Evaluated Kinetic Data for Combustion Modelling


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Evaluated Kinetic Data for Combustion Modeling. Supplement I
Evaluated Kinetic Data for Combustion Modelling

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

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

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1. Introduction

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

2. Guide to the Data Sheets

2.1. Scope and Reaction Ordering

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

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

O Atom Reactions
O2 Reactions
H Atom Reactions
H2 Reactions
OH Radical Reactions
H2O Reactions
HO2 Radical Reactions
H2O2 Reactions
N Atom Reactions
NH Radical Reactions
NH2 Radical Reactions
C2 Radical Reactions
CH Radical Reactions

Thus the reaction

\[ \text{CN} + \text{CH}_4 \rightarrow \text{HCN} + \text{CH}_3 \]

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

\[ \text{OH} + \text{CH}_3 + \text{M} \rightarrow \text{CH}_3\text{OH} + \text{M} \]

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 O2 and NO are treated as radicals only in their reactions with non-radical species.
For each reaction a data sheet is presented setting out relevant thermodynamic data, rate coefficient measurements, an 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\(^1\). Our format follows theirs closely but we have made more extensive use of graphs because of the need to convey some idea of the quality of the data over a wide temperature range.

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

### 2.2. Conventions Concerning Rate Coefficients

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

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

\[ A + A \rightarrow B + C \]

is given by

\[ \text{Rate} = -(i)\frac{d[A]}{dt} = \frac{d[B]}{dt} = \frac{d[C]}{dt} = k[A]^2 \]

### 2.3. Guide to the Tables

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

These are followed by the thermodynamic quantities \( \Delta H^0 \) and \( \Delta S^0 \) at 298 K and an expression for the equilibrium constant, \( K \), in units of atmospheres, for each of the reaction channels for which there are data available. All data refer to a standard state of 1 atmosphere. The source of the thermodynamic data is discussed later in this Preface.

The kinetic data for the reactions are summarized under the two headings (i) Rate Coefficient Measurements (ii) Reviews and Evaluations. To keep the size of the compilation within reasonable bounds, in most cases only the rate coefficient measurements back to the most recent comprehensive review are recorded. Where there is no suitable review, or where there are only few measurements, all of the measured values are tabulated. Also to limit the size of the review, if in a particular study, measurements of the rate coefficient have been made over a range of temperatures, the results are tabulated as a temperature dependent expression (usually Arrhenius in form) rather than as the individually reported data points. For bimolecular reactions the temperature dependence of the rate coefficient is expressed either as \( k = A \exp(-B/T) \) or \( AT^n \exp(-C/T) \) whichever is the more appropriate, where \( A, n, B \) and \( C \) are constants. In some cases the form with \( C = 0 \), leading to \( k = AT^n \), gives the best representation. The expressions used for pressure dependent combination and dissociation reactions are discussed in detail later.

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

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

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

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

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

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

### 2.4. Treatment of Combination and Dissociation Reactions

The rates of combination and the reverse dissociation reactions

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

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

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 \( k_* \),

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

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

\[
k_0[M]/k_* = [M][M],
\]

where the "centre of the falloff curve" \([M_*]\) indicates the third body concentration for which the extrapolated \( k_0 \) would be equal to \( k_* \). The dependence of \( k_0 \) 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:

\[
k = \frac{k_0 k_* [M]}{k_0[M] + k_*} = k_0[M] \left( \frac{1}{1 + [M][M]} \right)^F
\]

where the first factors at the rhs represent the Linde­

mann-Hinshelwood expression, and the additional broadening factor \( F \), at not too high temperature, is approximately given by

\[
\log F = \frac{\log F_2}{1 + \left( \frac{\log ([M][M])}{N} \right)^2}
\]

where \( n = 0.75 - 1.27 \log F_2 \). In this way the three quantities, \( k_0, k_* \), and \( F \) with

\[
[M]_k = \frac{k_*}{k_0}.
\]

characterize the falloff curve for the present application.

Alternatively, the three quantities \( k_0, [M]_k \), and \( F \) (or \( k_0, [M]_k \), and \( F \)) can be used. The temperature dependence of \( F \), which is sometimes significant, can be estimated by the procedure of Troe. The results can usually be represented approximately by an equation

\[
F = (1 - a) \exp(-T/T^{**}) + a \exp(-T/T^*) + \exp(-T^{**}/T).
\]

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

Theoretical predictions of \( F \) have been derived from rigid RRKM-type models including weak collision effects. Systematic calculations of this type have been presented by Patrick and Golden for reactions of atmospheric interest. It is debatable whether these calculations can be applied to reactions with large, where rotational effects are important. Changes in \( F \) 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 \( F \) values.

If detailed calculations are made it is sometimes found that alternative expressions for \( F \) may be more appropriate.

The dependence of \( k_0 \) and \( k_* \) on the temperature is represented in the \( T \) exponent \( n \),

\[
k \propto T^{-n}
\]

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

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

2.5. Assignment of Errors

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

No attempt has been made to assign explicit error limits to the temperature coefficient of \( k \). The assignment of error limits in \( \Delta \log k \) at the extremes of the temperature range indicates how the quality of the data varies with temperature without attempting to define the form which this variation takes. In the opinion of the evaluators the available data rarely merits a more elaborate assignment of errors over a wide temperature range.
The assignment of error limits in \( k \) is a subjective assessment by the evaluators. Modern techniques are capable in favourable circumstances of measuring rate coefficients with a precision represented by a standard deviation as small as 10%. However, data obtained in different laboratories on the same reaction and often by the same technique are rarely concordant to the extent that might be expected from the precision of the measurements; mean values may differ by many standard deviations. This is indicative of systematic errors which are difficult to detect and which cannot be simply incorporated into quoted error limits.

2.6. Thermodynamic Data

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

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

Because of the great sensitivity of \( K \) to the thermodynamic quantities, particularly \( \Delta H^0 \), any rate coefficient calculated from the equilibrium constant and the rate coefficient for the reaction in one direction may be subject to substantial uncertainty.

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

2.7. Acknowledgements

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2.8 References


3. Index of Reactions and Summary Table

3.1. Guide to the Summary Tables

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

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

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

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

#### Table 1. Bimolecular reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$k$/cm$^3$ molecule$^{-1}$s$^{-1}$</th>
<th>Temp/K</th>
<th>Error limits ($\Delta$ log $k$)</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>O Atom Reactions</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O + H$_2$ → OH + H</td>
<td>$8.5 \times 10^{-28} e^{-0.07 \frac{T}{T}}$</td>
<td>300-2500</td>
<td>± 0.5 at 300 K falling to ± 0.2 for $T &gt; 500$ K</td>
<td>430</td>
</tr>
<tr>
<td>O + OH → O$_2$ + H</td>
<td>$2.0 \times 10^{-11}$ exp(112/T)</td>
<td>220-500</td>
<td>± 0.2</td>
<td>432</td>
</tr>
<tr>
<td></td>
<td>$2.4 \times 10^{-11}$ exp(-353/T)</td>
<td>1000-2000</td>
<td>± 0.1</td>
<td></td>
</tr>
<tr>
<td>O + HO$_2$ → OH + O$_2$</td>
<td>$5.3 \times 10^{-11}$</td>
<td>300-1000</td>
<td>± 0.3 at 300 K rising to ± 0.5 at 1000 K.</td>
<td>434</td>
</tr>
<tr>
<td>O + H$_2$O$_2$ → OH + HO$_2$</td>
<td>$1.1 \times 10^{-12}$ exp(-2000/T)</td>
<td>300-500</td>
<td>± 0.3</td>
<td>437</td>
</tr>
<tr>
<td>O + NH$_3$ → OH + NH$_2$</td>
<td>$1.6 \times 10^{-11}$ exp(-3670/T)</td>
<td>500-2500</td>
<td>± 0.5</td>
<td>439</td>
</tr>
<tr>
<td>O + CH → CO + H → CHO + e</td>
<td>$6.6 \times 10^{-11}$</td>
<td>300-2000</td>
<td>± 0.5</td>
<td>441</td>
</tr>
<tr>
<td></td>
<td>$4.2 \times 10^{-13}$ exp(-850/T)</td>
<td>300-2500</td>
<td>± 0.5</td>
<td></td>
</tr>
<tr>
<td>O + ³CH$_2$ → CO + 2H → CO + H$_2$</td>
<td>$2 \times 10^{-10}$</td>
<td>300-2500</td>
<td>± 0.2 at 300 K rising to ± 0.7 at 2500 K.</td>
<td>443</td>
</tr>
<tr>
<td></td>
<td>$k_{ij} = 0.6 \pm 0.3$ over whole range</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O + CH$_3$ → HCHO + H</td>
<td>$1.4 \times 10^{-18}$</td>
<td>300-2200</td>
<td>± 0.2</td>
<td>444</td>
</tr>
<tr>
<td>O + CH$_4$ → OH + CH$_3$</td>
<td>$1.5 \times 10^{-15}$ $T^{1.55}$ exp(-4270/T)</td>
<td>300-2500</td>
<td>± 0.3 at 300 K falling to ± 0.15 at 2500 K.</td>
<td>445</td>
</tr>
<tr>
<td>O + CHO → OH + CO → CO$_2$ + H</td>
<td>$5.0 \times 10^{-11}$</td>
<td>300-2500</td>
<td>± 0.3</td>
<td>448</td>
</tr>
<tr>
<td></td>
<td>$5.0 \times 10^{-11}$</td>
<td>300-2500</td>
<td>± 0.3</td>
<td></td>
</tr>
<tr>
<td>O + HCHO → OH + CHO</td>
<td>$6.9 \times 10^{-13}$ $T^{0.87}$ exp(-1390/T)</td>
<td>250-2200</td>
<td>± 0.1 at 250 K rising to ± 0.3 at 2200 K.</td>
<td>449</td>
</tr>
<tr>
<td>O + CH$_3$O → O$_2$ + CH$_3$ → OH + HCHO</td>
<td>$2.5 \times 10^{-11}$</td>
<td>300-1000</td>
<td>± 0.3 at 300 K rising to ± 0.7 at 1000 K.</td>
<td>451</td>
</tr>
<tr>
<td></td>
<td>$k_{ij} = (0.12 \pm 0.1)$ at 300 K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O + CN → CO + N(S) → CO + N(D)</td>
<td>$1.7 \times 10^{-11}$</td>
<td>300-5000</td>
<td>± 0.2 at 300 K rising to ± 0.6 × 5000 K.</td>
<td>452</td>
</tr>
<tr>
<td>O + NCO → NO + CO → O$_2$ + CN</td>
<td>$7.0 \times 10^{-11}$</td>
<td>1450-2600</td>
<td>± 0.8</td>
<td>454</td>
</tr>
<tr>
<td>O + HCN → NCO + H → CO + NH → OH + CN</td>
<td>$2.3 \times 10^{-18}$ $T^{2.1}$ exp(-3075/T)</td>
<td>450-2500</td>
<td>± 0.2 at 450 K rising to ± 0.3 at 2500 K.</td>
<td>455</td>
</tr>
<tr>
<td>O + CH$_3$OH → OH + CH$_2$COOH → OH + CH$_3$O$_2$</td>
<td>$6.9 \times 10^{-13}$ $T^{0.87}$ exp(-1390/T)</td>
<td>250-2200</td>
<td>± 0.1 at 250 K rising to ± 0.3 at 2200 K.</td>
<td>458</td>
</tr>
<tr>
<td></td>
<td>$k_{ij} = 0.12 \pm 0.1$ at 300 K rising to ± 0.3 at 2500 K.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O + C$_2$H → CO + CH</td>
<td>$1.7 \times 10^{-11}$</td>
<td>300-2500</td>
<td>± 1.0</td>
<td>458</td>
</tr>
<tr>
<td>O + C$_2$H$_2$ → CO + ³CH$_2$ → CHCO + H</td>
<td>$3.6 \times 10^{-20}$ $T^{2.4}$ exp(-250/T)</td>
<td>300-2500</td>
<td>± 0.2</td>
<td>459</td>
</tr>
<tr>
<td></td>
<td>$k_{ij} = 0.5 \pm 0.3$ over whole range.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O + C$_2$H$_3$ → OH + C$_2$H$_4$ → CO + CH$_3$ → HCO + CH$_2$</td>
<td>$5 \times 10^{-11}$</td>
<td>300-2000</td>
<td>± 0.5</td>
<td>463</td>
</tr>
<tr>
<td>O + C$_2$H$_4$ → CH$_2$CHO + H → HCHO + CH$_2$ → CH$_3$CO + H$_2$</td>
<td>$5.75 \times 10^{-18}$ $T^{2.08}$</td>
<td>300-2000</td>
<td>± 0.1 for $T &lt; 1000$ K rising to ± 0.3 at 2000 K.</td>
<td>464</td>
</tr>
<tr>
<td></td>
<td>$k_{ij} = 0.35 \pm 0.05$ at p &gt; 3 Torr</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$k_{ij} = 0.6 \pm 0.10$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O + C$_3$H$_4$ → CH$_2$CHO + H → HCHO + CH$_3$</td>
<td>$1.1 \times 10^{-10}$</td>
<td>300-2500</td>
<td>± 0.3 from 300 to 1000 K</td>
<td>467</td>
</tr>
<tr>
<td></td>
<td>$k_{ij} = 0.17 \pm 0.2$ at 300 K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>± 0.5 from 1000 to 2500 K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reaction</td>
<td>$k$/cm$^3$ molecule$^{-1}$s$^{-1}$</td>
<td>Temp/K</td>
<td>Error limits ($\Delta \log k$)</td>
<td>Page</td>
</tr>
<tr>
<td>----------</td>
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<td>--------</td>
<td>-------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>$O + C_2H_6 \rightarrow OH + C_2H_5$</td>
<td>$1.66 \times 10^{-15} T^{1.5} \exp (-2920/T)$</td>
<td>300-1200</td>
<td>$\pm 0.3$ at 300 K falling to $\pm 0.15$ at 1200 K.</td>
<td>468</td>
</tr>
<tr>
<td>$O + CHCO \rightarrow 2CO + H$</td>
<td>$1.6 \times 10^{-10}$</td>
<td>300-2500</td>
<td>$\pm 0.3$</td>
<td>470</td>
</tr>
<tr>
<td>$O + CH_2CO \rightarrow CH_2O + CO$</td>
<td>$3.8 \times 10^{-12} \exp (-680/T)$</td>
<td>230-500</td>
<td>$\pm 0.3$</td>
<td>471</td>
</tr>
<tr>
<td>$O + CH_3CHO \rightarrow OH + CH_2CO$</td>
<td>$9.7 \times 10^{-12} \exp (-910/T)$</td>
<td>300-1500</td>
<td>$\pm 0.05$ at 300 K rising to $\pm 0.1$ at 1500 K.</td>
<td>473</td>
</tr>
<tr>
<td>$O + C_2H_5OOH \rightarrow OH + C_2H_5OOH$</td>
<td>$6.9 \times 10^{-13} T^{0.77} \exp (-1390/T)$</td>
<td>250-2200</td>
<td>$\pm 0.1$ at 150 K rising to $\pm 0.3$ at 2200 K.</td>
<td>475</td>
</tr>
<tr>
<td>$O + C_2H_5 \rightarrow OH + C_2H_5$</td>
<td>$1.2 \times 10^{-11} T^{-1} \exp (-570/T)$</td>
<td>300-1000</td>
<td>$\pm 0.5$</td>
<td>475</td>
</tr>
<tr>
<td>$O + C_2H_5CH_2 \rightarrow HCO + C_2H_5$</td>
<td>$5.5 \times 10^{-10}$</td>
<td>300</td>
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<tr>
<td>$O + C_2H_3CH \rightarrow C_2H_5CH + H$</td>
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<tr>
<td>$O + C_2H_5CH_2 \rightarrow$ products</td>
<td>$5.3 \times 10^{-15} T^{1.1} \exp (-1260/T)$</td>
<td>300-2800</td>
<td>$\pm 0.1$ at 300 K rising to $\pm 0.4$ at 2800 K</td>
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<td>$O + p-C_6H_4(CH_3)_2 \rightarrow$ products</td>
<td>$2.6 \times 10^{-11} \exp (-1409/T)$</td>
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<td>$O_2 + CH_4 \rightarrow HO_2 + CH_3$</td>
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<td>$O_2 + C_2H_5 \rightarrow HO_2 + C_2H_3$</td>
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<tr>
<td>$H + O_2 + H_2 \rightarrow HO_2 + H_2$</td>
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<td>$H + H + Ar \rightarrow H_2 + Ar$</td>
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<td>$H + OH + H_2O \rightarrow H_2O + H_2O$</td>
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<td>$H + OH + Ar \rightarrow H_2O + Ar$</td>
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<td>$H + HO + N_2 \rightarrow H_2O + N_2$</td>
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<th>Reaction</th>
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<th>Temp/K</th>
<th>Error limits (Δ log $k$)</th>
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<tr>
<td>$H + HO_2 \rightarrow H_2 + O_2$</td>
<td>$2.8 \times 10^{-10}$ exp(-440/T)</td>
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<td>± 0.3</td>
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<td>$H + O_2 \rightarrow 2 H$</td>
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<td>$H + H_2O \rightarrow OH + H_2$</td>
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<td>± 0.3</td>
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<td>$H + NH \rightarrow H_2 + N$</td>
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<td>$H + HO \rightarrow H_2O + O$</td>
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<td>$H + H_2O \rightarrow OH + H_2$</td>
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<td>$H + H_2O_2 \rightarrow H_2 + HO_2$</td>
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<tr>
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<td>$H + NH_2 \rightarrow H_2 + NH$</td>
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<td>$H + ^3CH_2 \rightarrow H_2 + CH$</td>
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<td>$H + CH_3 \rightarrow H_2 + ^3CH_2$</td>
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<td>$H + CHO \rightarrow H_2 + CO$</td>
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<td>$H + HCHO \rightarrow H_2 + HCO$</td>
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<td>$H + CH_3O \rightarrow H_2 + HCHO$</td>
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<td>$H + NCO \rightarrow NH + CO$</td>
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<td>$H + H_2 + CH_3$</td>
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<td>1400-1500</td>
<td>± 0.5</td>
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<td>$H + C_2H_5 \rightarrow H_2 + C_2H_4$</td>
<td>$1.0 \times 10^{-10}$ exp(-14000/T)</td>
<td>1000-3000</td>
<td>± 1.0</td>
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<td>300-2500</td>
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<td>$H + C_3H_4 \rightarrow C_3H_2 + H_2$</td>
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<td>$H + C_3H_6 \rightarrow H_2 + C_3H_3$</td>
<td>$2.4 \times 10^{-15}$ T$^{1/2}$ exp(-3730/T)</td>
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<td>$H + C_2H_5 \rightarrow H_2 + CH_4$</td>
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<td>$H + C_3H_6 \rightarrow H_2 + C_3H_3$</td>
<td>$3.0 \times 10^{-11}$ exp(-1700/T)</td>
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<td>± 0.5 at 200 K rising to ± 1.0 at 2000 K</td>
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<td>$H + CH_3CO \rightarrow CH_3 + CO$</td>
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<td>$H + CH_3CO \rightarrow CH_3 + CO$</td>
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<td>$H + CH_3CHO \rightarrow H_2 + CH_2CO$</td>
<td>$6.8 \times 10^{-15}$ T$^{1/2}$ exp(-1210/T)</td>
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### Table 1. Bimolecular reactions — Continued

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<th>Reaction</th>
<th>$k$/cm$^3$ molecule$^{-1}$s$^{-1}$</th>
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<td>$H + C_2H_5OH \rightarrow C_3H_6O + H_2$</td>
<td>$1.9 \times 10^{-10} \exp(-6240/T)$</td>
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<td>$\rightarrow C_2H_6 + OH$</td>
<td>$3.7 \times 10^{-11} \exp(-3990/T)$</td>
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<td>$H + C_3H_6CH_2 + M \rightarrow C_3H_5CH_3 + M$</td>
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<td>See Table 3</td>
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<td>$H + C_3H_6CH_2 \rightarrow H_2 + C_3H_5CH_3$</td>
<td>$6.6 \times 10^{-22} T^{1.4} \exp(-1570/T)$</td>
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<td>$\pm 0.3$ at 600 K rising to $\pm 0.5$ at 2800 K.</td>
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<td>$\rightarrow H_2 + C_3H_5CH_3$</td>
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<td>$\rightarrow C_3H_6 + CH_3$</td>
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<td>$H + p-C_6H_5(CH_3)_2 \rightarrow \text{products}$</td>
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<td>$H + C_6H_5C_6H_4 \rightarrow H_2 + C_6H_5C_6H_4$</td>
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<td>$\pm 0.1$ at 300 K rising to $\pm 0.3$ at 2500 K.</td>
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<td>$OH + OH \rightarrow H_2O + O$</td>
<td>$2.5 \times 10^{-15} T^{1.4} \exp(-50/T)$</td>
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<td>$OH + OH + M \rightarrow H_2O_2 + M$</td>
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<td>$OH + HO_2 \rightarrow H_2O + O_2$</td>
<td>$4.8 \times 10^{-11} \exp(250/T)$</td>
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<td>$OH + H_2O_2 \rightarrow H_2O + HO_2$</td>
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<td>$OH + NH \rightarrow NO + H_2$</td>
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<td>$\rightarrow H_2O + N$</td>
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<td>$OH + NH_2 \rightarrow O + NH_2$</td>
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<td>$\pm 0.2$ at 300 K rising to $\pm 0.5$ at 2000 K.</td>
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<td>$\rightarrow H + CH_3O$</td>
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<td>$\rightarrow H_2O + ^3CH_2$</td>
<td>$2.6 \times 10^{-17} T^{1.63} \exp(-1400/T)$</td>
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<td>$\pm 0.07$ at 250 K rising to $\pm 0.15$ at 1200 K.</td>
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<td>300-2500</td>
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<td>$OH + CHO \rightarrow H_2O + CO$</td>
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<td>$\pm 0.1$ at 300 K rising to $\pm 0.7$ at 3000 K.</td>
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<td>$OH + HCN \rightarrow H_2O + CN$</td>
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**TABLE 1. Bimolecular reactions — Continued**

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<th>Reaction</th>
<th>$k$/cm$^3$ molecule$^{-1}$s$^{-1}$</th>
<th>Temp/K</th>
<th>Error limits (Δ log $k$)</th>
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<tbody>
<tr>
<td>OH + CH$_3$OH → H$_2$O + CH$_3$OH</td>
<td>$1.2 \times 10^{-12}$ exp(130/T)</td>
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<td>± 0.2 at 300 K rising to ± 0.4 at 1000 K</td>
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<td>→ H$_2$O + CH$_2$OOH</td>
<td>$1.8 \times 10^{-12}$ exp(220/T)</td>
<td>300-1000</td>
<td>± 0.1 at 300 K rising to ± 0.3 at 1000 K.</td>
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<td>OH + C$_2$H$_4$ → H$_2$O + C$_2$H$_4$</td>
<td>$1.0 \times 10^{-10}$ exp(-6500/T)</td>
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<td>OH + C$_2$H$_6$ → H$_2$O + C$_2$H$_6$</td>
<td>$3.4 \times 10^{-11}$ exp(-2990/T)</td>
<td>650-1500</td>
<td>± 0.5</td>
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<td>OH + C$_2$H$_6$ → H$_2$O + C$_2$H$_6$</td>
<td>$2.7 \times 10^{-16}$ T$^{1.42}$ exp(-730/T)</td>
<td>400-1500</td>
<td>± 0.3</td>
<td>595</td>
</tr>
<tr>
<td>OH + C$_2$H$_4$OH → H$_2$O + C$_2$H$_4$OH</td>
<td>$6.4 \times 10^{-11}$ exp(-1440/T)</td>
<td>See Table 3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OH + C$_2$H$_4$OH → H$_2$O + C$_2$H$_4$OH</td>
<td>$8.7 \times 10^{-12}$</td>
<td>773</td>
<td>± 0.1</td>
<td>603</td>
</tr>
</tbody>
</table>

**H$_2$O Reactions**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$k$/cm$^3$ molecule$^{-1}$s$^{-1}$</th>
<th>Temp/K</th>
<th>Error limits (Δ log $k$)</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O + M → H + OH + M</td>
<td></td>
<td></td>
<td>See Table 2</td>
<td>603</td>
</tr>
</tbody>
</table>

**HO$_2$ Radical Reactions**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$k$/cm$^3$ molecule$^{-1}$s$^{-1}$</th>
<th>Temp/K</th>
<th>Error limits (Δ log $k$)</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>HO$_2$ + HO$_2$ → HO$_2$ + O$_2$</td>
<td>$3.1 \times 10^{-12}$ exp(-775/T)</td>
<td>550-1250</td>
<td>± 0.15 at 550 K rising to ± 0.3 at 1250 K.</td>
<td>604</td>
</tr>
<tr>
<td>HO$_2$ + NO$_2$ → HNO + O$_2$</td>
<td>$2.6 \times 10^{-11}$</td>
<td>300-400</td>
<td>± 0.4</td>
<td>607</td>
</tr>
<tr>
<td>HO$_2$ + CH$_3$ → OH + CH$_2$O</td>
<td>$3 \times 10^{-11}$</td>
<td>300-2500</td>
<td>± 0.7</td>
<td>608</td>
</tr>
<tr>
<td>HO$_2$ + CH$_4$ → H$_2$O + CH$_3$</td>
<td>$1.5 \times 10^{-11}$ exp(-12400/T)</td>
<td>600-1000</td>
<td>± 0.2 at 600 K rising to ± 0.3 at 1000 K.</td>
<td>608</td>
</tr>
<tr>
<td>HO$_2$ + HCHO → H$_2$O$_2$ + CHO</td>
<td>$5.0 \times 10^{-12}$ exp(-6580/T)</td>
<td>600-1000</td>
<td>± 0.5</td>
<td>609</td>
</tr>
</tbody>
</table>
### Table 1. Bimolecular reactions — Continued

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$k/\text{cm}^3\text{ molecule}^{-1}\text{s}^{-1}$</th>
<th>Temp/K</th>
<th>Error limits ($\Delta \log k$)</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{O} + \text{C}_2\text{H}_4 \rightarrow \text{OH} + \text{C}_2\text{H}_4\text{O}$</td>
<td>$3.7 \times 10^{-12} \exp(-8650/T)$</td>
<td>600-900</td>
<td>± 0.15 at 600 K rising to ± 0.25 at 900 K.</td>
<td>612</td>
</tr>
<tr>
<td>$\text{H}_2\text{O} + \text{C}_2\text{H}_6 \rightarrow \text{H}_2\text{O}_2 + \text{C}_2\text{H}_5$</td>
<td>$2.2 \times 10^{-11} \exp(-10300/T)$</td>
<td>500-1000</td>
<td>± 0.2 at 500 K rising to ± 0.3 at 1000 K.</td>
<td>614</td>
</tr>
<tr>
<td>$\text{H}_2\text{O} + \text{CH}_2\text{CHO} \rightarrow \text{H}_2\text{O}_2 + \text{CH}_3\text{CO}$</td>
<td>$5.0 \times 10^{-12} \exp(-6000/T)$</td>
<td>900-1200</td>
<td>± 0.7</td>
<td>614</td>
</tr>
</tbody>
</table>

**$\text{H}_2\text{O}_2$ Reactions**

$\text{H}_2\text{O}_2 + \text{M} \rightarrow 2\text{OH} + \text{M}$  
See Table 2  
615

**$N$ Atom Reactions**

$\text{N} + \text{CN} \rightarrow \text{N}_2 + \text{C}$  
$3 \times 10^{-10}$  
300-2500  
± 1.0  
616

$\text{N} + \text{NCO} \rightarrow \text{NO} + \text{CN}$  
$\rightarrow \text{N}_2 + \text{CO}$  
$3.3 \times 10^{-11}$  
1700  
± 0.5  
617

**NH Radical Reactions**

$\text{NH} + \text{O}_2 \rightarrow \text{NO} + \text{OH}$  
$\rightarrow \text{NO}_2 + \text{H}$  
$\rightarrow \text{HNO} + \text{O}$  
$1.26 \times 10^{-12} \exp(-770/T)$  
270-550  
± 0.2 at 270 K rising to ± 0.5 at 550 K.  
617

$\text{NH} + \text{NO} \rightarrow \text{N}_2 + \text{OH}$  
$\rightarrow \text{HN}_2 + \text{O}$  
$\rightarrow \text{N}_2 + \text{H}_2$  
$5.0 \times 10^{-11}$  
270-380  
± 0.2  
618

**$NH_2$ Radical Reactions**

$\text{NH}_2 + \text{O}_2 \rightarrow \text{products}$  
$<3 \times 10^{-18}$  
298  
621

$\text{NH}_3 + \text{NO} \rightarrow \text{N}_2 + \text{H}_2\text{O}$  
$\rightarrow \text{N}_2 + \text{H} + \text{OH}$  
$\rightarrow \text{N}_2\text{H} + \text{OH}$  
$\rightarrow \text{N}_2\text{O} + \text{H}_2$  
$1.8 \times 10^{-12} \exp(650/T)$  
$220-2000$  
± 0.5  
622

**$^1\text{C}_2$ and $^3\text{C}_2$ Radical Reactions**

$\text{CH Radical Reactions}$

$\text{CH} + \text{O}_2 \rightarrow \text{CHU} + \text{O}$  
$\rightarrow \text{CO} + \text{OH}$  
$5.5 \times 10^{-11}$  
300-2000  
± 0.3 at 300 K rising to ± 0.5 at 2000 K.  
627

$\text{CH} + \text{H}_2 \rightarrow \text{CH}_2 + \text{H}$  
$\rightarrow \text{CH}_3$  
$2.4 \times 10^{-10} \exp(-1760/T)$  
300-1000  
± 0.3  
630

$\text{CH} + \text{H}_2\text{O} \rightarrow \text{products}$  
$9.5 \times 10^{-12} \exp(380/T)$  
300-1000  
± 1.0  
632

$\text{CH} + \text{CO} \rightarrow \text{products}$  
$4.6 \times 10^{-13} \exp(860/T)$  
300-1000  
± 1.0  
632

$\text{CH} + \text{CO}_2 \rightarrow \text{products}$  
$5.7 \times 10^{-12} \exp(-345/T)$  
300-1000  
± 1.0  
633

$\text{CH} + \text{CH}_4 \rightarrow \text{products}$  
$5.0 \times 10^{-11} \exp(200/T)$  
200-700  
± 1.0  
634

$\text{CH} + \text{C}_2\text{H}_2 \rightarrow \text{products}$  
$3.5 \times 10^{-10} \exp(61/T)$  
200-700  
± 1.0  
634

$\text{CH} + \text{C}_3\text{H}_4 \rightarrow \text{products}$  
$2.2 \times 10^{-10} \exp(173/T)$  
200-700  
± 1.0  
635

$\text{CH} + \text{C}_2\text{H}_6 \rightarrow \text{products}$  
$1.8 \times 10^{-10} \exp(132/T)$  
200-700  
± 1.0  
636

---


<table>
<thead>
<tr>
<th>Reaction</th>
<th>( k/\text{cm}^3\text{ molecule}^{-1}\text{s}^{-1} )</th>
<th>Temp/K</th>
<th>Error limits (( \Delta \log k ))</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH} + \text{C}_3\text{H}_6 \rightarrow \text{products} )</td>
<td>( 1.9 \times 10^{-10} \text{exp}(240/T) )</td>
<td>300-700</td>
<td>± 1.0</td>
<td>636</td>
</tr>
<tr>
<td>( \text{CH} + \text{n-C}<em>4\text{H}</em>{10} \rightarrow \text{products} )</td>
<td>( 4.4 \times 10^{-10} \text{exp}(28/T) )</td>
<td>250-700</td>
<td>± 1.0</td>
<td>637</td>
</tr>
<tr>
<td>( \text{CH} + \text{i-C}<em>4\text{H}</em>{10} \rightarrow \text{products} )</td>
<td>( 2.0 \times 10^{-10} \text{exp}(240/T) )</td>
<td>300-700</td>
<td>± 1.0</td>
<td>637</td>
</tr>
<tr>
<td>( \text{CH} + \text{neo-C}<em>5\text{H}</em>{12} \rightarrow \text{products} )</td>
<td>( 1.6 \times 10^{-10} \text{exp}(340/T) )</td>
<td>300-700</td>
<td>± 1.0</td>
<td>638</td>
</tr>
<tr>
<td>( \text{CH} + \text{CH}_3\text{C}_2\text{H} \rightarrow \text{products} )</td>
<td>No recommendation</td>
<td></td>
<td></td>
<td>638</td>
</tr>
<tr>
<td>( \text{CH} + \text{CH}_2\text{O} \rightarrow \text{products} )</td>
<td>( 1.6 \times 10^{-10} \text{exp}(260/T) )</td>
<td>300-700</td>
<td>± 1.0</td>
<td>639</td>
</tr>
</tbody>
</table>

\( ^3\text{CH}_2 \) Radical Reactions

\[
\begin{align*}
^{3}\text{CH}_2 + \text{O}_2 & \rightarrow \text{CO} + \text{H} + \text{OH} \\
& \rightarrow \text{CO}_2 + \text{H} + \text{H} \\
& \rightarrow \text{CO} + \text{H}_2 \text{O} \\
& \rightarrow \text{CH}_2 + \text{H}_2 \\
& \rightarrow \text{HCHO} + \text{O} \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2 + ^3\text{CH}_2 + \text{H}_2 & \rightarrow \text{C}_2\text{H}_2 + 2\text{H} \\
& \rightarrow \text{C}_2\text{H}_4 \\
\end{align*}
\]

\[
\text{CH}_2 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_4 + \text{H} \\
\rightarrow \text{e-C}_3\text{H}_4 \\
\rightarrow \text{CH}_2\text{CHCH}_2 + \text{H} \\
\]

\( ^1\text{CH}_2 \) Radical Reactions

\[
\begin{align*}
\text{CH}_2 + \text{Ar} & \rightarrow ^2\text{CH}_2 + \text{Ar} \\
& \rightarrow ^3\text{CH}_2 + \text{Ar} \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2 + \text{N}_2 & \rightarrow ^2\text{CH}_2 + \text{N}_2 \\
& \rightarrow ^3\text{CH}_2 + \text{N}_2 \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2 + \text{CH}_4 & \rightarrow ^2\text{CH}_2 + \text{CH}_4 \\
& \rightarrow ^3\text{CH}_2 + \text{CH}_4 \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2 + \text{CH}_4 & \rightarrow ^2\text{CH}_2 + \text{CH}_4 \\
& \rightarrow ^3\text{CH}_2 + \text{CH}_4 \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2 + \text{O}_2 & \rightarrow \text{CO} + \text{H} + \text{OH} \\
& \rightarrow \text{CO}_2 + \text{H}_2 \\
& \rightarrow \text{CO} + \text{H}_2 \text{O} \\
& \rightarrow ^3\text{CH}_2 + \text{O}_2 \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2 + \text{H}_2 & \rightarrow \text{CH}_3 + \text{H} \\
& \rightarrow \text{CH}_2\text{CHCH}_2 + \text{H} \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 + \text{M} & \rightarrow \text{CH}_2 + \text{H} + \text{M} \\
\end{align*}
\]

See Table 3

See Table 3

See earlier entry

See earlier entry

See earlier entry

See Table 2

### Table 1. Bimolecular reactions — Continued

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$k$/cm$^3$ molecule$^{-1}$s$^{-1}$</th>
<th>Temp/K</th>
<th>Error limits ($\Delta$ log $k$)</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$ + O$_2$ $\rightarrow$ CH$_3$O + O $\rightarrow$ HCHO + OH $\rightarrow$ CH$_2$O$_2$</td>
<td>2.2 x 10$^{-10}$ exp$(-15800/T)$</td>
<td>300-2500</td>
<td>$\pm$ 0.5</td>
<td>649</td>
</tr>
<tr>
<td>CH$_2$ + H$_2$ $\rightarrow$ CH$_4$ + H $\rightarrow$ C$_2$H$_4$ + H$_2$ $\rightarrow$ C$_2$H$_6$</td>
<td>1.14 x 10$^{-10}$ T$^{-2/4}$ exp$(-4740/T)$</td>
<td>300-2500</td>
<td>$\pm$ 0.15 in the range 300-700 K. $\pm$ 0.3 in the range 700-2500 K.</td>
<td>653</td>
</tr>
<tr>
<td>CH$_3$ + CH$_3$ $\rightarrow$ C$_2$H$_4$ + H $\rightarrow$ C$_2$H$_4$ + H$_2$ $\rightarrow$ C$_2$H$_6$</td>
<td>5 x 10$^{-11}$ exp$(-6800/T)$</td>
<td>300-2500</td>
<td>$\pm$ 0.6</td>
<td>655</td>
</tr>
<tr>
<td>CH$_3$ + HCHO $\rightarrow$ CH$_4$ + HCO</td>
<td>6.8 x 10$^{-12}$ exp$(-4450/T)$</td>
<td>300-1000</td>
<td>$\pm$ 0.3</td>
<td>659</td>
</tr>
<tr>
<td>CH$_3$ + C$_2$H$_4$ + M $\rightarrow$ C$_3$H$_4$ + M $\rightarrow$ CH$_4$ + C$_2$H</td>
<td>See Table 3</td>
<td></td>
<td>No recommendation (see data sheets)</td>
<td></td>
</tr>
<tr>
<td>CH$_3$ + C$_2$H$_4$ $\rightarrow$ C$_3$H$_4$ $\rightarrow$ n-C$_3$H$_7$</td>
<td>6.9 x 10$^{-12}$ exp$(-5600/T)$</td>
<td>300-2500</td>
<td>$\pm$ 0.5</td>
<td>663</td>
</tr>
<tr>
<td>CH$_3$ + C$_2$H$_4$ $\rightarrow$ C$_3$H$_4$ $\rightarrow$ C$_2$H$_5$</td>
<td>1.9 x 10$^{-12}$</td>
<td>300-800</td>
<td>$\pm$ 0.4</td>
<td>665</td>
</tr>
<tr>
<td>CH$_3$ + C$_2$H$_4$ $\rightarrow$ C$_3$H$_4$ $\rightarrow$ C$_2$H$_5$</td>
<td>2.5 x 10$^{-31}$ T$^6$ exp$(-3043/T)$</td>
<td>300-1500</td>
<td>$\pm$ 0.1 at 300 K rising to $\pm$ 0.2 at 1500 K.</td>
<td>668</td>
</tr>
<tr>
<td>CH$_3$ + CH$_3$CHO $\rightarrow$ CH$_4$ + CH$_3$CO $\rightarrow$ CH$_4$ + CH$_3$CHO</td>
<td>3.3 x 10$^{-30}$ T$^{5/4}$ exp$(-1240/T)$</td>
<td>300-1250</td>
<td>$\pm$ 0.3</td>
<td>671</td>
</tr>
</tbody>
</table>

**CHO Reactions**

| CH$_4$ + M $\rightarrow$ CH$_3$ + H + M | See Table 2 | 673 |

**CHO Radical Reactions**

| CHO + O$_2$ $\rightarrow$ CO + HOO$_2$ $\rightarrow$ OH + CO$_2$ $\rightarrow$ HCO$_3$ | 5.0 x 10$^{-12}$ | 300-2500 | $\pm$ 0.3                        | 677  |

| CHO + CHO $\rightarrow$ HCHO + CO | 5.0 x 10$^{-11}$ | 300 | $\pm$ 0.3                        | 680  |

**HCHO Reactions**

| HCHO + M $\rightarrow$ H + CHO + M $\rightarrow$ H$_2$ + CO + M | See Table 2 | 681 |

**CH$_2$OH Reactions**

| CH$_2$OH + O$_2$ $\rightarrow$ CH$_3$O + HO$_2$ | 2.6 x 10$^{-9}$ T$^{-10}$ exp$(-1800/T)$ | 300-1200 | $\pm$ 0.1 at 300 K rising to $\pm$ 0.3 at 1200 K. | 684  |

**CH$_3$O Radical Reactions**

| CH$_3$O + M $\rightarrow$ HCHO + H + M | See Table 2 | 687 |

| CH$_3$O + O$_2$ $\rightarrow$ HCHO + HO$_2$ | 6.7 x 10$^{-14}$ exp$(-1070/T)$ | 300-1000 | $\pm$ 0.2 at 500 K rising to $\pm$ 0.3 at 300 K and 1000 K. | 688  |

