)$	300–650	0.5	B7
$\rightarrow C_3H_8 + CH_2CH(CH_3)CHO$	$5.3\cdot10^{-14}\exp(-4780/T)$	500–650	0.5	B7
	t-Butyl Radicals			
$t\text{-}C_4H_9 + M \rightarrow i\text{-}C_4H_8 + H + M$	$k^\infty = 8.3\cdot10^{13}\exp(-19200/T)\ s^{-1}$	300–800	0.5	C1
$t\text{-}C_4H_9 + O_2 \rightarrow i\text{-}C_4H_8 + HO_2$	$5\cdot10^{-14}\exp(+2115/T)$	600–800	0.5	C2
$t\text{-}C_4H_9 + H_2 \rightarrow i\text{-}C_4H_{10} + H$	$3.1\cdot10^{-26}T^{4.24}\exp(-4510/T)$	300–1200	0.5	C3
$t\text{-}C_4H_9 + C_2H_2 \rightarrow (CH_3)_3CCH{=}CH$	$1.2\cdot10^{-13}\exp(-4320/T)$	300–600	0.5	C4
$t\text{-}C_4H_9 + C_2H_4 \rightarrow (CH_3)_3CCH_2CH_2$	$3.3\cdot10^{-14}\exp(-4020/T)$	300–650	0.5	C5
$t\text{-}C_4H_9 + t\text{-}C_4H_9 \rightarrow C_8H_{18}$	$k^\infty = 5.2\cdot10^{-8}T^{-1.73}$	300–1000	0.15 at 300 K rising to 0.3 at 1000 K	C6
$\rightarrow i\text{-}C_4H_{10} + i\text{-}C_4H_8$	$1.2\cdot10^{-7}T^{-1.73}$	300–1000	0.15 at 300 K rising to 0.5 at 1000 K	C6

TABLE 1. Evaluated rate data for some reactions of ethyl, i-propyl, and t-butyl radicals — Continued

Reaction	k/cm^3 molecule^{-1} s^{-1}	T/K	$\pm \Delta \log k$	Note
	t-Butyl Radicals — Continued			
$t\text{-}C_4H_9 + t\text{-}C_4H_9CHO \rightarrow i\text{-}C_4H_{10} + t\text{-}C_4H_9CO$	$1.0\cdot10^{-14}\exp(-3200/T)$	300–700	0.5	C7
$\rightarrow i\text{-}C_4H_{10} + CH_2C(CH_3)_2CHO$	$3.9\cdot10^{-14}\exp(-5540/T)$	500–700	0.5	C7

A1. $C_2H_5 + M$. See separate data sheet for a discussion of this reaction.

A2. $C_2H_5 + O_2$. See separate data sheet for a discussion of this reaction.

A3. $C_2H_5 + H_2$. The available literature data have recently been reviewed by Tsang[1], and we have adopted his recommendation here.

A4. $C_2H_5 + CH_3$. See separate data for the reaction $CH_3 + C_2H_5$.

A5. $C_2H_5 + C_2H_2$. For the addition reaction we have recommended the rate expression given by Kerr and Parsonage[4], with adjustment to allow for the change in k of the reference reaction, $k(C_2H_5 + C_2H_5 \rightarrow n\text{-}C_4H_{10}) = 1.9 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1} (see Note A7).

A6. $C_2H_5 + C_2H_4$. For the addition reaction we have recommended the rate expression given by Kerr and Parsonage[4], with adjustment to allow for the change in k of the reference reaction, $k(C_2H_5 + C_2H_5 \rightarrow n\text{-}C_4H_{10}) = 1.9 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1} (see Note A7).

A7. $C_2H_5 + C_2H_5$. See separate data sheet for a discussion of this reaction.

A8. $C_2H_5 + C_2H_5CHO$. The available literature data have been evaluated by McAdam and Walker[5] and we have adopted their recommendation, with adjustment to allow for the change in k of the reference reaction, $k(C_2H_5 + C_2H_5 \rightarrow \text{n-}C_4H_{10}) = 1.9 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1} (see Note A7).

A9. Only disproportion/combination ratios are available[22] for this reaction. We accept Tsang's[23] recommendations for the various paths and the RRKM calculations for fall-off.

B1. $i\text{-}C_3H_7 + M$. Taken from the recent direct study of Seakins *et al.*[6] using laser flash photolysis coupled with photoionisation mass spectrometry; rate expressions derived from a transition state model including literature data[7–11] for the forward and reverse reactions.

B2. $i\text{-}C_3H_7 + O_2$. Calculated from the ratio $k(i\text{-}C_3H_7 + i\text{-}C_3H_7CHO \rightarrow C_3H_8 + C_4H_7O)/k(\text{i-}C_3H_7 + O_2 \rightarrow C_3H_6 + HO_2) = 2.57 \exp(-4580/T)$, as determined by Gulati and Walker[12] over the temperature range 653–773 K, from measurements of the yields of C_3H_8 and C_3H_6 in the oxidation of $\text{i-}C_3H_7CHO$. Recommended k based on $k(i\text{-}C_3H_7 + i\text{-}C_3H_7CHO \rightarrow C_3H_8 + C_4H_7O) = 8.47 \cdot 10^{-14} \exp(-3290/T)$ cm^3 molecule^{-1} s^{-1}, as calculated for the temperature range 653–773 K from the data of Kerr and Trotman-Dickenson[18] (see Note B7).

B3. $i\text{-}C_3H_7 + H_2$. The only experimental data for this reaction were measured at 713 K, where the ratio $k(i\text{-}C_3H_7 + O_2 \rightarrow C_3H_6 + HO_2)/k(i\text{-}C_3H_7 + H_2 \rightarrow C_3H_8 + H) = 3.06 \cdot 10^3$ has been determined by Baldwin *et al.*[13] from measurements of the yields of C_3H_8 and C_3H_6 in the oxidation of $i\text{-}C_3H_7CHO$ in the presence of added H_2. This yields $k = 6.5 \cdot 10^{-17}$ cm^3 molecule^{-1} s^{-1} based on $k(i\text{-}C_3H_7 + O_2 \rightarrow C_3H_6 + HO_2) = 2.0 \cdot 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 713 K (see Note B2). To obtain a temperature dependence of k, we have taken the recommendation of Tsang[2], $k = 5.8 \cdot 10^{-23} T^{3.28} \exp(-4363/T)$ cm^3 molecule^{-1} s^{-1} (based on his evaluated data for the reverse reaction and the equilibrium constant) and adjusted the pre-exponential factor to fit the above value of k at 713 K.

B4. $i\text{-}C_3H_7 + C_2H_2$. For the addition reaction we have recommended the rate expression given by Kerr and Parsonage[4], with adjustment to allow for the change in k of the reference reaction, $k(i\text{-}C_3H_7 + i\text{-}C_3H_7 \rightarrow C_6H_{14}) = 6.8 \cdot 10^{-12}$ cm^3 molecule^{-1} s^{-1} (see Note B6).

B5. $i\text{-}C_3H_7 + C_2H_4$. For the addition reaction we have recommended the rate expression as evaluated by Kerr and Parsonage[4], with allowance for the change in k of the reference reaction, $k(i\text{-}C_3H_7 + i\text{-}C_3H_7 \rightarrow C_6H_{14}) = 6.8 \cdot 10^{-12}$ cm^3 molecule^{-1} s^{-1} (see Note B6).

B6. $i\text{-}C_3H_7 + i\text{-}C_3H_7$. There is good agreement on the room temperature total rate coefficient of the combination reaction (k_c) plus the disproportionation reaction (k_d) as measured by molecular modulation studies[14]. The preferred value is the mean of the results of Anastasi and Arthur[14], Parkes and Quinn[15], and Arrowsmith and Kirsch[16], i.e. $k_c + k_d = 1.1 \cdot 10^{-11}$ cm^3 molecule^{-1} s^{-1}. The recommended values of k_c and k_d were then derived from the ratio $k_d/k_c = 0.62$ at room temperature[14]. The value of $k_c = 5 \cdot 10^{-12}$ cm^3 molecule^{-1} s^{-1}, over the temperature range 683–808 K from very-low-pressure-pyrolysis studies[17], is in good agreement with the molecular modulation studies.

B7. $i\text{-}C_3H_7 + i\text{-}C_3H_7CHO$. The preferred data are from the study of Kerr and Trotman-Dickenson[18], with allowance for the change in the k of the reference reaction, $k(i\text{-}C_3H_7 + i\text{-}C_3H_7 \rightarrow C_6H_{14}) = 6.8 \cdot 10^{-12}$ cm^3 molecule^{-1} s^{-1} (see Note B6).