**CH$_2$OOH Reactions**

| CH$_2$OOH + M $\rightarrow$ CH$_3$O + OH + M | See Table 2 | 690 |

---

### TABLE 1. Bimolecular reactions — Continued

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$k$/cm$^3$ molecule$^{-1}$s$^{-1}$</th>
<th>Temp/K</th>
<th>Error limits ($\Delta \log k$)</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CN Radical Reactions</strong></td>
<td></td>
<td></td>
<td></td>
<td>691</td>
</tr>
<tr>
<td>$\text{CN} + \text{O}_2 \rightarrow \text{NCO} + \text{O}$</td>
<td>$1.1 \times 10^{-11} \exp(205/T)$</td>
<td>300-2500</td>
<td>$\pm 0.25$ at 300 K rising to $\pm 0.5$ at 2500 K.</td>
<td>691</td>
</tr>
<tr>
<td>$\text{CN} + \text{H}_2 \rightarrow \text{HCN} + \text{OH}$</td>
<td>$1.3 \times 10^{-11} \exp(-3750/T)$</td>
<td>500-3000</td>
<td>$\pm 0.3$ at 500 K rising to $\pm 0.5$ at 3000 K.</td>
<td>694</td>
</tr>
<tr>
<td>$\text{CN} + \text{CH}_4 \rightarrow \text{HCN} + \text{CH}_3$</td>
<td>$1.5 \times 10^{-11} \exp(-940/T)$</td>
<td>260-400</td>
<td>$\pm 0.3$</td>
<td>695</td>
</tr>
<tr>
<td><strong>NCO Radical Reactions</strong></td>
<td></td>
<td></td>
<td></td>
<td>697</td>
</tr>
<tr>
<td>$\text{NCO} + \text{M} \rightarrow \text{N} + \text{CO} + \text{M}$</td>
<td>See Table 2</td>
<td></td>
<td></td>
<td>697</td>
</tr>
<tr>
<td>$\text{NCO} + \text{NO} \rightarrow \text{N}_2\text{O} + \text{CO}$</td>
<td>$1.7 \times 10^{-11} \exp(200/T)$</td>
<td>300-600</td>
<td>$\pm 0.5$</td>
<td>698</td>
</tr>
<tr>
<td><strong>C$_2$H Radical Reactions</strong></td>
<td></td>
<td></td>
<td></td>
<td>699</td>
</tr>
<tr>
<td>$\text{C}_2\text{H} + \text{O}_2 \rightarrow \text{CO}_2 + \text{CH}$</td>
<td>$3.0 \times 10^{-11}$</td>
<td>300</td>
<td>$\pm 0.5$</td>
<td>699</td>
</tr>
<tr>
<td>$\text{C}_2\text{H} + \text{H}_2 \rightarrow \text{C}_2\text{H}_2 + \text{H}$</td>
<td>$2.5 \times 10^{-11} \exp(-1560/T)$</td>
<td>300-2500</td>
<td>$\pm 0.3$ at 300 K rising to $\pm 0.7$ at 2500 K</td>
<td>700</td>
</tr>
<tr>
<td>$\text{C}_2\text{H} + \text{C}_2\text{H}_2 \rightarrow \text{C}_4\text{H}_2 + \text{H}$</td>
<td>$5.0 \times 10^{-11}$</td>
<td>300-2700</td>
<td>$\pm 0.3$</td>
<td>702</td>
</tr>
<tr>
<td>$\text{C}_2\text{H} + \text{CH}_4 \rightarrow \text{products}$</td>
<td>$2.0 \times 10^{-13}$</td>
<td>298</td>
<td>$\pm 1$</td>
<td>702</td>
</tr>
<tr>
<td>$\text{C}_2\text{H} + \text{C}_2\text{H}_6 \rightarrow \text{products}$</td>
<td>No recommendation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>C$_2$H$_3$ Radical Reactions</strong></td>
<td></td>
<td></td>
<td></td>
<td>704</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_3 + \text{M} \rightarrow \text{C}_2\text{H}_2 + \text{H} + \text{M}$</td>
<td>See Table 2</td>
<td></td>
<td></td>
<td>704</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_3 + \text{O}_2 \rightarrow \text{HCHO} + \text{CHO}$</td>
<td>$9.0 \times 10^{-12}$</td>
<td>300-2000</td>
<td>$\pm 0.3$ at 300 K rising to $\pm 0.5$ at 2000 K</td>
<td>705</td>
</tr>
<tr>
<td><strong>C$_2$H$_5$ Radical Reactions</strong></td>
<td></td>
<td></td>
<td></td>
<td>706</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_5 + \text{O}_2 \rightarrow \text{C}_2\text{H}_4 + \text{HO}_2$</td>
<td>$1.7 \times 10^{-14} \exp(1100/T)$</td>
<td>600-1200</td>
<td>$\pm 0.3$</td>
<td>706</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_6 + \text{C}_2\text{H}_4$</td>
<td>$2.4 \times 10^{-13}$</td>
<td>300-1200</td>
<td>$\pm 0.4$</td>
<td>707</td>
</tr>
<tr>
<td>See Table 3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>C$_2$H$_6$ Reactions</strong></td>
<td></td>
<td></td>
<td></td>
<td>710</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_6 + \text{M} \rightarrow \text{CH}_3 + \text{CH}_3 + \text{M}$</td>
<td>See Table 2</td>
<td></td>
<td></td>
<td>710</td>
</tr>
<tr>
<td><strong>CHCO Reactions</strong></td>
<td></td>
<td></td>
<td></td>
<td>713</td>
</tr>
<tr>
<td>$\text{CHCO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{HCO}$</td>
<td>$2.7 \times 10^{-12} \exp(430/T)$</td>
<td>300-550</td>
<td>$\pm 0.7$</td>
<td>713</td>
</tr>
<tr>
<td>$\rightarrow \text{CH}_2\text{O} + \text{OH}$</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>$\rightarrow \text{CHO}_2\text{CO}$</td>
<td></td>
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</tr>
<tr>
<td><strong>CH$_2$CHO Radical Reactions</strong></td>
<td></td>
<td></td>
<td></td>
<td>714</td>
</tr>
<tr>
<td>$\text{CH}_2\text{CHO} + \text{O}_2 \rightarrow \text{HO}_2 + \text{CH}_2\text{CHO}$</td>
<td>$k_1 = 2.6 \times 10^{-13}$</td>
<td>250-1000</td>
<td>$\pm 0.2$</td>
<td>714</td>
</tr>
<tr>
<td>$\rightarrow \text{HCHO} + \text{CO} + \text{OH}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\rightarrow \text{O}_2\text{CH}_2\text{CHO}$</td>
<td>$k_2 = 3.0 \times 10^{-14}$</td>
<td>300</td>
<td>$\pm 0.3$</td>
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### Table 1. Bimolecular reactions — Continued

<table>
<thead>
<tr>
<th>Reaction</th>
<th>k/cm³ molecule⁻¹s⁻¹</th>
<th>Temp/K</th>
<th>Error limits (Δ log k)</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂H₅CO Radical Reactions</td>
<td></td>
<td></td>
<td></td>
<td>716</td>
</tr>
<tr>
<td>CH₃CO + O₂ + M → CH₃CO₂ + M</td>
<td></td>
<td></td>
<td>See Table 3</td>
<td>716</td>
</tr>
<tr>
<td>CH₃CHO Reactions</td>
<td></td>
<td></td>
<td></td>
<td>716</td>
</tr>
<tr>
<td>CH₃CHO + M → CH₃ + HCO + M</td>
<td></td>
<td></td>
<td>See Table 2</td>
<td>716</td>
</tr>
<tr>
<td>C₅H₇O Reactions</td>
<td></td>
<td></td>
<td></td>
<td>717</td>
</tr>
<tr>
<td>C₂H₅O + M → HCHO + CH₂ + M → CH₂CHO + H + M</td>
<td></td>
<td></td>
<td>See Table 2</td>
<td>717</td>
</tr>
<tr>
<td>C₂H₅O + O₂ → CH₂CHO + HO₂</td>
<td>1.0 × 10⁻¹³ exp(−830/T)</td>
<td>300–1000</td>
<td>± 0.3 at 300 K rising to ± 0.5 at 1000 K</td>
<td>717</td>
</tr>
<tr>
<td>C₆H₅OOH Reactions</td>
<td></td>
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</tr>
<tr>
<td>C₆H₅OOH + M → C₂H₅O + OH + M</td>
<td></td>
<td></td>
<td>See Table 2</td>
<td>718</td>
</tr>
<tr>
<td>C₆H₅ Radical Reactions</td>
<td></td>
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<td>718</td>
</tr>
<tr>
<td>C₆H₅ + M → C₆H₅ + C₂H₅ + M → C₆H₅ + C₂H₅ + M → linear-C₆H₅ + M</td>
<td></td>
<td></td>
<td>See Table 2</td>
<td>718</td>
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<tr>
<td>C₆H₅ Reactions</td>
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<td></td>
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<td>721</td>
</tr>
<tr>
<td>C₆H₅ + M → C₆H₅ + H + M → C₆H₄ + C₂H₂ + M</td>
<td></td>
<td></td>
<td>See Table 2</td>
<td>721</td>
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<tr>
<td>C₆H₅O Radical Reactions</td>
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<td>724</td>
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<tr>
<td>C₆H₅O + M → C₆H₅ + CO + M</td>
<td></td>
<td></td>
<td>See Table 2</td>
<td>724</td>
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<tr>
<td>C₆H₅CH₂ Radical Reactions</td>
<td></td>
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<td>725</td>
</tr>
<tr>
<td>C₆H₅CH₂ + M → C₆H₅ + 2C₂H₂ + M → C₆H₄ + C₂H₃ + M → C₆H₅ + C₂H₂ + M → C₆H₅(BCH) + M</td>
<td></td>
<td></td>
<td>See Table 2</td>
<td>725</td>
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<tr>
<td>C₆H₅CH₂ Reactions</td>
<td></td>
<td></td>
<td></td>
<td>728</td>
</tr>
<tr>
<td>C₆H₅CH₂ + M → C₆H₅CH₂ + H + M</td>
<td></td>
<td></td>
<td>See Table 2</td>
<td>728</td>
</tr>
<tr>
<td>p-C₆H₄(CH₃)₂ Reactions</td>
<td></td>
<td></td>
<td></td>
<td>731</td>
</tr>
<tr>
<td>p-C₆H₄(CH₃)₂ + M → C₆H₅CH₂CH₃ + H + M</td>
<td></td>
<td></td>
<td>See Table 2</td>
<td>731</td>
</tr>
<tr>
<td>C₆H₅C₂H₁ Reactions</td>
<td></td>
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<td></td>
<td>733</td>
</tr>
<tr>
<td>C₆H₅C₂H₁ + M → C₆H₅CH₂ + CH + M → C₆H₅ + C₂H₂ + M → C₆H₅CH₂CH₂ + H + M → C₆H₅ + C₂H₂ + M → C₆H₅CH₂CH₂ + H + M</td>
<td></td>
<td></td>
<td>See Table 2</td>
<td>733</td>
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</tbody>
</table>

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Table 2. Decomposition reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$k_a k_s^{-1}$</th>
<th>Temp/K</th>
<th>Error limits ($\Delta \log k$)</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2 + Ar \rightarrow 2H + Ar$</td>
<td>$k_0 = 3.7 \times 10^{-10} \exp(-48350/T)$</td>
<td>2500-8000</td>
<td>± 0.3</td>
<td>550</td>
</tr>
<tr>
<td>$H_2 + H_2 \rightarrow 2H + H_2$</td>
<td>$k_0 = 1.5 \times 10^{-9} \exp(-48350/T)$</td>
<td>2500-8000</td>
<td>± 0.5</td>
<td>550</td>
</tr>
<tr>
<td>$H_2O + N_2 \rightarrow H + OH + N_2$</td>
<td>$k_0 = 5.8 \times 10^{-9} \exp(-52920/T)$</td>
<td>2000-6000</td>
<td>± 0.5</td>
<td>603</td>
</tr>
<tr>
<td>$H_2O_2 + M \rightarrow 2OH + M$</td>
<td>$k_d(Ar) = 3 \times 10^{-8} \exp(-21600/T)$</td>
<td>1000-1500</td>
<td>± 0.2</td>
<td>615</td>
</tr>
<tr>
<td>$k_d(N_2) = 2 \times 10^{-7} \exp(-22900/T)$</td>
<td></td>
<td>700-1500</td>
<td>± 0.2</td>
<td></td>
</tr>
<tr>
<td>$k_\alpha = 3 \times 10^{14} \exp(-24400/T)$</td>
<td></td>
<td>1000-1500</td>
<td>± 0.5</td>
<td></td>
</tr>
<tr>
<td>$F_c(Ar) = 0.5$</td>
<td></td>
<td>700-1500</td>
<td>$\Delta F_c = \pm 0.1$</td>
<td></td>
</tr>
<tr>
<td>$CH_3 + M \rightarrow CH_2 + H + M$</td>
<td>$k_0 = 1.7 \times 10^{-8} \exp(-45600/T)$</td>
<td>1500-3000</td>
<td>± 0.5</td>
<td>648</td>
</tr>
<tr>
<td>$CH_4 + M \rightarrow CH_2 + H + M$</td>
<td>$k_d(Ar) = 1.2 \times 10^{-6} \exp(-47900/T)$</td>
<td>1000-3000</td>
<td>± 0.3</td>
<td>673</td>
</tr>
<tr>
<td>$k_d(CH_4) = 1.4 \times 10^{-13} \exp(-48100/T)$</td>
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<td>1000-2000</td>
<td>± 0.3</td>
<td></td>
</tr>
<tr>
<td>$k_* = 2 \times 10^{13} \exp(-52800/T)$</td>
<td></td>
<td>1000-3000</td>
<td>± 0.5</td>
<td></td>
</tr>
<tr>
<td>$F_c(Ar) = \exp(-0.45/T) \exp(-2321)$</td>
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<td>1000-3000</td>
<td>$\Delta F_c = \pm 0.1$</td>
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<tr>
<td>$F_c(CH_4) = \exp(-0.37/T) \exp(-2210)$</td>
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<td>1000-2000</td>
<td>$\Delta F_c = \pm 0.1$</td>
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<tr>
<td>$HCHO + M \rightarrow H + CHO + M \rightarrow H_2 + CO + M$</td>
<td>$k_0(1) = 2.1 \times 10^{-9} \exp(-39200/T)$</td>
<td>1500-2500</td>
<td>± 0.3</td>
<td>681</td>
</tr>
<tr>
<td>$k_{b2} = 0.5$ at 2200 K</td>
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<tr>
<td>$CH_2O + M \rightarrow HCHO + H + M$</td>
<td>$k_0 = 3.16 \times 10^7 T^{-27} \exp(-15400/T)$</td>
<td>300-1000</td>
<td>± 1.0</td>
<td>687</td>
</tr>
<tr>
<td>[estimate]</td>
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</tr>
<tr>
<td>$CH_2O + M \rightarrow CH_2O + OH + M$</td>
<td>$k_* = 4 \times 10^{15} \exp(-21600/T)$</td>
<td>400-1000</td>
<td>± 0.5 at 600 K rising to ± 1.0 at 400 and 1000 K</td>
<td>690</td>
</tr>
<tr>
<td>$NCO + Ar \rightarrow N + CO + Ar$</td>
<td>$k_0 = 1.7 \times 10^{-9} \exp(-2350/T)$</td>
<td>1450-2600</td>
<td>± 0.4</td>
<td>697</td>
</tr>
<tr>
<td>$C_2H_3 + M \rightarrow C_2H_2 + H + M$</td>
<td>$k_0 = 6.9 \times 10^{10} T^{-35} \exp(-22900/T)$</td>
<td>500-2500</td>
<td>± 0.5</td>
<td>704</td>
</tr>
<tr>
<td>$k_* = 2 \times 10^{14} \exp(-20000/T)$</td>
<td></td>
<td>500-2500</td>
<td>± 0.5</td>
<td></td>
</tr>
<tr>
<td>$F_c = 0.35$</td>
<td></td>
<td>500-2500</td>
<td>$\Delta F_c = \pm 0.1$</td>
<td></td>
</tr>
<tr>
<td>$C_2H_4 + M \rightarrow 2CH_2 + M$</td>
<td>$k_d(Ar) = 1.1 \times 10^{25} T^{-4.84} \exp(-47900/T)$</td>
<td>300-2000</td>
<td>± 0.5</td>
<td>710</td>
</tr>
<tr>
<td>$k_d(CH_4) = 4.5 \times 10^{-2} \exp(-41950/T)$.</td>
<td></td>
<td>300-2000</td>
<td>± 0.5</td>
<td></td>
</tr>
<tr>
<td>$k_* = 1.8 \times 10^{13} T^{-1.84} \exp(-45700/T)$</td>
<td></td>
<td>300-2000</td>
<td>± 0.3</td>
<td></td>
</tr>
<tr>
<td>$F_c(Ar) = 0.38 \exp(-T/273) + 0.62 \exp(-T/1180)$</td>
<td></td>
<td>300-2000</td>
<td>$\Delta F_c = \pm 0.1$</td>
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</tr>
<tr>
<td>$F_c(CH_4) = 0.54 \exp(-T/1250)$</td>
<td></td>
<td>300-2000</td>
<td>$\Delta F_c = \pm 0.1$</td>
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</tr>
<tr>
<td>$CH_3CHO + M \rightarrow CH_3 + CHO + M$</td>
<td>$k(1 \text{ atm.}) = 7 \times 10^{-15} \exp(-41100/T)$</td>
<td>750-1200</td>
<td>± 0.4</td>
<td>716</td>
</tr>
<tr>
<td>(pressure dependent region)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_2H_2O + M \rightarrow HCHO + CH_3 + M$</td>
<td>$k_* = 8 \times 10^{13} \exp(-10830/T)$</td>
<td>300-600</td>
<td>± 1.0</td>
<td>717</td>
</tr>
<tr>
<td>[estimate]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_2H_2O + M \rightarrow C_2H_2O + OH + M$</td>
<td>$k_* = 4 \times 10^{15} \exp(-21600/T)$</td>
<td>400-1000</td>
<td>± 1.0</td>
<td>718</td>
</tr>
<tr>
<td>$C_2H_5 + M \rightarrow C_2H_2 + C_2H_3 + M$</td>
<td>No recommendation</td>
<td>1450-1900</td>
<td>± 0.4</td>
<td>718</td>
</tr>
<tr>
<td>$\rightarrow \text{linear-CH}_2 + \text{M}$</td>
<td>4.0 $\times 10^{13} \exp(-36700/T)$</td>
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<td></td>
</tr>
<tr>
<td>$C_2H_4 + M \rightarrow C_2H_2 + H + M$</td>
<td>9.0 $\times 10^{15} \exp(-54060/T)$</td>
<td>1200-2500</td>
<td>± 0.4 at 1200 K reducing to ± 0.3 at 2500 K</td>
<td>721</td>
</tr>
<tr>
<td>$\rightarrow C_2H_4 + H_2 + M$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_2H_5 + M \rightarrow C_2H_2 + CO + M$</td>
<td>2.5 $\times 10^{11} \exp(-22100/T)$</td>
<td>1000-1580</td>
<td>± 0.2</td>
<td>724</td>
</tr>
</tbody>
</table>
## EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

### Table 2. Decomposition reactions — Continued

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$k_0/k_{s-1}$</th>
<th>Temp/K</th>
<th>Error limits ($\Delta \log k$)</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}_2\text{H}_4\text{CH}_2 + \text{M} \rightarrow \text{C}_2\text{H}_5 + 2\text{C}_2\text{H}_2 + \text{M}$</td>
<td>$k_0 \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$</td>
<td>1350-1900</td>
<td>± 0.3 at 1350 K rising to ± 0.5 1900 K</td>
<td>725</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_4\text{CH}_2 + \text{H} + \text{M} \rightarrow \text{C}_2\text{H}_5 + \text{CH}_3 + \text{M}$</td>
<td>$3.1 \times 10^{13} \exp(-36370/T)$</td>
<td>920-2200</td>
<td>± 0.3 at 900 K rising to ± 0.5 at 2200 K</td>
<td>728</td>
</tr>
<tr>
<td>$\text{p-C}_6\text{H}_4(\text{CH}_3)_2 + \text{M} \rightarrow \text{p-C}_6\text{H}_4\text{CH}_3\text{CH}_3 + \text{H} + \text{M}$</td>
<td>$4.0 \times 10^{13} \exp(-42600/T)$</td>
<td>1400-1800</td>
<td>± 0.5</td>
<td>731</td>
</tr>
<tr>
<td>$\text{C}_6\text{H}_5\text{C}_2\text{H}_4 + \text{M} \rightarrow \text{C}_6\text{H}_5\text{CH}_2 + \text{CH} + \text{M}$</td>
<td>$6.1 \times 10^{13} \exp(-37800/T)$</td>
<td>770-1800</td>
<td>± 0.1 at 770 K rising to ± 0.4 at</td>
<td>733</td>
</tr>
</tbody>
</table>

Error limits ($\Delta \log k$): ± 0.3 at 770 K rising to ± 0.4 at 2200 K.
Table 3. Combination reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$k_{\text{cm}}^3\text{molecule}^{-1}\text{s}^{-1}$</th>
<th>Temp/K</th>
<th>Error limits ($\Delta \log k$)</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>H + O$_2$ + Ar $\rightarrow$ HO$_2$ + Ar</td>
<td>$k_0 = 1.7 \times 10^{-30} T^{-9.8}$</td>
<td>300-2000</td>
<td>± 0.5</td>
<td>488</td>
</tr>
<tr>
<td>H + O$_2$ + H$_2$ $\rightarrow$ HO$_2$ + H$_2$</td>
<td>$k_0 = 5.8 \times 10^{-30} T^{-9.8}$</td>
<td>300-2000</td>
<td>± 0.5</td>
<td>488</td>
</tr>
<tr>
<td>H + O$_2$ + N$_2$ $\rightarrow$ HO$_2$ + N$_2$</td>
<td>$k_0 = 3.9 \times 10^{-30} T^{-9.8}$</td>
<td>300-2000</td>
<td>± 0.5</td>
<td>488</td>
</tr>
<tr>
<td>H + O$_2$ + H$_2$O $\rightarrow$ HO$_2$ + H$_2$O</td>
<td>$k_0 = 4.3 \times 10^{-30} T^{-9.8}$</td>
<td>300-2000</td>
<td>± 0.5</td>
<td>488</td>
</tr>
<tr>
<td>H + H + Ar $\rightarrow$ H + Ar</td>
<td>$k_0 = 1.8 \times 10^{-30} T^{-1.0}$</td>
<td>300-2500</td>
<td>± 0.5</td>
<td>492</td>
</tr>
<tr>
<td>H + H + H$_2$ $\rightarrow$ H + H$_2$</td>
<td>$k_0 = 2.7 \times 10^{-31} T^{-6.6}$</td>
<td>100-5000</td>
<td>± 0.5</td>
<td>495</td>
</tr>
<tr>
<td>H + OH + H$_2$O $\rightarrow$ HO + H$_2$O + H$_2$O</td>
<td>$k_0 = 3.9 \times 10^{-25} T^{-2.0}$</td>
<td>300-3000</td>
<td>± 0.3</td>
<td>497</td>
</tr>
<tr>
<td>H + OH + Ar $\rightarrow$ HO + Ar</td>
<td>$k_0 = 2.3 \times 10^{-26} T^{-2.0}$</td>
<td>300-3000</td>
<td>± 0.3</td>
<td>496</td>
</tr>
<tr>
<td>H + OH + N$_2$ $\rightarrow$ H$_2$O + N$_2$</td>
<td>$k_0 = 6.1 \times 10^{-30} T^{-2.0}$</td>
<td>300-3000</td>
<td>± 0.3</td>
<td>498</td>
</tr>
<tr>
<td>H + C$_2$H$_2$ + M $\rightarrow$ C$_2$H$_3$ + M</td>
<td>$k_0(\text{He}) = 6.2 \times 10^{-29} (T/3000)^{-1.8}$</td>
<td>300-1000</td>
<td>± 0.3</td>
<td>512</td>
</tr>
<tr>
<td>H + C$_2$H$_2$ + H$_2$O $\rightarrow$ C$_2$H$_3$ + H$_2$O</td>
<td>$k_0(\text{He}) = 3 \times 10^{-28} (T/300)^{-1.8}$</td>
<td>300-1000</td>
<td>± 0.5</td>
<td>512</td>
</tr>
<tr>
<td>H + C$_2$H$_2$ + M $\rightarrow$ C$_2$H$_3$ + He</td>
<td>$F_e = 0.44$</td>
<td>300-1000</td>
<td>Δ$F_e = ± 0.1$</td>
<td>512</td>
</tr>
<tr>
<td>H + C$_2$H$_2$ + M $\rightarrow$ C$_2$H$_3$ + M</td>
<td>No recommendation</td>
<td></td>
<td></td>
<td>528</td>
</tr>
<tr>
<td>H + C$_2$H$_3$ + M $\rightarrow$ C$_2$H$_4$ + M</td>
<td>No recommendation</td>
<td></td>
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<td>529</td>
</tr>
<tr>
<td>H + C$_2$H$_3$ + M $\rightarrow$ C$_2$H$_6$ + M</td>
<td>No recommendation</td>
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<td>531</td>
</tr>
<tr>
<td>H + C$_2$H$_3$ + M $\rightarrow$ C$_2$H$_4$ + M</td>
<td>$k_0 = 1.3 \times 10^{-30}$</td>
<td>1400-1700</td>
<td>± 0.5</td>
<td>541</td>
</tr>
<tr>
<td>H + C$_2$H$_3$ + M $\rightarrow$ C$_2$H$_4$ + M</td>
<td>$k_0 = 6.7 \times 10^{-11} \exp(-2170/T)$</td>
<td>300-1000</td>
<td>± 0.2</td>
<td>541</td>
</tr>
<tr>
<td>H + C$_2$H$_3$ + M $\rightarrow$ C$_2$H$_4$ + M</td>
<td>$k_0 = 4.2 \times 10^{-10}$</td>
<td>1000</td>
<td>± 0.3</td>
<td>544</td>
</tr>
<tr>
<td>OH + OH + M $\rightarrow$ H$_2$O$_2$ + M</td>
<td>$k_0(N_2) = 8 \times 10^{-31} (T/300)^{-0.76}$</td>
<td>250-1400</td>
<td>± 0.4</td>
<td>556</td>
</tr>
<tr>
<td>OH + OH + M $\rightarrow$ H$_2$O$_2$ + M</td>
<td>$k_0(H_2O) = 4 \times 10^{-30}$</td>
<td>300-400</td>
<td>± 0.5</td>
<td>556</td>
</tr>
<tr>
<td>OH + OH + M $\rightarrow$ H$_2$O$_2$ + M</td>
<td>$k_0(N_2) = 1.5 \times 10^{-11} (T/300)^{-0.57}$</td>
<td>200-1500</td>
<td>± 0.5</td>
<td>556</td>
</tr>
<tr>
<td>OH + OH + M $\rightarrow$ H$_2$O$_2$ + M</td>
<td>$F_e(N_2) = 0.5$</td>
<td>200-1500</td>
<td>Δ$F_e = ± 0.2$</td>
<td>556</td>
</tr>
<tr>
<td>OH + OH + M $\rightarrow$ H$_2$O$_2$ + M</td>
<td>No data available for this channel (See Table 1)</td>
<td></td>
<td></td>
<td>570</td>
</tr>
<tr>
<td>OH + C$_2$H$_2$ + M $\rightarrow$ C$_2$H$_3$OH + M</td>
<td></td>
<td></td>
<td></td>
<td>583</td>
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</table>
### EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

#### TABLE 3. Combination reactions — Continued

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( k \text{/cm}^3 \text{molecule}^{-1} \text{s}^{-1} )</th>
<th>Temp/K</th>
<th>Error limits (Δ log ( k ))</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{OH} + \text{C}_6\text{H}_6 + \text{M} \rightarrow \text{C}_6\text{H}_5\text{OH} + \text{M} )</td>
<td>( k_0 = 3.8 \times 10^{-12} \exp(-340/T) )</td>
<td>240-340</td>
<td>± 0.2</td>
<td>595</td>
</tr>
<tr>
<td>( \text{OH} + \text{C}_6\text{H}_5\text{OH} + \text{M} \rightarrow \text{C}_6\text{H}_5(\text{OH})_2 + \text{M} )</td>
<td>( k_0 = 2.8 \times 10^{-11} )</td>
<td>298</td>
<td>± 0.1</td>
<td>598</td>
</tr>
<tr>
<td>( \text{OH} + \text{C}_6\text{H}_5\text{CH}_3 + \text{M} \rightarrow \text{HOC}_6\text{H}_5\text{CH}_3 + \text{M} )</td>
<td>( k_0 = 3.8 \times 10^{-12} \exp(180/T) )</td>
<td>200-300</td>
<td>± 0.4</td>
<td>598</td>
</tr>
<tr>
<td>( \text{OH} + \text{C}_6\text{H}_6(\text{CH}_3)_2 + \text{M} \rightarrow \text{C}_6\text{H}_6(\text{CH}_3)_2\text{OH} + \text{M} )</td>
<td>( k_0 = 1.4 \times 10^{-11} )</td>
<td>300-320</td>
<td>± 0.1</td>
<td>601</td>
</tr>
<tr>
<td>( \text{OH} + \text{C}_6\text{H}_5\text{CH}_3 + \text{M} \rightarrow \text{HOC}_6\text{H}_5\text{CH}_3 + \text{M} )</td>
<td>( k_0 = 7.5 \times 10^{-12} ) at ( p \leq 1 \text{ atm.} )</td>
<td>298</td>
<td>± 0.1</td>
<td>603</td>
</tr>
<tr>
<td>( ^3\text{CH}_2 + \text{C}_2\text{H}_2 + \text{M} \rightarrow \text{C}_6\text{H}_6 + \text{M} )</td>
<td>( k_0 = 2.1 \times 10^{-11} \exp(-330/T) ) at ( p = \leq 10 \text{ Torr.} )</td>
<td>300-1000</td>
<td>± 0.3</td>
<td>642</td>
</tr>
<tr>
<td>( ^3\text{CH}_2 + \text{C}_2\text{H}_4 + \text{M} \rightarrow \text{C}_6\text{H}_6 + \text{M} )</td>
<td>( k_0 = 5.3 \times 10^{-12} \exp(-2660/T) )</td>
<td>300-1000</td>
<td>± 0.2 at 300 K rising to ± 0.3 at 1000 K</td>
<td>643</td>
</tr>
<tr>
<td>( ^3\text{CH}_2 + \text{C}_2\text{H}_4 + \text{M} \rightarrow \text{C}_6\text{H}_6 + \text{M} )</td>
<td>( k_0 = 3.7 \times 10^{-16} ) independent of ( p )</td>
<td>300-1000</td>
<td>± 0.3 at 300 K rising to ± 0.7 at 1000 K</td>
<td>646</td>
</tr>
<tr>
<td>( ^3\text{CH}_2 + \text{C}_2\text{H}_4 + \text{M} \rightarrow \text{C}_6\text{H}_6 + \text{M} )</td>
<td>( k_0 = 1.1 \times 10^{-15} ) independent of ( p )</td>
<td>300-1000</td>
<td>± 0.2 at 300 K rising to ± 0.5 at 1000 K</td>
<td>647</td>
</tr>
<tr>
<td>( \text{CH}_3 + \text{O}_2 + \text{M} \rightarrow \text{CH}_3\text{O}_2 + \text{M} )</td>
<td>( k_0(\text{Ar}) = 1.5 \times 10^{-22} T^{-3.3} )</td>
<td>300-800</td>
<td>± 0.3</td>
<td>650</td>
</tr>
<tr>
<td>( k_0(\text{N}_2) = 1.6 \times 10^{-22} T^{-3.3} )</td>
<td>300-800</td>
<td>± 0.3</td>
<td>650</td>
<td></td>
</tr>
<tr>
<td>( k_0 = 1.3 \times 10^{-13} T^{-12} )</td>
<td>300-800</td>
<td>± 0.3</td>
<td>650</td>
<td></td>
</tr>
<tr>
<td>( F_0 = 0.466 - 1.30 \times 10^{-4} T )</td>
<td>300-800</td>
<td>± 0.3</td>
<td>650</td>
<td></td>
</tr>
<tr>
<td>( \text{CH}_3 + \text{C}_2\text{H}_2 + \text{Ar} \rightarrow \text{C}_6\text{H}_6 + \text{Ar} )</td>
<td>( k_0 = 6 \times 10^{-11} )</td>
<td>300-2000</td>
<td>± 0.05 at 300 K rising to ± 0.3 at 2000 K</td>
<td>656</td>
</tr>
<tr>
<td>( k_0 = 3.5 \times 10^{-7} T^{-7.0} \exp(-1390/T) )</td>
<td>300-2000</td>
<td>± 0.3</td>
<td>656</td>
<td></td>
</tr>
<tr>
<td>( F_0 = 0.38 \exp(-T/773) + 0.62 \exp(-T/1180) )</td>
<td>300-2000</td>
<td>± 0.3</td>
<td>656</td>
<td></td>
</tr>
<tr>
<td>( \Delta F_0 = \pm 0.1 )</td>
<td>300-2000</td>
<td>± 0.3</td>
<td>656</td>
<td></td>
</tr>
<tr>
<td>( \text{CH}_3 + \text{C}_2\text{H}_2 \rightarrow \text{C}_6\text{H}_6 + \text{M} )</td>
<td>( k_0 = 1 \times 10^{-12} \exp(-3900/T) )</td>
<td>300-600</td>
<td>± 0.5</td>
<td>661</td>
</tr>
<tr>
<td>( 3.5 \times 10^{-13} \exp(-3700/T) )</td>
<td>300-600</td>
<td>± 0.3</td>
<td>663</td>
<td></td>
</tr>
<tr>
<td>( 3.7 \times 10^{-12} \exp(-3900/T) )</td>
<td>300-600</td>
<td>± 0.3</td>
<td>663</td>
<td></td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_5 + \text{C}_2\text{H}_4 \rightarrow \text{n-C}<em>6\text{H}</em>{14} + \text{M} )</td>
<td>( k_0 = 4.7 \times 10^{-11} )</td>
<td>300-800</td>
<td>± 0.3</td>
<td>665</td>
</tr>
<tr>
<td>( 4.7 \times 10^{-11} )</td>
<td>300-800</td>
<td>± 0.3</td>
<td>665</td>
<td></td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_5 + \text{C}_2\text{H}_4 \rightarrow \text{n-C}<em>6\text{H}</em>{14} + \text{M} )</td>
<td>( k_0 = 1.9 \times 10^{-11} )</td>
<td>300-1200</td>
<td>± 0.3</td>
<td>707</td>
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<tr>
<td>( 2 \times 10^{-12} ) for ( p = 1-4 \text{ Torr.} )</td>
<td>300-1200</td>
<td>± 0.3</td>
<td>716</td>
<td></td>
</tr>
</tbody>
</table>

4. Data Sheets

O + H₂ → OH + H

Thermodynamic Data
ΔH₂₀₉ = 7.76 kJ mol⁻¹
ΔS₂₀₉ = 6.67 J K⁻¹ mol⁻¹
Kₚ = 1.8 × 10⁶⁰⁷ exp(−917/T)

Rate Coefficient Data

<table>
<thead>
<tr>
<th>k [cm³ molecule⁻¹ s⁻¹]</th>
<th>T [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.7 × 10⁻¹⁰ exp(−6916/T)</td>
<td>1400–1900</td>
<td>Schott, Getzinger, and Seitz (1974)¹</td>
<td>(a)</td>
</tr>
<tr>
<td>5.2 × 10⁻¹¹ exp(−4950/T)</td>
<td>363–490</td>
<td>Campbell and Handy (1975)²</td>
<td>(b)</td>
</tr>
<tr>
<td>8.3 × 10⁻¹² exp(−4330/T)</td>
<td>347–832</td>
<td>Dubinsky and McKenney (1975)³</td>
<td>(c)</td>
</tr>
<tr>
<td>9.1 × 10⁻¹³</td>
<td>298</td>
<td>Light and Matsumoto (1980)⁴</td>
<td>(d)</td>
</tr>
<tr>
<td>3.8 × 10⁻¹⁹ exp(−6916/T)</td>
<td>2097–2481</td>
<td>Pamidimukkala and Skinner (1982)⁵</td>
<td>(e)</td>
</tr>
<tr>
<td>3.1 × 10⁻¹⁹ exp(−6976/T)</td>
<td>1700–2500</td>
<td>Frank and Just (1985)⁶</td>
<td>(f)</td>
</tr>
<tr>
<td>8.5 × 10⁻²⁰ T².⁶⁷ exp(−3163/T)</td>
<td>504–2495</td>
<td>Sutherland et al. (1986)⁷</td>
<td>(g)</td>
</tr>
</tbody>
</table>

Review and Evaluations
3.0 × 10⁻¹⁴ T¹.⁰ exp(−4474/T) | 400–2000 | Baulch et al. (1972)⁸ |
1.8 × 10⁻²⁰ T².⁸ exp(−2983/T) | 400–1600 | Cohen and Westberg (1983)⁹ |
2.5 × 10⁻¹⁷ T².⁹ exp(−3800/T) | 300–2500 | Warnatz (1984)¹⁰ |

Comments
(a) Shock wave initiated combustion of H₂/O₂/CO/CO₂/Ar mixtures; [OH] monitored by chemiluminescence of CO + O reaction. Numerical integration of 12 reaction mechanism with fitting of k(O + H₂)/k(H + O₂) to experimental results. Based on k(H + O₂) = 2.0 × 10⁻⁷ T⁻⁰⁵¹ exp(−8369/T) cm³ molecule⁻¹ s⁻¹.¹¹
(b) Diffusion-stirred discharge-flow reactor; [O] by air afterglow chemiluminescence. Total pressure = 0.4 kN m⁻².
(c) Discharge-flow system; [O] by resonance fluorescence at 130.6 nm and air afterglow chemiluminescence. Given parameters based on resonance fluorescence measurements.
(d) State-selective reaction rate for H₂ (ν = 0). Discharge-flow reactor; [OH (ν = 0)] and [OH (ν = 1)] from laser induced fluorescence. H₂ (ν = 1) suppressed by addition of CO₂ and controlled by VUV absorption. Total pressure 3 Torr.
(e) Shock heating of H₂/N₂/O/Ar mixtures; [O] by atomic resonance absorption spectroscopy. Numerical modelling of 11 reaction mechanism.
(f) Shock heating of H₂/N₂/O/Ar mixtures; [H] and [O] by atomic resonance absorption spectroscopy. Total densities 6 × 10⁻⁶–1.3 × 10⁻⁵ mol cm⁻³.
(g) Flash-photolysis – shock tube technique combined with atomic resonance absorption and resonance fluorescence spectroscopy.

Preferred Values
k = 8.5 × 10⁻²⁰ T².⁶⁷ exp(−3163/T) cm³ molecule⁻¹ s⁻¹ over range 300–2500 K

Reliability
Δlog k = ± 0.5 at 300 K reducing to ± 0.2 for T > 500 K

Comments on Preferred Values
The rate coefficient given by Sutherland et al.⁷ is taken as the recommendation due to the extremely large temperature range and the sophisticated methods used.

References
EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

O + H₂ → OH + H

T/K

EXPERIMENTAL DATA
- Dubinsky and McKenny 1975
- Dubinsky and McKenny 1975
- Campbell and Handy 1975
- Light and Matsuzaka 1980
- Pimentelkofsky and Skinner 1982
- Frank and Just 1985
- Sutherland et al. 1986
- Sutherland et al. 1986
- Clyne and Thrush 1983
- Wang and Potter 1985
- Balakinin et al. 1986
- Ridley and Carle 1987
- Gutman and Schott 1987
- Gutman et al. 1987
- Heymann et al. 1987
- Westenberg and Delhays 1987
- Westenberg and Delhays 1987
- Balakinin et al. 1988
- Campbell and Thrush 1988
- Kurizus 1988
- Browne et al. 1989
- Schott 1989
- Wakefield 1989
- Westenberg and Delhays 1989
- Balakinin et al. 1990
- Dew and Kistiakowsky 1970
- Jochimsowski and Houghton 1970
- Brobb et al. 1971

This Recommendation 1980

Thermodynamic Data

\[ \Delta H_{298}^\circ = -70.2 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298}^\circ = -24.9 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ K_p = 3.3 \times 10^{-3} \exp\left(\frac{8620}{T}\right) \]

Rate Coefficient Data

<table>
<thead>
<tr>
<th>( k [\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}] )</th>
<th>( T [\text{K}] )</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.4\times10^{-11}</td>
<td>425</td>
<td>Campbell and Handy (1977)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>2.0\times10^{-11} \exp(+112/T)</td>
<td>221-499</td>
<td>Lewis and Watson (1980)(^2)</td>
<td>(b)</td>
</tr>
<tr>
<td>3.8\times10^{-11}</td>
<td>298</td>
<td>Howard and Smith (1980)(^3)</td>
<td>(c)</td>
</tr>
<tr>
<td>6.7\times10^{-10} \ T^{-0.5}</td>
<td>250-515</td>
<td>Howard and Smith (1981)(^4)</td>
<td>(e)</td>
</tr>
<tr>
<td>3.1\times10^{-11}</td>
<td>300</td>
<td>Brune, Schwab, and Anderson (1983)(^5)</td>
<td>(d)</td>
</tr>
<tr>
<td>3.3\times10^{-11}</td>
<td>296</td>
<td>Temps (1983)(^6)</td>
<td>(e)</td>
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</tbody>
</table>

Reviews and Evaluations

<table>
<thead>
<tr>
<th>( k [\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}] )</th>
<th>( T [\text{K}] )</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.8\times10^{-11}</td>
<td>300</td>
<td>Baulch et al. (1972,1980)(^7,,,8)</td>
<td></td>
</tr>
<tr>
<td>3.0\times10^{-11}</td>
<td>300-2500</td>
<td>Waintz (1984)(^9)</td>
<td></td>
</tr>
<tr>
<td>7.5\times10^{-10} \ T^{-0.5} \exp(-30/T)</td>
<td>200-2500</td>
<td>Tsang and Hampson (1986)(^10)</td>
<td></td>
</tr>
</tbody>
</table>

Comments

(a) Discharge-flow system; reaction of \( \text{O}^3\text{P} \) atoms in \( \text{H}_2/\text{CO}/\text{N}_2 \) mixtures monitored by observing the chemiluminescence of \( \text{CO} + \text{O} \) recombination. Relative measurement \( k(\text{O} + \text{OH})/k(\text{CO} + \text{OH}) = 260 \). Given \( k \) based on \( k(\text{CO} + \text{OH}) = 1.7\times10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \).

(b) Low-pressure discharge-flow system. \([\text{OH}]\) and \([\text{O}]\) by resonance fluorescence. Results also described by \( k = 2.4\times10^{-10} \ T^{-0.362} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \).

(c) Flow system; \( \text{O} \) formed by microwave discharge, \( \text{OH} \) by flash photolysis of \( \text{H}_2\text{O} \). [OH] monitored by resonance fluorescence. Total pressure 3.75 Torr.

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

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

Preferred Values

\[ k = 2.0\times10^{-11} \exp\left(+112/T\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range 220-500 K} \]
\[ k = 2.4\times10^{-11} \exp\left(-353/T\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range 1000-2000 K} \]

Reliability

\( \Delta \log k = \pm 0.2 \text{ over range 220-500 K} \)
\( \Delta \log k = \pm 0.1 \text{ over range 1000-2000 K} \)

Comments on Preferred Values

According to the potential energy surface two sets of rate parameters are recommended. In the low temperature region the results of Lewis and Watson\(^2\) have been chosen whereas for higher temperatures the parameters have been calculated from the rate of the reverse reaction \( \text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH} \) and the equilibrium constant.