C1. $t\text{-}C_4H_9 + M$. The available literature data have recently been reviewed by Tsang[3] and we have adopted his recommendations here.

C2. $t\text{-}C_4H_9 + O_2$. The rate coefficient at 753 K, $k = 8.3 \cdot 10^{-13}$cm^3 molecule^{-1} s^{-1} was calculated from the ratio $k(t\text{-}C_4H_9 + O_2 \rightarrow i\text{-}C_4H_8 + HO_2)/k(\text{t-}C_4H_9 + H_2 \rightarrow i\text{-}C_4H_{10} + H) = 6.89 \cdot 10^3$ at 753 K, as determined by Evans and Walker[19], from measurements of yields of $i\text{-}C_4H_8$ and $i\text{-}C_4H_{10}$ in the decomposition of 2,2,3,3,-tetramethylbutane in the presence of O_2 and H_2, by taking $k(t\text{-}C_4H_9 + H_2 \rightarrow i\text{-}C_4H_{10} + H) = 1.1 \cdot 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 753 K (see Note C3). The temperature coefficient of k was then obtained by assuming the recommended value of $A = 5 \cdot 10^{-14}$ cm^3 molecule^{-1} s^{-1}, based on the analogous reactions of C_2H_5 and $i\text{-}C_3H_7$.

C3. $t\text{-}C_4H_9 + H_2$. There are no experimental data on the rate coefficient of this reaction, but we have accepted the recommendation of Tsang[3], which is based on reliable data for the reverse reaction $k(\mathrm{H} + i\text{-}\mathrm{C_4H_{10}})$ together with thermochemical data which now appears to be established.

C4. $t\text{-}\mathrm{C_4H_9} + \mathrm{C_2H_2}$. We have accepted the evaluation of Kerr and Parsonage[4] on the addition reaction, with adjustment of the rate coefficient of the reference reaction, $k(t\text{-}\mathrm{C_4H_9} + t\text{-}\mathrm{C_4H_9} \rightarrow \mathrm{C_8H_{18}}) = 2.7 \cdot 10^{-12} (T/300)^{-1.73}$ cm^3 molecule^{-1} s^{-1} (see Note C6).

C5. $t\text{-}\mathrm{C_4H_9} + \mathrm{C_2H_4}$. We have accepted the evaluation of Kerr and Parsonage[4] on the addition reaction, with adjustment of the rate coefficient of the reference reaction, $k(\mathrm{t\text{-}C_4H_9} + \mathrm{t\text{-}C_4H_9} \rightarrow \mathrm{C_8H_{18}}) = 2.7 \cdot 10^{-12} (T/300)^{-1.73}$ cm^3 molecule^{-1} s^{-1} (see Note C6).

C6. $t\text{-}\mathrm{C_4H_9} + t\text{-}\mathrm{C_4H_9}$. There is good agreement on the room temperature rate coefficient of the combination reaction (k_c), as measured by molecular modulation studies. The preferred data are from the evaluation of all the experimental data by Arthur[20], which differs slightly from the recommendation of Tsang[3], based on the earlier data of Parkes and Quinn[15]. The rate coefficient of the disproportionation reaction (k_d) has been calculated from the ratio $k_d/k_c = 2.3$ at room temperature[20].

C7. $t\text{-}\mathrm{C_4H_9} + \mathrm{t\text{-}C_4H_9CHO}$. The preferred data are from the study of Birrell and Trotman-Dickenson[21], with allowance for the change in the k of the reference reaction, $k(\mathrm{t\text{-}C_4H_9} + \mathrm{t\text{-}C_4H_9} \rightarrow \mathrm{C_8H_{18}}) = 2.7 \cdot 10^{-12} (T/300)^{-1.73}$ cm^3 molecule^{-1} s^{-1} (see Note C6). For the reaction $t\text{-}\mathrm{C_4H_9} + t\text{-}\mathrm{C_4H_9CHO} \rightarrow i\text{-}\mathrm{C_4H_{10}} + t\text{-}\mathrm{C_4H_9CO}$, the data of Birrell and Trotman-Dickenson[21] yield the value $k = 1.9 \cdot 10^{-15} \exp(-2540/T)$ cm^3 molecule^{-1} s^{-1}, which would appear to be a serious underestimation of the Arrhenius parameters, in relation to data for analogous reactions, $\mathrm{R} + \mathrm{RCHO} \rightarrow \mathrm{RH} + \mathrm{RCO}$. Accordingly, we have calculated the preferred rate equation from the experimental value of k at 550 K and an assumed value of $A = 1.0 \cdot 10^{-14}$ cm^3 molecule^{-1} s^{-1}.