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

References

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ \text{O} + \text{OH} \rightarrow \text{H} + \text{O}_2 \]

**Experimental Data**
- Campbell and Handy 1977
- Lewis and Watson 1980
- Howard and Smith 1980
- Howard and Smith 1981
- Brune et al. 1983
- Tempe et al. 1983
- Del Greco and Kaufman 1962
- Clyne 1963
- Kaufman and Del Greco 1963
- Kaufman 1964
- Westenberg and DeRoo 1965
- Breen and Glass 1970
- Westenberg et al. 1970
- This Recommendation 1989

**Rate Coefficient Data**

<table>
<thead>
<tr>
<th>Rate Coefficient Measurements</th>
<th>T[K]</th>
<th>Reference</th>
<th>Comments</th>
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<tbody>
<tr>
<td>5.5×10^-11</td>
<td>1050</td>
<td>Day, Thompson, and Dixon-Lewis (1973)³</td>
<td>(a)</td>
</tr>
<tr>
<td>7.1×10^-11</td>
<td>1000</td>
<td>Dixon-Lewis and Rhodes (1975)²</td>
<td>(b)</td>
</tr>
<tr>
<td>3.5×10^-11</td>
<td>293</td>
<td>Burrows, Harris and Thrush (1977)³</td>
<td>(c)</td>
</tr>
<tr>
<td>3.3×10^-11</td>
<td>298</td>
<td>Hack et al. (1979)⁴</td>
<td>(d)</td>
</tr>
<tr>
<td>3.1×10^-11</td>
<td>296</td>
<td>Burrows et al. (1979)⁵</td>
<td>(e)</td>
</tr>
<tr>
<td>7×10^-11</td>
<td>298</td>
<td>Li, Sauer, and Gordon (1980)⁶</td>
<td>(f)</td>
</tr>
<tr>
<td>5.4×10^-11</td>
<td>296</td>
<td>Sridharan, Qiu, and Kaufman (1982)⁷</td>
<td>(g)</td>
</tr>
<tr>
<td>6.2×10^-11</td>
<td>298</td>
<td>Ravishankara, Wine, and Nicovich (1983)⁹</td>
<td>(i)</td>
</tr>
<tr>
<td>5.2×10^-11</td>
<td>300</td>
<td>Brune, Schwab, and Anderson (1983)¹⁰</td>
<td>(j)</td>
</tr>
<tr>
<td>2.9×10^-11 exp(+228/T)</td>
<td>266-391</td>
<td>Nicovich and Wine (1987)¹¹</td>
<td>(k)</td>
</tr>
<tr>
<td>Reviews and Evaluations</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0×10^-10 exp(-349/T)</td>
<td>300-800</td>
<td>Haultt et al. (1976)¹²</td>
<td>(l)</td>
</tr>
<tr>
<td>3.2×10^-11</td>
<td>298</td>
<td>Baulch et al. (1979)⁴</td>
<td>(m)</td>
</tr>
<tr>
<td>3.3×10^-11</td>
<td>298</td>
<td>Kaufman and Sherwell (1983)¹⁴</td>
<td>(n)</td>
</tr>
<tr>
<td>3.3×10^-11</td>
<td>300-1000</td>
<td>Warrnatz (1984)¹⁵</td>
<td>(o)</td>
</tr>
<tr>
<td>2.8×10^-11 exp(+200/T)</td>
<td>300-1000</td>
<td>Tsang and Hampp (1986)¹⁶</td>
<td>(p)</td>
</tr>
</tbody>
</table>

**Comments**

(a) Computer simulation of burning velocities of rich H₂/ O₂/N₂ flames. No great accuracy.

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

(c) Fast flow system; [OH] and [H₂O₂] by laser magnetic resonance.

(d) Isothermal discharge-flow tube; total pressures 1–10 mbar He, [O] by ESR, [H₂O₂] by LMR.

(e) Fast flow system; total pressure = 1 Torr, [OH] and [H₂O₂] by laser magnetic resonance. Value of k based on either k(O + OH) or k(OH + H₂O₂) from Ref. 17.

(f) Pulse radiolysis of H₂/O₂/Ar mixtures at total pressure of 1200 Torr. [H₂O₂] and [O] by absorption measurements. Numerical integration of a system of 10 reactions and adjusting of k to fit the experimental results.

(g) Discharge-flow tube. [H₂O₂] monitored by rapid conversion to OH with large excess of NO, [OH] by laser induced fluorescence, [H] and [O] by VUV resonance fluorescence.

(h) Discharge-flow system. [H₂O₂] monitored by rapid conversion to OH with large excess of NO, [OH], [H], and [O] by resonance fluorescence.

(i) Laser photolysis of a mixture of H₂O₂ and O₃ in N₂ or Ar under slow flow conditions. [O] by time-resolved resonance fluorescence, [H₂O₂] by absorption measurements. k found to be independent of pressure in the range 10–500 Torr.

(j) Discharge-flow system. [H₂O₂] by LMR and conversion to OH by NO. [OH] by LMR and resonance fluorescence, [O] by resonance fluorescence and resonance absorption. No pressure dependence of k observed.

(k) Pulsed laser photolysis of H₂O₂/O₃/N₂ mixtures (80 Torr) under slow flow conditions. Time-resolved resonance fluorescence of O(¹P).

**Preferred Values**

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

**Reliability**

\[ \Delta \log k = \pm 0.3 \text{ at 300 K rising to } \pm 0.5 \text{ at 1000 K} \]

**Comments on Preferred Values**

The recommendation is based on the value of Sridharan et al.³ which is in agreement with the majority of the other measurements within the error limits.

**References**


EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

435

$O + HO_2 \rightarrow OH + O_2$

**T/K**

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

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

**EXPERIMENTAL DATA**
- Day et al. 1972
- Day et al. 1973
- Peeters and Mohnen 1973
- Dixon-Lewis and Rhodes 1975
- Burrows et al. 1977
- Hock et al. 1979
- Burrows et al. 1979
- Li et al. 1980
- Sridharan et al. 1982
- Keyser 1982
- Redishankara et al. 1983
- Burke et al. 1983
- Keyser 1983
- Nicovich and Wine 1987

**This Recommendation 1989**

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ \begin{align*}
\text{O} + \text{H}_2\text{O}_2 & \rightarrow \text{HO}_2 + \text{OH} \\
& \rightarrow \text{H}_2\text{O} + \text{O}_2
\end{align*} \] (1) (2)

**Thermodynamic Data**

\[ \begin{align*}
\Delta H_{\text{tot}} (1) &= -63.6 \text{ kJ mol}^{-1} \\
\Delta S_{\text{tot}} (1) &= 18.8 \text{ J K}^{-1}\text{mol}^{-1} \\
K_p(1) &= 1.02 \times 10^5 T^{-0.066} \exp(7390/T) \\
\Delta H_{\text{tot}} (2) &= -354.9 \text{ kJ mol}^{-1} \\
\Delta S_{\text{tot}} (2) &= 0.07 \text{ J K}^{-1}\text{mol}^{-1} \\
K_p(2) &= 5.27 \times 10^7 T^{-0.95} \exp(42370/T)
\end{align*} \]

**Rate Coefficient Data**

\[ k = k_1 + k_2 \]

<table>
<thead>
<tr>
<th>( k [\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}] )</th>
<th>( T[\text{K}] )</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.7 \times 10^{-11} \exp(-3220/T)</td>
<td>370–800</td>
<td>Albers et al. (1971)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>2.8 \times 10^{-12} \exp(-2125/T)</td>
<td>283–368</td>
<td>Davis, Wong, and Schiff (1974)(^2)</td>
<td>(b)</td>
</tr>
<tr>
<td>1.1 \times 10^{-12} \exp(-2000/T)</td>
<td>298–386</td>
<td>Wine et al. (1983)(^3)</td>
<td>(c)</td>
</tr>
<tr>
<td>( k_1 / k &gt; 0.2 )</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Reviews and Evaluations**

\[ \begin{align*}
4.0 \times 10^{-11} \exp(-3223/T) & \quad 300–1000 \\
1.6 \times 10^{-11} T^2 \exp(-2000/T) & \quad 300–2500 \\
\end{align*} \]

Warnatz (1984)\(^4\)  
Tsang and Hampson (1986)\(^5\)

**Comments**

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

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

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

**Preferred Values**

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

**Reliability**

\[ \Delta \log k = \pm 0.3 \text{ over range} \ 300–500 \text{ K} \]

**Comments on Preferred Values**

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

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

**References**

O + H_2O_2 → HO_2 + OH

**EVALUATED KINETIC DATA FOR COMBUSTION MODELLING**

O + NH₂ → OH + NH₂

**Thermodynamic Data**

\[ \Delta H_{\text{fus}} = 26.1 \, \text{kJ mol}^{-1} \]
\[ \Delta S_{\text{fus}} = 24.6 \, \text{J K}^{-1} \text{mol}^{-1} \]
\[ K_p = 478 \, T^{-0.405} \exp(-3420/T) \]

**Rate Coefficient Data**

<table>
<thead>
<tr>
<th>( k [\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}] )</th>
<th>( T [\text{K}] )</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5 \times 10^{-12} \exp(-3020/T)</td>
<td>300-1000</td>
<td>Baulch et al. (1973)⁴</td>
<td>(a)</td>
</tr>
<tr>
<td>1.8 \times 10^{-10} T^{21} \exp(-2620/T)</td>
<td>–</td>
<td>Cohen (1987)²</td>
<td>(b)</td>
</tr>
</tbody>
</table>

**Comments**

(a) Review of data up to 1973.

(b) Thorough review of Refs. up to 1987, results checked and recalculated. Recommended \( k \) value based upon evaluation of previous data and also upon transition state theory calculations resulting in a higher than usual value of the \( T^4 \) term.

**Preferred Values**

\[ k = 1.6 \times 10^{-11} \exp(-3670/T) \, \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range 500-2500 K} \]

**Reliability**

\[ \Delta \log k = \pm 0.5 \text{ over range 500-2500 K} \]

**Comments on Preferred Values**

Studies up to 1987 have been comprehensively reviewed by Cohen² and only review articles are tabulated here.

The \( k \) values at high temperatures have all been obtained by fitting experimental results of flame studies⁴ or shock tube studies⁵,⁶,⁷,⁸,⁹ to assumed reaction mechanisms. Hence the accuracy of the resulting \( k \) value is dependent upon the sensitivity of the experimentally measured quantities to the rate of this particular reaction; in this respect the work of Salimian et al.¹⁶ is the most sensitive, although all of the quoted \( k \) values agree to within a factor of 3. There is similar agreement between the studies at low temperatures, which have used discharge flow techniques⁴,⁵,⁹,¹¹, stirred flow reactors⁶ and static photolysis techniques¹² with the exception of the more recent study of Perry¹³ using laser photolysis of \( O_2 \) and [O] detection by NO₂ chemiluminescence. This study is favoured by Cohen² as the technique should be free from complicating secondary reactions. The expression given by Cohen² has a large \( T^4 \) value based on transition state theory and leading to a high degree of curvature in the Arrhenius plot at high temperatures which is not evident in the experimental data.

The recommended values are based on the work of Salimian et al.¹⁶ at high temperatures. At low temperatures it seems likely that most of the earlier studies are affected by secondary reactions and only that of Perry¹³ is likely to be exempt from that criticism.

However, until Perry’s results are confirmed, we adopt an expression with substantial error limits and lying between the results of Perry¹³ and the older measurements. No \( T^4 \) term has been included due to lack of direct experimental evidence for it but some curvature of the Arrhenius plot is likely.

**References**

$O + NH_3 \rightarrow OH + NH_2$

$T/K$

**Diagram**

**EXPERIMENTAL DATA**

- Fenimore and Jones 1961
- Avramenko et al. 1962
- Wong and Potter 1963
- Arasanyan and Nalbandyan 1965
- Kurylo et al. 1969
- Albers et al. 1969
- Kirchner et al. 1974
- Lolo and Vermeil 1980
- Perry 1984
- Baulch et al. 1984
- Fujii et al. 1984
- Salminen et al. 1984
- Fujii et al. 1986
- Wong and Potter 1985
- This Recommendation 1989

**Equation**

$\log(k/cm^3 \text{ molecule}^{-1} \cdot s^{-1})$

$10^3 T^{-1} / K^{-1}$
EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ O + CH \rightarrow H + CO \]
\[ \rightarrow CHO^+ + e^- \]

\[ \Delta H_{\text{so}} (1) = -736 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{so}} (1) = -31.7 \text{ K}^{-1} \text{mol}^{-1} \]
\[ k_T(1) = 3.3 \times 10^{-2} \exp(\frac{88500}{T}) \]

**Thermodynamic Data**

**Rate Coefficient Data**

<table>
<thead>
<tr>
<th>( k [\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}] )</th>
<th>( T [\text{K}] )</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 = 2.8 \times 10^{-13} \exp(-3020/T) )</td>
<td>2000-2400</td>
<td>Peeters and Vinckier (1975)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>( k_2 = 9.5 \times 10^{-13} \exp(-3020/T) )</td>
<td>1700-2100</td>
<td>Matsui and Nomaguchi (1978)(^2)</td>
<td>(b)</td>
</tr>
<tr>
<td>( k_3 = 2.4 \times 10^{-14} )</td>
<td>295</td>
<td>Vinckier (1979)(^3)</td>
<td>(c)</td>
</tr>
<tr>
<td>( E_1 / R = 805 \text{ K} )</td>
<td>298</td>
<td>Messing et al. (1980)(^4)</td>
<td>(d)</td>
</tr>
<tr>
<td>( k_1 = 9.4 \times 10^{-11} )</td>
<td>298</td>
<td>Homann and Schweinfurth (1981)(^5)</td>
<td>(e)</td>
</tr>
<tr>
<td>( k_2 = 3.3 \times 10^{-11} )</td>
<td>298</td>
<td>Becker et al. (1982)(^6)</td>
<td>(f)</td>
</tr>
<tr>
<td>( k_3 = 1.2 \times 10^{-13} )</td>
<td>298</td>
<td>Frank, Bhaskaran, and Just (1986)(^8)</td>
<td>(g)</td>
</tr>
<tr>
<td>( k_4 = (1.7-2.5) \times 10^{-10} )</td>
<td>1500-2500</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Comments**

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

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

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

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

(e) Discharge-flow system; reaction of C\(_2\)H\(_2\) with O and H atoms. Total pressure 1.4-8 mbar. Mass spectrometric observation of formation of C\(_2\)H\(_3\), C\(_2\)H\(_5\), and CH\(_3\)O. Computer modelling of 25 reaction mechanism.

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

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

**Preferred Values**

\[ k_1 = 6.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range 300-2000 K} \]
\[ k_2 = 4.2 \times 10^{-13} \exp(-850/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range 300-2500 K} \]

**Reliability**

\[ \Delta \log k_1 = \pm 0.5 \text{ over range 300-2000 K} \]
\[ \Delta \log k_2 = \pm 0.5 \text{ over range 300-2500 K} \]

**Comments on Preferred Values**

The recommendation of \( k_1 \) is based on the given experimental data\(^6\). The value of \( k_2 \) is derived from the measurements at high and low temperatures available\(^1,2,5\).

**References**

O + CH → CO + H
→ CHO⁺ + e
EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ O + ^3CH_2 \rightarrow CO + 2H \quad (1) \]
\[ \rightarrow CO + H_2 \quad (2) \]

**Thermodynamic Data**

\[ \Delta H_{298}^\circ (1) = -310.8 \, \text{kJ mol}^{-1} \]
\[ \Delta H_{298}^\circ (2) = 746.7 \, \text{kJ mol}^{-1} \]
\[ \Delta S_{298}^\circ (1) = 70.3 \, \text{J K}^{-1}\text{mol}^{-1} \]
\[ \Delta S_{298}^\circ (2) = -28.3 \, \text{J K}^{-1}\text{mol}^{-1} \]
\[ K_p(1) = 3.81 \times 10^{11} \exp(\frac{37600}{T}) \text{ atm} \]
\[ K_p(2) = 0.122 T^{-0.166} \exp(\frac{89700}{T}) \]

**Rate Coefficient Data**

\[ k = k_1 + k_2 \]

<table>
<thead>
<tr>
<th>Rate Coefficient Measurements</th>
<th>( T ) [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3 \times 10^{-11}</td>
<td>290-600</td>
<td>Vinckier and De Bruyn (1978, 1979)²</td>
<td>(a)</td>
</tr>
<tr>
<td>8 \times 10^{-11}</td>
<td>298</td>
<td>Homann and Schweinfurth (1981)³</td>
<td>(b)</td>
</tr>
<tr>
<td>1.4 \times 10^{-11}</td>
<td>296</td>
<td>Böhland, Temps, and Wagner (1984)⁴</td>
<td>(c)</td>
</tr>
<tr>
<td>( k_1 = 2 \times 10^{-10} )</td>
<td>1500-2500</td>
<td>Frank, Bhaskaran, and Just (1987)⁵</td>
<td>(d)</td>
</tr>
<tr>
<td>( k_2 = 1 \times 10^{-10} )</td>
<td>800-2000</td>
<td>Warnatz (1984)⁶</td>
<td>(e)</td>
</tr>
<tr>
<td>8 \times 10^{-11}</td>
<td>298</td>
<td>Tsang and Hampson (1986)⁷</td>
<td>(f)</td>
</tr>
</tbody>
</table>

**Comments**

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

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

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

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

(e) Evaluation based on Refs. 1–3.

(f) Based on an evaluation by Laufer⁸ of the data from Ref. 1 reputed to determine \( k(\text{CH}_2+O)/k(\text{CH}_2+\text{C}_2\text{H}_2) \). The low value of \( k(\text{CH}_2+\text{C}_2\text{H}_2) \) renders this analysis erroneous.

**Preferred Values**

\[ k = 2 \times 10^{-10} \, \text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1} \] over range 300–2500 K

\[ k_1/k = 0.6 \]

**References**

O + CH₃ → HCHO + H

**Thermodynamic Data**
\[ \Delta H_{\text{r}} = -293 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{r}} = -23.0 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_p = 1.43 \times 10^{-1} \exp \left( \frac{+3.54 \times 10^4}{T} \right) \]

**Rate Coefficient Data**

<table>
<thead>
<tr>
<th>Rate Coefficient Measurements</th>
<th>T [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3-10⁻¹⁰</td>
<td>1700-2300</td>
<td>Bhaskaran, Frank, and Just (1979)¹</td>
<td>(a)</td>
</tr>
<tr>
<td>1.14-10⁻¹⁰</td>
<td>295</td>
<td>Plumb and Ryan (1982)²</td>
<td>(b)</td>
</tr>
<tr>
<td>1.4-10⁻¹⁰</td>
<td>294-900</td>
<td>Slagle, Sarzynski, and Gutman (1987)³</td>
<td>(c)</td>
</tr>
<tr>
<td>Reviews and Evaluations</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.2-10⁻¹⁰</td>
<td>300-2500</td>
<td>Warnatz (1984)⁴</td>
<td></td>
</tr>
<tr>
<td>1.3-10⁻¹⁰</td>
<td>295</td>
<td>Tsang and Hampson (1986)⁵</td>
<td></td>
</tr>
</tbody>
</table>

**Comments**

(a) Shock-tube decomposition of C₂H₆/O₂ mixtures with direct detection of H and O by atomic resonance absorption spectrometry. Rate coefficient derived from a computer simulation of [H] and [O] profiles.

(b) Flow-discharge with mass spectrometric detection of O and CH₃, decay of [CH₃] measured under pseudo first-order conditions with [O] >> [CH₃].

(c) Flow system with generation of CH₃ and O(¹P) from the simultaneous in situ photolysis of CH₃COCH₃ and SO₂ and determination of [CH₃] and [O] by photoionization mass spectrometry. Experiments were performed under conditions such that [O]/[CH₃] > 20 and the rate coefficients were determined from the decay of CH₃, k found to be independent of pressure over the range 1–22 Torr. k confirmed by measurements of the rate of formation of HCHO, the sole observable product.

**Preferred Values**

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

**Reliability**

\[ \Delta \log k = \pm 0.2 \text{ over range 300–2500 K} \]

**Comments on Preferred Values**

The experiments of Plumb and Ryan² and Slagle et al.³ are in accord with the evaluations of Warnatz⁴ and of Tsang and Hampson⁵. Here we have recommended the rate coefficient reported by Slagle and et al.³, a study which also confirms that the reaction involves only one channel forming HCHO and H.

**References**

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

O + CH₄ → OH + CH₃

Thermodynamic Data

\[ \Delta H_{\text{f,298}} = 10.4 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{f,298}} = 30.6 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_p = 3.28 \times 10^3 T^{-0.786} \exp(-1560/T) \]

Rate Coefficient Data

<table>
<thead>
<tr>
<th>Rate Coefficient Measurements</th>
<th>Temperature [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1.16 \times 10^{-11} \exp(-3875/T))</td>
<td>450-600</td>
<td>Brown and Thrush (1967)</td>
<td>(a)</td>
</tr>
<tr>
<td>(1.66 \times 10^{-10} \exp(-5033/T))</td>
<td>375-576</td>
<td>Wong and Potter (1967)</td>
<td>(b)</td>
</tr>
<tr>
<td>(3.3 \times 10^{-11} \exp(-4630/T))</td>
<td>297-904</td>
<td>Westenberg and DeHaas (1969)</td>
<td>(c)</td>
</tr>
<tr>
<td>(2.61 \times 10^{-10} \exp(-4000/T))</td>
<td>1750-2575</td>
<td>Dean and Kistiakowsky (1971)</td>
<td>(d)</td>
</tr>
<tr>
<td>(3.2 \times 10^{-10} \exp(-5900/T))</td>
<td>1200-2000</td>
<td>Brabbs and Brokaw (1975)</td>
<td>(e)</td>
</tr>
<tr>
<td>(6.8 \times 10^{-10} \exp(-7030/T))</td>
<td>1200-2230</td>
<td>Roth and Juji (1977)</td>
<td>(f)</td>
</tr>
<tr>
<td>(2.01 \times 10^{-10} \exp(-5435/T))</td>
<td>474-1156</td>
<td>Klemm et al. (1981)</td>
<td>(g)</td>
</tr>
<tr>
<td>(2.63 \times 10^{-10} T^{2.6} \exp(-3730/T))</td>
<td>420-1670</td>
<td>Felder and Fontijn (1981)</td>
<td>(h)</td>
</tr>
<tr>
<td>(9.2 \times 10^{-10} T^{2.4} \exp(-2838/T))</td>
<td>763-1755</td>
<td>Klemm et al. (1986)</td>
<td>(i)</td>
</tr>
</tbody>
</table>

Reviews and Evaluations

\(3.5 \times 10^{-11} \exp(-4550/T)\) | 350-2000 | Herron (1969) | (j) |
\(3.5 \times 10^{-11} \exp(-4550/T)\) | 300-1000 | Herron and Huie (1973) | (j) |
\(8.5 \times 10^{-14} T^{2} \exp(-3240/T)\) | 300-2000 | Shaw (1970) | (j) |
\(5.24 \times 10^{-12} T^{0.5} \exp(-517/T)\) | 475-2250 | Klemm et al. (1981) | (k) |
\(2.0 \times 10^{-17} T^{2.1} \exp(-3837/T)\) | 300-2200 | Warnatz (1984) | (l) |
\(2.69 \times 10^{-10} T^{2.3} \exp(-3570/T)\) | - | Cohen (1986) | (m) |
\(3.44 \times 10^{-10} T^{3.3} \exp(-3713/T)\) | 400-2000 | Wagner (1986) | (n) |
\(1.7 \times 10^{-15} T^{1.3} \exp(-4330/T)\) | 400-2200 | Tsang and Hampson (1986) | (p) |
\(1.15 \times 10^{-15} T^{1.6} \exp(-4270/T)\) | 400-2250 | Klemm et al. (1986) | (q) |

Comments

(a) Discharge flow; ESR detection of O atoms. Some doubt about stoichiometry of reaction.
(b) Discharge, stirred reactor; time-of-flight mass spectrometry. Assumed \(\Delta [O]/\Delta [CH_4] = 4\), but Cohen suggests a value of 6 to 7 at 400 K. k values probably high at least 50% (not plotted).
(c) Discharge flow; ESR detection of O atoms. Cohen suggests points below 400 K are too high due to use of incorrect stoichiometry.
(d) Shock tube; fitting of \(d[CO_2]/dt\) profiles; complex system.
(e) Shock tube; monitoring CO flame band emission; complex system.
(f) Shock tube; vacuum UV detection of O atoms.
(g) Flash photolysis–resonance fluorescence (474–520 K); discharge flow–resonance fluorescence (548–1156 K). Very pure CH₄ used.
(h) Flash photolysis–resonance fluorescence. Purity of CH₄ not stated.
(i) Flash photolysis–shock tube. Very pure CH₄ used.
(j) Review of early data.
(k) Parameters based on 'collision' model of reaction.
(l) Recommended value based on Refs. 6 and 8.
(m) Temperature range not specified, but 400–2000 K likely.
(o) Fit to rate constants calculated from activated complex theory.

Preferred Values

\[ k = 1.15 \times 10^{-15} T^{1.56} \exp(-4270/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]
over range 300–2500 K

Reliability

\[ \Delta \log k = \pm 0.15 \text{ at } 2500 \text{ K} \]
\[ = \pm 0.05 \text{ between } 1000 \text{ and } 500 \text{ K}, \text{ rising to } 0.1 \]
at 400 K and at least 0.3 at 300 K.

Comments on Preferred Values

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

References

BAULCH ET AL.

**EVALUATED KINETIC DATA FOR COMBUSTION MODELLING**

\[ O + CH_4 \rightarrow OH + CH_3 \]

**Experimental Data**
- Westenberg and de Haas 1969
- Wang and Potter 1967
- Cadle and Allen 1965
- Brown and Thrush 1967
- Froben 1968
- Dean and Kistelkowski 1971
- Basevich and Kogarko 1966
- Basevich and Kogarko (b) 1966
- Azotyon and Filippov 1960
- Roth and Just 1977
- Roth and Just (b) 1977
- Westenberg and de Haas 1967
- Brabbs and Brakow 1975
- Felder and Fontijn 1979
- Klemm et al. 1981
- Felder and Fontijn 1981
- Sutherland et al. 1986
- Borassin and Combourieu 1974
- Shaw – theor. 1978
- Wagner et al. – theor. 1986
- Mishra et al. – theor. 1989
- Cohen and Westberg – theor. 1986

This Recommendation 1989

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**Thermodynamic Data**

\[ \Delta H_{\text{f}}^\circ (1) = -364 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{f}}^\circ (1) = -4.32 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_p(1) = 20.7 \ T^{-0.462} \exp(43600/T) \]

\[ \Delta H_{\text{f}}^\circ (2) = -468 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{f}}^\circ (2) = -57.1 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_p(2) = 8.76 \times 10^{-6} \ T^{-0.462} \exp(56600/T) \]

**Rate Coefficient Data** \((k = k_1 + k_2)\)

<table>
<thead>
<tr>
<th>(k) [cm(^3) molecule(^{-1}) s(^{-1})]</th>
<th>(T) [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_1 = 5 \times 10^{-11})</td>
<td>1000–1700</td>
<td>Browne et al. (1969)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>(k_1 / k = 0.8)</td>
<td>300</td>
<td>Niki, Daby, and Weinstock (1969)(^2)</td>
<td>(b)</td>
</tr>
<tr>
<td>(k_2 / k_1 = 0.73)</td>
<td>298</td>
<td>Westenberg and de Haas (1972)(^3)</td>
<td>(c)</td>
</tr>
<tr>
<td>(k_2 = 0.46)</td>
<td>300</td>
<td>Mack and Thrush (1973)(^4)</td>
<td>(d)</td>
</tr>
<tr>
<td>(k = 2.1 \times 10^{-10})</td>
<td>297</td>
<td>Washida, Martinez, and Bayes (1974)(^5)</td>
<td>(e)</td>
</tr>
<tr>
<td>(k_1 / k = 0.4)</td>
<td>425</td>
<td>Campbell and Handy (1978)(^6)</td>
<td>(f)</td>
</tr>
</tbody>
</table>

**Reviews and Evaluations**

| \(k_1 = 5 \times 10^{-11}\) | 300–2000 | Warnatz (1984)\(^7\) |
| \(k_2 = 5 \times 10^{-11}\) | 300–2000 |
| \(k_3 = 5 \times 10^{-11}\) | 300–2500 | Tsang and Hampson (1986)\(^8\) |
| \(k_4 = 5 \times 10^{-11}\) | 400–7500 |

**Comments**

(a) Modelling study of rich and lean acetylene flames at low pressures; species profiles by gas chromatography and by absorption measurements (OH, CH, and C\(_2\)).

(b) Discharge-flow system, C\(_2\)H\(_2\) + O reaction; time-of-flight mass spectrometry.

(c) Fast flow system; O atoms generated by microwave discharge. [O] monitored by ESR, [CO\(_2\)] by mass spectrometry.

(d) Discharge-flow system; reaction CH\(_2\)O + O studied. Products analysed by gas chromatography, [O] and [H] by ESR.

(e) Fast flow reactor; C\(_2\)H\(_4\) + O system free of O\(_3\); photoionisation mass spectrometry. \(k\) derived from the rate of approach of [CHO] to its steady-state value.

(f) Stirred flow reactor; O/H\(_2\)/N\(_2\) or Ar system with various amounts of CO added. [O] monitored by CO + O chemiluminescence.

**Preferred Values**

\(k_1 = 5 \times 10^{-11}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) over range 300–2500 K

\(k_2 = 5 \times 10^{-11}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) over range 300–2500 K

**Reliability**

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

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

**Comments on Preferred Values**

The recommendations of Warnatz\(^7\) and Tsang and Hampson\(^8\) are adopted.

**References**

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

O + HCHO → OH + CHO

Thermodynamic Data

\[ \Delta H_{298} = -50.8 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298} = 28.6 \text{ J K}^{-1} \text{ mol}^{-1} \]
\[ K_0 = 6.88 \times 10^2 \ T^{-0.315} \exp(5810/T) \]

Rate Coefficient Data

<table>
<thead>
<tr>
<th>( k ) [cm³ molecule⁻¹ s⁻¹]</th>
<th>( T ) [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5 \times 10^{-13}</td>
<td>300</td>
<td>Herron and Penzhorn (1969)¹</td>
<td>(a)</td>
</tr>
<tr>
<td>1.6 \times 10^{-13}</td>
<td>298</td>
<td>Niki et al. (1968)²</td>
<td>(b)</td>
</tr>
<tr>
<td>1.0 \times 10^{-10}</td>
<td>1400-2200</td>
<td>Izod et al. (1971)³</td>
<td>(c)</td>
</tr>
<tr>
<td>1.5 \times 10^{-13}</td>
<td>300</td>
<td>Mack and Thrush (1973)⁴</td>
<td>(d)</td>
</tr>
<tr>
<td>8.3 \times 10^{-11} \exp(-2300/T)</td>
<td>1875-2240</td>
<td>Bowman (1975)⁵</td>
<td>(e)</td>
</tr>
<tr>
<td>2.8 \times 10^{-13} \exp(-1525/T)</td>
<td>250-498</td>
<td>Klemm (1979)⁶</td>
<td>(f)</td>
</tr>
<tr>
<td>3.8 \times 10^{-11} \exp(-1583/T)</td>
<td>296-437</td>
<td>Chang and Barker (1979)⁷</td>
<td>(g)</td>
</tr>
<tr>
<td>3.0 \times 10^{-11} \exp(-1554/T)</td>
<td>298-748</td>
<td>Klemm et al. (1980)⁸</td>
<td>(h)</td>
</tr>
</tbody>
</table>

Reviews and Evaluations

| \( 5.8 \times 10^{-11} \exp(-1768/T) \) | 300-2500 | Warratz (1984)⁹         | (i) |
| \( 3.0 \times 10^{-11} \exp(-1550/T) \) | 298-750  | NASA (1985)¹⁰         | (j) |
| \( 3.0 \times 10^{-11} \exp(-1550/T) \) | 250-750  | Tsang and Hampson (1986)¹¹ | (k) |

Reliability

\[ \Delta \log k = \pm 0.3 \text{ at } 2000 \text{ K} \text{ reducing to } \pm 0.1 \text{ at } 298 \text{ K} \]

Comments on Preferred Values

The preferred values are based on the low temperature data which are all in good agreement, and on the higher temperature value of Bowman¹. The earlier high temperature values of Izod et al.³ exceed the preferred values by factors of 3.4 and 6.3 at 2200 and 1400 K respectively. These results are considered unreliable, however, since they were inferred from the computer modelling of reagent and product time dependences using an assumed chemical model. Three other rate coefficients were simultaneously determined, and the derived \( k \) values necessarily depend on other rate constants in the model.

Preferred Values

\[ k = 6.85 \times 10^{-13} \ T^{0.57} \exp(-1390/T) \text{ cm}³ \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range } 250-2200 \text{ K} \]

Comments

(a) Room temperature study using discharge flow of Ar/\( \text{O}_2 \) or \( \text{N}_2/\text{NO} \). Mass spectrometric detection of reagents and products. [\( \text{O} \)] determined by titration.
(b) Room temperature discharge flow study of \( \text{O} + \text{CH}_4 \). Value of \( k \) concluded from mass spectrometric detection of product time profiles.
(c) CO/Ar/\( \text{O}_2 \) mixtures investigated in incident shock waves. Time profiles for CO and product CO₂ used for computer fitting of 4 variable rate constants. Not a true determination of \( k \).
(d) Room temperature study using discharge flow of \( \text{N}_2/\text{NO} \). [\( \text{O} \)] determined by titration and ESR.
(e) CH₄/\( \text{O}_2/\text{Ar} \) mixtures investigated in incident shock waves. \( k \) determined from computer fitting.
(f) Flash photolysis; resonance fluorescence detection of \( \text{O} \) atoms.
(g) Discharge flow; mass spectrometric detection of \( \text{O} \) atoms.
(h) Discharge flow; resonance fluorescence detection of \( \text{O} \) atoms.
(i) Uses high temperature data of Bowman⁵ and low temperature data as cited on this sheet.
(j) Based on the results of Klemm⁶, Chang and Barker⁷, and Klemm et al.⁸.
(k) Accepts the NASA evaluation¹⁰.

References

\[ O + HCHO \rightarrow OH + CHO \]

**EXPERIMENTAL DATA**
- Herron and Penzhorn 1969
- Niki et al 1968
- Izod et al 1971
- Meck and Thrush 1973
- Bowman 1975
- Klemm 1979
- Chang and Barker 1979
- Klemm et al 1980
- Peeters and Wamen 1973
- This Recommendation 1989

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EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ O + CH_3O \rightarrow O_2 + CH_3 \] (1)
\[ \rightarrow OH + HCHO \] (2)

**Thermodynamic Data**

\[ \Delta H_{298}^{\circ} (1) = -119.6 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298}^{\circ} (1) = 9.6 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ K_p (1) = 88.8 \times 10^{-4} \exp(14100/T) \]

\[ \Delta H_{298}^{\circ} (2) = -342 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298}^{\circ} (2) = 12.8 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ K_p (2) = 3.84 \times 10^5 \times 10^{-2} \exp(40900/T) \]

**Rate Coefficient Data** \( (k = k_1 + k_2) \)

<table>
<thead>
<tr>
<th>( k ) [cm(^3) molecule(^{-1}) s(^{-1})]</th>
<th>( T ) [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5 \times 10^{-11}</td>
<td>298</td>
<td>Ewig, Rhasa and Zellner (1987)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>( k_2 ) / ( k ) = 0.12</td>
<td>298</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0 \times 10^{-11}</td>
<td>300-2500</td>
<td>Tsang and Hampson (1986)(^2)</td>
<td>(b)</td>
</tr>
</tbody>
</table>

**Comments**

(a) Laser photolysis of CH\(_3\)ONO/O\(_3\)/N\(_2\) mixtures at 248 nm; CH\(_3\)O detected by LIF in presence of excess O.
(b) Estimate with uncertainty of a factor of 5 quoted.

**Preferred Values**

\[ k = 2.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range 300–1000 K} \]
\[ k_2 / k = 0.12 \text{ at 298 K} \]

**Reliability**

\[ \Delta \log k = \pm 0.7 \text{ at 1000 K reducing to } \pm 0.3 \text{ at 300 K} \]
\[ \Delta k_2 / k = \pm 0.1 \text{ at 298 K} \]

**Comments on Preferred Values**

The recent direct measurement of this rate constant confirms that this highly exothermic reaction occurs rapidly, as predicted. The recommended value is based on the single experimental measurement at 298 K with an assumed zero temperature dependence. The branching ratio measured in recent work of Zellner and co-workers\(^1\) at room temperature is also recommended. CH\(_3\)O is unstable at high temperatures prevalent in most combustion systems.

**References**

Thermodynamic Data

\[ \Delta H_{298} (1) = -322 \text{kJ mol}^{-1} \]
\[ \Delta T_{298} (1) = -12.8 \text{J K}^{-1} \text{mol}^{-1} \]
\[ K_c (1) = 0.361 T^{-0.077} \exp (+38700/T) \]

\[ \Delta H_{298} (2) = -92 \text{kJ mol}^{-1} \]
\[ \Delta T_{298} (2) = 1.1 \text{J K}^{-1} \text{mol}^{-1} \]
\[ K_c (2) = 1.92 T^{-0.077} \exp (+11036/T) \]

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

<table>
<thead>
<tr>
<th>Rate Coefficient Measurements</th>
<th>T[K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 8.0 \times 10^{-12} )</td>
<td>1500</td>
<td>Shaub and Bauer (1978)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>( 3.1 \times 10^{-11} )</td>
<td>2000</td>
<td>Louge and Hanson (1984)(^2)</td>
<td>(b)</td>
</tr>
<tr>
<td>( 1.7 \times 10^{-11} )</td>
<td>298</td>
<td>Baulch \emph{et al.} (1981)(^3)</td>
<td>(c)</td>
</tr>
<tr>
<td>( 1.7 \times 10^{-11} )</td>
<td>298</td>
<td>CODATA (1984)(^4)</td>
<td>(d)</td>
</tr>
</tbody>
</table>

Comments

(a) Shock tube study on C2H2/NO/O2 mixtures. Gas chromatographic analysis of products. Computer fit of results to reaction mechanism.
(b) Shock tube study of (CN)2/O2/Ar mixtures. [CN] monitored by absorption at 388 nm. Computer fit of results to reaction mechanism.
(c) All data reviewed, recommendation made for low temperatures only.
(d) Low temperature data only.

Preferred Values

\[ k = 1.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range 300–5000 K} \]

Reliability

\[ \Delta \log k = \pm 0.2 \text{ at 298 K rising to } \pm 0.6 \text{ at 5000 K} \]

Comments on Preferred Values

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

At low temperatures there is good agreement among the data from Refs. 8–12. At higher temperatures there are two recent shock tube studies\(^1,2\) in fair agreement and compatible with the low temperature results if the temperature coefficient of the rate constant is very small. The preferred values are based on the results of Louge and Hanson\(^2\) and Shaub and Bauer\(^1\) at high temperatures, Boden and Thrush\(^6\) between 570 and 687 K, and Refs. 8–12 at low temperatures.

Schmatjko and Wolfrum\(^11,12\) have reported a branching ratio \( k_1 / k_2 = 0.8 \pm 0.1 \) at 298 K.

References

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ O + CN \rightarrow CO + N(^S) \quad (1) \]
\[ \rightarrow CO + N(^D) \quad (2) \]

T/K

<table>
<thead>
<tr>
<th>$10^3T^{-1}/K^{-1}$</th>
<th>$10^3T^{-1}/K^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.5</td>
<td>0.5</td>
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<tr>
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</tr>
<tr>
<td>3.5</td>
<td>3.5</td>
</tr>
</tbody>
</table>

EXPERIMENTAL DATA

- Selser and Thrush 1965
- Boden and Thrush 1968
- Reichardt et al. 1969
- Schloss and Wolfrum 1972
- Schlock and Wolfrum 1973
- Albers et al. 1975
- Shoub 1976
- Schmeide and Wolfrum 1977
- Schmeid and Wolfrum 1978
- Shoub and Bauer 1978
- Louge and Hanson 1984
- This Recommendation 1989

**Thermodynamic Data**

\[
\Delta H_{298}^{\circ} (1) = -429 \text{ kJ mol}^{-1} \\
\Delta H_{298}^{\circ} (2) = 26.6 \text{ kJ mol}^{-1} \\
\Delta S_{298}^{\circ} (1) = 15.1 \text{ J K}^{-1}\text{ mol}^{-1} \\
\Delta S_{298}^{\circ} (2) = 14.5 \text{ J K}^{-1}\text{ mol}^{-1} \\
K_p(1) = 9.66 \times 10^7 T^{-1.07 \exp(51200/T)} \\
K_p(2) = 2.91 \times 10^3 T^{-0.915 \exp(-3500/T)}
\]

**Rate Coefficient Data** \(k = k_1 + k_3\)

<table>
<thead>
<tr>
<th>(k_1)</th>
<th>(k_2)</th>
<th>(T)</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.32 \times 10^{-11}</td>
<td>1500</td>
<td>Mulvihill and Phillips (1975)</td>
<td>(a)</td>
<td></td>
</tr>
<tr>
<td>1.66 \times 10^{-12}</td>
<td>1500</td>
<td>Phillips (1976)</td>
<td>(b)</td>
<td></td>
</tr>
<tr>
<td>1.66 \times 10^{-11}</td>
<td>1700</td>
<td>Lifshitz and Frenklach (1980)</td>
<td>(c)</td>
<td></td>
</tr>
<tr>
<td>6.61 \times 10^{-11}</td>
<td>1450–2600</td>
<td>Higashihara, Saito, and Murakami (1983)</td>
<td>(d)</td>
<td></td>
</tr>
<tr>
<td>9.34 \times 10^{-11}</td>
<td>1450</td>
<td>Louge and Hanson (1984)</td>
<td>(e)</td>
<td></td>
</tr>
<tr>
<td>5.25 \times 10^{-11}</td>
<td>1680–2250</td>
<td>Higashihara et al. (1985)</td>
<td>(f)</td>
<td></td>
</tr>
</tbody>
</table>

**Comments**

(a) Flame study of \(H_2/N_2/O_2/C_2N_2\) mixtures. Analysis of products by quadrupole mass spectrometry. \(k\) derived from computer fit of data to assumed reaction mechanism.

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

(c) Shock tube study of \(C_2N_2/O_2/Ar\) mixtures. Induction times measured. Results fitted by computer modelling of 15 reaction mechanism. Only approximate value of \(k\) obtained.

(d) Shock tube study of \(HCN/O_2/NO\) mixtures. Induction times measured. Ultraviolet emission at 306 nm due to OH and infrared emission at 5.34 \(\mu\)m, mainly due to NO with some contribution from HCN and H\(_2\)O, monitored as a function of time.

(e) Shock tube study of \(C_2N_2/O_2/N_2O\). [NCO] monitored as a function of time by absorption spectroscopy at 440.5 nm.

(f) Shock tube study of \(BrCN/O_2/Ar\) mixtures. [NO] monitored as a function of time by infrared emission spectroscopy.

**Preferred Values**

\(k = 7.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) over range 1450–2600 K

**Reliability**

\(\Delta \log k = \pm 0.8\) over range 1450–2600 K

**Comments on Preferred Values**

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

Comparison of the results of Louge and Hanson\(^2\), measuring \(k\), and those of Higashihara et al., measuring \(k_1\), suggest that channel (1) is dominant at temperatures in the range 1450–2600 K, but the data are too imprecise to recommend a branching ratio.

**References**

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

O + HCN → NCO + H → CO + NH → OH + CN

**Thermodynamic Data**

(See Comments on Preferred Values)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \Delta H_{298}^o )</th>
<th>( \Delta S_{298}^o )</th>
<th>( K_p(3) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>-7.0 kJ mol(^{-1})</td>
<td>-16.0 J K(^{-1})mol(^{-1})</td>
<td>8.6·10(^{-12})</td>
</tr>
<tr>
<td>(2)</td>
<td>-138 kJ mol(^{-1})</td>
<td>16.0 J K(^{-1})mol(^{-1})</td>
<td>2.3·10(^{-18})</td>
</tr>
</tbody>
</table>

**Rate Coefficient Data**

\( k = k_1 + k_2 + k_3 \)

<table>
<thead>
<tr>
<th>( k ) [cm(^3) molecule(^{-1}) s(^{-1})]</th>
<th>( T ) [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.6·10(^{-12}) exp(-4090/T)</td>
<td>450-650</td>
<td>Davies and Thrush (1968)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>1.94·10(^{-18}) exp (-7460/T)</td>
<td>1800-2500</td>
<td>Roth, Löhri, and Hirmanns (1980)(^2)</td>
<td>(b)</td>
</tr>
<tr>
<td>( k_1 ) = 1.21·10(^{-9}) exp(-7460/T)</td>
<td>574-840</td>
<td>Perry and Melius (1985)(^3)</td>
<td>(c)</td>
</tr>
<tr>
<td>9.8·10(^{-12}) exp(-4000/T)</td>
<td>1440</td>
<td>Louie and Hanson (1985)(^4)</td>
<td>(d)</td>
</tr>
<tr>
<td>( k_2 ) = 8.3·10(^{-12}) exp(-7740/T)</td>
<td>1800-2600</td>
<td>Seekel, Hanson, and Bowman (1985)(^5)</td>
<td>(e)</td>
</tr>
<tr>
<td>( k_3 ) &lt; 8.3·10(^{-11}) exp(-11000/T)</td>
<td>2000-2500</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Preferred Values**

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

**Reliability**

\( \Delta \log k = \pm 0.2 \) at 450 K rising to \( \pm 0.3 \) at 2500 K

**Comments on Preferred Values**

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

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

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

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

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

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

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

(d) Shock tube measurements on HCN/O\(_2\)/N\(_2\)O/Ar mixtures. [NCO] monitored as a function of time by laser absorption at 440.479 nm. \( k_1/k(O+C_2N_2) = 2.4 \pm 0.6 \) obtained from computer fit. \( k(O+C_2N_2) = 7.47·10^{-12} \exp(-440/T) \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) used\(^6\) to obtain \( k_1 \).

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

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ \text{O} + \text{HCN} \rightarrow \text{NCO} + \text{H} \] (1)
\[ \rightarrow \text{CO} + \text{NH} \] (2)
\[ \rightarrow \text{OH} + \text{CN} \] (3)

![Graph showing the evaluated kinetic data for combustion modelling.](image-url)
\[ O + CH_3OOH \rightarrow OH + CH_3OO \quad (1) \]
\[ \rightarrow OH + CH_2OOH \quad (2) \]

Thermodynamic Data
\[ \Delta H_{298}^\circ (1) = -61.0 \text{ kJ mol}^{-1} \]
\[ \Delta H_{298}^\circ (2) = -16.0 \text{ kJ mol}^{-1} \]

Comment
There are no experimental data for the reaction of \( \text{O}^3\text{P} \) with \( CH_3OOH \). The rate constant for the reaction of \( \text{OH} \) with \( CH_3OOH \) is equal to that for \( \text{OH} + HCHO \), and since relative reactivities of \( O \) and \( \text{OH} \) towards H abstraction are similar, the overall expression for \( k = k_1 + k_2 \) is the same as for \( O + HCHO \) i.e. \( k = 6.85 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) over the range 300-1000 K. Comparison with the rate constant for the reaction \( O + H_2O_2 \rightarrow \text{OH} + HO_2 \) indicates that abstraction of the peroxic H is slower and provisionally it is suggested that channel (2) is dominant.

\[ O + C_2H \rightarrow CH + CO \]

Thermodynamic Data
\[ \Delta H_{298}^\circ = -326 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298}^\circ = 12.1 \text{ J K}^{-1} \text{ mol}^{-1} \]
\[ K_p = 3.67 \times 10^2 \text{ T}^{-0.645} \exp(39000 / T) \]

Rate Coefficient Data

<table>
<thead>
<tr>
<th>Rate Coefficient Measurements</th>
<th>( T [K] )</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 2.4 \times 10^{-11} \exp(-1585 / T) )</td>
<td>1400-2600</td>
<td>Shaub and Bauer (1978)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>( = 1.7 \times 10^{-11} )</td>
<td>298</td>
<td>Homann and Schweinfurth (1981)(^2)</td>
<td>(b)</td>
</tr>
<tr>
<td>( = 1.2 \times 10^{-12} )</td>
<td>298</td>
<td>Grebe and Homann (1982)(^3)</td>
<td>(c)</td>
</tr>
</tbody>
</table>

Reviews and Evaluations
\( 1.7 \times 10^{-11} \) | 300-2500 | Warnatz (1984)\(^4\) |
\( 3.0 \times 10^{-11} \) | 300-2500 | Tsang and Hampson (1986)\(^5\) |

Comments
(a) Shock heating of \( C_2H_3O_2/Ar \) mixtures; final product concentrations from gas chromatography. Numerical modelling of 17 reaction mechanism, \( k \) adjusted to give best fit to experimental results.
(b) Discharge-flow system; \( C_2H_3/O \) system with and without added H. \( [C_2H_2], [C_2H_3], \) and \( [CH_2O] \) by mass spectrometry. Numerical modelling of 27 reaction mechanism; reaction plays only a minor role.
(c) Discharge-flow reactor; \( C_2H_3/H/O \) system. Measurement of CH (\( A^2\Delta \rightarrow X^2\Pi \)) and C\(_6\)(\( d^3\Pi_e \rightarrow A^2\Pi_u \)) chemiluminescence at 431.4 nm and 516.5 nm and the quasi-continuous \( C_2H^* \) radiation. Numerical modelling of 37 reaction mechanism. Rate coefficient given for formation of \( CH(A^2\Delta) \).

Preferred Values
\[ k = 1.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \] over range 300-2500 K

Reliability
\[ \Delta \log k = \pm 1.0 \text{ over range 300-2500 K} \]

References
### Thermodynamic Data

\[
\Delta H_{\text{f}}(1) = -200 \text{ kJ mol}^{-1} \\
\Delta H_{\text{f}}(2) = -80.4 \text{ kJ mol}^{-1} \\
\Delta S_{\text{f}}(1) = 31.2 \text{ K} \cdot \text{Kmol}^{-1} \\
\Delta S_{\text{f}}(2) = 6.9 \text{ K} \cdot \text{Kmol}^{-1} \\
K_p(1) = 7.3 \times 10^2 \ T^{-1.40} \exp(+23500/T) \\
K_p(2) = 1.17 \ T^{1.15} \exp(+9600/T)
\]

### Rate Coefficient Data \((k = k_1 + k_2)\)

<table>
<thead>
<tr>
<th>(k [\text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1}])</th>
<th>(T [\text{K}])</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3 \times 10^{-11} \exp(-1600/T)</td>
<td>230-450</td>
<td>Westenberg and de Haas (1969)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>2.0 \times 10^{-11} \exp(-1500/T)</td>
<td>243-673</td>
<td>Hoyermann, Wagner, and Wolfrum (1969)(^2)</td>
<td>(b)</td>
</tr>
<tr>
<td>(k_1/k = 0.42)</td>
<td>404</td>
<td>Williamson (1971)(^3)</td>
<td>(c)</td>
</tr>
<tr>
<td>8.6 \times 10^{-11} \exp(-1860/T)</td>
<td>1200-1700</td>
<td>Peeters and Malinen (1973)(^4)</td>
<td>(d)</td>
</tr>
<tr>
<td>(k_2/k &lt; 0.03)</td>
<td>298</td>
<td>Blumenberg, Hoyermann, and Sievert (1976)(^5)</td>
<td>(e)</td>
</tr>
<tr>
<td>1.2 \times 10^{-13} \exp(-2000/T)</td>
<td>297</td>
<td>Westenberg and de Haas (1977)(^6)</td>
<td>(f)</td>
</tr>
<tr>
<td>1.1 \times 10^{-10} \exp(-2000/T)</td>
<td>700-1430</td>
<td>Vandooren and Van Tilgeelen (1977)(^7)</td>
<td>(g)</td>
</tr>
<tr>
<td>(k_1 = 2.0 \times 10^{-10} \exp(-3300/T))</td>
<td>1500-2570</td>
<td>Löh and Roth (1981)(^8)</td>
<td>(h)</td>
</tr>
<tr>
<td>(k_2 = 7.2 \times 10^{-10} \exp(-6100/T) \times 3 \times 10^{-11} \exp(-1620/T))</td>
<td>298-608</td>
<td>Aleksandrov, Arutyunov, and Košlov (1981)(^9)</td>
<td>(i)</td>
</tr>
<tr>
<td>(k_2/k = 0.5 \exp(-660/T))</td>
<td>300-1300</td>
<td>Homann and Wellmann (1983)(^10)</td>
<td>(j)</td>
</tr>
<tr>
<td>(k_2/k &lt; 0.5)</td>
<td>1000</td>
<td>Homann and Wellmann (1983)(^11)</td>
<td>(j)</td>
</tr>
<tr>
<td>(k_2/k = 0.6)</td>
<td>287-555</td>
<td>Peeters, Schaecker, and Vinkler (1986)(^12)</td>
<td>(k)</td>
</tr>
<tr>
<td>(k_1 = 2.7 \times 10^{-10} \exp(-4975/T))</td>
<td>1500-2500</td>
<td>Frank, Bhaskaran, and Just (1986)(^13)</td>
<td>(l)</td>
</tr>
<tr>
<td>(k_2 = 6.6 \times 10^{-10} \exp(-5365/T) \times 1.1 \times 10^{-19} T^{7/6} \exp(-330/T))</td>
<td>290-1510</td>
<td>Mahmud and Fontijn (1987)(^14)</td>
<td>(m)</td>
</tr>
<tr>
<td>(k_2/k = 0.8)</td>
<td>287</td>
<td>Peeters et al. (1987)(^15)</td>
<td>(n)</td>
</tr>
<tr>
<td>6.6 \times 10^{-11} \exp(-1900/T)</td>
<td>370-876</td>
<td>Russell et al. (1988)(^16)</td>
<td>(o)</td>
</tr>
</tbody>
</table>

### Reviews and Evaluations

| \(k_1 = 6.8 \times 10^{-16} \ T^{-1.1} \exp(-850/T)\) | 300-2500 | Warnatz (1984)\(^17\) | (p) |
| \(k_1 = 7.2 \times 10^{-10} \exp(-6100/T)\) | 1000-2500 | NASA (1985)\(^18\) | (g) |
| \(2.9 \times 10^{-11} \exp(-1600/T)\) | 200-450 | Tsang and Hampson (1986)\(^19\) | (r) |
| \(2.9 \times 10^{-11} \exp(-1600/T)\) | 200-700 | Cvetanovic (1987)\(^20\) | (s) |
| \(2.7 \times 10^{-12} \exp(-1550/T)\) | 250-1300 | | |
| \(k_1 = 3.5 \times 10^5 T^{-0.5} \exp(-850/T)\) | 300-2500 | | |
| \(k_1 = 1.5 \times 10^{-11} \exp(-2300/T)\) | 300-600 | | |
| \(k_1 = 7.0 \times 10^{-10} \exp(-6100/T)\) | 1000-2500 | | |

### Comments

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

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

(c) Applies to \(O + C_2D_2\). O generated from Hg photolized decomposition of \(N_2O\). D yield determined from HD produced by scavenging with H3. HD measured relative to H2.

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

(e) Mass spectrometric detection from a laval nozzle reactor. Ratios based on H, CO, and \(C_2H_2\) signals although CH2 and CHCO were also observed.

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

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

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

(i) O generated by discharge through \(N_2O\), admitted through movable nozzle. H and O detection by resonance fluorescence, absolute calibration being achieved via equilibrium concentrations of H and O in H2 and O2 at 1300–1500 K. k determined from decay of O signal, \(k_2/k\) from the absolute H signal.
(j) Discharge flow (O/C2H5/He), nozzle beam sampling with mass spectrometric detection.
(k) Flow reactor, O generated by discharge through O2, molecular beam sampling with mass spectrometric detection.
(l) Reflected shock wave study on N2O/C2H5/Ar, O, H, and CO detected by resonance absorption spectrometry. Channel (2) was essential if the initial shape of the H profile was to be reproduced.
(m) Flash photolysis, resonance fluorescence. O generated from photolysis of O2 or CO2.
(n) Flow reactor, O and H generated by discharge. k2/k determined from the dependence of the CH2 signal on [H]/[O], based on secondary generation of CH2 via H + HCCO.
(p) Evaluation, based on the low temperature data summarised by Cvetanovic and the high temperature data of Peeters and Mahnen, Vandooren and Van Tiggelen, Löh and Roth, and Homann and Wollmann. k2 based on data of Löh and Roth and Homann and Wollmann.
(q) NASA panel evaluation based on low temperature data over the period 1965–1981.
(r) Accepted the NASA evaluation but extended range.
(s) Low temperature evaluation of data prior to 1986. Cvetanovic selected a dependence close to that of Homann and Wollmann.

Preferred Values

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

\[ k_2 / k = 0.5 \text{ over range 300–2500 K} \]

Reliability

\[ \Delta \log k = \pm 0.2 \]

\[ \Delta (k_2/k) = \pm 0.3 \]

Comments on Preferred Values

(i) Overall rate constant

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

(ii) Channel efficiencies

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

References

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ O + C_2H_2 \rightarrow CH_2 + CO \quad (1) \]
\[ \quad \rightarrow H + C_2HO \quad (2) \]

\[ T/K \]

\[ \log(k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}) \]

\[ 10^3T^{-1}/K^{-1} \]

EXPERIMENTAL DATA

- Peeters and Mohnen 1973
- Vondooron and Van Tiggelen 1977
- Lohr and Roth 1981
- Aleksandrov et al. 1981
- Homann and Wellmann 1983
- Frank et al. 1986
- Mahmud and Fontijn 1987
- Russell et al. 1988
- Westenberg and de Haas 1969
- Hoyermon et al. 1969
- Westenberg and de Haas 1977

\[ \times \] This Recommendation 1989
O + C2H2 → 3CH2 + CO \hspace{1cm} (1)
→ H + C2HO \hspace{1cm} (2)

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ \text{O + C}_2\text{H}_3 \rightarrow \text{H + CH}_2\text{CO} \quad (1) \]
\[ \rightarrow \text{CH}_3 + \text{CO} \quad (2) \]

**Thermodynamic Data**

\[ \Delta H_{298}^\circ (1) = -369 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298}^\circ (1) = -36.1 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_p(1) = 7.9 \times 10^{-11} T^{0.36} \exp( + 44600/T) \]
\[ \Delta H_{298}^\circ (2) = -500 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298}^\circ (2) = -0.87 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_p(2) = 1.10 \times 10^7 T^{-0.636} \exp(- 59800/T) \]

**Rate Coefficient Data** \( (k = k_1 + k_2) \)

<table>
<thead>
<tr>
<th>( k ) [cm(^3) molecule(^{-1}) s(^{-1})]</th>
<th>( T ) [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3 \times 10^{-11}</td>
<td>298</td>
<td>Homann and Schweinfurth (1981)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>5 \times 10^{-11}</td>
<td>200</td>
<td>Heinemann et al. (1986)(^2)</td>
<td>(b)</td>
</tr>
<tr>
<td>= 200</td>
<td>(see comments)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Reviews and Evaluations**

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

**Preferred Values**

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

**Reliability**

\[ \Delta \log k = \pm 0.5 \text{ over the whole range} \]

**Comments on Preferred Values**

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

**References**


Thermodynamic Data

\[ \Delta H_{\text{m}}(1) = -58.5 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{m}}(1) = 2.3 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ K_p(1) = 0.127 \, T^{0.440} \exp(7030/T) \]
\[ \Delta H_{\text{m}}(2) = -112 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{m}}(2) = 38.5 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ K_p(2) = 4.5 \times 10^{-12} \, T^{-0.7116} \exp(13100/T) \]
\[ \Delta H_{\text{m}}(3) = -30.5 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{m}}(3) = 33.9 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ K_p(3) = 6.08 \times 10^{4} \, T^{-0.948} \exp(3210/T) \]
\[ \Delta H_{\text{m}}(4) = -353.0 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{m}}(4) = -7.73 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ K_p(4) = 0.369 \, T^{0.143} \exp(42280/T) \]

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

<table>
<thead>
<tr>
<th>( k [\text{cm}^{3} \text{ molecule}^{-1} \text{ s}^{-1}] )</th>
<th>( T [\text{K}] )</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 6.73 \times 10^{-13} )</td>
<td>298</td>
<td>Fonderie et al. (1983)</td>
<td>(a)</td>
</tr>
<tr>
<td>( 2.42 \times 10^{-12} )</td>
<td>552</td>
<td>Browarzik and Stuhl (1984)</td>
<td>(b)</td>
</tr>
<tr>
<td>( 4.61 \times 10^{-12} )</td>
<td>736</td>
<td>Smalley et al. (1986)</td>
<td>(c)</td>
</tr>
<tr>
<td>( 8.43 \times 10^{-12} \exp(-757/T) )</td>
<td>197-372</td>
<td>Mahmud et al. (1987)</td>
<td>(e)</td>
</tr>
<tr>
<td>( k_{ijk} = 0.27 )</td>
<td>300</td>
<td>Klemm et al. (1987)</td>
<td>(f)</td>
</tr>
<tr>
<td>( (244-1052 \exp(-830/T) + )</td>
<td>290-1510</td>
<td>Herron and Huie (1973)</td>
<td>(g)</td>
</tr>
<tr>
<td>( 1.90 \times 10^{-10} \exp(-6940/T) )</td>
<td>230-940</td>
<td>Warnatz (1984)</td>
<td>(h)</td>
</tr>
<tr>
<td>( 1.02 \times 10^{-11} \exp(-753/T) )</td>
<td>244-1052</td>
<td>Tsang and Hampson (1986)</td>
<td>(i)</td>
</tr>
<tr>
<td>( 1.72 \times 10^{-16} \exp(-4220/T) )</td>
<td>200-500</td>
<td>Cvetanovic (1987)</td>
<td>(j)</td>
</tr>
</tbody>
</table>

Comments

(a) Discharge flow–mass spectrometry with molecular beam sampling. Decay of \( \text{C}_2\text{H}_4 \) in large excess of \( \text{O} \). Data in table obtained at 2 Torr; no effect of pressure between 0.5–5 Torr was found at any of the three temperatures investigated.

(b) Laser photolysis of \( \text{NO} \) to produce \( \text{O} \) which was monitored by \( \text{O} + \text{NO} \) chemiluminescence in excess \( \text{C}_2\text{H}_4 \).

(c) Branching ratio for the \( \text{H} + \text{CH}_2\text{CHO} \) product channel determined from measured \( \Pi \)- and \( \text{O} \)-atom profiles in this flash photolysis–resonance fluorescence study. Relative detector sensitivities for \( \text{O} \) and \( \text{H} \) determined, giving accurate value of \( k_{ijk} \). The branching ratio increased slightly with temperature, based on measurements at 300, 515, 608, 677, and 769 K.

(d) Branching ratio determined from measurement of \( \text{CHO} \) (CDO) and \( \text{CH}_2\text{CHO} \) (CD$_2$CDO) yields using time-resolved microwave spectroscopy in pulsed Hg-photonsensitised reaction of \( \text{N}_2\text{O}/\text{C}_2\text{H}_4 \) mixtures. Pressure \( = 30 \) mTorr.

(e) High temperature flash photolysis of \( \text{CO}_2 \) to produce \( \text{O} \)(3P); resonance fluorescence detection. Pressure 60–500 Torr.

(f) Two techniques used: flash photolysis–resonance fluorescence (244–1052 K) and discharge flow–resonance fluorescence (298–1017 K). NO was used as photolytic source of \( \text{O} \)(3P) at \( T > 600 \) K to avoid problems from secondary reactions involving \( \text{O}_2 \).

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

(h) Based on experimental data up to 1980, including high temperature data of Peet and Mahnen19.

(i) Fit to results of Davis et al.11, Westenberg and de-Haas12 for \( T < 500 \) K, Atkinson and Pitts13, Singleton and Cvetanovic14, Atkinson and Pitts15, Nicovich and Ravishankara16, and Perry17. Uncertainty of 20%.

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

Preferred Values

\[ k = 5.75 \times 10^{-18} \, T^{0.08} \text{ cm}^{3} \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range } 300-2000 \text{ K} \]

\[ k_1 / k = 0.35 \text{ at } p \geq 3 \text{ Torr and } T \geq 300 \text{ K} \]

\[ k_2 / k = 0.60 \]
EVALUATED KINETIC DATA FOR COMBUSTION MODELLING 465

Reliability
\[ \Delta \log k = \pm 0.1 \text{ for } T < 1000 \text{ K increasing to } \pm 0.3 \text{ at } 2000 \text{ K} \]
\[ \Delta k_1/k = \pm 0.05 \]
\[ \Delta k_2/k = \pm 0.10 \]
\[ \Delta k_3/k = \pm 0.10 \]

Comments on Preferred Values
There is a large amount of data on this reaction which has been reviewed regularly. Only those recent data not presented by Cvetanovic\(^{10}\) are listed here. The recent direct studies at higher temperatures\(^{1,5,6,16,17}\) show clear non-Arrhenius behaviour at temperatures > 500 K. The recent study of Browarzik and Stuhl\(^{2}\) extends the temperature range down to 197 K. All the data are in excellent agreement, within the stated experimental uncertainty. Both recent studies at temperatures > 1000 K suggest a biexponential representation of the overall \(k\). The expression given by Klemm et al.\(^{6}\) does not include the higher temperature data of Mahmud et al.\(^{5}\), but nevertheless gives a good fit to all the data over the range 250–1500 K. The preferred expression is derived by performing a 3 parameter \(A T^n \exp(E/RT)\) fit to the curve generated from the expression of Klemm et al. over the range 250–1500 K. The exponential term was negligible, the curve being accurately described by an \(AT^n\) expression. The results from Ref. 1 show that \(k\) is independent of pressure at \(T > 300\) K. The recent determination of the branching ratio, \(k_1/k\), confirms that H atom elimination is a major pathway in this reaction. Koda et al.\(^{4}\) have rationalised these results, as well as their observed isotope effect, with a model involving unimolecular dissociation on a triplet biradical surface (channel 1) and a competitive triplet-to-singlet crossing. The small temperature effect may reflect an increase in rate of fragmentation of the initial adduct with increasing energy of the reactants, which is also consistent with the results of Buss et al.\(^{19}\) who found \(k_1/k = \approx 1.0\) at high kinetic energies of reactants in molecular beam experiments. The recommended values of the branching ratios are based on these studies. Earlier attempts to determine the branching ratios by mass spectrometry appear to have given an erroneous picture.

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

**Experimental Data**

- Nicovich and Rovitha (1969)
- Fonderie et al. (1983)
- Perry (1984)
- Browarcik and Stuhl (1984)
- Mahmud et al. (1987)
- Klemm et al. (1987)
- This Recommendation (1989)
EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ \text{O} + \text{C}_2\text{H}_6 \rightarrow \text{CH}_3\text{CHO} + \text{H} \]  \hspace{1cm} (1)  
\[ \rightarrow \text{HCHO} + \text{CH}_3 \]  \hspace{1cm} (2)

**Thermodynamic Data**

\[ \Delta H_{\text{fm}} (1) = -314 \text{ kJ mol}^{-1} \]
\[ \Delta H_{\text{fm}} (2) = -337 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{fm}} (1) = -34.2 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ \Delta S_{\text{fm}} (2) = -0.07 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ K_e (1) = 1.3 \times 10^{-4} \exp\left( +37900/T \right) \]
\[ K_e (2) = 64.8 \ T^{-0.54} \exp\left( +40200/T \right) \]

**Rate Coefficient Data \( (k = k_1 + k_2) \)**

<table>
<thead>
<tr>
<th>( k [\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}] )</th>
<th>( T [\text{K}] )</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1/k_2 = 5 \pm 1 )</td>
<td>300</td>
<td>Hoyermann and Sievert (1979)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>9.5 \times 10^{-11}</td>
<td>720–785</td>
<td>Peeters and Caymax (*)(^2)</td>
<td>(b)</td>
</tr>
</tbody>
</table>

**Reviews and Evaluations**

<table>
<thead>
<tr>
<th>( k_1/k_2 )</th>
<th>( T [\text{K}] )</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.3 \times 10^{-11}</td>
<td>700–2000</td>
<td>Warnatz (1984)(^3)</td>
</tr>
<tr>
<td>1.6 \times 10^{-10}</td>
<td>300–2500</td>
<td>Tsang and Hampson (1986)(^4)</td>
</tr>
</tbody>
</table>

**Comments**

(a) Low pressure flow system with nozzle reactor and mass spectrometric analysis. Products CH\(_3\)CHO and HCHO taken as confirmation for channels (1) and (2). Absence of OH and C\(_2\)H\(_2\) products indicates that channel \( \text{O} + \text{C}_2\text{H}_6 \rightarrow \text{OH} + \text{C}_2\text{H}_4 \) does not occur in this system.

(b) Discharge-flow technique with molecular beam sampling for mass spectrometry. O atoms (microwave discharge) reacted with C\(_2\)H\(_6\) at total pressures of 2 Torr. \( k \) derived from measurements of [O] (titration) and [C\(_2\)H\(_3\)] (mass spectrometry) at the approach to the stationary state of C\(_2\)H\(_3\).

(c) Estimated value.

(d) Assumed value taken to be equal to \( k (\text{O} + \text{CH}_3) \).

**Preferred Values**

\[ k = 1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range 300–2500 K} \]
\[ k_1/k_2 = 0.17 \text{ at 300 K} \]

**Reliability**

\[ \Delta \log k = \pm 0.3 \text{ over range 300–1000 K} \]
\[ = \pm 0.5 \text{ over range 1000–2500 K} \]
\[ \Delta k_1/k_2 = \pm 0.03 \text{ at 300 K} \]

**Comments on Preferred Values**

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

**References**

\(^2\)J. Peeters and M. Caymax, awaiting publication.
O + C₂H₆ → OH + C₂H₅

**Thermodynamic Data**

\[ \Delta H_{\text{fus}} = -9.1 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{fus}} = 45.3 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ K_s = 5.29 \times 10^4 T^{-0.36} \exp(+744/T) \]

**Rate Coefficient Data**

<table>
<thead>
<tr>
<th>Rate Coefficient Measurements</th>
<th>Temperature [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.39 \times 10^{-10} \exp(-3770/T)</td>
<td>853-933</td>
<td>Azatayan, Nalbandyan, and Meng-yuan (1962)¹</td>
<td>(a)</td>
</tr>
<tr>
<td>3.0 \times 10^{-11} \exp(-2650/T)</td>
<td>320-589</td>
<td>Westenberg and DeHaas (1967)²</td>
<td>(b)</td>
</tr>
<tr>
<td>3.0 \times 10^{-11} \exp(-2650/T)</td>
<td>272-615</td>
<td>Westenberg and DeHaas (1969)³</td>
<td>(c)</td>
</tr>
<tr>
<td>1.38 \times 10^{-11} \exp(-3620/T)</td>
<td>336-595</td>
<td>Herron and Huie (1969)⁴</td>
<td>(d)</td>
</tr>
<tr>
<td>4.6 \times 10^{-11} \exp(-3270/T)</td>
<td>303-364</td>
<td>Papadopoulos, Ashmore, and Tyler (1969)⁵</td>
<td>(e)</td>
</tr>
<tr>
<td>3.2 \times 10^{-10} \exp(-4806/T)</td>
<td>600-1030</td>
<td>Caymax and Peeters (1983)⁶</td>
<td>(f)</td>
</tr>
</tbody>
</table>

| Reviews and Evaluations | | | |
| 4.2 \times 10^{-11} \exp(-3200/T) | 298-650 | Herron and Huie (1973)⁷ | (g) |
| 5.0 \times 10^{-20} T^2 \exp(-2575/T) | 300-1500 | Warnatz (1984)⁸ | (h) |
| 1.55 \times 10^{-20} T^{-2} \exp(-2890/T) | - | Cohen (1986)⁹ | |
| 2.0 \times 10^{-12} T^4 \exp(-3680/T) | 500-1000 | Tsang and Hampson (1986)¹⁰ | (i) |

**Comments**

(a) Effect of C₂H₆ on lower explosion limit of CO + O₂ mixtures.
(b) Discharge flow with ESR detection of O atoms.
(c) Reinvestigation using same technique; report same parameters. In both studies stoichiometry measured only at 500 K and assumed temperature independent.
(d) Discharge flow with mass spectrometric detection of reagents. Secondary reactions avoided by large [O]/[C₂H₆D] ratios.
(e) Flow discharge, [O] by NO titration. Detailed determination of stoichiometry at 310 K.
(f) Discharge flow, molecular beam sampling and mass spectrometric analysis.
(g) Details of early studies given.
(h) T range not given, but < 1000 K.
(i) Recommend Cohen's¹¹ expression determined from transition state theory.

**Preferred Values**

\[ k = 1.66 \times 10^{-15} T^{0.5} \exp(-2920/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]
over range 300-1200 K

**Reliability**

\[ \Delta \log k = \pm 0.15 \text{ between } 500 \text{ K and } 1200 \text{ K rising to } 0.3 \text{ at } 300 \text{ K} \]

**Comments on Preferred Values**

The rate constants are only reasonably reliable between 500 and 1000 K. Cohen¹¹ suggests that all the experimental values below 500 K are too high by factors rising up to 4 at 300 K due to incorrect stoichiometry used in the determination of k. The preferred value is based on Cohens¹¹ analysis of the low temperature data.

**References**

²¹N. Cohen, Aerospace Report. No. ATR-84(7073)-1, August 1984 (reported in Ref. 10).
EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

$O + C_2H_6 \rightarrow OH + C_2H_5$

![Graph showing the reaction rate constant as a function of temperature]
**Thermodynamic Data**

\[ \Delta H_{298} = -429.8 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298} = 94.6 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ K_p = 2.38 \times 10^6 T^{-0.439} \exp(-51460/T) \]

**Rate Coefficient Data**

<table>
<thead>
<tr>
<th>( k [\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}] )</th>
<th>Temperature [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0 \times 10^{-12}</td>
<td>298</td>
<td>Jones and Bayes (1973)</td>
<td>(a)</td>
</tr>
<tr>
<td>3.2 \times 10^{-10} \exp(-300/T)</td>
<td>285-535</td>
<td>Vinckier et al. (1985)</td>
<td>(b)</td>
</tr>
<tr>
<td>1.6 \times 10^{-10}</td>
<td>1500-1700</td>
<td>Frank et al. (1986)</td>
<td>(c)</td>
</tr>
</tbody>
</table>

**Comments**

(a) Discharge flow study with O atoms generated from \( N + NO \). CHCO produced as an intermediate from \( O + C_2H_2 \) with [CHCO] and [O] measured by photo-ionisation mass spectroscopy. \( k \) measured from steady state value of [CHCO] at relatively long reaction times with simplifying assumptions concerning the mechanism.

(b) Flow study with O atoms generated by \( O_2 \) discharge, and measured by standard titration technique. Radical concentrations measured by molecular beam mass spectrometry. Conditions selected so that CHCO is effectively removed only by reaction with O atoms. Value of \( k \) at 535 K determined from best fit to [CHCO] profile at 535 K. Activation energy determined from measurements of [CHCO].

(c) Shock tube study, with simultaneous measurement of [H], [O], and [CO] by atomic and molecular absorption spectrometry. \( O + CHCO \) important in later stages of \( O + C_2H_2 \) system. \( k \) determined from [O] profile under optimised stoichiometry.

**Preferred Values**

\[ k = 1.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \] over range 300-2500 K

**Reliability**

\[ \Delta \log k = \pm 0.3 \text{ over range 300-2500 K} \]

**Comments on Preferred Values**

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

**References**

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ O + CH_2CO \rightarrow CH_2O + CO \quad (1) \]
\[ \rightarrow CHO + H + CO \quad (2) \]
\[ \rightarrow CHO + CHO \quad (3) \]

**Thermodynamic Data**

\[ \Delta H_{298} (1) = -424 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298} (1) = 13.4 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ K_r (1) = 2.0 \times 10^6 T^{1.26} \exp(+50600/T) \]

\[ \Delta H_{298} (2) = -46.4 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298} (2) = 134 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ K_r (2) = 2.39 \times 10^8 T^{0.378} \exp(+5260/T) \text{ atm} \]

\[ \Delta H_{298} (3) = -110 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298} (3) = 46.3 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ K_r (3) = 6.66 \times 10^5 T^{-1.15} \exp(+12900/T) \]

**Rate Coefficient Data**

\[ k = k_1 + k_2 + k_3 \]

\[ k \text{[cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}] \quad T[\text{K}] \quad \text{Reference} \quad \text{Comments} \]

**Rate Coefficient Measurements**

- \[ 8.8 \times 10^{-13} \]
- \[ 5.67 \times 10^{-13} \]
- \[ 2.92 \times 10^{-12} \exp(-680/T) \]
- \[ 3.3 \times 10^{-11} \exp(-1155/T) \]

<table>
<thead>
<tr>
<th>[ T[\text{K}] ]</th>
<th>[ 298 ]</th>
<th>[ 293 ]</th>
<th>[ 230-449 ]</th>
<th>[ 300 ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ \text{Reference} ]</td>
<td>Carr, Glass, and Niki (1968) (^1)</td>
<td>Mack and Thrush (1974) (^2)</td>
<td>Washida et al. (1983) (^3)</td>
<td>Warnatz (1984) (^4)</td>
</tr>
</tbody>
</table>

**Comments**

(a) Discharge flow system. O atoms produced by reaction \( N + NO \rightarrow O + N_2 \) \( CH_2CO \) in excess. Analysis by mass spectrometry. CO\(_2\), CO, H\(_2\)O, H\(_2\) and H\(_2\)CO observed in the products. Experiments using \(^1\)O mixtures of \( CH_2CO \) and \( CD_2CO \) suggest channels (2) and (3) not of major importance.

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

(c) Two experimental methods used.

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

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

**Preferred Values**

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

**Reliability**

\[ \Delta \log k = \pm 0.3 \text{ over range } 230-500 \text{ K} \]

**Comments on Preferred Values**

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

Carr et al. \(^1\) concluded that the probable initial step is formation of \( CH_2CO_2 \) which may rapidly decompose. Results from the isotope study \(^4\) and product analysis \(^2\) by gas chromatography indicate that channels (2) and (3) may be dominant but more recently \( CH_2O \) has been observed as a major product suggesting that reaction (1) is also of importance. No recommendations are made for the branching ratios.

**References**


O + CH₂CO → CH₂O + CO
→ CHO + H + CO
→ CHO + CHO

T/K

EXPERIMENTAL DATA
EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ \text{O} + \text{CH}_3\text{CHO} \rightarrow \text{OH} + \text{CH}_3\text{CO} \quad (1) \]
\[ \rightarrow \text{OH} + \text{CH}_2\text{CHO} \quad (2) \]

**Thermodynamic Data**

\[ \Delta H_{298} (1) = -67.5 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298} (1) = 25.6 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_r (1) = 2.18 \times 10^9 T^{-0.444} \exp( +7780/T) \]

\[ \Delta H_{298} (2) = -19.8 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298} (2) = 26.6 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_r (2) = 9.6 \times 10^2 T^{-0.455} \exp(2050/ T) \]

**Rate Coefficient Data** \( (k = k_1 + k_2) \)

<table>
<thead>
<tr>
<th>( k ) [cm(^3) molecule(^{-1}) s(^{-1})]</th>
<th>( T ) [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 4.8 \times 10^{-13} )</td>
<td>300</td>
<td>Mack and Thrush (1974)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>( 1.7 \times 10^{-11} \exp(-2010/T) )</td>
<td>1550–1850</td>
<td>Beeley et al. (1977)(^2)</td>
<td>(b)</td>
</tr>
<tr>
<td>( 4.9 \times 10^{-13} )</td>
<td>298</td>
<td>Michael and Lee (1977)(^3)</td>
<td>(c)</td>
</tr>
<tr>
<td>( 9.2 \times 10^{-11} \exp(-990/T) )</td>
<td>298–472</td>
<td>Singleton et al. (1977)(^4)</td>
<td>(d)</td>
</tr>
</tbody>
</table>

**Comments**

(a) Discharge flow system. Oxygen atoms monitored by EPR and air afterglow.
(b) Ignition of CH\(_3\)CHO/O_{2}/Ar mixtures behind incident shock waves. Stable and transient species monitored by UV and IR emission. \( k \) determined from modelling the system.
(c) Discharge flow system. Oxygen atoms monitored by resonance fluorescence.
(d) Modulated photolysis of N\(_2\)O/CH\(_3\)CHO. Oxygen atoms monitored by air afterglow.

**Preferred Values**

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

**Reliability**

\[ \Delta \log k = \pm 0.5 \text{ at 1500 K reducing to } \pm 0.05 \text{ at 298 K} \]

**Comments on Preferred Values**

Preferred values are based on the low temperature data of Mack and Thrush\(^1\), Michael and Lee\(^3\), and Singleton et al.\(^4\). Temperature dependence based on the data of Singleton et al.\(^4\). Although the data of Beeley et al.\(^2\) agrees with the extrapolation based on a simple Arrhenius expression, the determination was indirect and subject to uncertainty. No information is available on the branching ratio. If it is assumed that \( k_2 = 1/2 k_0 + C_{2H_6} \) then the second channel only becomes significant (\( k_2/k > 0.1 \)) at \( T > 700 \text{ K} \). However the extrapolated value is a factor of 2 higher than the overall rate given by Beeley et al.\(^2\). The contribution of the second channel is negligible at \( T < 500 \text{ K} \), where the only reliable studies were conducted.