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TABLE 2. Evaluated rate data for some reactions of allyl radicals

Reaction	k/cm^3 molecule^{-1} s^{-1}	T/K	$\pm\ \Delta \log k$	Note
$C_3H_5 + M \rightarrow CH_2=C=CH_2 + H + M$	$k^\infty = 1.5\cdot 10^{11} T^{0.84} \exp(-30050/T)\ s^{-1}$	800–1500	0.3	A1
$C_3H_5 + O_2 \rightarrow CH_2=C=CH_2 + HO_2$	$1.7\cdot 10^{-12} \exp(-11400/T)$	600–1200	0.3 at 600 rising to 0.5 at 1200 K	A2
$\rightarrow CO$ + products	$7.6\cdot 10^{-12} \exp(-9450/T)$	600–1200	0.3	
$C_3H_5 + H_2 \rightarrow C_3H_6 + H$	$1.8\cdot 10^{-19} T^{2.4} \exp(-9550/T)$	300–1100	0.7 at 300 K reducing to 0.3 at 1100 K	A3
$C_3H_5 + CH_4 \rightarrow C_3H_6 + CH_3$	$6.6\cdot 10^{-23} T^{3.4} \exp(-11670/T)$	300–1200	0.4	A4
$C_3H_5 + C_2H_6 \rightarrow C_3H_6 + C_2H_5$	$3.9\cdot 10^{-22} T^{3.3} \exp(-9990/T)$	300–1200	0.4	A5
$C_3H_5 + C_3H_8 \rightarrow C_3H_6 + CH_3CH_2CH_2$ (a)	$3.9\cdot 10^{-22} T^{3.3} \exp(-9990/T)$	300–1200	0.4 over the range 600 to 1000 K rising to 0.7 at other temperatures.	A6
$\rightarrow C_3H_6 + CH_3CHCH_3$ (b)	$1.3\cdot 10^{-22} T^{3.3} \exp(-8660/T)$	300–1200		
$C_3H_5 + i\text{-}C_4H_{10} \rightarrow C_3H_6 + (CH_3)_2CHCH_2$ (a)	$5.9\cdot 10^{-22} T^{3.3} \exp(-9990/T)$	300–1200	0.4 over the range 600 to 1000 K rising to 0.7 at other temperatures.	A7
$\rightarrow C_3H_6 + (CH_3)_3C$ (b)	$0.7\cdot 10^{-22} T^{3.3} \exp(-7800/T)$	300–1200		
$C_3H_5 + HCHO \rightarrow C_3H_6 + HCO$	$1.2\cdot 10^{-16} T^{1.8} \exp(-9155/T)$	300–1000	0.4	A8
$C_3H_5 + C_6H_5CH_3 \rightarrow C_3H_6 + C_6H_5CH_2$	$3.3\cdot 10^{-12} \exp(-8660/T)$	600–1000	0.4	A9
$C_3H_5 + C_2H_4 \rightarrow C_3H_6 + C_2H_3$ (a)	$6.6\cdot 10^{-23} T^{3.4} \exp(-13120/T)$	600–1200	0.5	A10
$\rightarrow c\text{-}C_5H_8 + H$ (b)	$1.0\cdot 10^{-13} \exp(-9620/T)$	600–1200	0.7	
$C_3H_5 + 2\text{-}C_4H_8 \rightarrow C_3H_6 + CH_2CHCHCH_3$ (a)	$6.6\cdot 10^{-12} \exp(-8180/T)$	600–1000	0.5	A11
$\rightarrow C_3H_6 + CH_3C=CHCH_3$ (b)	$3.3\cdot 10^{-23} T^{3.4} \exp(-12160/T)$	600–1000	0.5	
$\rightarrow CH_2=CHCH_2CH(CH_3)CHCH_3$ (c)	$k_c^\infty = 1.0\cdot 10^{-13} \exp(-9620/T)$	600–1200	0.7	
$C_3H_5 + H \rightarrow C_3H_6$ (a)	$(k_a^\infty + k_b) = 2.8\cdot 10^{-10}$	300–1000	0.2 at 300 K rising to 0.5 at 1000 K	A12
$\rightarrow C_2H_3 + CH_3$ (b)				
$\rightarrow C_3H_4 + H_2$ (c)	$k_c = 3\cdot 10^{-11}$	300–1000	0.5	
$C_3H_5 + O \rightarrow H + CH_2=CHCHO$ (a)	$3.0\cdot 10^{-10}$	300–1000	0.2 over the range 300 to 600 K and 0.4 over the range 600 to 1000 K.	A13
$\rightarrow C_2H_3 + HCHO$ (b)	$<3\cdot 10^{-11}$			
$C_3H_5 + OH \rightarrow C_3H_4 + H_2O$ (a)	$k_a = 1.0\cdot 10^{-11}$	300–1000	0.5	A14
$\rightarrow CH_2=CHCH_2OH$ (b)	$(k_b^\infty + k_c) = 2.5\cdot 10^{-11}$	300–1000	0.3	
$\rightarrow CH_2 = CHCHO + 2H$ (c)				
$C_3H_5 + HO_2 \rightarrow C_3H_6 + O_2$ (a)	$4.4\cdot 10^{-12}$	300–1000	0.3 over the range 600 to 800 K rising to 0.5 at other temperatures.	A15
$\rightarrow CO$ + products (b)	$1.1\cdot 10^{-11}$	500–900	0.3	
$C_3H_5 + CH_3 \rightarrow CH_4 + CH_2=C=CH_2$ (a)	$3.5\cdot 10^{-13}$	500–1200	0.5	A16
$\rightarrow C_2H_5CH=CH_2$ (b)	$k_b^\infty = 1.7\cdot 10^{-10} T^{-0.32} \exp(66/T)$	500–1200	0.2	
$C_3H_5 + CH_3O_2 \rightarrow CH_2=CHCH_2O + CH_3O$	$2.0\cdot 10^{-11}$	500–1200	0.5	A17
$C_3H_5 + C_2H_5 \rightarrow CH_2=C=CH_2 + C_2H_6$ (a)	$1.6\cdot 10^{-12} \exp(66/T)$	500–1200	0.3	A18
$\rightarrow C_3H_6 + C_2H_4$ (b)	$4.3\cdot 10^{-12} \exp(66/T)$	500–1200	0.4	
$\rightarrow CH_3CH_2CH_2CH=CH_2$ (c)	$k_c^\infty = 3.3\cdot 10^{-11} \exp(66/T)$	500–1200	0.4	
$C_3H_5 + C_3H_5 \rightarrow CH_2=CHCH_2CH_2CH=CH_2$ (a)	$k_a^\infty = 1.7\cdot 10^{-11} \exp(132/T)$	300–600	0.2	A19
	$k_a^\infty = 2.0\cdot 10^{-11}$	600–1000	0.4	
$\rightarrow C_3H_6 + CH_2=C=CH_2$ (b)	$k_b = 1.0\cdot 10^{-13} \exp(132/T)$	300–1000	0.7	