**References**

\[ \text{O} + \text{CH}_3\text{CHO} \rightarrow \text{OH} + \text{CH}_3\text{CO} \]
\[ \quad \rightarrow \text{OH} + \text{CH}_2\text{CHO} \]

-11.5

-12.0

-12.5

-13.0

0.5

1.0

1.5

2.0

2.5

3.0

3.5

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

Log(k/cm^3 molecule^{-1}s^{-1})
EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ \text{O} + \text{C}_2\text{H}_5\text{OOH} \rightarrow \text{OH} + \text{C}_2\text{H}_5\text{OO} \] (1)
\[ \rightarrow \text{OH} + \text{C}_2\text{H}_4\text{OOH} \] (2)

**Thermodynamic Data**

\[ \Delta H_{298}^\circ (1) = -60.15 \text{ kJ mol}^{-1} \]
\[ \Delta H_{298}^\circ (2) = -20.7 \text{ kJ mol}^{-1} \]

**Comment**

There are no experimental data for the reaction of \( \text{O}(^3\text{P}) \) with \( \text{C}_2\text{H}_5\text{OOH} \). As for \( \text{CH}_3\text{OOH} \) the rate expression

\[ k = 6.85 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \exp(-1390/T) \]

with channel (2) dominant, is recommended by analogy with H abstraction from HCHO and \( \text{H}_2\text{O}_2 \).

\[ \text{O} + \text{C}_6\text{H}_6 \rightarrow \text{OH} + \text{C}_6\text{H}_5 \] (1)
\[ \text{O} + \text{C}_6\text{H}_6 (+ \text{M}) \rightarrow \text{C}_6\text{H}_5\text{OH} (+ \text{M}) \] (2)

**Thermodynamic Data**

\[ \Delta H_{298}^\circ (1) = 35.3 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298}^\circ (1) = 41.7 \text{ J K}^{-1} \text{ mol}^{-1} \]
\[ K_p(1) = 9.8 \times 10^{-4} T^{-0.88} \exp(-4701/T) \]
\[ \Delta H_{298}^\circ (2) = -428.5 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298}^\circ (2) = -115.4 \text{ J K}^{-1} \text{ mol}^{-1} \]
\[ K_p(2) = 4.3 \times 10^{-6} T^{-0.20} \exp(+5141/T) \text{ atm}^{-1} \]

**Rate Coefficient Data** \((k = k_1 + k_2)\)

<table>
<thead>
<tr>
<th>(k) [cm³ molecule⁻¹ s⁻¹]</th>
<th>(T) [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(6.0 \times 10^{-14})</td>
<td>298</td>
<td>Mani and Sauer (1968)¹</td>
<td>(a)</td>
</tr>
<tr>
<td>(2.5 \times 10^{-10} \exp(-2768/T))</td>
<td>883–963</td>
<td>Mkryan et al. (1971)²</td>
<td>(b)</td>
</tr>
<tr>
<td>(k_1 = 5.3 \times 10^{-10} \exp(-3019/T))</td>
<td>1300–1700</td>
<td>Fujii and Asaba (1972)³</td>
<td>(c)</td>
</tr>
<tr>
<td>(k_2 = 6.3 \times 10^{-11} \exp(-2214/T))</td>
<td>255–305</td>
<td>Bommanno et al. (1972)⁴</td>
<td>(d)</td>
</tr>
<tr>
<td>(2.4 \times 10^{-14})</td>
<td>300</td>
<td>Atkinson and Pitts (1974)⁵</td>
<td>(e)</td>
</tr>
<tr>
<td>(1.8 \times 10^{-11} \exp(-2214/T))</td>
<td>298–462</td>
<td>Colussi et al. (1975)⁶</td>
<td>(f)</td>
</tr>
<tr>
<td>(1.8 \times 10^{-11} \exp(-2005/T))</td>
<td>299–392</td>
<td>Atkinson and Pitts (1975)⁷</td>
<td>(g)</td>
</tr>
<tr>
<td>(1.7 \times 10^{-11} \exp(-2010/T))</td>
<td>299–440</td>
<td>Atkinson and Pitts (1979)⁸</td>
<td>(h)</td>
</tr>
<tr>
<td>(4.6 \times 10^{-11} \exp(-2470/T))</td>
<td>298–867</td>
<td>Nicovich et al. (1982)⁹</td>
<td>(i)</td>
</tr>
<tr>
<td>(k_1 = 5.3 \times 10^{-10} \exp(-3020/T))</td>
<td>1600–2300</td>
<td>Hsu et al. (1984)¹⁰</td>
<td>(j)</td>
</tr>
<tr>
<td>(2.5 \times 10^{-11} \exp(-2130/T))</td>
<td>298–600</td>
<td>Cvetanovic (1987)¹¹</td>
<td>(k)</td>
</tr>
</tbody>
</table>

**Comments**

(a) Pulsed radiolysis with product analysis by gas chromatography. \( \text{O} \) atoms originate from radiolysis of \( \text{CO}_2 \) and \( \text{NO}_2 \) 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 \( \text{O} \) atoms was monitored by ESR detection and changes in benzene concentration followed by mass spectrometry. It was found that \( \text{O} \) atoms removal is much faster than benzene decrease. Therefore it was assumed that the \( \text{O} \) atoms react with radicals produced in the initiation reaction. The rate coefficient for channel (2) was evaluated from the mass spectrometric measurements.
(e) Same method as in comment (a).
(f) Phase shift–\( \text{O} + \text{NO} \) chemiluminescence. \( \text{O} \) atoms are generated during Hg photosensitized decomposition of \( \text{NO}_2 \).
(g) Same method as in comment (f).
(h) Flash photolysis–resonance fluorescence. \( \text{O} \) atoms are generated by VUV photolysis of \( \text{O}_2 \) and \( \text{NO} \).
(i) Flash photolysis–resonance fluorescence. \( \text{O} \) atoms are generated by VUV photolysis of \( \text{O}_2 \).
(j) The oxidation of benzene under fuel lean conditions was studied behind reflected shock waves using a stabilized cw CO laser to monitor CO production. The formed CO was modelled by a 25 step reaction mechanism. A rate coefficient for channel (1) was determined.
(k) Critical evaluation and compilation of chemical kinetic data of \( \text{O}(^3\text{P}) \) atoms with unsaturated hydrocarbons.

Preferred Values

\[ k = 1.2 \times 10^{-22} T^{3.68} \exp \left( -\frac{570}{T} \right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range } 300-1000 \text{ K} \]

Reliability

\[ \Delta \log k = \pm 0.5 \text{ over range } 300-1000 \text{ K} \]

Comments on Preferred Values

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

References

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ \ce{O + C_6H_6 -> OH + C_6H_5} \]
\[ \ce{O + C_6H_6 (+ M) -> C_6H_5OH (+ M)} \]

\[ \text{Log}(k/\text{cm}^3\text{ molecule}^{-1}\text{s}^{-1}) \]

\[ 10^3T^{-1}/K^{-1} \]

EXPERIMENTAL DATA
- Mor and Sauer 1968
- Miyaro et al 1971
- Fujii and Asaba (k1) 1972
- Bonanno et al (k2) 1972
- Atkinson and Pitts 1974
- Colussi et al 1975
- Colussi et al 1977
- Atkinson and Pitts 1979
- Hsu et al (k1) 1982
- Atkinson and Pitts 1989

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\[
\begin{align*}
O + C_6H_5CH_2 & \rightarrow HCO + C_6H_6 & \text{(1)} \\
\rightarrow CH_2O + C_6H_5 & \rightarrow H + C_6H_5CHO & \text{(2)} \\
\end{align*}
\]

**Thermodynamic Data**

\[
\begin{align*}
\Delta H_{298}^0 (1) &= -322.8 \text{ kJ mol}^{-1} \\
\Delta S_{298}^0 (1) &= 16.7 \text{ J K}^{-1} \text{mol}^{-1} \\
K_p (1) &= 3.5 \times 10^6 T^{-2.8} \exp(+38474/T) \\
\Delta H_{298}^0 (2) &= -236.7 \text{ kJ mol}^{-1} \\
\Delta S_{298}^0 (2) &= 29.9 \text{ J K}^{-1} \text{mol}^{-1} \\
K_p (2) &= 8.0 \times 10^6 T^{-1.84} \exp(+27932/T) \\
\end{align*}
\]

**Rate Coefficient Data** \((k = k_1 + k_2 + k_3)\)

<table>
<thead>
<tr>
<th>(k) (\text{[cm}^3\text{molecule}^{-1}\text{s}^{-1}])</th>
<th>(T [K])</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate Coefficient Measurements</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(k_2 = 1.7 \times 10^{-11})</td>
<td>1700–2800</td>
<td>McLain et al. (1979) (^{(1)})</td>
<td>(a)</td>
</tr>
<tr>
<td>(k_1 + k_3 = 5.5 \times 10^{-10})</td>
<td>298</td>
<td>Bartels et al. (1988) (^{(2)})</td>
<td>(b)</td>
</tr>
</tbody>
</table>

**Comments**

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

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

**Preferred Values**

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

**Reliability**

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

**Comments on Preferred Values**

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

**References**


**O + C\(_6\)H\(_5\)CH\(_3\) → products**

**Rate Coefficient Data**

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

**Reviews and Evaluations**

\(2.7 \times 10^{-11} \exp(-1720/T)\) | 298–932 | Cvetanovic (1987) \(^{(11)}\) | (k) |

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

Comments

(a) O atoms from Hg photosensitized decomposition of N₂O. Ratio derived from relative k data in competing experiments. Reference reaction was O + cyclopentene → products. Evaluated by Cvetanovic.
(b) Same method as in (a). Reference reaction was O + benzene → products. Evaluated by Cvetanovic.
(c) O atoms from pulse radiolysis of CO₂ and N₂O at high pressures. Rate coefficient from absorption spectra of transient species.
(d) Phase shift - O + NO chemiluminescence. O atoms from Hg photosensitized decomposition of N₂O.
(e) Same method as in (a).
(f) Same method as in (d).
(g) Microwave discharge - fast flow reactor. O atoms from N + NO.
(h) Flash photolysis - resonance fluorescence. O atoms from VUV photolysis of O₂ and NO.
(i) Incident shock wave investigation of the oxidation mechanism of C₆H₆/O₂/Ar and C₅H₅NO/Ar mixtures by monitoring UV and IR emission of CO, CO₂, and the product [O]_[CO]. Arrhenius expression for the product channel C₄H₅CH₂ + OH estimated by comparison with data for benzene.
(j) Flash photolysis - resonance fluorescence. O atoms from VUV photolysis of O₂.
(k) Critical evaluation and compilation of chemical kinetic data of O(³P) atoms with unsaturated hydrocarbons.

Preferred Values

\[ k = 5.3 \times 10^{-15} \, T^{1.21} \exp(-1260/T) \, \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} \text{ over range } 298-2800 \, \text{K} \]

Reliability

\[ \Delta \log k = \pm 0.4 \text{ at } 2800 \, \text{K reducing to } \pm 0.1 \text{ at } 300 \, \text{K} \]

Comments on Preferred Values

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

References

O + C_5H_5CH_3 → products

EXPERIMENTAL DATA

Jones and Ovetic 1981
Mori and Sauer 1968
Groenerstein and Mosher 1970
Atkinson and Pitts 1974
Colussi et al 1975
Atkinson and Pitts 1975
Mclain et al 1979
Nicovich et al 1982

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EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\( O + p\text{-C}_6\text{H}_4(\text{CH}_3)_2 \rightarrow \text{products} \)

Rate Coefficient Data

<table>
<thead>
<tr>
<th>( k [\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}] )</th>
<th>( T ) [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate Coefficient Measurements</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 7.5 \times 10^{-13} )</td>
<td>298</td>
<td>Mani and Sauer (1968)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>( 1.8 \times 10^{-13} )</td>
<td>300</td>
<td>Atkinson and Pitts, Jr. (1974)(^2)</td>
<td>(b)</td>
</tr>
<tr>
<td>( 1.3 \times 10^{-14}\exp(-1280/T) )</td>
<td>299–392</td>
<td>Atkinson and Pitts, Jr. (1975)(^3)</td>
<td>(c)</td>
</tr>
<tr>
<td>( 3.9 \times 10^{-14}\exp(-1540/T) )</td>
<td>298–600</td>
<td>Cvetanovic et al. (1982)(^4)</td>
<td>(d)</td>
</tr>
<tr>
<td>Reviews and Evaluations</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 2.0 \times 10^{-13} )</td>
<td>298</td>
<td>Cvetanovic (1987)(^5)</td>
<td>(e)</td>
</tr>
<tr>
<td>( 2.6 \times 10^{-11}\exp(-1409/T) )</td>
<td>298–600</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Comments

(a) O from pulse radiolysis of CO\(_2\) or N\(_2\)O. \( k \) from absorption spectra of transients (not positively identified). \( p \approx 60 \text{ bar} \).

(b) Phase shift–O + NO chemiluminescence. O-atoms from Hg-photosensitized decomposition of N\(_2\)O. \( p = 72 \text{ mbar} \).

(c) Same method as in (b).

(d) Flash photolysis–resonance fluorescence. O-atoms from VUV photolysis of O\(_2\). Density range \( 2 \times 10^{10} \text{–} 2 \times 10^{13} \text{ cm}^{-3} \).

(e) Critical evaluation and compilation of chemical kinetic data of O\(^{16}\P\) atoms with unsaturated hydrocarbons.

Preferred Values

\[
k = 2.6 \times 10^{-11}\exp(-1409/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range 298–600 K}
\]

Reliability

\[ \Delta \log k = \pm 0.3 \]

Comments on Preferred Values

The preferred value is based on the evaluation of Cvetanovic\(^5\).

References

\(^1\) I. Mani and M. C. Sauer, Jr., Advanc. Chem. Ser. No. 82, 142 (1968).
O + p-C<sub>6</sub>H<sub>4</sub> (CH<sub>3</sub>)<sub>2</sub> → products

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

O + C₂H₂C₃H₆ → products

Rate Coefficient Data

<table>
<thead>
<tr>
<th>Rate Coefficient Measurements</th>
<th>Temperature [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.3×10⁻¹³</td>
<td>298</td>
<td>Mani and Sauer (1968)¹</td>
<td>(a)</td>
</tr>
<tr>
<td>1.0×10⁻¹³</td>
<td>303</td>
<td>Grovenstein and Mosher (1970)²</td>
<td>(b)</td>
</tr>
</tbody>
</table>

Reviews and Evaluations

| 1.0×10⁻¹³ | 298 | Cvetanovic (1987)³ |

Comments

(a) O from pulse radiolysis of CO₂ or N₂O. k from absorption spectra of transients (not positively identified). p = 53 bar.
(b) Ratio derived from relative k data in competing experiments. Reference reaction was O + benzene → products. p = 1 bar. Evaluated by Cvetanovic³.
(c) Critical evaluation and compilation of chemical kinetic data of O(¹P) atoms with hydrocarbons.

Preferred Values

k = 1.0×10⁻¹³ cm³ molecule⁻¹ s⁻¹ at 298 K and 1 bar

Thermodynamic Data

ΔH₀ = 231.0 kJ mol⁻¹
ΔS₀ = 31.9 J K⁻¹mol⁻¹
Kp = 39.6 T⁻⁰.¹⁰⁵ exp(-27930/T)

O₂ + CH₄ → HO₂ + CH₃

Rate Coefficient Data

<table>
<thead>
<tr>
<th>Rate Coefficient Measurements</th>
<th>Temperature [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>No experimental measurements have been made.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Reviews and Evaluations

6.6×10⁻¹¹ exp(-28600/T) 500-2000 Walker (1974)¹ |

Comments

(a) Based on experimental value³ for HCHO + O₂ → HO₂ + HCO, which is effectively 3.3×10⁻¹¹ exp(-ΔH/RT) cm³ molecule⁻¹ s⁻¹. Assuming equal A factors per C—H bond k = 6.6×10⁻¹¹ exp(-ΔH/RT) cm³ molecule⁻¹ s⁻¹.

Preferred Values

k = 6.6×10⁻¹¹ exp(-28600/T) cm³ molecule⁻¹ s⁻¹ over range 500–2000 K

References

O₂ + C₂H₆ → HO₂ + C₂H₅

**Thermodynamic Data**

\[ \Delta H_{\text{fne}} = 211.5 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{fne}} = 46.6 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_p = 6.39 \times 10^{4} T^{-0.44} \exp(-25630/T) \]

**Rate Coefficient Data**

<table>
<thead>
<tr>
<th>( k [\text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1}] )</th>
<th>( T[\text{K}] )</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 3.4 \times 10^{-11} \exp(-19580/T) )</td>
<td>713-813</td>
<td>Baldwin et al. (1974)¹</td>
<td>(a)</td>
</tr>
<tr>
<td>( 7.5 \times 10^{-11} \exp(-20630/T) )</td>
<td>878-952</td>
<td>Vardanyan et al. (1975)²</td>
<td>(b)</td>
</tr>
<tr>
<td>( 6.3 \times 10^{-11} \exp(-20100/T) )</td>
<td>650-900</td>
<td>Walker (1975)³</td>
<td>(c)</td>
</tr>
<tr>
<td>( 3.4 \times 10^{-11} \exp(-19600/T) )</td>
<td>300-2000</td>
<td>Tsang and Hampson (1986)⁴</td>
<td>(d)</td>
</tr>
</tbody>
</table>

**Comments**

(a) Oxidation of HCHO in KCl coated vessels under conditions where the chain length is near unity.
(b) Thermal oxidation of HCHO; expression for \( k \) cited from earlier work published in Armenian Chemical Journal³.
(c) Based on Ref. 1; recommended Arrhenius parameters for general reaction RH + O₂ → R + HO₂ are \( E = \Delta H^o \) and \( A = 6.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \). Accuracy estimated to be \( \pm \) a factor of 2–4 in the temperature range 650–900 K.
(d) Accepts the value in Ref. 1.

**Preferred Values**

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

O₂ + HCHO → HO₂ + CHO

**Thermodynamic Data**

\[ \Delta H_{\text{fne}} = 170 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{fne}} = 29.9 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_p = 0.083 T^{-0.167} \exp(-20600/T) \]

**Rate Coefficient Data**

<table>
<thead>
<tr>
<th>( k [\text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1}] )</th>
<th>( T[K] )</th>
<th>Reference</th>
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</thead>
<tbody>
<tr>
<td>( 3.4 \times 10^{-11} \exp(-19580/T) )</td>
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<tr>
<td>( 7.5 \times 10^{-11} \exp(-20630/T) )</td>
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<td>(b)</td>
</tr>
<tr>
<td>( 6.3 \times 10^{-11} \exp(-20100/T) )</td>
<td>650-900</td>
<td>Walker (1975)³</td>
<td>(c)</td>
</tr>
<tr>
<td>( 3.4 \times 10^{-11} \exp(-19600/T) )</td>
<td>300-2000</td>
<td>Tsang and Hampson (1986)⁴</td>
<td>(d)</td>
</tr>
</tbody>
</table>

**Comments**

(a) Oxidation of HCHO in KCl coated vessels under conditions where the chain length is near unity.
(b) Thermal oxidation of HCHO; expression for \( k \) cited from earlier work published in Armenian Chemical Journal³.
(c) Based on Ref. 1; recommended Arrhenius parameters for general reaction RH + O₂ → R + HO₂ are \( E = \Delta H^o \) and \( A = 6.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \). Accuracy estimated to be \( \pm \) a factor of 2–4 in the temperature range 650–900 K.
(d) Accepts the value in Ref. 1.

**Preferred Values**

\( k = 1.0 \times 10^{-10} \exp(-20460/T) \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \) over range 700–1000 K
EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

Reliability
\[ \Delta \log k = \pm 0.5 \text{ over range 700-1000 K} \]

Comments on Preferred Values
The results of Baldwin et al.\(^1\) appear reliable and are confirmed by the rate parameters cited from the Russian work. The preferred value is obtained using the approach of Walker\(^3\), using the currently accepted \( \Delta H^0 \) and the \( A \) factor adjusted to fit the value of \( k = 3.4 \times 10^{-22} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \) at 773 K from Ref. 2.

Thermodynamic Data
\[
\begin{align*}
\Delta H_{298}^0 &= 153 \text{ kJ mol}^{-1} \\
\Delta S_{298} &= 26.8 \text{ J K}^{-1} \text{ mol}^{-1} \\
K_c &= 2.63 \times 10^{-10} \exp(-18600/\theta)
\end{align*}
\]

Rate Coefficient Data

<table>
<thead>
<tr>
<th>Rate Coefficient Measurements</th>
<th>( T[K] )</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.32 \times 10^{-11} \exp(-21240/\theta)</td>
<td>700-1100</td>
<td>Colket et al. (1977)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>6.7 \times 10^{-11} \exp(-20100/\theta)</td>
<td>650-900</td>
<td>Walker (1975)(^2)</td>
<td>(b)</td>
</tr>
</tbody>
</table>

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

(b) Recommended expression using \( E = \Delta H^0 = 167 \text{ kJ mol}^{-1} \) and \( A = 6.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \), based on work of Baldwin et al.\(^1\).

Preferred Values
\[ k = 5.0 \times 10^{-11} \exp(-19700/\theta) \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \text{ over range 600-1100 K} \]

Reliability
\[ \Delta \log k = \pm 0.5 \text{ at 600 K rising to } \pm 1.0 \text{ at 1100 K} \]

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**H + O₂ → O + OH**

**Thermodynamic Data**

\[ \Delta H_{\text{f}} = 70.2 \text{ kJ mol}^{-1} \]

\[ \Delta S_{\text{f}} = 24.9 \text{ J K}^{-1}\text{mol}^{-1} \]

\[ K_p = 3.02 \times 10^2 \text{T}^{-0.034} \exp(-8620/\text{T}) \]

**Rate Coefficient Data**

<table>
<thead>
<tr>
<th>( k [\text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1}] )</th>
<th>( T [\text{K}] )</th>
<th>Reference</th>
<th>Comments</th>
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<tr>
<td>4.5 \times 10^{-10} \exp(-8354/T)</td>
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<td>Kochubei and Moin (1973)(^1)</td>
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<tr>
<td>2.0 \times 10^{-7} \exp(-8369/T)</td>
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<td>Schott (1973)(^2)</td>
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<td>1.0 \times 10^{-9} \exp(-8450/T)</td>
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<td>Bowman (1975)(^3)</td>
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<td>Chiang and Skinner (1979)(^4)</td>
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<td>962-1705</td>
<td>Klemm et al. (1989)(^7)</td>
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**Comments**

(a) Oxidation of H₂ in O₂/CO₂/N₂ mixtures; static system. Product analysis by gas chromatography. Total pressures 80–900 Torr.

(b) Shock heating of lean and rich H₂/CO/O₂/Ar mixtures, time-resolved chemiluminescence near the visible and ultraviolet region (λ > 340 nm). Total pressures 20–350 Torr.

(c) Shock heating of stoichiometric and rich CH₄/O₂/Ar mixtures, [OH] by absorption at 308 nm, [O] from chemiluminescence near 370 nm, [CO] and [CO₂] from infrared emission at 4.8 μm and 6.3 μm. Total densities \((1.4-2.3) \times 10^{-5} \text{ mol cm}^{-3}\). Numerical modelling of 23 reaction mechanism of methane oxidation and adjusting of sensitive rates.

(d) Shock tube; H₂/O₂/Ar mixtures; [H] by Lyman α-resonance absorption. Total pressure = 2 atm.

(e) Shock heating of rich and stoichiometric H₂/O₂/Ar mixtures; [O] by resonance absorption. Total pressures = 1.5–2.5 atm.

(f) Shock heating of N₂O/H₂/O₂/Ar mixtures; [H] and [O] by time-resolved atomic resonance absorption. Total densities \((6 \times 10^{-6}–1.3 \times 10^{-5}) \text{ mol cm}^{-3}\). Numerical modelling of 10 reaction mechanism and adjusting of rate parameters.

(g) Shock tube; H atoms produced by flash photolysis of either NH₃ or H₂O in the reflected shock regime; [H] by atomic resonance absorption. Total pressures 10–30 Torr.

**Preferred Values**

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

**Reliability**

\[ \Delta \log k = \pm 0.1 \text{ at low temperatures rising to } \pm 0.2 \text{ at 2500 K} \]

**Comments on Preferred Values**

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

**References**

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

H + O₂ → O + OH

T/K

Log(k) (cm³ molecule⁻¹ s⁻¹)

10³T⁻¹ / K⁻¹

EXPERIMENTAL DATA
Booman 1974
Kochhebel and Maen 1973
Schoßl 1973
Ohm and Skinner 1979
Biland et al 1976
Azotyon and Namadzve 1977
Frank and Just 1985
Ponomarchenko and Skinner 1982
Azotyon et al 1981
Just and Wagner 1990
Azotyon et al 1992
Azotyon et al 1994
Hirsche and Ryssen 1964
Azebi et al 1965
Skinner et al 1966
Azotyon et al 1967
Gulman et al 1967
Gulman and Schoßl 1967
Jenkins et al 1967
Kurzus and Boudart 1968
Wyrrson and Wall 1968
Parshmazyan et al 1968
Brown et al 1969
Bunow et al 1969
Schoßl 1969
Zobalowski and Houghton 1970
Bolte et al 1971
Klemm et al 1988

This Recommendation 1989

H + O₂ (+ M) → HO₂ (+ M)

**Thermodynamic Data**

\[ \Delta H_{298} = -208 \text{ kJ mol}^{-1} \]

\[ \Delta S_{298} = -90.6 \text{ J K}^{-1} \text{mol}^{-1} \]

\[ K_p = 6.9 \times 10^{-3} T^{-0.8} \exp(+24800/T) \text{ atm}^{-1} \]

**Rate Coefficient Data**

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<tr>
<th>( k [\text{cm}^3 \text{ molecule}^{-2} \text{s}^{-1}] )</th>
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**Reviews and Evaluations**

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**Comments**

(a) Hg sensitized photodecomposition of H₂; H monitored by Lyman α spectroscopy. Reaction was found to be third order over total pressure range. Relative efficiencies H₂ : Kr : He : Ar : Ne = 2 : 0.8 : 1.2 : 1 : 0.2.

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

(c) Flash photolysis of CH₄ or C₂H₆/He/Ar, or Ar/N₂ mixtures. [H] monitored by Lyman α resonance fluorescence. Relative collision efficiencies CH₄ : N₂ : He : Ar = 15.7 : 3.4 : 1.0 : 1.0.

(d) Oxidation of H₂ in O₂/CO₂/N₂ mixtures; product analysis by gas chromatography. H₂ in excess.

(e) VUV flash photolysis of CH₄/O₂/M mixtures. [H] by Lyman α resonance fluorescence. Relative efficiencies Ar : He : H₂ : N₂ : CH₄ = 1 : 0.93 : 2.8 : 22 at 300 K.

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

(g) Numerical simulation of H₂/O₂/N₂ flames. Relative efficiencies H₂ : O₂ : N₂ : H₂O = 1 : 0.35 : 0.44 : 6.5.

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

(i) Shock heating of H₂/air mixtures. OH and H₂O observed by emission at 307 nm and 2.7 μm, respectively. Modelling of induction times near to the second explosion limit; results very sensitive to k.

(j) Decomposition of H₂/O₂/Ar mixtures behind reflected shock waves; [H] by Lyman α resonance absorption.
EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

(k) Pulse radiolysis of H₂ with small amounts of O₂; [H₂O₂] monitored by absorption at 230 nm.

(l) Shock heating of rich and stoichiometric H₂/O₂/Ar mixtures. [O] by resonance absorption.

(m) Discharge-flow system; [H₂O₂] by gas chromatography, other products by mass spectrometry.

(n) Laser flash photolysis of NH₃ in the presence of excess O₂. Total pressures between 1 and 200 bar. H₂O₂ monitored by absorption at 220 nm. Reaction found to be in the fall-off range; extrapolation to limiting low- and high-pressure rate coefficients.

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

(p) Flash photolysis of either NH₃ or H₂O in the reflected shock regime. [H] monitored by atomic resonance absorption spectroscopy.

Preferred Values

\[
\begin{align*}
    k &= 1.7 \times 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \text{ over range 300–2000 K for M = Ar} \\
    k &= 5.8 \times 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \text{ over range 300–2000 K for M = H₂} \\
    k &= 3.9 \times 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \text{ over range 300–2000 K for M = N₂} \\
    k &= 4.3 \times 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \text{ over range 300–2000 K for M = H₂O}
\end{align*}
\]

Reliability

\[\Delta \log k = \pm 0.5 \text{ over range 300–2000 K}\]

Comments on Preferred Values

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

For clarity, rate data measured before 1972 are included in the Arrhenius plot (see Baulch et al.² for Ref.).

References

$H + O_2 + Ar \rightarrow HO_2 + Ar$

![Graph showing the reaction rate constant as a function of temperature.](image-url)
EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ \text{H} + \text{O}_2 + \text{H}_2 \rightarrow \text{HO}_2 + \text{H}_2 \]

\[ \text{T \hspace{0.2cm} K} \]

**EXPERIMENTAL DATA**
- Ahumada et al. 1972
- Kochubei and Main 1973
- Wong and Davis 1974
- Dixon-Lewis et al. 1975
- Nielsen et al. 1982
- Burgess and Robb 1957
- Robertsson et al. 1987
- Kurzius 1964
- Bishop and Dorfman 1970
- This Recommendation 1989

**Equation**

\[ \text{Log} \left( k \text{cm}^6 \text{molecules}^{-2} \text{s}^{-1} \right) \]

\[ 10^3 \frac{T^{-1}}{K^{-1}} \]

**Source**

**Thermodynamic Data**

\[
\Delta H_{\text{f,298}} = -436 \text{ kJ mol}^{-1} \\
\Delta S_{\text{f,298}} = -98.6 \text{ JK}^{-1}\text{mol}^{-1} \\
K_p = 3.19 \times 10^{-18} \exp(52100/T) \text{ atm}^{-1}
\]

**Rate Coefficient Data**

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<th>(T[K])</th>
<th>(M)</th>
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**Comments**

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

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

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

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

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

(f) Flow tube, EPR detection.

\[k = 1.8 \times 10^{-30} T^{-1.0} \text{ cm}^3\text{molecule}^{-2}\text{s}^{-1} \text{ over range 300-2500 K for M = Ar}\]

**Reliability**

\[\Delta \log k = \pm 0.5 \text{ over whole temperature range}\]

**Comments on Preferred Values**

The value preferred by Baulch et al.²⁵ has been adopted. The arguments given there are accepted, and the values measured after 1972 do not contradict this recommendation.

For clarity, rate data measured before 1972 are included in the Arrhenius plot (see Baulch et al.²⁵ for Ref.).

**References**


EVALUATED KINETIC DATA FOR COMBUSTION MODELLING


H + H + Ar → H₂ + Ar

Temperature (T/K)

Log (k/cm·molecules⁻²·s⁻¹)

10³T⁻¹/K⁻¹

EXPERIMENTAL DATA
- Mallard and Owen 1974
- Volakisogi and Kauffman 1975
- Trainor et al. 1973
- Lynch et al. 1976
- Grigoryan 1980
- Schott 1980
- Patch 1982
- Rin 1987
- Sutton 1982
- Larkin and Thrush 1964
- Russo et al. 1964
- Schott and Bird 1964
- Jacobs et al. 1965
- Larkin and Thrush/Larkin 1968
- Gelzinger and Blair 1966
- Jacobs et al. 1967
- Azarbayani et al. 1968
- Guv and Pratt 1969
- Gelzinger and Blair 1969
- Holstein and Jenkins 1969
- Hurle et al. 1969
- Roberts et al. 1969
- This Recommendation 1989

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ H + H + H_2 \rightarrow H_2 + H_2 \]

This Recommendation 1989

Thermodynamic Data

\[ \Delta H_{\text{fum}} = -499 \text{kJ mol}^{-1} \]
\[ \Delta S_{\text{fum}} = -109 \text{J K}^{-1}\text{mol}^{-1} \]
\[ K_p = 3.6 \times 10^{-3} T^{-1.2} \exp\left(\frac{-59800}{T}\right) \text{atm}^{-1} \]

Rate Coefficient Data

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<td>&lt; 1 \times 10^{-32}</td>
<td>1900</td>
<td>CO, CO(_2)</td>
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<td>2.1 \times 10^{-32}</td>
<td>2130</td>
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<tr>
<td>8.3 \times 10^{-33} \exp\left(\frac{+750}{T}\right)</td>
<td>300-1800</td>
<td>N(_2)</td>
<td>Friswell and Sutton (1972)(^4)</td>
<td></td>
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<tr>
<td>4.3 \times 10^{-35} T^{-7.6}</td>
<td>220-300</td>
<td>He</td>
<td>Dixon-Lewis et al. (1975)(^5)</td>
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<tr>
<td>1.0 \times 10^{-28} T^{-1}</td>
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</table>

Reviews and Evaluations

<table>
<thead>
<tr>
<th>( k ) [cm(^6) molecule(^{-2}) s(^{-1})]</th>
<th>( T ) [K]</th>
<th>( M )</th>
<th>Reference</th>
<th>Comments</th>
</tr>
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<tbody>
<tr>
<td>2.3 \times 10^{-26} T^{-2.0}</td>
<td>1000-3000</td>
<td>Ar</td>
<td>Baulch et al. (1972)(^8)</td>
<td></td>
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<tr>
<td>6.1 \times 10^{-26} T^{-2.0}</td>
<td>300-3000</td>
<td>N(_2)</td>
<td></td>
<td></td>
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<tr>
<td>3.9 \times 10^{-25} T^{-2.0}</td>
<td>300-3000</td>
<td>H(_2)O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.1 \times 10^{-26} T^{-2.0}</td>
<td>300-3000</td>
<td>N(_2)</td>
<td>Tsang and Hampson (1986)(^9)</td>
<td></td>
</tr>
</tbody>
</table>

Comments

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

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

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

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


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

Preferred Values

\[ k = 2.3 \times 10^{-26} T^{-2.0} \text{cm}^6 \text{molecule}^{-2} \text{s}^{-1} \text{ over range 300-3000 K for } M = \text{Ar} \]
\[ k = 6.1 \times 10^{-26} T^{-2.0} \text{cm}^6 \text{molecule}^{-2} \text{s}^{-1} \text{ over range 300-3000 K for } M = \text{N}_2 \]
\[ k = 3.9 \times 10^{-25} T^{-2.0} \text{cm}^6 \text{molecule}^{-2} \text{s}^{-1} \text{ over range 300-3000 K for } M = \text{H}_2\text{O} \]

Reliability

\[ \Delta \log k = \pm 0.3 \text{ for } M = \text{Ar} \]
\[ \Delta \log k = \pm 0.5 \text{ for } M = \text{N}_2 \]
\[ \Delta \log k = \pm 0.5 \text{ for } M = \text{H}_2\text{O} \]

Comments on Preferred Values

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

References

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ \text{H} + \text{OH} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O} + \text{H}_2\text{O} \]

\[ T/\text{K} \]

\[ \log(k/\text{cm}^6\text{molecules}^{-2}\text{s}^{-1}) \]

\[ 10^3 T^{-1}/\text{K}^{-1} \]

EXPERIMENTAL DATA
- Homer and Hurka 1969
- Holleod and Jenkins 1970
- Friswell and Sutton 1972
- Boyd et al 1973
- Jensen and Jones 1974
- Dixon-Lewis 1975
- Goodings and Hoyhurst 1988
- Frost and Oldenberg 1936
- Oldenberg and Riese 1939
- Bulewicz and Sugden 1958
- Padley and Sugden 1958
- Black and Porter 1962
- Dixon-Lewis et al 1962
- Mckandrew and Wheeler 1962
- Rosenfeld and Sugden 1964
- Dixon-Lewis et al 1965
- Zeegers and Alkemade 1965
- Getzinger and Blair 1969
- Jenkins et al 1967
- McFarland and Topps 1967
- Gay and Pratt 1969

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\[ H + OH + N_2 \rightarrow H_2O + N_2 \]

\[ T/K \]

**Experimental Data**
- Halstead and Jenkins 1970
- Dixon-Lewis 1975
- Black and Porter 1962
- Dixon-Lewis et al. 1962
- MeAndrew and Wheeler 1962
- Rosenfeld and Sugden 1964
- Schott and Bird 1964
- Dixon-Lewis et al. 1965
- Zeegers and Alkemade 1965
- Getzinger and Blair 1969
- Gay and Pratt 1969

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EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[
\begin{align*}
\text{H} + \text{HO}_2 & \rightarrow \text{H}_2 + \text{O}_2 \quad (1) \\
& \rightarrow \text{OH} + \text{OH} \quad (2) \\
& \rightarrow \text{O} + \text{H}_2\text{O} \quad (3)
\end{align*}
\]

Thermodynamic Data
\[
\begin{align*}
\Delta H_{fu} (1) &= -228 \text{ kJ mol}^{-1} \\
\Delta S_{fu} (1) &= -7.96 \text{ J K}^{-1} \text{mol}^{-1} \\
K_p(1) &= 4.58 T^{-0.30} \exp(+ 27300/T) \\
\Delta H_{fu} (2) &= -150 \text{ kJ mol}^{-1} \\
\Delta S_{fu} (2) &= 23.6 \text{ J K}^{-1} \text{mol}^{-1} \\
K_p(2) &= 2.5 \times 10^7 T^{-0.30} \exp(+ 17800/T) \\
\Delta H_{fu} (3) &= -221 \text{ kJ mol}^{-1} \\
\Delta S_{fu} (3) &= 6.06 \text{ J K}^{-1} \text{mol}^{-1} \\
K_p(3) &= 1.56 \times 10^7 T^{-0.62} \exp(+ 26300/T)
\end{align*}
\]

Rate Coefficient Data

<table>
<thead>
<tr>
<th>(k[\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}])</th>
<th>(T[\text{K}])</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_1 / k_2 / k_3 = 0.62 : 0.27 : 0.11)</td>
<td>300-1000</td>
<td>Westenberg and deHaas (1972)</td>
<td>(a)</td>
</tr>
<tr>
<td>(k_1 = 2.7 \times 10^{-11} \exp(-180/T))</td>
<td>293</td>
<td>Day et al. (1973)</td>
<td>(b)</td>
</tr>
<tr>
<td>(k_2 = 3.8 \times 10^{-38} \exp(-930/T))</td>
<td>758-850</td>
<td>Hack, Wagner, and Hoyermann (1978)</td>
<td>(c)</td>
</tr>
<tr>
<td>(k_3 / k_1 = 0.1)</td>
<td>298</td>
<td>Baldwin and Walker (1979)</td>
<td>(d)</td>
</tr>
<tr>
<td>(k_1 = 4.6 \times 10^{-11})</td>
<td>349</td>
<td>Pagsberg et al. (1979)</td>
<td>(e)</td>
</tr>
<tr>
<td>(k_2 = 9.0 \times 10^{-38} \exp(-915/T))</td>
<td>298</td>
<td>Thrush and Wilkinson (1981)</td>
<td>(f)</td>
</tr>
<tr>
<td>(k_3 = 8.3 \times 10^{-11} \exp(-915/T))</td>
<td>298</td>
<td>Sridharan, Qiu, and Kaufman (1982)</td>
<td>(g)</td>
</tr>
<tr>
<td>(k_2 = 3.3 \times 10^{-11})</td>
<td>304</td>
<td>Pagsberg et al. (1979)</td>
<td>(h)</td>
</tr>
<tr>
<td>(k_1 = 6.7 \times 10^{-12})</td>
<td>231-464</td>
<td>Pratt and Wood (1983)</td>
<td>(i)</td>
</tr>
<tr>
<td>(k_2 = 6.4 \times 10^{-11})</td>
<td>245-300</td>
<td>Keyser (1986)</td>
<td>(j)</td>
</tr>
</tbody>
</table>

Reviews and Evaluations
\[
\begin{align*}
\text{(a) Discharge-flow system; absolute [H] and steady-state [OH] and [O] by electron spin resonance.} \\
\text{(b) Numerical modelling of burning velocities of rich H}_2/\text{O}_2/\text{N}_2 \text{ flames. Parameters not very accurate.} \\
\text{(c) Discharge-flow system; HO}_2 \text{ from H} + \text{O}_2 \text{ recombination, [H], [O], and [OH] monitored by electron spin resonance. Total pressure near 5 \times 10^5 \text{ Pa.} k \text{ estimated to lie in the range (3.3-7.3) \times 10^{-11} cm}^3 \text{ molecule}^{-1} \text{s}^{-1}.} \\
\text{(d) Discharge-flow system; HO}_2 \text{ from F} + \text{H}_2\text{O} \text{ reaction or from H} + \text{O}_2 + \text{M recombination. [OH] and [HO}_2 \text{ observed by laser magnetic resonance. Total pressures 500-800 Pa and 130 Pa.} } \\
\text{(e) Recalculated because of a revised value for} k(\text{H} + \text{O}_2) \rightarrow \text{OH} + \text{O}. \\
\text{(f) Pulse radiolysis of gaseous ammonia -- oxygen mixtures at atmospheric pressure; [NH], [NH], and [OH] measured by UV absorption spectroscopy. Numerical integration of 23 reaction mechanism and fitting of unknown rate parameters to experimental results.} \\
\text{(g) Discharge-flow system; HO}_2 \text{ steady-state concentration measured by laser magnetic resonance. Total pressures 2.5-3.2 Torr. Given rate based on a relative collision efficiency of O}_2/\text{Ar} = 3 : 1 \text{ in H} + \text{O}_2 + \text{M recombination.}}
\end{align*}
\]

(h) Flow system; \( \text{HO}_2 \) from \( F + \text{H}_2\text{O}_2 \) reaction. [\( \text{HO}_2 \)] monitored by conversion to \( \text{OH} \) with excess \( \text{NO} \), [\( \text{H} \)] and [\( \text{O} \)] by VUV resonance fluorescence, [\( \text{OH} \)] by laser induced fluorescence. Total pressures near 2.5 Torr He.

(i) Discharge-flow system; \( \text{HO}_2 \) from \( \text{H} + \text{O}_2 + \text{M} \) recombination. Product analysis by mass spectrometry and gas chromatography. Total pressures 2-10 Torr Ar.

(j) Flow system; \( \text{HO}_2 \) from \( F + \text{H}_2\text{O}_2 \) reaction. [\( \text{OH} \)], [\( \text{O} \)], and [\( \text{H} \)] monitored by resonance fluorescence, [\( \text{HO}_2 \)] by quantitatively converting it to \( \text{OH} \) with an excess of \( \text{NO} \).

Preferred Values

\[
\begin{align*}
\text{k}_1 & = 7.1 \cdot 10^{-11} \exp(-710/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range } 300-1000 \text{ K} \\
\text{k}_2 & = 2.8 \cdot 10^{-10} \exp(-440/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range } 300-1000 \text{ K} \\
\text{k}_3 & = 5.0 \cdot 10^{-11} \exp(-866/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range } 300-1000 \text{ K}
\end{align*}
\]

Reliability

\( \Delta \log k = \pm 0.3 \) for total rate coefficient over range 300–1000 K

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

Comments on Preferred Values

For the reaction leading to \( \text{H}_2 \) and \( \text{O}_2 \) the recommendation is based on the relatively small rate coefficients at low temperature measured with modern methods and on the spare high temperature values. For the reaction leading to \( \text{OH} + \text{OH} \), the recommendation of Tsang and Hampson\(^\text{14}\) is adopted which is similar to the recommendation of Warnatz\(^\text{14}\).

For clarity, rate data measured before 1972 are included in the Arrhenius plot (see Baulch et al.\(^\text{11}\) for Ref.).

References

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

H + HO₂ → H₂ + O₂

T/K

Log(κ/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1})

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

EXPERIMENTAL DATA

Sridharon et al. 1982
Hackett et al. 1978
Day et al. 1973
Baldwin et al. 1974
Westenberg and DeHaas 1972
Koywar 1977
Pratt and Wood 1983
Baldwin and Walker 1979
Clyne and Thrush 1963
Albers 1969

Dodge and Thrush 1966
Dodd et al. 1969
Dixon-Lewis et al. 1970
Bennet and Blackmore 1971

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\[ H + HO_2 \rightarrow OH + OH \]

**Experimental Data**
- Sridharan et al. 1982
- Hock et al. 1978
- Day et al. 1973
- Baldwin et al. 1974
- Westenberg and DeHaas 1972
- Keyser 1986
- Pratt and Wood 1983
- Baldwin and Walker 1979
- Burgess and Rabbit 1958
- Semenov 1959
- Dixon-Lewis and Williams 1962
- Baldwin et al. 1967
- Albers 1989
- Brown et al. 1969
- Getzinger (Dove et al. 1969) 1969

**This Recommendation 1989**

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EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

$H + HO_2 \rightarrow H_2O + O$

$T / K$

Log($k$/cm$^3$/molecule$^{-1}$/s$^{-1}$) vs. $10^3T^{-1}/K^{-1}$

EXPERIMENTAL DATA:
- Sridharan et al. 1982
- Hock et al. 1978
- Day et al. 1973
- Baldwin et al. 1974
- Westenberg and DeHaas 1972
- Keyser 1986
- Baldwin and Walker 1986
- Clyne and Thrush 1963
- Albers 1969
- Dodanov et al. 1969

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Thermodynamic Data

\[ \Delta H_{\text{fus}} = 62.9 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{fus}} = 10.9 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_p = 8.85 \times 10^{0.84} \exp(-7680/T) \]

Rate Coefficient Data

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

Comments

(a) Flash photolysis of \(\text{H}_2\text{O}\); \([\text{OH}]\) by time resolved resonance fluorescence. Total pressures near 200 Torr. Experimental difficulties due to \(\text{H}\) atom diffusion.

(b) Shock tube; \(\text{H}\) atoms produced by flash photolysis of \(\text{H}_2\text{O}/\text{Ar}\) mixtures. \([\text{H}]\) as a function of time by atomic resonance absorption spectroscopy.

Preferred Values

\[ k = 7.5 \times 10^{-16} T^{1.8} \exp(-9270/T) \text{ cm}^3\text{ molecule}^{-1}\text{s}^{-1} \text{ over range 300–2500 K} \]

Reliability

\[ \Delta \log k = \pm 0.2 \text{ over range 300–2500 K} \]

Comments on Preferred Values

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

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

References

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

H + H₂O → OH + H₂

T/K

Log(k/cm³ molecule⁻¹ s⁻¹)

10³T⁻¹/K⁻¹

EXPERIMENTAL DATA

Madronich and Felder 1984
Fenimore and Jones 1958
Dixon-Lewis and Williams 1963
Dixon-Lewis et al 1965
Mayer et al. 1967
Michael and Sutherland 1988
This Recommendation 1989

H + H₂O₂ → HO₂ + H₂ (1)
→ OH + H₂O (2)

**Thermodynamic Data**

<table>
<thead>
<tr>
<th></th>
<th>ΔH‡\text{sw} (1) = -71.4 kJ mol⁻¹</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>ΔS‡\text{sw} (1) = 12.1 J K⁻¹mol⁻¹</td>
</tr>
<tr>
<td>( k_0 (1) )</td>
<td>5.65·10⁻² T⁻¹exp(+8310/T)</td>
</tr>
</tbody>
</table>

\[ \Delta H_{\text{sw}}(2) = -285 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{sw}}(2) = 24.8 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ k_0(2) = 1.59·10^{-18} T^{-1.94} \exp (+33700/T) \]

**Rate Coefficient Data (k = k₁ + k₂)**

<table>
<thead>
<tr>
<th>( k[\text{cm}^{3} \text{ molecule}^{-1} \text{ s}^{-1}] )</th>
<th>( T[\text{K}] )</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_2 / k_1 = 10 )</td>
<td>870–1000</td>
<td>Kijewski and Troe (1971)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>( k_2 / k_1 = 3.0 )</td>
<td>298</td>
<td>Gorse and Volman (1974)(^2)</td>
<td>(b)</td>
</tr>
<tr>
<td>( k_2 / k_1 = 1.3 )</td>
<td>798</td>
<td>Heicklen and Meagher (1974)(^3)</td>
<td>(c)</td>
</tr>
<tr>
<td>( (E_F-E_D) / R = 2030 \text{ K} )</td>
<td>294–753</td>
<td>Baldwin et al. (1974)(^4)</td>
<td>(d)</td>
</tr>
<tr>
<td>( A_2 / A_1 = 100 )</td>
<td>5.2·10⁻¹² \exp(-1400/T)</td>
<td>Klemm et al. (1975)(^5)</td>
<td>(e)</td>
</tr>
</tbody>
</table>

**Reviews and Evaluations**

| \( k_2 = 2.8·10⁻¹² \exp(-1890/T) \) | 300–800     | Baulch et al. (1972)\(^6\)          |         |
| \( k_2 = 3.7·10⁻⁹ \exp(-5906/T) \) | 400–800     | Warnatz (1984)\(^7\)               |         |
| \( k_2 = 2.8·10⁻¹² \exp(-1890/T) \) | 300–800     |                                   |         |
| \( k_2 = 1.7·10⁻¹⁰ \exp(-1805/T) \) | 300–1000    |                                   |         |
| \( k_2 = 8.0·10⁻¹⁰ \exp(-4005/T) \) | 300–2500    | Tsang and Hampson (1986)\(^8\)  |         |
| \( k_2 = 4.0·10⁻¹⁰ \exp(-2000/T) \) | 300–2500    |                                   |         |

**Comments**

(a) Thermal decomposition of H₂O₂ behind reflected shock waves in Ar carrier gas (density = 5·10⁻⁵ mol cm⁻³) with added H₂, [H₂O₂] by absorption measurements at 280 nm, [H₂O₂] by absorption at 230 nm. Relative rate estimated from the maximum H₂O yield in the quasi-stationary period of the reaction. Computer simulations of the system were only successful with \( k_1 \) > 1.7·10⁻¹³ cm³ molecule⁻¹ s⁻¹.

(b) Photolysis of H₂O₂ at 254 nm in the presence of CO₂ mass spectrometric analysis. \( k_2 / k_1 \) derived from relative yields of CO₂ and H₂.

(c) Photolysis of H₂O₂ at 253.7 nm in the presence of CO. Rate of CO₂ production monitored by quadrupole mass spectrometry. Total pressure near 50 Torr N₂.

(d) Combination of the results of Baldwin et al.\(^9\) with those of Albers et al.\(^10\) for H₂O₂ + D assuming small isotopic effects.

(e) VUV flash photolysis of H₂O₂/He to yield H. [H] monitored by Lyman-α resonance fluorescence. Below 1000 K channel (2) was found to be predominant.

**Preferred Values**

<table>
<thead>
<tr>
<th>( k_1 )</th>
<th>( 2.8·10⁻¹² \exp(-1890/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_2 )</td>
<td>( 1.7·10⁻¹⁰ \exp(-1800/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} )</td>
</tr>
</tbody>
</table>

\[ \Delta \log k_1 = \pm 0.3 \text{ over range 300–1000 K} \]
\[ \Delta \log k_2 = \pm 0.3 \text{ over range 300–1000 K} \]

**Reliability**

**Comments on Preferred Values**

The values preferred by Warnatz\(^7\) have been adopted. The arguments given there are accepted, and the values measured after 1984 do not contradict this recommendation.

For clarity, rate data measured before 1972 are included in the Arrhenius plot (see Baulch et al.\(^6\) for Ref.).

**References**

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ H + \text{H}_2\text{O}_2 \rightarrow \text{H}_2 + \text{HO}_2 \]

\[ T/K \]

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

\[ 10^3T^{-1}/\text{K}^{-1} \]

EXPERIMENTAL DATA
- Gorse and Voiman 1974
- Baldwin and Walker 1970
- Heicklen and Meagher 1974
- Foner and Hudson 1982
- Baldwin et al. 1970
- Albers et al. 1971
- Kijewski and True 1971
- This recommendation 1989

H + H₂O₂ → H₂O + OH

**BAULCH ET AL.**

![Graph showing the reaction rate constant as a function of temperature.](image)

Log($k$/cm³ molecule⁻¹ s⁻¹) vs. $10^3 T^{-1}$/K⁻¹

**EXPERIMENTAL DATA**

- Gorse and Volman 1974
- Klemm et al. 1975
- Michael et al. 1977
- Baldwin and Walker 1979
- Heicklen and Meagher 1974
- Geb 1934
- Forst and Gigure 1958
- Baldwin and Mayor 1960
- Sotakiewicz et al. 1997
- Baldwin et al. 1970
- Kijewski and Troe 1971

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EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

H + NH → H₂ + N

Thermodynamic Data (See Comments on Preferred Values)

\[ \Delta H_{\text{f,m}} = -102 \text{kJ mol}^{-1} \]
\[ \Delta S_{\text{f,m}} = -12.0 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ K_p = 0.497 T^{-0.168} \exp\left(\frac{12200}{T}\right) \]

Rate Coefficient Data

<table>
<thead>
<tr>
<th>( k ) [cm³ molecule⁻¹ s⁻¹]</th>
<th>( T ) [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate Coefficient Measurements</td>
<td>( \approx 1.7 \times 10^{-11} )</td>
<td>1790–2200</td>
<td>Morley (1981)¹</td>
</tr>
<tr>
<td>Reviews and Evaluations</td>
<td>( \approx 5 \times 10^{-11} )</td>
<td>1790–2200</td>
<td>Hanson and Salimian (1984)²</td>
</tr>
</tbody>
</table>

Comments

(a) \( \text{H}_2/\text{O}_2/\text{Ar} \) flames doped with \( \text{CH}_3\text{CN} \). [NH] monitored by laser induced fluorescence. Accuracy limited by calibration for NH. \( k \) also calculated from the results of Haynes³ assuming mole fraction of \( \text{H}_2 = 5.7 \times 10^{-2} \)
and \( K = 3 \) in his conditions.
(b) Review of experimental measurements. Recommends value of Morley¹.

Preferred Values

\( k = 1.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) over range 1500–2500 K

Reliability

\( \Delta \log k = \pm 1.0 \) over the range 1500–2500 K

Comments on Preferred Values

The only experimental determinations are those of Morley¹ and of Haynes³ recalculated by Morley¹.

Thermodynamic Data

\[ \Delta H_{\text{f,m}} = -51.9 \text{kJ mol}^{-1} \]
\[ \Delta S_{\text{f,m}} = 2.54 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ K_p = 5.24 T^{-0.158} \exp\left(\frac{6090}{T}\right) \]

Rate Coefficient Data

<table>
<thead>
<tr>
<th>( k ) [cm³ molecule⁻¹ s⁻¹]</th>
<th>( T ) [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reviews and Evaluations</td>
<td>( 5.0 \times 10^{-11} \exp\left(-\frac{4600}{T}\right) )</td>
<td>1800–3000</td>
<td>Baulch et al. (1974)⁴</td>
</tr>
<tr>
<td></td>
<td>( 3.16 \times 10^{-11} )</td>
<td>2400–3000</td>
<td>Lesclaux (1984)²</td>
</tr>
</tbody>
</table>

Comments

(a) Review of data to 1973. Alternative addition channel yielding \( \text{NH}_3 \) assumed dominant.
(b) Evaluation. Value of \( k \) based on Yumura et al.⁶.
(c) Review of data.

d \( k = 1.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) over range 2000–3000 K

Reliability

\( \Delta \log k = \pm 1.0 \) over the range 2000–3000 K

References

Comments on Preferred Values

All of the available data have been reviewed\textsuperscript{1,2,3}. At low temperatures there are two measurements of \( k \) differing by a factor of 4. There is an alternative channel (\( H + NH_3 + M \rightarrow NH_2 + M \)) which may be important at low temperatures (see data sheet on \( NH_3 + M \)). We make no recommendation for this temperature regime.

At high temperatures (1800-3000 K) the results from three studies\textsuperscript{5,6,7} of shock tube pyrolysis of \( NH_3 \) scatter over an order of magnitude. Two of these\textsuperscript{5,7} depend upon measurements of \( k_1 \) and equilibrium data. The value of Roose\textsuperscript{5} plotted is a value which supersedes an older value from the same laboratory\textsuperscript{9}. The recommended value is based on the values from all three studies with substantial error limits.

The thermodynamic data should be used with caution. There may be significant errors in the data on \( NH_3 \).

References


\[ H + ^3CH_2 \rightarrow H_2 + CH \]

\textbf{Thermodynamic Data}

\[ \Delta H_{298} = -10.6 \text{kJ mol}^{-1} \]
\[ \Delta S_{298} = 3.44 \text{J K}^{-1}\text{mol}^{-1} \]
\[ K_p = 3.64 \times 10^{-11} \exp(1220/T) \]

\textbf{Rate Coefficient Data}

<table>
<thead>
<tr>
<th>( k ) [cm(^3) molecule(^{-1}) s(^{-1})]</th>
<th>( T ) [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.7\times10^{-10}</td>
<td>298</td>
<td>Böhland and Temps (1984)\textsuperscript{1}</td>
<td>(a)</td>
</tr>
<tr>
<td>1.3\times10^{-11}</td>
<td>2000-2800</td>
<td>Frank, Bhaskaran, and Just (1986)\textsuperscript{2}</td>
<td>(b)</td>
</tr>
<tr>
<td>1.8\times10^{-10}</td>
<td>298</td>
<td>Böhland, Temps, and Wagner (1987)\textsuperscript{3}</td>
<td>(a)</td>
</tr>
</tbody>
</table>

\textbf{Comments}

(a) Discharge flow with LMR detection of \(^3\)CH\(_2\). H produced from discharge through \( H_2 \), \(^3\)CH\(_2\) by discharge through ketene.
(b) Absorption spectroscopy study of H and CO following thermal dissociation of dilute ketene in argon behind reflected shocks.
(c) Based on Ref. 1.

\textbf{Preferred Values}

\[ k = 1.0 \times 10^{-11} \exp(+900/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range 300-3000 K} \]

\textbf{Reliability}

\[ \Delta \log k = \pm 0.7 \]

\textbf{Comments on Preferred Values}

Böhland \textit{et al.}\textsuperscript{5} demonstrated that, when their value is combined with the reverse rate coefficient of Zabarnick \textit{et al.}\textsuperscript{3}, an estimate of 389 kJ mol\(^{-1}\) is obtained for \( \Delta H_{298}(^3\text{CH}_2) \), in good agreement with the accepted value.

Frank \textit{et al.}\textsuperscript{2} argue that the rate coefficient must decrease with temperature and that a value as high as that of Böhland \textit{et al.}\textsuperscript{2} is not compatible with their high temperature data. Lühr and Roth\textsuperscript{6} found some evidence for a high temperature value of 5\times10^{-11} cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) but the technique was less direct than that of Frank \textit{et al.}, and subject to significant uncertainty. In view of the large discrepancy between the estimates of Refs. 2 and 3, a negative temperature dependence is proposed, compatible with a mechanism involving a CH\(_3\) association complex. Large uncertainties are attached.
EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ H + CH_3 \rightarrow H_2 + ^1CH_2 \]  \hspace{1cm} (1)
\[ H + CH_3 (+ M) \rightarrow CH_4 (+ M) \]  \hspace{1cm} (2)

\textbf{Thermodynamic Data}
\[ \Delta H^{298}_\text{f} (1) = 61.0 \text{ kJ mol}^{-1} \]
\[ \Delta S^{298}_\text{f} (1) = 10.7 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_p(1) = 23.7 T^{-0.57} \exp(-7640/T) \]
\[ \Delta H^{298}_\text{f} (2) = -439 \text{ kJ mol}^{-1} \]
\[ \Delta S^{298}_\text{f} (2) = -123 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_p(2) = 1.76 \times 10^{-4} T^{-1.06} \exp(+52700/T) \text{ atm}^{-1} \]

\textbf{Rate Coefficient Data}

<table>
<thead>
<tr>
<th>( k ) [cm(^3) molecule(^{-1}) s(^{-1})]</th>
<th>( T ) [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate Coefficient Measurements</td>
<td>( k_l = 3.0 \times 10^{-10} \exp(-7580/T) )</td>
<td>1700–2300</td>
<td>Bhaskaran \textit{et al.} (1979)(^1)</td>
</tr>
</tbody>
</table>

\textbf{Comments}

(a) Shock tube study using atomic resonance absorption spectroscopy.

\textbf{Preferred Values}

\[ k = 1.0 \times 10^{-10} \exp(-7600/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range 300–2500 K} \]

\textbf{Reliability}

\[ \Delta \log k = \pm 1.0 \]

\textbf{Comments on Preferred Values}

Combining the well established low temperature rate coefficient for the reverse reaction (1.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, this evaluation) with \( K_p \) gives \( k = 2.8 \times 10^{-9} T^{-0.93} \exp(-7640/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range 300–1000 K, a factor, at 1000 K, of } 6 \text{ below that predicted by extrapolation of the Arrhenius expression of Bhaskaran \textit{et al.}} \.) It is possible, although unlikely, that the rate coefficient for the reverse reaction increases with temperature. A preferred rate coefficient midway between the thermodynamic value and that of Bhaskaran \textit{et al.} has been adopted to accommodate this possibility.

\textbf{Reference}

**H + CH₃(+M) → CH₄(+M)**

**Thermodynamic Data**

\[ \Delta H_{298} = -439 \text{ kJ mol}^{-1} \]

\[ \Delta S_{298} = -123 \text{ J K}^{-1} \text{mol}^{-1} \]

\[ K_p = 1.76 \times 10^{-16} T^{-1/2} \exp(+52700/T) \text{ atm}^{-1} \]

---

**Rate Coefficient Data**

<table>
<thead>
<tr>
<th>( k [\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}] )</th>
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<th>( \text{[M]} [\text{molecule cm}^{-3}] )</th>
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<th>Comments</th>
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<tbody>
<tr>
<td><strong>Rate Coefficient Measurements</strong></td>
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<tr>
<td><strong>Low Pressure Range</strong></td>
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<tr>
<td>[He] 3.2 \times 10^{-12}</td>
<td>504</td>
<td>(4.8-76.7) \times 10^{17} (He)</td>
<td>Brouard et al. (1985)</td>
<td>(a)</td>
</tr>
<tr>
<td>[He] 4.0 \times 10^{-29}</td>
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<td>(4.5-163.5) \times 10^{17} (He)</td>
<td>Brouard et al. (1989)</td>
<td>(a)</td>
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<td><strong>Intermediate Fall-off Range</strong></td>
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<td>6.6 \times 10^{-12}</td>
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<td>(5.2-10.0) \times 10^{10} (Ar)</td>
<td>Brown et al. (1966)</td>
<td>(b)</td>
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<td>Dodonov et al. (1969)</td>
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<td>Michael et al. (1973)</td>
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<td>(i)</td>
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<td>(k)</td>
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<td>(k)</td>
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<td><strong>High Pressure Range</strong></td>
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<td>1.5 \times 10^{-10}</td>
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<td>(1.6-32.2) \times 10^{18} (Ar, SF₆)</td>
<td>Patrick et al. (1980)</td>
<td>(l)</td>
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<td>(a)</td>
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<td>Brouard et al. (1989)</td>
<td>(a)</td>
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<td><strong>Reviews and Evaluations</strong></td>
<td></td>
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<tr>
<td>( k_o = [\text{Ar} \times 2.2 \times 10^{-21} T^{-3} \text{ s}^{-1}] )</td>
<td>300-2500</td>
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<td>Warnatz (1984)</td>
<td>(m)</td>
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<td>( k_o = 1.0 \times 10^{-7} T^{-1} )</td>
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<tr>
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<td>300-1100</td>
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<td>Tsang and Hampson (1986)</td>
<td>(n)</td>
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</table>
Comments

(a) 193 nm photolysis of acetone, [CH₃] and [H] by time-resolved UV absorption and resonance fluorescence respectively. [CH₃] >> [H]. kₐ by RRKM/master equation fit.

(b) Discharge flow study of H + C₂H₄ system. CH₃ generated by H + C₂H₃ → 2 CH₄. ESR detection of H. Relied on Toby and Schiff's product yield analysis to interpret data.

(c) Mass spectrometric study of species distribution in diffusion cloud; CH₃ generated from H + C₂H₆, H + C₂H₅, H generated in discharge.

(d) Discharge flow study of H + C₂H₄ system; used GC analysis of CH₃, C₂H₆, CH₃, C₂H₄, and C₂H₆.

(e) Discharge flow study of H + C₂H₄ system; products analysed by GC and simulated by numerical integration.


(g) Discharge flow study of H + C₂H₄ system. GC detection of CH₃, C₂H₆, and C₂H₄. Rate coefficients from fitting the reaction scheme using numerical integration. Assumed k₁ independent of temperature.

(h) Discharge flow study of H + C₂H₄ system. Products detected by mass spectrometry. Rate coefficients by fitting 7 reaction scheme using numerical integration.

(i) Steady-state Hg photosensitisation of C₂H₆. Products detected by mass spectrometry. kₐ by Lindemann plot.

(j) Discharge flow study of H + CH₄ system. Products detected by gas chromatography. Rate coefficients from numerical integration of 14 reaction scheme.

(k) 160 nm photolysis of H₂O/CH₄ mixtures. CH₃ detected as function of time at 216 nm. Rate coefficient determined by fitting to 11 reaction scheme with H₂ and N₂ 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 CH₃ + CH₃ and low rate coefficient was used for CH₃ recombination, (ii) H + azomethane was neglected. kₐ by RRKM fit.

(m) Review of literature prior to 1980.

(n) The results of Cheng et al.¹¹, Sworski et al.¹³, and Patrick et al.¹⁴ have been combined with the reverse rate determination of Chen et al.²⁵ to derive the recommended expression. A tabulation of log k/kₐ over the temperature range 300–2500 K from RRKM calculations is also given.

(o) Single-channel hindered Gorin model RRKM calculations of the CH₄ decomposition with a fit to experimental results. Conversion to kₐ via the equilibrium constant.

(p) The results of Cheng et al.¹¹, Sworski et al.¹³, and Patrick et al.¹⁴ have been combined with the reverse rate determination of Chen et al.²⁵ to derive the recommended expression.

(q) Theoretical calculation based on kₐ calculations from Ref. 21, the representation of fall-off curves from Ref. 22, and the kₐ treatment from Ref. 23. Collision efficiencies βₑ at 300 K of 0.07 for M = He and of 0.15 for M = C₂H₆ point to particularly inefficient energy transfer for which <ΔE> values may increase proportional to the temperature. Therefore, the temperature coefficient of kₐ at T ≤ 1000 K was chosen as in the strong collision limit, i.e., assuming βₑ to be temperature independent. The temperature coefficient of kₐ was derived from SACP-modified PST calculations of Ref. 23 which also predicts the absolute value of kₐ to be as recommended. The broadening factors contain a considerable weak collision contribution, strong collision broadening factors being given by Fₑ = exp(−0.09−T/3316).

Preferred Values

\[
\begin{align*}
k₀ &= [\text{He}] 6.2 \times 10^{−29} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range } 300–1000 \text{ K} \\
k₀ &= [\text{Ar}] 6.0 \times 10^{−29} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range } 300–1000 \text{ K} \\
k₀ &= [\text{C}_2\text{H}_6] 3.0 \times 10^{−28} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range } 300–1000 \text{ K} \\
kₐ &= 3.5 \times 10^{−10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range } 300–1000 \text{ K} \\
Fₑ &= \exp(−0.45−T/3231) \text{ for } M = \text{He, Ar} \\
Fₑ &= \exp(−0.34−T/3053) \text{ for } M = \text{C}_2\text{H}_6
\end{align*}
\]

Reliability
\[ \Delta \log k_0 = \pm 0.3 \text{ for } M = \text{He over range } 300-1000 \text{ K} \]
\[ \Delta \log k_0 = \pm 0.5 \text{ for } M = \text{Ar, C}_2\text{H}_6 \text{ over range } 300-1000 \text{ K} \]
\[ \Delta F_c = \pm 0.1 \text{ over range } 300-1000 \text{ K} \]

Comments on Preferred Values
The preferred values are chosen from a comparison of a recent theoretical modelling by Cobos and Troe with the most extensive experimental data from Pilling and coworkers for the bath gas He. This model points to comparably low \( \beta_3 \) and \( \langle \Delta E \rangle \) values such that a positive temperature coefficient of \( \langle \Delta E \rangle \) and a temperature independent \( \beta_3 \), in agreement with the fit to the experiments appears not unconceivable. The high pressure limit is based mainly on the data by Cheng and Yeh in accord with the theoretical prediction from Ref. 23. The values for \( M = \text{Ar} \) are uncertain, Ref. 3 indicating a larger \( k_0 \) value than for \( M = \text{He} \) which is in contrast to the more detailed results from Ref. 5. More experiments close to the low and high pressure limits are required to arrive at a conclusive picture.

References
EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

$\text{CH}_3 + \text{H} + \text{He} \rightarrow \text{CH}_4 + \text{He}$

**EXPERIMENTAL DATA**

- Brouard et al., 301K 1989
- Brouard et al., 401K 1989
- Brouard et al., 504K 1989
- Brouard et al., 601K 1989
- Chang and Yeh (M = C$_2$H$_4$), 1989

---

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

**Log ([M]/molecules cm$^{-3}$)**

Thermodynamic Data

$$\Delta H_{298} = 2.6 \text{ kJ mol}^{-1}$$
$$\Delta S_{298} = 24.0 \text{ J K}^{-1} \text{ mol}^{-1}$$
$$K_{p} = 1.81 \times 10^{16} T^{-0.225} \exp(-638/T)$$

Rate Coefficient Data

<table>
<thead>
<tr>
<th>Rate Coefficient Measurements</th>
<th>Temperature [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.7 \times 10^{-14} \exp(-2265/T)$</td>
<td>372-436</td>
<td>Bertie and LeRoy (1954)$^1$</td>
<td>(a)</td>
</tr>
<tr>
<td>$6.3 \times 10^{-11} \exp(-5185/T)$</td>
<td>1150-1900</td>
<td>Fenimore and Jones (1961)$^2$</td>
<td>(b)</td>
</tr>
<tr>
<td>$1.15 \times 10^{-10} \exp(-5539/T)$</td>
<td>426-747</td>
<td>Kurylo and Timmons (1969)$^3$</td>
<td>(c)</td>
</tr>
<tr>
<td>$1.04 \times 10^{-10} \exp(-5838/T)$</td>
<td>500-732</td>
<td>Kurylo, Hollinden, and Timmons (1970)$^4$</td>
<td>(d)</td>
</tr>
<tr>
<td>$5.33 \times 10^{-12} \exp(-2265/T)$</td>
<td>1600</td>
<td>Peeters and Mahnen (1970)$^5$</td>
<td>(e)</td>
</tr>
<tr>
<td>$3.55 \times 10^{-19} T^3 \exp(-8889/T)$</td>
<td>1300-1750</td>
<td>Biordi, Papp, and Lazzara (1974)$^6$</td>
<td>(f)</td>
</tr>
<tr>
<td>$1.02 \times 10^{-11} \exp(-5185/T)$</td>
<td>1700</td>
<td>Biordi, Papp, and Lazzara (1975)$^7$</td>
<td>(g)</td>
</tr>
<tr>
<td>$1.2 \times 10^{-10} \exp(-7580/T)$</td>
<td>1700-2300</td>
<td>Roth and Just (1975)$^8$</td>
<td>(h)</td>
</tr>
<tr>
<td>$3.02 \times 10^{-10} \exp(-6627/T)$</td>
<td>640-818</td>
<td>Peeters and Mahnen (1973)$^9$</td>
<td>(i)</td>
</tr>
<tr>
<td>$5.33 \times 10^{-12} \exp(-2265/T)$</td>
<td>1300-1750</td>
<td>Biordi, Papp, and Lazzara (1974)$^6$</td>
<td>(j)</td>
</tr>
<tr>
<td>$3.55 \times 10^{-19} T^3 \exp(-8889/T)$</td>
<td>1300-1750</td>
<td>Biordi, Papp, and Lazzara (1974)$^6$</td>
<td>(k)</td>
</tr>
<tr>
<td>$1.02 \times 10^{-11} \exp(-5185/T)$</td>
<td>1700</td>
<td>Biordi, Papp, and Lazzara (1975)$^7$</td>
<td>(l)</td>
</tr>
<tr>
<td>$1.2 \times 10^{-10} \exp(-7580/T)$</td>
<td>1700-2300</td>
<td>Roth and Just (1975)$^8$</td>
<td>(m)</td>
</tr>
<tr>
<td>$3.02 \times 10^{-10} \exp(-6627/T)$</td>
<td>640-818</td>
<td>Peeters and Mahnen (1973)$^9$</td>
<td>(n)</td>
</tr>
</tbody>
</table>

Comments

(a) Only low temperature data available; $k$ values more reliable than A and E. H atoms measured by catalytic recombination.

(b) Low pressure flames. $k$ determined relative to $k(H + N_2O)$ for which $1.26 \times 10^{-10} \exp(-7600/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$ is used$^{15}$.

(c) Flow discharge; ESR detection of H atoms.

(d) Flow discharge; ESR detection of H atoms; excellent agreement with authors’ earlier results.

(e) Flame study; molecular beam sampling, mass spectrometric detection of all species.

(f) Low pressure flames, modulated molecular beam with mass spectrometric detection. Authors do not quote $k$ values; Arrhenius parameters determined from published graph.

(g) CF$_3$Br-inhibited CH$_4$ flames, techniques as in (f).

(h) Shock tube–resonance fluorescence study of CH$_4$ pyrolysis.

(i) Discharge flow; computer fit to C$_3$H$_6$ yields determined by gas chromatography.

(j) Reviews early work critically and discusses reliability of data.

(k) Simplified BEBO form of calculating $k$ values. Gave good fit to reliable data between 300 and 1800 K.

(l) Non-critical review of rate constants; useful coverage of data up to 1978.

Preferred Values

$$k = 2.18 \times 10^{-20} T^{10} \exp(-4045/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over range 300-2000 K

Reliability

$$\Delta \log k = \pm 0.05$$ over range 500–1000 K rising to $\pm 0.1$ at 2000 K and $\pm 0.2$ at 2500 K

$$= \pm 0.2$$ at 300 K

Comments on Preferred Values

Extensive literature on this reaction is available. Walker$^{10}$ has shown that a number of early studies are unreliable. The value of $k$ is defined very accurately between 500 and 2000 K, but no reliable data are available at room temperature. The preferred expression gives a slightly better fit to the high temperature data than Clark and Dove’s, but the two expressions give very similar rate constants at all temperatures and both involve a $T^3$ term.
EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

References

BAULCH ET AL.

H + CH₄ → CH₃ + H₂

T/K

EXPERIMENTAL DATA

Berle and LeRoy 1954
Fenimore and Jones 1961
Kurylo and Timmons 1969
Kurylo et al 1970
Blandi et al 1974
Shoemaker and Mahnen 1973
Blandi et al 1975
Roth and Just 1975
Szephred et al 1979
Azaryan et al 1964
Dixon-Lewis and Williams 1967
Bustard and Dyer 1970
Overend 1971
Arai et al 1981
Gorban and Nalbandyan 1962
Karpilov and Vovkonskii 1965
Takeshita and Tseng 1986
Walker 1985
Baldwin et al 1970
Nalbandyan and Gorban 1961
Baldwin et al 1977
Geller and Khayat 1965
Bock and Van Der Auwer 1962
Azaryan 1967
This Recommendation 1989

## EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

### H + CHO → CO + H₂

#### Thermodynamic Data

\[ \Delta H_{298} = -372 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298} = -11.0 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_p = 11.4 \times 10^{-209} \exp\left(\frac{+44500}{T}\right) \]

#### Rate Coefficient Data

<table>
<thead>
<tr>
<th>Rate Coefficient Measurements</th>
<th>T[K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k ) [cm³ molecule⁻¹ s⁻¹]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.3 × 10⁻¹⁰</td>
<td>1000-1700</td>
<td>Browne et al. (1969)¹</td>
<td>(a)</td>
</tr>
<tr>
<td>( k ) / k_{CHO + O} = 3</td>
<td>300</td>
<td>Niki, Daby, and Weinstock (1969)²</td>
<td>(b)</td>
</tr>
<tr>
<td>( k ) / k_{CHO + O} = 4.0</td>
<td>298</td>
<td>Mack and Thrush (1973)³</td>
<td>(c)</td>
</tr>
<tr>
<td>( k ) / k_{CHO + O} = 2.1</td>
<td>425</td>
<td>Campbell and Handy (1978)⁴</td>
<td>(d)</td>
</tr>
<tr>
<td>( k ) / k_{CHO + O} = 1.5</td>
<td>3.5 × 10⁻¹⁰</td>
<td>Reilly et al. (1978)⁵</td>
<td>(e)</td>
</tr>
<tr>
<td>( k ) / k_{CHO + O} = 1.0</td>
<td>2.9 × 10⁻¹⁰</td>
<td>Nadtochenko, Sarkisov, and Vedeneev (1979)⁶</td>
<td>(f)</td>
</tr>
<tr>
<td>( k ) / k_{CHO + O} = 0.8</td>
<td>2.6 × 10⁻¹⁰</td>
<td>Hochanadel, Sworsky, and Ogren (1980)⁷</td>
<td>(g)</td>
</tr>
<tr>
<td>( k ) / k_{CHO + O} = 0.6</td>
<td>2.9 × 10⁻¹¹</td>
<td>Cherian et al. (1981)⁸</td>
<td>(h)</td>
</tr>
<tr>
<td>( k ) / k_{CHO + O} = 0.4</td>
<td>3.5 × 10⁻¹¹</td>
<td>Timonen, Ratajczak, and Gutman (1987)⁹</td>
<td>(i)</td>
</tr>
<tr>
<td>( k ) / k_{CHO + O} = 0.2</td>
<td>4.1 × 10⁻¹¹</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### Reviews and Evaluations

- 3.3 × 10⁻¹⁰: 300-2500 | Warnatz (1984)¹⁰ |
- 2.0 × 10⁻¹⁰: 300-2500 | Tsang and Hampson (1986)¹¹ |

#### Comments

(a) Modelling of lean and rich acetylene flames at low pressures. Species profiles by gas chromatography, [OH], [CH], and [C₂] by absorption measurements.

(b) C₂H₄/O discharge-flow system; mass spectrometry. Total pressure 1-2.3 Torr.

(c) Discharge-flow system; CH₃/O reaction; gas chromatography, air afterglow chemiluminescence observed, [O] and [H] by electron spin resonance. Total pressure = 1.5-3 Torr.

(d) Stirred flow reactor, microwave discharge of N₂; CHO formed by addition of various amounts of CO to O/H₂ mixtures. [O] from O + CO chemiluminescence. Total densities = (1-3)×10⁻⁴ mol cm⁻³ Ar or N₂.

(e) Near-UV pulsed photolysis of CH₂O; intracavity dye laser spectroscopy of CHO absorption at either 613.8 nm or 614.5 nm. Total pressure 10 Torr pure CH₂O. Numerical solution of a kinetic scheme and fitting of rates to experimental data; results are rather insensitive to k.

(f) Pulsed photolysis of CH₂CHO/Ar at 10-200 Torr; intracavity dye laser spectroscopy of CHO absorption.

(g) Flash photolysis of H₂O or H₂O/CO (CH₄ or H₂) mixtures at 1-3 atm; UV absorption of CHO at 230 nm and of CH₃ at 213 nm monitored. Numerical integration of 17 reaction mechanism.

(h) Numerical modelling of burning velocities of flat H₂/O₂/N₂ flames at atmospheric pressure using a 27 reaction mechanism and assuming zero activation energy for k.

(i) Pulsed laser photolysis of CH₃CHO/H/He mixtures at 308 nm; H atoms from microwave discharge. Mass spectrometry, [H] monitored by NO titration.

\[ k = 1.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range 300–2500 K} \]

#### Preferred Values

Reliability

\[ \Delta \log k = \pm 0.3 \text{ over range 300–2500 K} \]

Comments on Preferred Values

The preferred values are based on the expectation that the rate coefficient will have a negligibly small temperature coefficient and on the reasonable concordant values of \( k \) at 298 K. The assumption of a small temperature coefficient is supported by the high value found for k at 298 K and the few high temperature values indicating little change with temperature.

#### References

BAULCH ET AL.

\[ \text{H} + \text{CHO} \rightarrow \text{CO} + \text{H}_2 \]

\[ \frac{\text{T}}{\text{K}} \]

**Graphical Representation**

The graph shows the logarithm of the rate constant (\(k/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}\)) plotted against the reciprocal of the temperature in Kelvin (\(10^3T^{-1}/\text{K}^{-1}\)) for the reaction \(\text{H} + \text{CHO} \rightarrow \text{CO} + \text{H}_2\). The data points represent various experimental studies:

- Niki et al. 1969
- Manuel and Thrush 1973
- Combs and Handy 1978
- Reilly et al. 1978
- Nadtochenko et al. 1979
- Hochanadel et al. 1980
- Chertov et al. 1981
- Tsimen et al. 1987
- Browne et al. 1969
- This Recommendation 1989

**Experimental Data**

The graph includes various symbols representing different experimental data points. The data is spread across a range of temperatures, with the rate constant values decreasing as the temperature increases. The graph also includes a line representing the recommendation from 1989.
EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

H + HCHO → H₂ + CHO

Thermodynamic Data
\[ \Delta H_{\text{fus}} = -58.5 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{fus}} = 21.9 \text{ J K}^{-1} \text{ mol}^{-1} \]
\[ k_p = 3.8 \times 10^{-12} \exp(+6730/T) \]

Rate Coefficient Data

<table>
<thead>
<tr>
<th>( k ) [cm³ molecule⁻¹ s⁻¹]</th>
<th>( T ) [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3 \times 10^{-11} \exp(-1660/T)</td>
<td>1400-2200</td>
<td>Schechter and Jost (1969)¹</td>
<td>(a)</td>
</tr>
<tr>
<td>2.2 \times 10^{-11} \exp(-1892/T)</td>
<td>297-652</td>
<td>Westenberg and de Haas (1972)²</td>
<td>(b)</td>
</tr>
<tr>
<td>5.4 \times 10^{-14}</td>
<td>297</td>
<td>Ridley et al. (1972)³</td>
<td>(c)</td>
</tr>
<tr>
<td>3.3 \times 10^{-11} \exp(-1847/T)</td>
<td>264-479</td>
<td>Klemm (1979)⁴</td>
<td>(d)</td>
</tr>
<tr>
<td>5.5 \times 10^{-14} \exp(-5280/T)</td>
<td>1700-2500</td>
<td>Dean et al. (1980)⁵</td>
<td>(e)</td>
</tr>
<tr>
<td>4.2 \times 10^{-11} \exp(-2009/T)</td>
<td>300-2500</td>
<td>Warnatz (1984)⁶</td>
<td>(f)</td>
</tr>
<tr>
<td>3.6 \times 10^{-14} T^{1.77} \exp(-1510/T)</td>
<td>264-2500</td>
<td>Tsang and Hampson (1986)⁷</td>
<td>(g)</td>
</tr>
</tbody>
</table>

Comments

(a) Thermal dissociation of HCHO/Ar in a shock tube; species monitored by UV absorption and IR emission.

(b) Microwave discharge of H₂/He; behaviour of H atoms in the presence of excess HCHO determined by ESR.

(c) Pulsed vacuum UV photolysis of HCHO; behaviour of H atoms in the presence of excess HCHO determined by Lyman α resonance fluorescence.

(d) Flash photolysis; resonance fluorescence detection of H atoms.

(e) HCHO/O₂/Ar and HCHO/N₂O/Ar mixtures investigated in reflected shock waves; HCHO detected by IR emission.

(f) Based on low temperature data of Westenberg and de Haas², Ridley et al.³, and Klemm⁴, which are in good agreement, and the high temperature data of Schechter and Jost¹.

(g) Based on the data of Westenberg and de Haas², Ridley et al.³, Klemm⁴, and Dean et al.⁵, and fitted using transition state frequencies as defined from BEBO calculations.

Preferred Values

\[ k = 3.8 \times 10^{-14} T^{1.05} \exp(-1650/T) \text{ cm}³ \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range } 250-2200 \text{ K} \]

Reliability

\[ \Delta \log k = \pm 0.5 \text{ at } 2000 \text{ K reducing to } \pm 0.1 \text{ at } 300 \text{ K} \]

Comments on Preferred Values

The preferred values are based on the low temperature data of Ridley et al.³, Klemm⁴, and the high temperature data of Dean et al.⁵.

References

⁵A. M. Dean, R. L. Johnson, and D. C. Steiner, Comb. Flame 37, 41 (1980).
H + HCHO → H₂ + HCO

BAULCH ET AL.

T/K

Log(k/[cm³ molecule⁻¹ s⁻¹])

10³T⁻¹/K⁻¹

EXPERIMENTAL DATA
- Shechter and Jost 1969
- Westenberg and de Haas 1972
- Ridley et al. 1974
- Klamm 1979
- Dean et al. 1980
- This Recommendation 1989

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

H + CH₃O → H₂ + HCHO

**Thermodynamic Data**

\[ \Delta H_{\text{fus}} = -330 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{fus}} = 6.1 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ K_p = 2.12 \times 10^{-0.41} \exp (+41800/T) \]

<table>
<thead>
<tr>
<th>Rate Coefficient Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k [\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}] )</td>
</tr>
<tr>
<td>-----------------------</td>
</tr>
<tr>
<td><strong>Rate Coefficient Measurements</strong></td>
</tr>
<tr>
<td><strong>Reviews and Evaluations</strong></td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

**Comments**

(a) Discharge flow–mass spectrometric detection. Rate determined relative to \( k(C_2H_6 + H) \) for which this evaluation gives 6\times10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. Pressure = 1 \text{Torr}.
(b) Based on the work of Hoyermann et al.; uncertainty is a factor 3.

**Preferred Values**

\[ k = 3.0\times10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range 300–1000 K} \]

**Reliability**

\[ \Delta \log k = \pm 0.5 \text{ over range 300–1000 K} \]

\[ \text{H} + \text{HNCO} \rightarrow \text{NH}_2 + \text{CO} \quad \text{(1)} \]

**Thermodynamic Data**

\[ \Delta H_{\text{fus}} \text{(1)} = -34.0 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{fus}} \text{(1)} = -38.8 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ K_p \text{(1)} = 1.58\times10^6 \ T^{-0.41} \exp (+3610/T) \]

\[ \Delta H_{\text{fus}} \text{(2)} = 45.6 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{fus}} \text{(2)} = 9.39 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ K_p \text{(2)} = 23.6 \ T^{-0.70} \exp (-5640/T) \]

| Rate Coefficient Data (\( k = k_1 + k_2 \)) |
|----------------|----------------|-------------|
| \( k [\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}] \) | \( T [K] \) | Reference | Comments |
|----------------|----------------|-------------|
| **Rate Coefficient Measurements** | 2.3\times10^{-11} | 1700-1800 | Beer et al. (1981) | (a) |
| | 5.3\times10^{-13} | 1700-1800 | |

**Comments**

(a) Combustion of a 0.7% N No. 6 Fuel Oil with air in a furnace assembly, with on line gas analysis instruments (unspecified) for CO, CO₂, and O₂ measurement and a chemiluminescent analyser for NO analysis. The results were fitted to a 34 reaction mechanism from which the quoted values resulted.

\[ k_2 = 3.4\times10^{-10} \ T^{-0.27} \exp (-10190/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range 500–1000 K} \]

**Reliability**

\[ \Delta \log k = \pm 1.0 \text{ over range 500–1000 K} \]

References

Comments on Preferred Values

There are no direct experimental measurements of rate constants for either of the channels or the total reaction. The values tabulated are of doubtful quality.