A1. C_3H_5 + M. Tsang and Walker[1] obtained the high pressure value $k^\infty = 40 \pm 10\ s^{-1}$ at 1080 K from single pulse shock tube studies of 1,7-octadiene decomposition. Combination with low-temperature data on H atom addition to allene to form allyl gave the recommended expression for k^∞. No other high temperature data are available, but Walker[2] recommended $k^\infty = 10^{14.0}\exp(-31270/T)\ s^{-1}$, based on thermochemical estimates, which gives $k^\infty = 27\ s^{-1}$ at 1080 K in excellent agreement with Tsang's experimental value. Tsang[3] gives data for fall-off effects in his review.

A2. $C_3H_5 + O_2$. Walker *et al.*[4–6] used the decomposition of 4,4-dimethylpent-1-ene in the presence of O_2 and the direct oxidation of C_3H_6 to study the reactions of allyl radicals with O_2 between 673 and 773 K. Analysis of allene and CO was used to monitor the reactions. All the reactions have a high energy barrier. Rate constants determined as $k/k_r^{1/2}$ where $k_r = 1.69\cdot10^{-11}\exp(132/T)$ cm^3 molecule^{-1} s^{-1} for the recombination of allyl radicals. Reactions to give CO probably involve the formation of a cyclic peroxy intermediate, so that alternative pathways may occur outside the temperature range studied. Walker and Stothard[7] found evidence for a radical branching reaction ($C_3H_5 + O_2 \rightarrow 2$ radicals + products) and give $k = 2.7\cdot10^{-13}\exp(-8720/T)$ cm^3 molecule^{-1} s^{-1}. Formation of allylperoxy radicals will not be important under combustion conditions.