Values of both $k_1$ and $k_2$ have been used in modelling high temperature systems (1600-1800 K) but all are from unpublished sources. In all cases $k_1$ has been assumed to be much larger than $k_2$.

Perry et al.\(^3\) have obtained a value for $k_2$ over the range 591-913 K which may be combined with the equilibrium data to give the expression for $k_2$ quoted above.

\[
H + NCO \rightarrow NH + CO \quad (1)
\]
\[
\rightarrow HCN + O \quad (2)
\]

**Thermodynamic Data (See Comments on Preferred Values)**

\[
\Delta H_{298}^° (1) = -131 \text{ kJ mol}^{-1}
\]
\[
\Delta S_{298}^° (1) = 32.0 \text{ J K}^{-1}\text{ mol}^{-1}
\]
\[
K_p (1) = 3.52 \times 10^4 T^{-1.29} \exp(15300/T)
\]

\[
\Delta H_{298}^° (2) = 6.95 \text{ kJ mol}^{-1}
\]
\[
\Delta S_{298}^° (2) = 16.0 \text{ J K}^{-1}\text{ mol}^{-1}
\]
\[
K_p (2) = 2.62 \times 10^7 T^{-0.33} \exp(-995/T)
\]

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

<table>
<thead>
<tr>
<th>$k$ [cm$^3$ molecule$^{-1}$ s$^{-1}$]</th>
<th>$T$ [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate Coefficient Measurements</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$1.74 \times 10^{-10} \exp(-1000/T)$</td>
<td>1400-1500</td>
<td>Louge and Hanson (1984)$^1$</td>
<td>(a)</td>
</tr>
</tbody>
</table>

Comments

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

Preferred Values

$k = 8.7 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ over range 1400-1500 K

Reliability

$\Delta \log k = \pm 0.5$ over range 1400-1500 K

Comments on Preferred Values

There is only one direct determination of $k$, that of Louge and Hanson$^1$. Although they derive a temperature coefficient for the reaction the temperature range covered is small and we therefore recommend a constant value of $k$ over the range 1400-1500 K with substantial error limits.

A number of other values of $k$ have been quoted in the literature and used in modelling a range of reaction systems$^{2,3,4,5}$. However, none of the systems studied was sufficiently sensitive to the chosen value of $k$ for these values to be considered in this evaluation.

There are no data on the branching ratios. Channel (1) is usually assumed to be more important than (2); the available data on $k_2$ and $K_p(2)$ support this. There are other channels possible leading to OH + CN and HCO + N but both are substantially endothermic.

The thermodynamic data given for channel (1) should be used with caution. There may be significant errors in the data for NH.

References

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[
\begin{align*}
H + C_2H_2 & \rightarrow H_2 + C_2H \\
H + C_2H_2( + M) & \rightarrow C_2H_3( + M)
\end{align*}
\]

(1) \quad (2)

Thermodynamic Data

\[
\begin{align*}
\Delta H^\text{ref} (1) &= 116 \text{ kJ mol}^{-1} \\
\Delta S^\text{ref} (1) &= 22.5 \text{ J K}^{-1}\text{mol}^{-1} \\
K_0 (1) &= 7.2 \times 10^3 \text{T}^{-1} \exp(-14300/T)
\end{align*}
\]

\[
\begin{align*}
\Delta H^\text{ref} (2) &= -158 \text{ kJ mol}^{-1} \\
\Delta S^\text{ref} (2) &= -84 \text{ J K}^{-1}\text{mol}^{-1} \\
K_0 (2) &= 0.412 \text{T}^{-1} \exp(+18900/T) \text{ atm}^{-1}
\end{align*}
\]

Rate Coefficient Data \((k = k_1)\)

<table>
<thead>
<tr>
<th>(k ) [cm(^3) molecule(^{-1})s(^{-1})]</th>
<th>(T ) [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(5 \times 10^{-12} )</td>
<td>1600</td>
<td>Porter et al. (1967)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>(9 \times 10^{-10} \exp(-9600/T))</td>
<td>1000-1700</td>
<td>Brown et al. (1969)(^2)</td>
<td>(b)</td>
</tr>
<tr>
<td>(8 \times 10^{-11} \exp(-8500/T))</td>
<td>1073-1700</td>
<td>Yampolskii et al. (1974)(^3)</td>
<td>(c)</td>
</tr>
<tr>
<td>(1.3 \times 10^{-17} \exp(-240/T))</td>
<td>1700-3400</td>
<td>Tanzawa and Gardiner (1978)(^4)</td>
<td>(d)</td>
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<tr>
<td>(1.7 \times 10^{-11} \exp(-9600/T))</td>
<td>2000</td>
<td>Warnatz et al. (1982)(^5)</td>
<td>(e)</td>
</tr>
</tbody>
</table>

Reviews and Evaluations

| \(1.3 \times 10^{-17} \exp(-12900/T)\) | 1850-3000 | Frank and Just (1980)\(^6\) | (f) |
| \(1 \times 10^{-10} \exp(-11900/T)\) | 300-3000 | Warnatz (1984)\(^7\) | (g) |
| \(1 \times 10^{-10} \exp(-11200/T)\) | | Tsang and Hampson (1986)\(^8\) | (h) |

Comments

(a) Acetylene and methane flames probed in absorption and emission. Assumed \(O_2\) removed exclusively by \(H + O_2 \rightarrow OH + O\).
(b) Probing of concentration, by absorption and emission spectroscopy, and temperature in acetylene flames. Numerical integration of complex mechanism.
(c) Pyrolysis of acetylene in presence of \(D_2\), \(CD_4\). Analysis by mass spectrometry. Assumed reaction (1) was sole mechanism for \(H_2\) production.
(d) Thermal decomposition of acetylene behind shock wave. Laser schlieren, computer modelling.
(e) Burner stabilised laminar flat \(C_2H_2/O_2/Ar\) flame. Sampling nozzle with mass spectrometric detection. Studied the formation of \(C_4H_2\).
(f) Reflected shock waves in \(C_2H_2/Ar\); atomic resonance absorption on \(H\). Data not sensitive to \(k\), but they review earlier data.
(g) Based on reverse reaction and thermodynamics. Took \(\Delta H^\text{ref}(1) = 87 \text{ kJ mol}^{-1}\text{and } k_{-1} = 2.5 \times 10^{-11} \exp(-1560/T) \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}\).
(h) Based on thermodynamics and \(k_{-1} = 1.9 \times 10^{-11} \exp(-1450/T) \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}\).

Preferred Values

\[ k_1 = 1 \times 10^{-12} \exp(-14000/T) \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}\text{over range } 1000-3000 \text{ K} \]

Reliability

\[ \Delta \log k_1 = \pm 1.0 \]

Comments on Preferred Values

The experimental investigations are very indirect, with the possible exception of that of Tanzawa and Gardiner\(^4\), and make sweeping assumptions. The most direct approach is to use thermodynamic data and \(k_{-1}\). The preferred value is based on \(k_{-1} = 2.5 \times 10^{-11} \exp(-1560/T) \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}\).

The value used for \(\Delta H^\text{ref}(1)\) corresponds to \(\Delta H^\text{ref}(C_2H) = 560 \text{ kJ mol}^{-1}\), which is consistent, within experimental error, with the value quoted by McMillen and Golden\(^9\) (564±4 kJ mol\(^{-1}\)) and with more recent spectroscopic data\(^10\).

References

H + C_2H_2 → H_2 + C_2H

\( T/K \)

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

EXPERIMENTAL DATA
- Porter et al. 1967
- Browne et al. 1969
- Yampolski et al. 1974
- Tonzawa and Gardiner 1978
- Warnatz et al. 1982
- This Recommendation 1989

\(10^3T^{-1}/K^{-1}\)

**EVALUATED KINETIC DATA FOR COMBUSTION MODELLING**

\[
H + C_2H_2 (+ M) \rightarrow C_2H_3 (+ M)
\]

**Thermodynamic Data**

\[\Delta H_{298} = -158 \text{ kJ mol}^{-1}\]
\[\Delta S_{298} = -84 \text{ J K}^{-1}\text{mol}^{-1}\]
\[K_p = 0.412 \text{ exp}(18900/T) \text{ atm}^{-1}\]

**Rate Coefficient Data**

<table>
<thead>
<tr>
<th>Rate Coefficient Measurements</th>
<th>Intermediate Fall-off Range</th>
<th>High Pressure Range</th>
<th>Reviews and Evaluations</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k ) [molecule(^{-1}) cm(^{-3}) s(^{-1})]</td>
<td>(T) [K]</td>
<td>([M]) [molecule cm(^{-2})]</td>
<td>Reference</td>
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<tr>
<td>2.3(\times)10(^{-14})</td>
<td>298</td>
<td>1.7(\times)10(^{16}) (He)</td>
<td>Michael and Niki (1967)(^1)</td>
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<tr>
<td>3.9(\times)10(^{-14})</td>
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<td>4.5(\times)10(^{16}) (He)</td>
<td>Hoyermann et al. (1968)(^2)</td>
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<tr>
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<td>7.1(\times)10(^{-14})</td>
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<td>3.0(\times)10(^{-13})</td>
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<td>5.8(\times)10(^{16})</td>
<td>Keil et al. (1976)(^3)</td>
</tr>
<tr>
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<td>6.9(\times)10(^{-14})</td>
<td>2.6(\times)10(^{16})</td>
<td>Payne and Stief (1976)(^4)</td>
</tr>
<tr>
<td>1.9(\times)10(^{-14})</td>
<td>1.9(\times)10(^{-14})</td>
<td>4.0(\times)10(^{16})</td>
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</tr>
<tr>
<td>1.4(\times)10(^{-14})</td>
<td>1.4(\times)10(^{-14})</td>
<td>4.2(\times)10(^{16})</td>
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<tr>
<td>3.7(\times)10(^{-14})</td>
<td>3.7(\times)10(^{-14})</td>
<td>2.1(\times)10(^{17})</td>
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</tr>
<tr>
<td>5.1(\times)10(^{-14})</td>
<td>5.1(\times)10(^{-14})</td>
<td>2.3(\times)10(^{17})</td>
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<td>3.2(\times)10(^{-14})</td>
<td>2.4(\times)10(^{17})</td>
<td></td>
</tr>
<tr>
<td>1.1(\times)10(^{-13})</td>
<td>1.1(\times)10(^{-13})</td>
<td>2.5(\times)10(^{17})</td>
<td></td>
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<tr>
<td>2.5(\times)10(^{-13})</td>
<td>2.5(\times)10(^{-13})</td>
<td>7.5(\times)10(^{17})</td>
<td></td>
</tr>
<tr>
<td>2.3(\times)10(^{-13})</td>
<td>2.3(\times)10(^{-13})</td>
<td>2.4(\times)10(^{18})</td>
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<td>1.7(\times)10(^{-13})</td>
<td>1.7(\times)10(^{-13})</td>
<td>1.7(\times)10(^{18})</td>
<td></td>
</tr>
</tbody>
</table>

**High Pressure Range**

\[3.8\times10^{-13}\text{exp}(1374/T)\]
\[1.4\times10^{-11}\text{exp}(1363/T)\]

<table>
<thead>
<tr>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sugawara et al. (1981)(^5)</td>
<td>(e)</td>
</tr>
<tr>
<td>Ellul et al. (1981)(^6)</td>
<td>(f)</td>
</tr>
<tr>
<td>Warnatz (1984)(^7)</td>
<td>(g)</td>
</tr>
<tr>
<td>Tsang and Hampson (1986)(^8)</td>
<td>(h)</td>
</tr>
</tbody>
</table>

**Preferred Values**

\[k_\infty = 1.4\times10^{-11}\text{exp}(-1300/T) \text{ cm}^{-3}\text{molecule}^{-1}\text{s}^{-1}\text{ over range 200-400 K}\]
\[k_0 = [\text{He}] 3.3\times10^{-39}\text{exp}(-740/T) \text{ cm}^{-3}\text{molecule}^{-1}\text{s}^{-1}\text{ over range 200-400 K}\]
\[F_e = 0.44 \text{ over range 200-400 K}\]

**Reliability**

\[\Delta\log k_\infty = \pm 0.3 \text{ over range 200-400 K}\]
\[\Delta\log k_0 = \pm 0.5 \text{ for over range 200-400 K}\]
\[\Delta\log F_e = \pm 0.1 \text{ over range 200-400 K}\]

**Comments**

(a) The reaction was studied in a fast discharge-flow system coupled to a time-of-flight mass spectrometer. The reaction mechanism was confirmed by an isotopic study.

(b) The reaction was investigated in a fast flow-system coupled to ESR and mass spectrometer.

(c) The reaction was studied in a conventional discharge flow reactor coupled to a time-of-flight mass spectrometer. RRKM treatment of the results.

(d) The technique of flash photolysis coupled with time resolved detection of H via resonance fluorescence was employed in this investigation.

(e) The reaction was investigated using the pulse radiolysis/resonance absorption technique.

(f) Pulsed photolysis/resonance absorption study. The reaction was followed monitoring 121.6 nm Lyman \(\alpha\) absorption.

(g) Data evaluation and simplified fall-off construction.

(h) Construction of RRKM fall-off curves.

Comments on Preferred Values

The preferred values are based on the experimental data from Ref. 4 and a construction of the corresponding fall-off curve from the present evaluation.

References


\[
\text{H} + \text{C}_2\text{H}_3 \rightarrow \text{H}_2 + \text{C}_2\text{H}_2 \quad (1)
\]

\[
\text{H} + \text{C}_2\text{H}_3 (\text{+ M}) \rightarrow \text{C}_2\text{H}_4 (\text{+ M}) \quad (2)
\]

Thermodynamic Data

\[
\begin{align*}
\Delta H_{\text{f},\text{m}}(1) &= -277 \text{ kJ mol}^{-1} \\
\Delta S_{\text{f},\text{m}}(1) &= 14.6 \text{ J K}^{-1} \text{mol}^{-1} \\
K_p(1) &= 7.75 \times 10^{-2} \text{ exp}(+33200/T) \text{ K atm}^{-1}
\end{align*}
\]

\[
\begin{align*}
\Delta H_{\text{f},\text{m}}(2) &= -452 \text{ kJ mol}^{-1} \\
\Delta S_{\text{f},\text{m}}(2) &= -127 \text{ J K}^{-1} \text{mol}^{-1} \\
K_p(2) &= 6.83 \times 10^{-5} \text{ T}^{-0.001} \text{ exp}(+54400/T) \text{ atm}^{-1}
\end{align*}
\]

Rate Coefficient Data

<table>
<thead>
<tr>
<th>( k [\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}] )</th>
<th>( T [\text{K}] )</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 = 7 \times 10^{-12} )</td>
<td>1170-1780</td>
<td>Benson and Haugen (1967)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>( k_1 = 3 \times 10^{-11} )</td>
<td>1100-1500</td>
<td>Skinner, Sweet, and Davis (1971)(^2)</td>
<td>(b)</td>
</tr>
<tr>
<td>( k_1 = 1 \times 10^{-11} )</td>
<td>298</td>
<td>Keil \textit{et al.} (1976)(^3)</td>
<td>(c)</td>
</tr>
<tr>
<td>( k_1 = 1.7 \times 10^{-11} )</td>
<td>1300-2500</td>
<td>Olson, Tanzawa, and Gardiner (1979)(^4)</td>
<td>(d)</td>
</tr>
</tbody>
</table>

Reviews and Calculations

| \( k_1 = 3 \times 10^{-11} \) | 300-2500 | Wamatz (1984)\(^5\) | (e) |
| \( k_1 = 1.6 \times 10^{-10} \) | - | Tsang and Hampson (1986)\(^6\) | (f) |

Comments

(a) Steady state analysis of the shock tube data of Skinner and Sokolski\(^7\) on H and H/D exchange with C\(_2\)H\(_3\) and its isotopomers.
(b) Shock tube study at 3 atm of H and H/D exchange with C\(_2\)H\(_3\), C\(_2\)H\(_2\), and their isotopomers. Steady state analysis.
(c) Analysis of effects of atom/radical reactions on H + C\(_2\)H\(_3\) system. Simulation by numerical integration and comparison of discharge flow – mass spectrometry, flash photolysis – resonance fluorescence and flash photolysis – resonance fluorescence experiments.
(d) Shock tube study of ethane dissociation in argon by laser schlieren. Numerical integration of a 14 reaction scheme.
(e) Evaluation based on tabulated data plus a privately communicated value from Hoyermann at 298 K of \(7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\).
(f) Estimate.

Reliability

\( \Delta \log k_1 = \pm 0.5 \)

Comments on Preferred Values

All of the determinations are very indirect, hence the wide error limits. The large exothermicity of reaction (1) suggests that there is a negligible probability of forming stabilised C\(_2\)H\(_4\) except under conditions of very high pressure.

References


Preferred Values

\( k_1 = 2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) over range 300-2500 K
EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

H + C₂H₄ → H₂ + C₂H₃  (1)
H + C₂H₄ (+ M) → C₂H₅ (+ M)  (2)

Thermodynamic Data

\[ \Delta H_{\text{f}}^{\circ} (1) = 15.8 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{f}}^{\circ} (1) = 28.3 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ K_p (1) = 4.67 \times 10^9 \; T^{-0.67} \exp(-2270/T) \]
\[ \Delta H_{\text{f}}^{\circ} (2) = -153 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{f}}^{\circ} (2) = -82.1 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ K_p (2) = 5.83 \times 10^{-2} \; T^{1.13} \exp(18300/T) \text{ atm}^{-1} \]

Rate Coefficient Measurements

<table>
<thead>
<tr>
<th>Rate Coefficient Measurements</th>
<th>T [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2 \times 10^{-13} \exp(-3000/T)</td>
<td>813</td>
<td>Baldwin, Simmons, and Walker (1966)⁵</td>
<td>(a)</td>
</tr>
<tr>
<td>1.0 \times 10^{-10} \exp(-7000/T)</td>
<td>1170-1780</td>
<td>Benson and Haugen (1967)²</td>
<td>(b)</td>
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<tr>
<td>2.6 \times 10^{-10} \exp(-1200/T)</td>
<td>1100-1500</td>
<td>Skinner, Sweet, and Davis (1971)¹</td>
<td>(c)</td>
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<tr>
<td>1.8 \times 10^{-10} \exp(-4300/T)</td>
<td>1200-1700</td>
<td>Peeters and Mahnen (1974)⁴</td>
<td>(d)</td>
</tr>
<tr>
<td>8.3 \times 10^{-10} \exp(-11500/T)</td>
<td>1700-2000</td>
<td>Just, Roth, and Damm (1977)⁵</td>
<td>(e)</td>
</tr>
<tr>
<td>7.10^{-14}</td>
<td>773</td>
<td>Baldwin et al. (1984)⁶</td>
<td>(f)</td>
</tr>
<tr>
<td>1.5 \times 10^{-13}</td>
<td>900</td>
<td>Jayaweera and Pacey (1988)⁷</td>
<td>(g)</td>
</tr>
</tbody>
</table>

Reviews and Evaluations

<table>
<thead>
<tr>
<th>Reviews and Evaluations</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5 \times 10^{-10} \exp(-5100/T)</td>
<td>700-2000</td>
<td>Warnatz (1984)⁶</td>
</tr>
<tr>
<td>2.2 \times 10^{-18} ; T^{2.55} \exp(-6160/T)</td>
<td>-</td>
<td>Tsang and Hampson (1986)⁹</td>
</tr>
</tbody>
</table>

Comments

(a) Inhibition of first and second limits of H₂ + O₂ reaction by C₂H₄. Assuming ‘reasonable’ A factor, they give \( k_1 = 1.7 \times 10^{-10} \exp(-4900/T) \).
(b) Reinterpretation of the data of Skinner and Sokolski⁸ on hydrogen, deuterium exchange in C₂H₄ and its isotopomers.
(c) Shock tube study of H, D exchange in C₂H₄ and its isotopomers. GC/MS analysis.
(d) Molecular beam – mass spectrometer sampling of C₂H₂/O₂ flames.
(e) Thermal decomposition of C₂H₄ in reflected shock waves. H atom profile by atomic resonance absorption spectroscopy.
(f) Addition of C₂H₄ to slowly reacting mixtures of H₂ + O₂ and observation of pressure change corresponding to 50% loss of additive. k was measured relative to H + O₂ \rightarrow OH + O (k(H + C₂H₄)/k(H + O₂) = 12 ± 4) and the value of k(H + O₂) recommended in this evaluation \((5.8 \times 10^{-10}) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} \text{at 773 K}) has been assumed.
(g) Pyrolysis of ethene in a flow system and measurement of H₂ formation. The value of k depends on the equilibrium constant for H + C₂H₄ \rightarrow C₂H₃ and the rate coefficient for C₂H₃ + H₂ \rightarrow C₂H₄ + C₂H₅, previously measured by McKenzie et al.¹³.
(h) Approximate representation of Refs. 1–5.
(i) Based on a BEBO fit to the data of Ref. 5.

Preferred Values

\[ k = 9 \times 10^{-10} \exp(-7500/T) \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \text{ over range } 700-2000 \text{ K} \]

Reliability

\[ \Delta \log k = \pm 0.5 \]

Comments on Preferred Values

With the exception of the data of Skinner et al.³, there is good agreement in the magnitude of the high temperature values, although the temperature dependencies are not well defined. Similarly the more recent and more reliable lower temperature value of Baldwin et al.⁶ is compatible with that of Jayaweera and Pacey⁷. The recommended rate coefficient expression is a compromise between the high and low temperature data. The high A factor may indicate a curved Arrhenius plot, but the data only permit a linear expression with wide error limits.

References

H + C₂H₄ → C₂H₃ + H₂

T/K

Log(k/cm³ molecule⁻¹ s⁻¹)

10³T⁻¹/K⁻¹

EXPERIMENTAL DATA
Baldwin et al 1966
Benson and Hagen 1967
Skinner et al 1971
Poelers and Wahlend 1973
Just et al 1977
Baldwin et al 1984
Jayaweera and Pacey 1988
This Recommendation 1989

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ H + C_2H_5 \rightarrow 2 CH_3 \]  \hspace{1cm} (1)

\[ H + C_2H_5 (+ M) \rightarrow C_2H_6 (+ M) \]  \hspace{1cm} (2)

**Thermodynamic Data**

\[ \Delta H_{298} (1) = -43.8 \text{ kJ mol}^{-1} \]

\[ \Delta S_{298} (1) = 21.9 \text{ J K}^{-1} \text{mol}^{-1} \]

\[ K_p(1) = 4.52 \times 10^3 T^{-0.74} \exp(4790/T) \]

\[ \Delta H_{298} (2) = -419 \text{ kJ mol}^{-1} \]

\[ \Delta S_{298} (2) = -137 \text{ J K}^{-1} \text{mol}^{-1} \]

\[ K_p(2) = 1.09 \times 10^{-6} T^{-0.59} \exp(50400/T) \text{ atm}^{-1} \]

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

<table>
<thead>
<tr>
<th>( k ) [cm(^3) molecule(^{-1}) s(^{-1})]</th>
<th>( T ) [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_2 ) = 6.0 \times 10^{-11} \hspace{1cm}</td>
<td>298</td>
<td>Kurylo, Peterson, and Braun (1970)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>( k_1 = (4-9) \times 10^{-11} \hspace{1cm}</td>
<td>303-603</td>
<td>Teng and Jones (1972)(^2)</td>
<td>(b)</td>
</tr>
<tr>
<td>( k_1 = 2.5 \times 10^{-11} \hspace{1cm}</td>
<td>298</td>
<td>Michael, Osborne, and Suess (1973)(^3)</td>
<td>(c)</td>
</tr>
<tr>
<td>( k_1 = 6 \times 10^{-11} \hspace{1cm}</td>
<td>503-753</td>
<td>Camilleri, Marshall, and Purnell (1974)(^4)</td>
<td>(d)</td>
</tr>
<tr>
<td>( k_1 ) = 1.1 \times 10^{-10} \exp(-50/T) \hspace{1cm}</td>
<td>321-521</td>
<td>Pratt and Veltmann (1976)(^5)</td>
<td>(e)</td>
</tr>
<tr>
<td>( k_1 = 1.2 \times 10^{-11} \hspace{1cm}</td>
<td>1950-2770</td>
<td>Tabayashi and Bauer (1979)(^6)</td>
<td>(f)</td>
</tr>
<tr>
<td>( k_1 = 8 \times 10^{-11} \exp(-127/T) \hspace{1cm}</td>
<td>230-568</td>
<td>Pratt and Wood (1984)(^7)</td>
<td>(g)</td>
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<tr>
<td>( k_1 ) = 5.0 \times 10^{-11} \hspace{1cm}</td>
<td>300-1500</td>
<td>Warnatz (1984)(^8)</td>
<td>(h)</td>
</tr>
<tr>
<td>( k_1 = 6.0 \times 10^{-11} \hspace{1cm}</td>
<td></td>
<td>Tsang and Hampson (1986)(^9)</td>
<td>(i)</td>
</tr>
</tbody>
</table>

**Comments**

(a) Flash photolysis – resonance fluorescence study of H + C\(_2\)H\(_5\). Computer simulation of increase in apparent rate constant as [H]/[C\(_2\)H\(_5\)] was increased. Suggested they were measuring \( k_2 \).

(b) Discharge flow study of H + C\(_2\)H\(_5\); products analysed by GC. Computer simulation of product yields.

(c) Pulsed Hg photosensitized decomposition of H\(_2\) – resonance absorption, discharge flow – time-of-flight mass spectrometry studies of H + C\(_2\)H\(_5\) system. \( k_1 \) from analysis of stoichiometry.

(d) Discharge flow study of H + C\(_2\)H\(_5\). Products by gas chromatography. Numerical integration.


(f) Shock tube study of CH\(_3\)/Ar, CH\(_4\)/O\(_2\)/Ar. Laser schlieren.

(g) Discharge flow study of CH\(_3\) + O\(_2\). CH\(_3\) formed from H + C\(_2\)H\(_5\). Products analysed by GC and simulated by numerical integration.

(h) Evaluation, mean of low temperature data.

(i) Evaluation based on Refs. 1, 3, and 4. A strong collision analysis of \( k_1/k_2 \) is presented.

**Preferred Values**

\( k_1 = 6.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) over range 300–2000 K

**Reliability**

\( \Delta \log k = \pm 0.3 \) at 300 K rising to \( \pm 0.7 \) at 2000 K

References


BAULCH ET AL.

\[ \text{H} + \text{C}_2\text{H}_5 \rightarrow \text{CH}_3 + \text{CH}_3 \]
\[ \rightarrow \text{C}_2\text{H}_6 \]

\[ T/\text{K} \]

---

EXPERIMENTAL DATA

- Teng and Jones (k1) 1972
- Michael et al (k1) 1973
- Camilleri et al (k1) 1974
- Pratt and Veltmann (k1) 1976
- Tabayashi and Itoh (k1) 1979
- Pratt and Wood (k1) 1984
- Kurylo et al (k2) 1970

This Recommendation (k1) 1989

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EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

H + C₂H₆ → H₂ + C₂H₅

Thermodynamic Data
ΔH₂₀ = −16.9 kJ mol⁻¹
ΔS₂₀ = 38.6 J K⁻¹mol⁻¹
κ = 2.92·10⁻⁴ T⁻⁰.⁷³⁷ exp(+/660/T)

Rate Coefficient Data

<table>
<thead>
<tr>
<th>Rate Coefficient Measurements</th>
<th>Temperature [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.65·10⁻¹² exp(−3420/T)</td>
<td>353-436</td>
<td>Berlie and LeRoy (1953)¹</td>
<td>(a)</td>
</tr>
<tr>
<td>7.94·10⁻¹¹ exp(−4310/T)</td>
<td>990-1500</td>
<td>Fenimore and Jones (1961)²</td>
<td>(b)</td>
</tr>
<tr>
<td>8.3·10⁻¹¹ exp(−3960/T)</td>
<td>853-953</td>
<td>Parsamyan et al. (1968)³</td>
<td>(c)</td>
</tr>
<tr>
<td>3.09·10⁻¹⁰ exp(−4920/T)</td>
<td>503-753</td>
<td>Purnell et al. (1974)⁴</td>
<td>(d)</td>
</tr>
<tr>
<td>1.78·10⁻¹⁰ exp(−4643/T)</td>
<td>385-544</td>
<td>Purnell et al. (1977)⁵</td>
<td>(e)</td>
</tr>
<tr>
<td>8.3·10⁻¹¹ exp(−4580/T)</td>
<td>281-347</td>
<td>Lede and Villерmaux (1978)⁶</td>
<td>(f)</td>
</tr>
<tr>
<td>4.06·10⁻¹³ exp(−6440/T)</td>
<td>773</td>
<td>Baldwin and Walker (1979)⁷</td>
<td>(g)</td>
</tr>
<tr>
<td>8.7·10⁻¹⁰ exp(−6440/T)</td>
<td>876-1016</td>
<td>Cao and Back (1984)⁸</td>
<td>(h)</td>
</tr>
</tbody>
</table>

Reviews and Evaluations
2.17·10⁻¹⁰ exp(−4885/T)         | 300-1500        | Baldwin and Melvin (1964)⁹ | (i) |
8.9·10⁻²² T⁻³ exp(−2615/T)      | 300-1800        | Clark and Dove (1973)¹⁰  | (j) |
2.19·10⁻¹⁰ exp(−4715/T)         | 300-1300        | Purnell et al. (1974)¹⁰  | (k) |
8.9·10⁻²² T⁻³ exp(−2615/T)      | 300-2000        | Warnatz (1984)¹¹         | (l) |
8.9·10⁻²² T⁻³ exp(−2615/T)      | 300-1800        | Tsang and Hampson (1986)¹²| (m) |

Comments
(a) H atom concentration determined by catalytic recombination. Constant stoichiometry assumed at all temperatures, but (Ref. 5) k values not seriously in error.
(b) Low pressure C₂H₆ + H₂ + O₂ flames: effectively measured k/k(H + O₂ → OH + O). Results recalculated¹¹ using k(H + O₂) = 2.0·10⁻⁷ T⁻⁰.⁹¹ exp(−8310/T) cm³ molecule⁻¹ s⁻¹.  
(c) Inhibition of H₂ + O₂ limit by C₂H₆. Results recalculated using k(H + O₂) in (b).
(d) Flow discharge, computer fit of all products.
(e) Flow discharge, mass spectrometry. Both excess C₂H₆ and excess H₂ atom used, and stoichiometry measured over temperature range used.
(f) Discharge flow, H atoms formed Hg from HgO target, and released Hg vapour measured spectrophotometrically.
(g) Addition of C₂H₆ to H₂ + O₂ reaction gives k/k(H + O₂) Value of k(H + O₂) given in (b).
(h) H₂ ≈ 2 H equilibrium used to control and effectively measure H atom concentration.
(i) Review of early measurements of k.
(j) Simplified BEBO calculation of rate constants.
(k) Recalculated assumed stoichiometry of earlier workers; argue strongly for Arrhenius expression between 300 and 1300 K.
(l) Recommends Clark and Dove’s expression without comment.
(m) Recommend Clark and Dove’s expression, but emphasize that it may overestimate k above 1500 K.

Preferred Values

k = 2.35·10⁻¹⁵ T⁻¹.⁵ exp(−3725/T) cm³ molecule⁻¹ s⁻¹ over range 300–2000 K

Reliability

Δlog k = ± 0.15 between 300 K and 1500 K rising to ± 0.3 at 2000 K

Comments on Preferred Values

The agreement between the various sets of experimental values of k is less good than might be expected. No particular temperature dependence of the pre-exponential term is dictated by the results. Between 300 and 1300 K, the Arrhenius expression (1.89 ± 0.60)·10⁻¹⁰ exp(−4635 ± 200/T) cm³ molecule⁻¹ s⁻¹ fits the results as well as the preferred values, but is unlikely to give relatively accurate values of k above 2000 K. The rate constant expression suggested by Clark and Dove, and recommended by Warnatz and by Tsang and Hampson, gives values of k too high at 300 and above 1300 K. Above 2000 K, the Clark and Dove expression is recommended.

References

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

$H + C_2H_6 \rightarrow C_2H_5 + H_2$

$T/K$

EXPERIMENTAL DATA
Berlie and Leftoy 1953
Garban and Nalbandyan 1960
Garban and Nalbandyan 1962
Baldwin and Melvin 1964
Parsamyan et al 1968
Azotyan et al 1969
Baldwin et al 1070
Azotyan and Romanovich 1971
Azotyan 1971
Camilleri et al 1974
Kalinenko et al 1974
Jurea et al 1977
Lede and VillermoUlf 1977
Lede and VillermoUlf 1978
Clark et al 1971
Baldwin and Walker 1979
Azotyan 1987
Yang and Gant, 1961
Davis and Williamson 1959
Cao and Bock 1984

This Recommendation 1989

$\text{H} + \text{CHCO} \rightarrow \text{CH}_2 + \text{CO}$ \hspace{1cm} (1)
$\rightarrow \text{C}_2\text{O} + \text{H}_2$ \hspace{1cm} (2)
$\rightarrow \text{HCCOH}$ \hspace{1cm} (3)

**Thermodynamic Data**

$\Delta H^\circ_m (1) = -175.3 \text{ kJ mol}^{-1}$
$\Delta S^\circ_m (1) = 24.3 \text{ J K}^{-1} \text{ mol}^{-1}$

$K_p (1) = 6.23 \times 10^5 T^{-1.35} \exp (+13865/T)$

$\Delta H^\circ_m (2) = -108.9 \text{ kJ mol}^{-1}$
$\Delta S^\circ_m (2) = -5.2 \text{ J K}^{-1} \text{ mol}^{-1}$

$K_p (2) = 5.39 T^{-0.337} \exp (+12990/T)$

$\Delta H^\circ_m (3) = -310.1 \text{ kJ mol}^{-1}$
$\Delta S^\circ_m (3) = -123.1 \text{ J K}^{-1} \text{ mol}^{-1}$

$K_p (3) = 3.26 \times 10^{-5} T^{-0.765} \exp (-37270/T)$

**Rate Coefficient Data**

$k = k_1 + k_2 + k_3$

<table>
<thead>
<tr>
<th>$k$ [cm$^3$ molecule$^{-1}$ s$^{-1}$]</th>
<th>Temperature [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5 \times 10^{-11}$</td>
<td>1600-2000</td>
<td>Löhö and Roth (1981)$^1$</td>
<td>(a)</td>
</tr>
<tr>
<td>$5 \times 10^{-12}$</td>
<td>1000</td>
<td>Homann and Wellmann (1983)$^2$</td>
<td>(b)</td>
</tr>
<tr>
<td>$2.5 \times 10^{-10}$</td>
<td>535</td>
<td>Vinckier et al. (1985)$^3$</td>
<td>(c)</td>
</tr>
<tr>
<td>$2.5 \times 10^{-10}$</td>
<td>1500-1700</td>
<td>Frank et al. (1986)$^4$</td>
<td>(d)</td>
</tr>
</tbody>
</table>

**Comments**

(a) Direct measurement of [H] and [O] in reaction zone behind shock waves generated in O + C$_2$H$_2$ mixtures. Reaction H + CHCO needed to give good fit to [O] and [H] time profiles. Derived $k$ is best-fit value and assumed to be $k_1$.

(b) High temperature flow reactor coupled to a quadrupole mass spectrometer. Value of $k$ obtained from best fit to [CO]-time profiles. However, value of $k$ is based partly on the Jones and Bayes$^5$ value for $k$(O + CHCO) which is almost certainly too low by a factor of at least 50 (see comment on O + CHCO reaction).

(c) Discharge flow study of O + C$_2$H$_2$, radical concentrations being monitored by molecular beam mass spectrometry. Value of $k$ determined from best fit to [CHCO]-time profile at 535 K and determined from ratio $k/k$(O + CHCO) = 1.4 with $k$(O + CHCO) = 1.8$\times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. Value of $k$(O + CHCO) is effectively indistinguishable from recommended value = 1.6$\times 10^{-10}$, see comment on O + CHCO reaction).

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

**Preferred Values**

$k = 2.5 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ over range 300-2500 K

**Reliability**

$\Delta \log k = \pm 0.4$ over range 300-2500 K

**Comments on Preferred Values**

Based on computer fitting of intermediate products, reaction (1) is the preferred path.$^{13}$ Faubel and Wagner$^6$ have suggested, however, that reaction (2) could be an important route for C$_2$O formation in the O + C$_2$H$_2$ system. The values of $k$ differ by a factor of 50, but that obtained by Homann and Wellmann is almost certainly too low by a factor of at least 10 (see comments). With an activation energy of effectively zero the values obtained by Frank et al. and by Vinckier et al. are in excellent agreement, and are the bases of the preferred value of $k$.

**References**

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

H + CH₂CO → CH₃ + CO  (1)
→ CH₂CHO  (2)

Thermodynamic Data

\[ \Delta H_{\text{f}}^\circ (1) = -131 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{f}}^\circ (1) = 35.2 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ k_r (1) = 1.4 \times 10^9 \text{ T}^{-1.45} \exp(15300/T) \]
\[ \Delta H_{\text{f}}^\circ (2) = -141 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{f}}^\circ (2) = -88.6 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ k_r (2) = 1.1 \times 10^{-2} \text{ T}^{-1.61} \exp(16900/T) \]

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

<table>
<thead>
<tr>
<th>( k ) [cm³ molecule⁻¹ s⁻¹]</th>
<th>( T ) [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3 \times 10^{-13}</td>
<td>298</td>
<td>Carr et al. (1968)¹</td>
<td>(a)</td>
</tr>
<tr>
<td>6.0 \times 10^{-12} \exp(-1176/T)</td>
<td>218–363</td>
<td>Slemr and Warnek (1975)²</td>
<td>(b)</td>
</tr>
<tr>
<td>1.88 \times 10^{-11} \exp(-1725/T)</td>
<td>298–500</td>
<td>Michael et al. (1979)³</td>
<td>(c)</td>
</tr>
<tr>
<td>7.3 \times 10^{-14}</td>
<td>298</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.48 \times 10^{-11} \exp(-975/T)</td>
<td>240–440</td>
<td>Umemoto et al. (1985)⁴</td>
<td>(d)</td>
</tr>
<tr>
<td>3.0 \times 10^{-11}</td>
<td>1650–1850</td>
<td>Frank et al. (1986)⁵</td>
<td>(e)</td>
</tr>
<tr>
<td>7.0 \times 10^{-12} \exp(-1515/T)</td>
<td>300–500</td>
<td>Warnatz (1984)⁶</td>
<td>(f)</td>
</tr>
</tbody>
</table>

Comments

(a) Discharge flow system. H atoms produced from H₂/He mixtures flowing through a microwave discharge. CH₂CO in excess. Analysis by mass spectrometer. CH₄ and CO observed to be major products. C₂H₄, C₂H₂, and CH₂O also observed.

(b) Discharge flow system, H atoms in excess. H generated from H₂/He mixtures flowing through a microwave discharge, ketene produced by continuous pyrolysis of diketene. Analysis by mass spectrometer.

(c) Two techniques used.
   (i) Flash photolysis of CH₄/CH₂Cl/Ar mixtures, analysis by resonance fluorescence for [H].
   (ii) Discharge flow system, analysis by resonance fluorescence for [H], CH₂CO in excess. Results at 298 K only.

(d) Pulse radiolysis of H₂/ketene mixtures, ketene in excess. [H] decay measured by resonance absorption.

(e) Shock tube study, CH₂CO/Ar mixtures. [H] and [CO] measured with respect to time by atomic and molecular resonance absorption spectroscopy.

(f) Only low temperature results available.

Preferred Values

\( k_1 = 3.0 \times 10^{-11} \exp(-1700/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) over range 200–2000 K

Reliability

\( \Delta \log k_1 = \pm 0.5 \) at 200 K rising to \( \pm 1.0 \) at 2000 K

Comments on Preferred Values

All the experimental data available is for the total rate constant \( (k = k_1 + k_2) \). No determination of the importance of the separate channels has yet been made. However, it has been assumed²,³,⁴ that channel (1) is dominant and channel (2) is of negligible importance.

The absolute values of the rate constants obtained in the different low temperature studies¹,²,³,⁴ are in good agreement but there are significant differences in the temperature coefficients obtained. Use of the largest temperature coefficient² to extrapolate to high temperatures still leaves the extrapolated value of \( k \) slightly lower at 1800 K than the experimental results of Frank et al.². This may imply curvature of the Arrhenius plot or merely reflect the errors in the measurements.

The preferred values are based on the temperature coefficient of \( k \) of Michael et al.³ and a value of \( k = 1.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) at 298 K.