A3. $C_3H_5 + H_2$. This rate constant has not been measured experimentally. We accept Tsang's[3] recommendation which is based on a thermochemical calculation involving

$$k = 2.87\cdot10^{-19}T^{2.5}\exp(-1255/T)\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

for the reverse reaction, which is itself based on the experimental value for $k(H + 2\text{-}C_4H_8 \rightarrow H_2 + CH_3CHCHCH_2)$[3].

A4. $C_3H_5 + CH_4$. No experimental data are available. We accept Tsang's[3] recommendation which is based on a thermochemical calculation with $k(CH_3 + C_3H_6 \rightarrow CH_4 + CH_2CHCH_2) = 3.7\cdot10^{-24}T^{3.5}\exp(-2860/T)$ cm^3 molecule^{-1} s^{-1}.

A5. $C_3H_5 + C_2H_6$. No experimental data are available. We accept Tsang's[3] recommendation which is based on a thermochemical calculation with $k(C_2H_5 + C_3H_6 \rightarrow C_2H_6 + CH_2CHCH_2) = 3.7\cdot10^{-24}T^{3.5}\exp(-3340/T)$ cm^3 molecule^{-1} s^{-1} which itself is based on Tsang's[3] recommendation for $k(CH_3 + C_3H_6)$(see above). A simple check supports the validity of the data on allyl + CH_4 and allyl + C_2H_6. At 750 K, $k(C_3H_5 + C_2H_6)/k(C_3H_5 + CH_4) = 29$ compared with $k(HO_2 + C_2H_6)/k(HO_2 + CH_4) = 23$ from Walker's[9,10] experimental HO_2 data. As the allyl reactions are only about 10 kJ mol^{-1} more endothermic than the HO_2 reactions, the allyl ratio should be marginally higher than the HO_2 value as observed.

A6. $C_3H_5 + C_3H_8$. No experimental data are available. We accept Tsang's[3] recommendation for abstraction at a primary position (equal to $k(C_3H_5 + C_2H_6)$, see A5). For abstraction at the secondary position, Tsang recommends the same *A* factor (per C—H bond) and a reduction in activation energy of 7 kJ mol^{-1}. However, at 750 K, $k(C_3H_5 + CH_3CH_2CH_3 \rightarrow CH_3CHCH_3)/k(C_3H_5 + C_2H_6) = 1.0$ compared with the analogous HO_2 reaction ratio = 1.7 which arises[9,10] from the fact that the allyl reactions are about 10 kJ mol^{-1} more endothermic than the equivalent HO_2 reactions. A difference of 11 kJ mol^{-1} in the allyl activation energies is therefore recommended giving $k_b = 1.3\cdot10^{-22}T^{3.3}\exp(-8660/T)$ cm^3 molecule^{-1} s^{-1} for abstraction by allyl at the secondary C—H positions.

A7. $C_3H_5 + i\text{-}C_4H_{10}$. No experimental data are available. The expression for primary abstraction is the same as for allyl + C_2H_6 with allowance for path degeneracy (i.e. 3/2(k for allyl + C_2H_6)). The expression for attack at the tertiary position is derived by comparison with HO_2 data[9,10] (see A6) and we recommend $k = 0.7\cdot10^{-22}T^{3.3}\exp(-7800/T)$ cm^3 molecule^{-1} s^{-1}.

A8. C_3H_5 + HCHO. No experimental data are available. Tsang[3] gives $k = 2.4\cdot10^{-16}T^{1.8}\exp(-9154/T)$, calculated thermochemically from an estimate of the reverse reaction. In combination with the recommended value for k(allyl + C_2H_6), then k/k(allyl + C_2H_6) = 84 at 770 K compared with $k(HO_2 + HCHO)/k(HO_2 + C_2H_6) = 29$ from Walker's HO_2 data[9–11]. The difference in the ratios is a little larger than expected (see A6) and we recommend a reduction in Tsang's A factor for allyl + HCHO by a factor of 2.

A9. $C_3H_5 + C_6H_5CH_3$. $\text{Log}(k/k_1) = -0.55 - 3760/T$ was obtained by Throssell[12] from the measurement of propene and but-1-ene in the decomposition of 4-phenylbut-1-ene and hexa-1,5-diene between 850 and 950 K, where reaction (1) is $CH_3 + C_3H_5 \rightarrow C_4H_8\text{–}1$. A value of $k_1 = 2.3\cdot10^{-11}$ cm^3 molecule^{-1} s^{-1} is used to calculate k, which at 725 K is a factor of 10 higher than the only other experimental value of $6.6\cdot10^{-18}$ cm^3 molecule^{-1} s^{-1} obtained by Louw[13] from studies of the decomposition of diallyloxalate, as a source of allyl radicals, in the presence of toluene. We consider the value used for k_1 to be slightly high and reduce Throssell's A factor by a factor of 2, leading to the recommended value of k. Use of this and the recommended data for allyl + HCHO (see A8) gives $k(C_3H_5 + HCHO)/k(C_3H_5 + C_6H_5CH_3) = 6$ at 770 K compared with the analogous HO_2 ratio from Walker's data[9,10] equal to 10, comparable values being expected from the similar thermochemistry involved (see A5 and A6 above).

A10. $C_3H_5 + C_2H_4$. There are no experimental data for the addition and abstraction paths. The recommended expression for abstraction is based on $k(C_3H_5 + CH_4)$ with an increase of 12 kJ mol^{-1} in the activation energy on thermochemical grounds. For the addition path which will be reversed at combustion temperatures, the recommendation is based[14] on the *A* factors for addition of C_2H_5, n-C_3H_7 and i-C_3H_7 to C_2H_4 (A $= 1\cdot10^{-13}$ cm^3 molecule^{-1} s^{-1}) and an increase in the activation energy (E = 30 kJ mol^{-1}) by 50 kJ mol^{-1}, the delocalization energy of allyl radicals[1]. Tsang[3] reports evidence at 1100 K that the decomposition of 4-pentenyl radicals leads to 2.5% conversion to cyclopentene. It is possible, therefore, that addition of allyl to C_2H_4 may lead to cyclopentane through the sequence $C_3H_5 + C_2H_4 \rightarrow$ 4-pentenyl $\rightarrow$ cyclopentyl $\rightarrow$ cyclopentane + H.

A11. C_3H_5 + 2-C_4H_8. No experimental data are available for any path. The recommended value for abstraction at the allyl position is based on $k(C_3H_5 + C_6H_5CH_3)$ with adjustments due to path degeneracy (3 to 6) and to a slight weakening of the C—H bond in 2-C_4H_8(ca. 6 kJ mol^{-1}). For the alternative abstraction, the recommendation is based on $k(C_3H_5 + C_2H_4)$ with adjustments for path degeneracy (4 to 2) and for the weaker C—H bond (E lower by 12 kJ mol^{-1}). The recommended expression for addition is based on kinetic data for alkyl + alkene[14] with E increased by 50 kJ mol^{-1} delocalization energy.

A12. C_3H_5 + H. The only experimental data were obtained by Hanning-Lee and Pilling[15] who used laser flash photolysis of hexa-1,5-diene at 291 K, measuring [H] and [C_3H_5] by resonance fluorescence and absorption spectroscopy, respectively. The rate coefficient showed no significant variation between 100 and 400 Torr. The value is consistent with an estimate by Tsang[3], who has calculated fall-off values for $k_a/(k_a + k_b)$. Allera and Shaw[16] estimate $k_c/(k^\infty_a + k_b + k_c) \approx 0.1$, used as the basis of the recommended value of k_c. Negligible temperature coefficient is expected between 300 and 1000 K.

A13. C_3H_5 + O. Studied directly by Pilling *et al.*[17] between 300 and 600 K using laser flash photolysis and detection firstly by photo-ionization mass spectrometry and secondly by absorption spectroscopy and resonance fluorescence for C_3H_5 and O, respectively. The mass spectrometry results suggest a slight decrease in k with temperature ($2.3\cdot10^{-10}\exp(120/T)$ cm^3 molecule^{-1} s^{-1}), but no such trend is observed from absorption spectroscopy. The only detectable product by mass spectrometry was acrolein suggesting that the major channel is $O + C_3H_5 \rightarrow C_3H_4O$ + H. In particular, no C_2H_3 or HCHO was observed and $k_b < 3\cdot10^{-11}$ is recommended.

A14. C_3H_5 + OH. There are no experimental data. Tsang[3] recommends $k_a = 1\cdot10^{-11}$ for the abstraction process (based on comparable reactions) and $(k_b^\infty + k_c) = 2.5\cdot10^{-11}$ cm^3 molecule^{-1} s^{-1} for the high pressure limit for the addition channel. Tsang[3] has carried out RRKM calculations for the fall-off effects which are unimportant below about 1200 K.

A15. $C_3H_5 + HO_2$. There is only one, indirect, study[4]. Measurement of propene and CO yields in the decomposition of 4,4-dimethylpent-1-ene in the presence of O_2 gives $k_a/k_b = 0.38 \pm 0.10$ between 670 + 750 K, and further studies[5] with added propene give k_b. [C_3H_5] is determined from the rate of formation of hexa-1,5-diene and [HO_2] from the rate of formation of propene oxide in the reaction $HO_2 + C_3H_6 \rightarrow C_3H_6O + OH$ (k is accurately known). Small corrections are made for the formation of propene in the molecular decomposition of 4,4-dimethylpent-1-ene[4]. Original values modified first by use of the value of k for allyl recombination recommended in this table and, secondly, (5%) for the formation of CO in the reaction $C_3H_5 + O_2$. The mechanism of (b) almost certainly involves addition followed by rapid loss of OH and further decomposition to form HCHO + C_2H_3 radicals which react uniquely with O_2 under the conditions used to form CO. Other paths including formation of acrolein may be possible.

A16. $C_3H_5 + CH_3$. There are no experimental data. Tsang[3] recommends $k_b^\infty = 1.69\cdot10^{-10}T^{-0.32}\exp(66/T)$ cm^3 molecule^{-1} s^{-1} based on use of the cross-combination rule with data for CH_3 radical combination and C_3H_5 recombination (recommended value used). At 1000 K, $k_b^\infty = 1.75\cdot10^{-11}$ cm^3 molecule^{-1} s^{-1} in satisfactory agreement with $2.3\cdot10^{-11}$ cm^3 molecule^{-1} s^{-1} calculated thermochemically by Throssell[12] from the kinetics of but-1-ene homolysis into C_3H_5 and CH_3 radicals. Tsang[3] has carried out RRKM calculations for the fall-off in k_b. Based on data[18] for the disproportion/combination ratio of methylallyl + CH_3 (= 0.02), $k_a = 3.5\cdot10^{-13}$ cm^3 molecule^{-1} s^{-1} is recommended for the disproportionation path.

A17. $C_3H_5 + CH_3O_2$. There are no experimental data or suggested mechanisms for this reaction. The main path almost certainly involves combination followed by rapid loss of CH_3O radicals to give CH_2=$CHCH_2O$ radicals which will undergo homolysis and react with O_2 to give a variety of products such as CO, HCHO and acrolein. A value of $k = 2\cdot10^{-11}$ cm^3 molecule^{-1} s^{-1} is recommended for the overall reaction, based on the specific rate constant for CO formation in the reaction $C_3H_5 + HO_2$ (see recommendation).

A18. $C_3H_5 + C_2H_5$. Only disproportionation/combination ratios are available[19] for this reaction. We accept Tsang's[3] recommendations for the various paths and the RRKM calculations for fall-off.

A19. $C_3H_5 + C_3H_5$. The only direct high pressure study was carried out by Tulloch *et al.*[20] who used laser flash photolysis coupled with absorption spectroscopy to measure [C_3H_5]. The absorption coefficient was assumed independent of temperature. Mixtures of hexa-1,5-diene (1 Torr) and argon (up to 250 Torr) gave the high pressure limit k_a^∞. Other studies (see Tsang[3]) were either indirect or involved low pressure pyrolysis with extensive extrapolation to high pressure. The values obtained by Tulloch *et al.* show a slight negative temperature coefficient between 300 and 600 K. Above 600 K, there is some evidence of a slight increase in k_a^∞ and in consequence, between 600 and 1000 K in the absence of independent evidence, a temperature independent value is recommended. Fall-off becomes important in combustion above about 1200 K[3]. James and Kambanis[21] give $k_b/k_a^\infty = 0.008$ between 400 and 460 K, but Tsang and Walker[1] found a value below 0.005 above 1000 K. A value of $k_b = 1.0 \cdot 10^{-13} \exp(132/T)$ is recommended.

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