References


H + CH₂CO → CH₃ + CO

T/K

EXPERIMENTAL DATA
Carr et al 1988
Sistr and Worneck 1975
Michael et al 1979
Michael et al 1979
Umemoto et al 1984
Frank et al 1986
This Recommendation 1989

Log(k/cm³ molecule⁻¹ s⁻¹)

10³T⁻¹/K⁻¹

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ \begin{align*}
H + CH_3CHO & \rightarrow H_2 + CH_3CO \quad (1) \\
& \rightarrow H_2 + CH_3CHO \quad (2)
\end{align*} \]

**Thermodynamic Data**

\[
\begin{align*}
\Delta H_{298}^0 (1) & = -75.3 \text{ kJ mol}^{-1} \\
\Delta S_{298}^0 (1) & = 18.9 \text{ J K}^{-1} \text{ mol}^{-1} \\
K_p (1) & = 1.21 \times 10^9 T^{-0.646} \exp(+8690/T)
\end{align*}
\]

\[
\begin{align*}
\Delta H_{298}^0 (2) & = -27.6 \text{ kJ mol}^{-1} \\
\Delta S_{298}^0 (2) & = 20.0 \text{ J K}^{-1} \text{ mol}^{-1} \\
K_p (2) & = 53.2 \times 10^{-48} \exp(+2967/T)
\end{align*}
\]

**Rate Coefficient Data**

\[
\begin{align*}
\log k & = \log k_1 + \log k_2 \\
\log k_1 & = 4.3 \times 10^{-12} \exp(-1310/T) \text{ (Aders and Wagner, 1973)} \\
\log k_2 & = 5.3 \times 10^{-14} \text{ (Slemr and Wameck, 1975)} \\
\log k_1 & = 2.2 \times 10^{-11} \exp(-1660/T) \text{ (Whytock et al., 1976)} \\
\log k_2 & = 1.4 \times 10^{-11} \exp(-3490/T) \text{ (Beeley et al., 1977)} \\
\log k_1 & = 9.8 \times 10^{-14} \exp(-3490/T) \text{ (Michael and Lee, 1977)}
\end{align*}
\]

**Comments**

(a) Fast flow reactor. Transients and products measured by ESR and mass spectroscopy.
(b) Discharge flow mass spectroscopic measurement of stable species. \( k \) measured relative to the reaction of hydrogen atoms with ketene.
(c) Flash photolysis – resonance fluorescence (Lyman \( \alpha \)).
(d) Ignition of \( CH_3CHO/O_2/Ar \) mixtures behind incident shock waves. Stable and transient species monitored by UV and IR emission. \( k \) determined from modelling the system.
(e) Discharge flow – resonance fluorescence (Lyman \( \alpha \)).

**Preferred Values**

\[
\log k = 6.8 \times 10^{-15} T^{1.16} \exp(-1210/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range 300–2000 K}
\]

**Reliability**

\[
\Delta \log k = \pm 0.4 \text{ at 2000 K reducing to } \pm 0.1 \text{ at 300 K}
\]

**Comments on Preferred Values**

Preferred values are based on the data of Whytock et al., and Michael and Lee at low temperature. Arrhenius plot curved to fit the data of Beeley et al., at high temperature. Temperature dependence data of Whytock et al., indicates possibility of curvature. No experimental information is available on the contribution of the second channel. Assuming \( k_2 = 0.5 k (H + C_2H_2) \), \( k_2/k \) increases from 0.04 at 700 K to 0.5 at 1700 K. The contribution at lower temperatures where most of the measurements have been made is negligible.

**References**

\[ \text{H} + \text{CH}_3\text{CHO} \rightarrow \text{H}_2 + \text{CH}_3\text{CO} \\
\rightarrow \text{H}_2 + \text{CH}_2\text{CHO} \]

\[ \log(k/\text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1}) \]

\[ 10^3T^{-1}/\text{K}^{-1} \]

**Experimental Data**
- Acters and Wagner 1973
- Slawe and Warneck 1975
- Whylock et al. 1976
- Beasley et al. 1977
- Michael and Lee 1977
- This Recommendation 1989
EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

H + C<sub>6</sub>H<sub>5</sub> (+ M) → C<sub>6</sub>H<sub>6</sub> (+ M)

**Thermodynamic Data**

\[ \Delta H_{298}^{\circ} (1) = -463.5 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298}^{\circ} (1) = -133.7 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ K_p (1) = 1.0 \times 10^{-6} T^{-0.4} \exp( +55840/T) \text{ atm}^{-1} \]

**Rate Coefficient Data**

<table>
<thead>
<tr>
<th>([\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}])</th>
<th>(T[\text{K}])</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.7 \times 10^{-11}</td>
<td>1500-2000</td>
<td>Frenklach et al. (1985)&lt;sup&gt;1&lt;/sup&gt;</td>
<td>(a)</td>
</tr>
<tr>
<td>1.3 \times 10^{-10}</td>
<td>1380-1700</td>
<td>Braun-Unkhoff et al. (1989)&lt;sup&gt;2&lt;/sup&gt;</td>
<td>(b)</td>
</tr>
</tbody>
</table>

(a) Modelling of soot formation under the conditions in shock tube pyrolysis. Initial concentrations of about 1% acetylene in argon were used at post shock pressures of 5–7 bar. No sensitivity of the rate constant value with respect to the measured profiles is presented.

(b) Dissociation of phenyl radicals behind reflected shock waves was investigated by monitoring H atoms with ARAS. Nitrosobenzene served as thermal source for the phenyl radicals. The test gas mixtures consisted of argon with relative concentrations of 1–100 ppm nitrosobenzene. It was found that besides the dissociation reaction sequence of phenyl, the recombination step has strongest influence on the measured H atom concentration level.

\[ \Delta H_{298}^{\circ} (2) = 112.3 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298}^{\circ} (2) = -78.9 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ K_p (2) = 6.4 \times 10^{-1} T^{-1.27} \exp( -14060/T) \text{ atm}^{-1} \]

**Rate Coefficient Data \((k = k_1 + k_2)\)**

<table>
<thead>
<tr>
<th>([\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}])</th>
<th>(T[\text{K}])</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3 \times 10^{-11} \exp(-1661/T)</td>
<td>300-357</td>
<td>Sauer and Ward (1967)&lt;sup&gt;1&lt;/sup&gt;</td>
<td>(a)</td>
</tr>
<tr>
<td>9.8 \times 10^{-11} \exp(-2164/T)</td>
<td>298-393</td>
<td>Sauer and Mani (1970)&lt;sup&gt;2&lt;/sup&gt;</td>
<td>(b)</td>
</tr>
<tr>
<td>(k_1 = 3.40 \times 10^{-11} \exp(-4378/T))</td>
<td>883-963</td>
<td>Mkryan et al. (1971)&lt;sup&gt;3&lt;/sup&gt;</td>
<td>(c)</td>
</tr>
<tr>
<td>(k_2 = 6.6 \times 10^{-10} \exp(-3623/T))</td>
<td>1400-1900</td>
<td>Asaba and Fujii (1971)&lt;sup&gt;4&lt;/sup&gt;</td>
<td>(d)</td>
</tr>
<tr>
<td>(k_3 = 3.0 \times 10^{-14})</td>
<td>303</td>
<td>Knutti and Buchler (1972)&lt;sup&gt;5&lt;/sup&gt;</td>
<td>(e)</td>
</tr>
<tr>
<td>(k_4 = 1.7 \times 10^{-11} \exp(-2013/T))</td>
<td>540</td>
<td>Louw and Lucas (1973)&lt;sup&gt;6&lt;/sup&gt;</td>
<td>(f)</td>
</tr>
<tr>
<td>(k_5 = 1.2 \times 10^{-11} \exp(-1864/T))</td>
<td>296-493</td>
<td>Hoyermann et al. (1975)&lt;sup&gt;7&lt;/sup&gt;</td>
<td>(g)</td>
</tr>
<tr>
<td>(k_6 = 1.3 \times 10^{-10} \exp(-5032/T))</td>
<td>1200-1900</td>
<td>Fujii and Asaba (1977)&lt;sup&gt;8&lt;/sup&gt;</td>
<td>(h)</td>
</tr>
<tr>
<td>(k_7 = 1.1 \times 10^{-11} \exp(-4780/T))</td>
<td>1273-2073</td>
<td>Smith (1979)&lt;sup&gt;9&lt;/sup&gt;</td>
<td>(i)</td>
</tr>
<tr>
<td>(k_8 = 6.7 \times 10^{-11} \exp(-2170/T))</td>
<td>298-1000</td>
<td>Nicolich and Ravishankara (1984)&lt;sup&gt;10&lt;/sup&gt;</td>
<td>(j)</td>
</tr>
<tr>
<td>(k_9 = 4.7 \times 10^{-11} \exp(-8052/T))</td>
<td>1630-1940</td>
<td>Rao and Skinner (1984)&lt;sup&gt;11&lt;/sup&gt;</td>
<td>(k)</td>
</tr>
<tr>
<td>(k_10 = 4.2 \times 10^{-10} \exp(-8052/T))</td>
<td>1900-2200</td>
<td>Kiefer et al. (1985)&lt;sup&gt;12&lt;/sup&gt;</td>
<td>(l)</td>
</tr>
</tbody>
</table>

References

Comments

(a) Pulsed radiolysis with product analysis by gas chromatography. Transient species were monitored as function of time by absorption in the wavelength range 260-340 \(\mu\text{m}\). The results are close to the high pressure limiting rate coefficient.

(b) H atom reactions with a series of monosubstituted benzenes, naphthalene, the xylene, and pyridine were investigated using the pulsed-radiolysis method. Optical absorption changes occurring after the electron pulses were monitored for the wavelength range 260-400 \(\mu\text{m}\). Measurements of the overall reaction are close to the high pressure limits.

(c) Evaluation of an overall rate coefficient from a flow reactor study. Mixtures of 10-20\% benzene with argon were pyrolyzed in a single pulse shock tube at 2-8 atm. The products formed were analyzed by gas chromatography. Additionally absorption spectroscopy was applied. A complex mechanism was used for modelling the experimental data.

(d) Low pressures study (mbar range) in a fast gas flow system. The time dependence of adducts, transient species, and of products were measured by mass spectroscopy. The rate expression is deduced from a kinetic model.

(e) The conversion of benzene and of deuterated benzenes into biphenyl was examined in a tank flow reactor at atmospheric pressure. Formation of biphenyl was detected by gas chromatography.

(f) The experiments were carried out in an isothermal flow reactor using ESR, MS, and GC detection techniques. The reactions of H atoms with cyclohexene and cyclohexadiene have also been measured.

(g) The high temperature pyrolysis of benzene was studied in a single pulse shock. Gas samples were heated by reflected shock waves; the products were analyzed by GC. The reaction rate was also followed by light absorption at 200-600 nm (benzene, biphenyl). The experimental data are interpreted by a chain mechanism consisting of 7 elementary reactions.

(h) The pyrolysis of mixtures of toluene and benzene were studied in a high temperature Knudsen cell by using modulated molecular beam mass spectrometric methods.

(i) Observed rate coefficient for the consumption of H atoms using the flash photolysis-resonance fluorescence technique for \(p = 10-200\) Torr. H-atoms were produced by photolysis of benzene or \(\text{H}_2\text{O}\). Time-dependent detection of H-resonance fluorescence at 121.5 nm (channel (2)). An estimated rate coefficient for channel (1) \((k_1 = 5 \times 10^{-12}\ \text{exp}(-4076/T) \text{cm}^3\ \text{molecule}^{-1} \text{s}^{-1})\) gives negligible contribution to the overall rate at any temperature less than 1000 K. Consequently a limiting high pressure rate expression for channel (2) is evaluated for temperature range below 1000 K.

(k) Dilute mixtures of deuterated benzene and of chlorobenzene were pyrolyzed behind reflected shock waves at total pressures of 2-3 atm. The formation of D or H atoms was monitored by a time resolved ARAS.

(l) The shock tube laser schlieren technique was used to investigate the high temperature pyrolysis of benzene in mixtures with krypton. The measured density gradient profiles were modelled by a 26 step mechanism (channel (1)).

Preferred Values

\[ k_{2a} = 6.7 \times 10^{-11} \exp(-2170/T) \text{ cm}^3\ \text{molecule}^{-1} \text{s}^{-1} \text{ over range } 300-1000 \text{ K} \]

Reliability

\(\Delta \log k_2 = \pm 0.2\)

Comments on Preferred Values

The present data do not allow an evaluation of a rate expression for the abstraction channel (1) because of the scattering of the experimental data at high temperatures. For the adduct reaction channel (2) a high pressure limiting rate coefficient is evaluated based on the data of Ref. 10.

References

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ \text{H} + \text{C}_6\text{H}_6 \rightarrow \text{H}_2 + \text{C}_6\text{H}_5 \]
\[ \rightarrow \text{C}_6\text{H}_7 \]

\[ T / \text{K} \]

Experimentally Determined Data:
- Sauer and Ward 1967
- Sauer and Menk 1970
- Moryon et al. (k1) 1971
- Asaba and Fujii (k1) 1971
- Knutti and Buehler (k2) 1972
- Louw and Lucas (k2) 1973
- Hoyermenn et al. (k2) 1975
- Fujii and Asaba (k1) 1977
- Smith (k1) 1979
- Nicovich et al. 1984
- Roo and Skinner (k1) 1984
- Keifer et al. (k1) 1985

This Recommendation (k2) 1989

H + C₆H₆O (+ M) → C₆H₅OH (+ M)

**Thermodynamic Data**

\[ \Delta H_{298} = -362.1 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298} = -107.6 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ K_p = 4.6 \times 10^{-10} \text{ exp}(+4373/T) \text{ atm}^{-1} \]

**Rate Coefficient Data**

<table>
<thead>
<tr>
<th>([\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}])</th>
<th>([\text{T}[\text{K}])</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2 \times 10^{-10}</td>
<td>≈ 1000</td>
<td>He et al. (1988)</td>
<td></td>
</tr>
</tbody>
</table>

**Comments**

(a) Obtained solely by computer simulation of the system phenol + H (see appropriate data sheet), based on GC measurements of the two stable end products isobutene and benzene. No literature is found on the potential role of bimolecular channels.

**Preferred Values**

In the absence of any other measurements the rate coefficient of He et al. is recommended.

**References**


---

\[ H + C₆H₅OH \rightarrow C₆H₆O + H₂ \quad (1) \]
\[ \rightarrow C₆H₆ + OH \quad (2) \]

**Thermodynamic Data**

\[ \Delta H_{298} (1) = -73.9 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298} (1) = 8.9 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ K_p(1) = 1.1 \times 10^7 T^{-0.358} \text{ exp}(+8693/T) \]
\[ \Delta H_{298} (2) = 0.3 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298} (2) = 23.5 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ K_p(2) = 2.1 \times 10^4 T^{-1.112} \text{ exp}(-262/T) \]

**Rate Coefficient Data \((k = k_1 + k_2)\)**

<table>
<thead>
<tr>
<th>([\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}])</th>
<th>([\text{T}[\text{K}])</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_1 = 1.9 \times 10^{-16} \text{ exp}(-6249/T))</td>
<td>1000–1150</td>
<td>He et al. (1988)</td>
<td>(a)</td>
</tr>
<tr>
<td>(k_2 = 3.7 \times 10^{-11} \text{ exp}(-3990/T))</td>
<td>1000–1150</td>
<td>He et al. (1988)</td>
<td>(a)</td>
</tr>
</tbody>
</table>

**Comments**

(a) Shock tube; 2.5–5 atm of Ar. H source is the decomposition of C₆H₁₅ to H atoms and isobutene. Phenol is in large excess over C₆H₁₅ and is thus the main H sink. Benzene is produced via reaction (2) and measured by GC, together with isobutene yields. This establishes the branching ratio for reactions (1) and (2). Absolute rate data are obtained by using CH₄ + H as an internal standard, i.e., by observing the change of benzene yields under addition of several percent of CH₄. Kinetic complications were investigated by varying the stoichiometry and by computer simulation.

**Preferred Values**

In the absence of any other study the expressions of He et al. are preferred.

**References**

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

H + C₆H₅CH₂ (+ M) → C₆H₅CH₃ (+ M)

**Thermodynamic Data**

\[ \Delta H_{\text{fm}} = -368.0 \text{kJ mol}^{-1} \]
\[ \Delta S_{\text{fm}} = -110.9 \text{JK}^{-1}\text{mol}^{-1} \]
\[ k_p = 1.8 \times 10^{-2} \text{T}^{-1/49} \exp\left(\frac{44028}{T}\right) \text{atm}^{-1} \]

**Rate Coefficient Data**

<table>
<thead>
<tr>
<th>( k [\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}] )</th>
<th>( T[K] )</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3 \times 10^{-10} \text{to} 1.3 \times 10^{-9}</td>
<td>1450–1900</td>
<td>Brouwer et al. (1988)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>5.5 \times 10^{-10}</td>
<td>298</td>
<td>Bartels et al. (1989)(^2)</td>
<td>(b)</td>
</tr>
</tbody>
</table>

**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.

**Preferred Values**

\[ k = 5.5 \times 10^{-10} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} \text{ over the range 300–2000 K} \]

**Reliability**

\[ \Delta \log k = \pm 0.2 \text{ at room temperature increasing to } \pm 0.7 \text{ at 2000 K} \]

**Comments on Preferred Values**

The only direct measurements performed at room temperature provide evidence for the recombination channel to toluene. Owing to the high exothermicity of this reaction no barrier is expected to be involved, and the recommendation has been extended to the range up to 2000 K.

**References**

Rate Coefficient Measurements

\( k_1 = 1.4 \times 10^{-10} \exp(-4630/T) \)

\( k_2 = 8.5 \times 10^{-14} \)

\( k_3 = 8.3 \times 10^{-11} \exp(-1864/T) \)

\( k_4 = 1.3 \times 10^{-20} T^{3/2} \exp(-171/T) \)

\( k_5 = 5.4 \times 10^{-6} \exp(-7584/T) \)

\( k_6 = 5.4 \times 10^{-6} \exp(-9561/T) \)

\( k_7 = 2.1 \times 10^{-14} \exp(-1862/T) \)

\( k_8 = 1.8 \times 10^{-20} T^{3/2} \exp(-1183/T) \)

\( k_9 = 1.1 \times 10^{-21} T^{4/2} \exp(-377/T) \)

\( k_{10} = 7.3 \times 10^{-24} T^{4/2} \exp(-1057/T) \)

\( k_{11} = 5.0 \times 10^{-11} \)

\( k_{12} = 9.7 \times 10^{-13} \)

\( k_{13} = 4.2 \times 10^{-10} \exp(-8052/T) \)

\( k_{14} = 8.3 \times 10^{-16} \exp(-6290/T) \)

Comments

(a) Static system. Detection by gas chromatography and mass spectrometry. Rate expression for channel (3) deduced by comparison with H addition to benzene.

(b) Pulsed radiolysis with product analysis by gas chromatography. Transient species were monitored as function of time by absorption in the wavelength range 260–340 nm. A \( k \)-value for the overall reaction (4) at room temperature was deduced.

(c) Evaluation of a \( k \)-expression for channel (1) from a flow reactor study.

(d) Fast flow reactor with product analysis by mass spectrometry. H atoms produced in microwave discharge. Rate expression evaluated for the overall reaction (channel (4)).

(e) Shock tube study with toluene/Ar mixtures. Toluene and benzyl were monitored as function of time by absorption in the 200–350 nm range. A rate expression for channel (1) was derived on the assumption that the benzyl radical exhibits sufficient thermal stability.

(f) Shock tube study with initial mixtures of toluene-\( d_8 \)/Ar and neopentane/toluene-\( d_8 \)/Ar mixtures. D and H atoms were monitored as function of time by ARAS. Investigation covered a temperature range from 1200–1460 K for neopentane/toluene, and from 1410–1730 K for toluene experiments. Together with unpublished results of Ravishankara and Nicovich a non-Arrhenius expression for \( T = 600–1700 \) K was deduced for channel (1).

(g) Shock tube study with mixtures of toluene and ethylbenzene, respectively. Products were monitored as function of time by time-of-flight mass spectrometry. The rate expression for formation of benzyl radicals and hydrogen (channel (1)) is reevaluated from the data of Ref. 6. Rate expressions for the formation of methyl phenyl radicals and hydrogen (channel (2)) and of benzene and methyl radicals (channel (3)) are deduced from experiments.

(h) Single pulse shock tube. The source of H atoms was the thermal decay of small quantities of hexamethylenethane. The \( k \)-values have been derived on the basis of competitive process \( H + CH_4 \rightarrow CH_3 + H_2 \) with \( k = 2.2 \times 10^{-20} T^{3/2} \exp(-4045/T) \). Rate expressions for the formation of benzene and methyl radicals (channel (3)) and of benzyl radicals and hydrogen (channel (1)) were obtained.

(i) Small amounts of toluene (0.05–0.5%) have been added to slowly reacting mixtures of hydrogen and oxygen at 773 K. Under the experimental conditions the \( H_2 + O_2 \) system provides a reproducible source of H, O, and OH radicals. The measurements of the rel-
ative consumption of H₂ and of the additive permits the evaluation of rate constants for the reaction of H, O, and OH with toluene.

(j) Shock tube study on high temperature pyrolysis of ethylbenzene with the laser schlieren technique. Rate expression for channel (1).

(k) Two independent shock tube techniques (time-offlight mass spectrometry and laser schlieren densitometry) were used to investigate the high temperature pyrolysis of toluene in mixtures with Kr and Ne, respectively. A rate coefficient for the formation of methyl phenyl (channel (2)) was obtained.

(l) Shock tube study with very low initial concentrations of toluene in Ar. Hydrogen atom formation is monitored by ARAS. The measured H profiles were sensitive to \( k_1 \) in the later stage of observation time. A rate coefficient for channel (1) was deduced which is slightly smaller than the rate constant of Rao and Skinner².

### Preferred Values

\[
k_1 = 6.6 \times 10^{-22} \ T^{3.44} \exp(-1570/T) \ \text{cm}^3 \ \text{molecule}^{-1} \ \text{s}^{-1}
\]
\[
k_4 = 1.2 \times 10^{-13} \ \text{cm}^3 \ \text{molecule}^{-1} \ \text{s}^{-1} \ \text{at} \ T = 298 \ \text{K}
\]

**Reliability**

\[
\Delta \log k_1 = \pm 0.5 \ \text{at} \ 2800 \ \text{K} \ \text{reducing to} \ \pm 0.3 \ \text{at} \ 600 \ \text{K}
\]
\[
\Delta \log k_4 = \pm 0.2 \ \text{at} \ 298 \ \text{K}
\]

**Comments on Preferred Values**

Most of the available measurements give evidence for the product channel (1) leading to benzyl radicals and molecular hydrogen. It has to be noted that only a few experiments permit a discrimination between the channels at elevated temperatures. Therefore from the majority of the data, the different product pathways have been deduced not by direct measurement of product distribution and concentration but by modelling with the aid of plausible reaction systems. By combining the few room temperature data with the rate constant values at elevated temperatures, it has to be assumed that a change in the reaction mechanism occurs, possibly from channel (4) at room temperature to channel (1) dominating at temperatures above 1000 K¹¹. The data are insufficient to permit a recommendation of a rate expression for the overall H-consuming reaction over the whole temperature range. For the addition reaction (4) it is only possible to evaluate a room temperature value.

### References

BAULCH ET AL.

\[ \begin{align*}
  H &+ C_6H_5CH_3 \rightarrow H_2 + C_6H_5CH_2 \\
  & \rightarrow H_2 + C_6H_5CH_2 \\
  & \rightarrow C_6H_5CH_2
\end{align*} \]

T/K

EXPERIMENTAL DATA

- Minyn et al. (k1) 1972
- Astnerz et al. (k1) 1981
- Rao and Skinner (k1) 1984
- Pamldimukkola and Kern (k1) 1985
- Robaugh and Tsang (k1) 1986
- Mizerak and Kiefer (k1) 1988
- Braun-Unkhoff et al. (k1) 1989
- Benson and Shriver (k2) 1987
- Pamldimukkola and Kern (k2) 1985
- Pamldimukkola and Kern (k3) 1985
- Robaugh and Tsang (k3) 1986
- Sauer and Ward (k4) 1987
- Inghel and Duinker (k5) 1976
- Baldwin et al. (k5) 1987
- Baldwin et al. (k5) 1987
- Pamldimukkola et al. (k2) 1987

This Recommendation (k1) 1989
This Recommendation (k4) 1989

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ \text{H} + \text{p-C}_6\text{H}_4(\text{CH}_3)_2 (+ \text{M}) \rightarrow \text{products} \]

### Rate Coefficient Data

<table>
<thead>
<tr>
<th>Rate Coefficient Measurements</th>
<th>5.8 \times 10^{-13}</th>
<th>298</th>
<th>Sauer, Jr., and Mani (1970)(^1)</th>
<th>(a)</th>
</tr>
</thead>
</table>

#### Comments

(a) Pulse-radiolysis study at pressures around 75 bar. Analysis from transient spectra.

#### Preferred Values

\[ k = 5.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K} \]

#### Reliability

\[ \Delta \log k = \pm 0.1 \]

### Thermodynamic Data

\[ \Delta H_{298} (1) = -94.6 \text{ kJ mol}^{-1} \]

\[ \Delta S_{298} (1) = 11.7 \text{ J K}^{-1} \text{ mol}^{-1} \]

\[ K_p (1) = 2.4 \times 10^4 T^{-0.10} \exp \left( +1180/T \right) \]

### Rate Coefficient Data (\(k = k_1 + k_2\))

<table>
<thead>
<tr>
<th>Rate Coefficient Measurements</th>
<th>3.3 \times 10^{-13}</th>
<th>298</th>
<th>Sauer, Jr., and Mani (1970)(^1)</th>
<th>(a)</th>
</tr>
</thead>
</table>

#### Comments

(a) Pulse-radiolysis study at pressures around 75 bar. Analysis from transient spectra.

#### Preferred Values

\[ k = 3.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K} \]

#### Reliability

\[ \Delta \log k = \pm 0.1 \]

### Reference

\(^1\)M. C. Sauer, Jr., and I. Mani, J. Phys. Chem. 74, 59 (1970).
**Thermodynamic Data**

\( \Delta H_{\text{m}} = 436 \text{ kJ mol}^{-1} \)

\( \Delta S_{\text{m}} = 98.6 \text{ J K}^{-1}\text{mol}^{-1} \)

\( \kappa_r = 31.3 \text{ T}^{1.28} \exp(-52100/T) \text{ atm} \)

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**Rate Coefficient Data**

<table>
<thead>
<tr>
<th>( k ) [cm(^3) molecule(^{-1}) s(^{-1})]</th>
<th>( T ) [K]</th>
<th>M</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 1.6 \times 10^{-10} \exp(-44740/T) )</td>
<td>3500-8000</td>
<td>Ar</td>
<td>Breshears and Bird (1973)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>( 5.5 \times 10^{-9} \exp(-52990/T) )</td>
<td>3500-8000</td>
<td>( \text{H}_2 )</td>
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<td></td>
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</tbody>
</table>

**Reviews and Evaluations**

<table>
<thead>
<tr>
<th>( k ) [cm(^3) molecule(^{-1}) s(^{-1})]</th>
<th>( T ) [K]</th>
<th>M</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 3.7 \times 10^{-10} \exp(-48350/T) )</td>
<td>2500-5000</td>
<td>Ar</td>
<td>Baulch et al. (1972)(^2)</td>
</tr>
<tr>
<td>( 1.5 \times 10^{-9} \exp(-48350/T) )</td>
<td>2500-5000</td>
<td>( \text{H}_2 )</td>
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</tr>
<tr>
<td>( 7.6 \times 10^{-5} T^{-1.4} \exp(-52525/T) )</td>
<td>600-2000</td>
<td>( \text{N}_2 )</td>
<td>Tsang and Hampson (1986)(^3)</td>
</tr>
</tbody>
</table>

---

**Comments**

(a) Dissociation of \( \text{H}_2 \) in Ar behind incident shock waves. Postshock density gradients measured by laser schlieren technique.

**Preferred Values**

\( k = 3.7 \times 10^{-10} \exp(-48350/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) over range 2500-8000 K for M = Ar

\( k = 1.5 \times 10^{-9} \exp(-48350/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) over range 2500-8000 K for M = \( \text{H}_2 \)

**Reliability**

\( \Delta \log k = \pm 0.3 \) for M = Ar

\( \Delta \log k = \pm 0.5 \) for M = \( \text{H}_2 \)

---

**Comments on Preferred Values**

The value preferred by Baulch et al.\(^2\) has been adopted. The arguments given there are accepted, and the values measured after 1972 do not contradict this recommendation.

For clarity, rate data measured before 1972 are included in the Arrhenius plot (see Baulch et al.\(^2\) for Ref.).

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**References**


EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ \text{H}_2 + \text{Ar} \rightarrow \text{H} + \text{H} + \text{Ar} \]

\( T/K \)

Thermodynamic Data

\[
\Delta H^{\text{fus}} = -62.9 \text{ kJ mol}^{-1} \\
\Delta S^{\text{fus}} = -10.9 \text{ J K}^{-1} \text{mol}^{-1} \\
K_p = 0.113 T^{0.039} \exp(7680/T)
\]

Rate Coefficient Data

<table>
<thead>
<tr>
<th>(k) [cm(^3) molecule(^{-1}) s(^{-1})]</th>
<th>(T) [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(7.1 \times 10^{-13})</td>
<td>300</td>
<td>Stuhl and Niki (1972)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>(8.6 \times 10^{-13} \exp(-3271/T))</td>
<td>1200-1800</td>
<td>Gardiner et al. (1973)(^2)</td>
<td>(b)</td>
</tr>
<tr>
<td>(4.6 \times 10^{-12})</td>
<td>1050</td>
<td>Day, Thompson, and Dixon-Lewis (1973)(^3)</td>
<td>(c)</td>
</tr>
<tr>
<td>(7.6 \times 10^{-13})</td>
<td>298</td>
<td>Westenberg and deHaas (1973)(^4)</td>
<td>(d)</td>
</tr>
<tr>
<td>(1.8 \times 10^{-14})</td>
<td>352</td>
<td>Smith and Zellner (1974)(^5)</td>
<td>(e)</td>
</tr>
<tr>
<td>(3.3 \times 10^{-14})</td>
<td>403</td>
<td>Atkinson, Hansen, and Pitts (1973)(^6)</td>
<td>(f)</td>
</tr>
<tr>
<td>(1.4 \times 10^{-13})</td>
<td>518</td>
<td>Overend et al. (1973)(^7)</td>
<td>(g)</td>
</tr>
<tr>
<td>(3.7 \times 10^{-13})</td>
<td>628</td>
<td>Smith and Zellner (1974)(^8)</td>
<td>(h)</td>
</tr>
<tr>
<td>(6.6 \times 10^{-13})</td>
<td>745</td>
<td>Trainor and von Rosenberg (1975)(^9)</td>
<td>(i)</td>
</tr>
<tr>
<td>(8.6 \times 10^{-11})</td>
<td>870-1100</td>
<td>Gardiner, Mallard, and Owen (1974)(^6)</td>
<td>(j)</td>
</tr>
<tr>
<td>(5.9 \times 10^{-15})</td>
<td>295</td>
<td>Trainor and von Rosenberg (1975)(^7)</td>
<td>(k)</td>
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<tr>
<td>(5.3 \times 10^{-17})</td>
<td>300</td>
<td>Schmidt et al. (1985)(^15)</td>
<td>(l)</td>
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<tr>
<td>(1.2 \times 10^{-11} \exp(-2333/T))</td>
<td>1200-1500</td>
<td>Smith and Zellner (1974)(^5)</td>
<td>(m)</td>
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<tr>
<td>(8.6 \times 10^{-11})</td>
<td>210-460</td>
<td>Sworsky, Hoehanadel, and Ogren (1980)(^11)</td>
<td>(n)</td>
</tr>
<tr>
<td>(4.1 \times 10^{-12} \exp(-1281/T))</td>
<td>210-460</td>
<td>Tully et al. (1980,1981)(^12,13)</td>
<td>(o)</td>
</tr>
<tr>
<td>(5.0 \times 10^{-13})</td>
<td>295</td>
<td>Frank and Just (1985)(^14)</td>
<td>(p)</td>
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<tr>
<td>(1.05 \times 10^{-10} \exp(-4045/T))</td>
<td>227-729</td>
<td>Schmidt et al. (1985)(^15)</td>
<td>(q)</td>
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<tr>
<td>(5.0 \times 10^{-15})</td>
<td>295</td>
<td>Zellner (1979)(^18)</td>
<td>(r)</td>
</tr>
<tr>
<td>(1.1 \times 10^{-12})</td>
<td>300-2000</td>
<td>Cohen and Westberg (1983)(^20)</td>
<td>(s)</td>
</tr>
<tr>
<td>(1.7 \times 10^{-16} \exp(-1660/T))</td>
<td>240-2400</td>
<td>Cohen and Westberg (1983)(^20)</td>
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<td>Overend et al. (1973)(^7)</td>
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<td>Sworsky, Hoehanadel, and Ogren (1980)(^11)</td>
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<td>Michael and Sutherland (1988)(^16)</td>
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<td>Smith and Zellner (1974)(^5)</td>
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<td>1700-2500</td>
<td>Smith and Zellner (1974)(^5)</td>
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<td>Smith and Zellner (1974)(^5)</td>
<td>(b)</td>
</tr>
<tr>
<td>(1.05 \times 10^{-10} \exp(-4045/T))</td>
<td>1246-2297</td>
<td>Smith and Zellner (1974)(^5)</td>
<td>(c)</td>
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Comments

(a) Pulsed VUV photolysis of H\(_2\)O; [OH] by resonance fluorescence. Total pressure 20 Torr He.
(b) Combustion of rich H\(_2\)/O\(_2\)/Ar mixtures behind incident shock waves; [OH] by absorption spectroscopy, [CO\(_2\)] by emission at 4.2 \(\mu\)m, CO + O chemiluminescence. Numerical integration of 12 reaction mechanism.
(c) Calculation of burning velocities and concentration profiles in rich H\(_2\)/D\(_2\)/O\(_2\)/N\(_2\) flames.
(d) Discharge-flow reactor; [OH] by ESR. Total pressures 1–3 Torr.
(e) Flash photolysis of either H\(_2\)O or N\(_2\)O/H\(_2\) mixtures; time-resolved resonance absorption of OH. Total pressures at least 10 Torr.
(f) Shock-initiated combustion of rich H\(_2\)/O\(_2\)/Ar mixtures; [OH] by resonance absorption. Numerical integration of 12 reaction mechanism; \(k\) adjusted to fit the experimental OH concentration profiles.
(g) Flash photolysis of H\(_2\)O/H\(_2\)/N\(_2\) mixtures; [OH] by time-resolved resonance UV absorption spectroscopy. Total pressures near 100 Torr.
(h) Pulsed VUV photolysis of H\(_2\)O; [OH] by resonance fluorescence at 306.4 nm. Total pressures 15–25 Torr Ar.
(j) Lean CO/H\(_2\)/O\(_2\) flames on a flat burner; molecular beam sampling coupled with mass spectrometry. Total pressure 40 Torr. \(k\) determined from mole flux of H\(_2\)O.
(k) Flash photolysis of H\(_2\)/O\(_2\)/CH\(_4\) mixtures with and without H\(_2\) or N\(_2\) at atmospheric pressures; [CH\(_3\)] by absorption at 216 nm. Numerical integration of 11 reaction mechanism.
(l) Flash photolysis of H\(_2\)/H\(_2\)/Ar mixtures; [OH] by resonance fluorescence.

(m) Shock heating of N₂O/H₂O₂/Ar mixtures; [H] and [O] by time-resolved atomic resonance absorption. Total densities (6×10⁻⁶–1.3×10⁻⁵) mol cm⁻³. Numerical integration of 10 reaction mechanisms.

(n) Excimer laser photolysis of H₂O₂ or HNO₃ in synthetic air at a total pressure of 1 atm; [OH] by laser induced fluorescence near 300 nm.

(o) Flash photolysis - shock tube study of k₁; [H] by atomic resonance absorption. k calculated from equilibrium data.

Preferred Values

\[ k = 1.7 \times 10^{-16} T^{1.6} \exp(-1660/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]
over range 300–2500 K

Reliability
\[ \Delta \log k = \pm 0.3 \] at 2500 K reducing to \[ \pm 0.1 \] below 1000 K

Comments on Preferred Values

The rate coefficient recommended by Zellner¹⁸ is adopted, which represents the ample experimental material very well.

References

OH + H₂ → H₂O + H

**Experimental Data**

- Stuhl and Niki 1972
- Garvin et al. 1973
- Day et al. 1973
- Westenberg and Deloof 1973
- Smith and Zellner 1974
- Gardiner et al. 1974
- Trainer and Van Rossum 1975
- Atkinson et al. 1975
- Overend et al. 1975
- Vandenbrouke et al. 1975
- Swiderski et al. 1980
- Tully et al. (2 works) 1981
- Frank and Just 1985
- Schmidt et al. 1985
- Michael and Sutherland 1988
- Bermann et al. 1976
- Ahl et al. 1977
- Singh and Sawyer 1970
- Bera et al. 1987
- Dixon-Lewis et al. 1966
- Ripley and Gardiner 1966
- Aradim et al. 1987
- Graiser 1987
- Jenkin et al. 1967
- Damm et al. 1969
- Dobrov et al. 1999
- Graiser 1969
- Wang and Jelles 1970
- Drabek et al. 1971

This Recommendation 1989
**EVALUATED KINETIC DATA FOR COMBUSTION MODELLING**

**OH + OH → O + H₂O**

### Thermodynamic Data

\[ \Delta H_{298}^o = -70.6 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298}^o = -17.5 \text{ J K}^{-1} \text{ mol}^{-1} \]
\[ K_p = 6.24 \times 10^{-2} \cdot 7^{0.007} \exp(+8600/T) \]

### Rate Coefficient Data

<table>
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<tr>
<th>( k ) [cm³ molecule⁻¹ s⁻¹]</th>
<th>( T ) [K]</th>
<th>Reference</th>
<th>Comments</th>
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<tr>
<td>( 9.1 \times 10^{-11} \exp(-3523/T) )</td>
<td>1500–2000</td>
<td>Gardiner et al. (1973)¹</td>
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<tr>
<td>( 2.2 \times 10^{-12} )</td>
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<td>McKenzie, Mulcahy, and Steven (1973)²</td>
<td>(b)</td>
</tr>
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<td>( 2.3 \times 10^{-12} )</td>
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<td>Westenberg and deHaas (1973)³</td>
<td>(c)</td>
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<td>( 1.4 \times 10^{-13} )</td>
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<td>Clyne and Down (1974)⁴</td>
<td>(d)</td>
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<td>Trainor and von Rosenberg (1974)⁵</td>
<td>(e)</td>
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<tr>
<td>( 5.6 \times 10^{-11} \exp(-2536/T) )</td>
<td>1180–1890</td>
<td>Ernst, Wagner, and Zellner (1977)⁶</td>
<td>(f) and Zellner (1979)⁷</td>
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<td>( 3.2 \times 10^{-12} \exp(-277/T) )</td>
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<td>Zellner and Wagner (1980)⁸</td>
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<td>( 3.2 \times 10^{-12} \exp(-242/T) )</td>
<td>250–580</td>
<td>Wagner and Zellner (1981)⁹</td>
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### Comments on Preferred Values

The rate coefficient preferred by Ernst, Wagner, and Zellner⁶ is taken as the recommendation due to the fact that it is based on experimental work over a large temperature range and careful evaluation of literature data.

For clarity, rate data measured before 1972 are included in the Arrhenius plot (see Bauch et al.¹⁰ for reference).

### References

**Thermodynamic Data**

\[ \Delta H_{298} = -214 \text{ kJ mol}^{-1} \]

\[ \Delta S_{298} = -134 \text{ J K}^{-1} \text{mol}^{-1} \]

\[ K_p = \frac{2.26 \times 10^{-9}}{T^{0.01} \exp\left(+26000/T\right)} \text{ atm}^{-1} \]

**Rate Coefficient Data**

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<th>(T) [K]</th>
<th>(M) [molecule cm(^{-3})]</th>
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<td>253</td>
<td>((0.06-2.7) \times 10^{19})</td>
<td>Zellner et al. (1988)(^1)</td>
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<td>(2.9 \times 10^{19})</td>
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<td>([\text{H}_2\text{O}]) (4.0 \times 10^{-20})</td>
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<td>([\text{H}_2\text{O}]) (4.1 \times 10^{-20})</td>
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<td>Reviews and Evaluations</td>
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<tr>
<td>(k_0 = [\text{N}_2] 1.6 \times 10^{-33} T^{-3})</td>
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<td>Tsang and Hampson (1986)(^2)</td>
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<tr>
<td>(k_0 = 8.0 \times 10^{-33} (T/300)^{-0.7})</td>
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<td>Brouwer et al. (1987)(^3)</td>
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<tr>
<td>(k_w = 1.5 \times 10^{-11} (T/300)^{-0.37})</td>
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<tr>
<td>(F_c(\text{N}_2) = 0.5)</td>
<td>200–1500</td>
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**Comments**

(a) Flash photolysis of H\(_2\)O vapour in N\(_2\). Detection of OH by laser induced fluorescence. Discussion of earlier more scattered data.

(b) As comment (a). Extrapolation to \(k_w = 1.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) using \(F_c = 0.6\).

(c) Based on results of the reverse dissociation of H\(_2\)O and RRKM calculations.

(d) Theoretical construction of fall-off curves for the forward and reverse reaction based on the experimental results from Ref. 1 and consistent with non-thermal H\(_2\)O dissociation lifetime measurements.

**Preferred Values**

\[ k_0 = [\text{N}_2] 8.0 \times 10^{-33} (T/300)^{-0.7}\text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\] over range 250–1400 K

\[ k_0 = [\text{H}_2\text{O}] 4.0 \times 10^{-30} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\] over range 300–400 K

\[ k_w = 1.5 \times 10^{-11} (T/300)^{-0.37} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\] over range 200–1500 K

\(F_c = 0.5\) for M = N\(_2\) over range 200–1500 K

**Reliability**

\[ \Delta \log k_0 = \pm 0.4\] over range 250–1400 K for M = N\(_2\)

\[ \Delta \log k_w = \pm 0.5\] over range 200–1500 K

**Comments on Preferred Values**

The preferred values are from the analysis in Ref. 3 of theoretical modelling and experimental results from Ref. 1. Since the earlier experimental data scatter considerably, new experiments are required before safe recommendations can be made.

**References**

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ \text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O} \]
\[ \rightarrow \text{H}_2\text{O}_2 \]

**Experimental Data**
- Albers et al. 1971
- Gardiner et al. 1973
- McKeech et al. 1973
- Westenberg and Deloaches 1973
- Clyne and Down 1974
- Trainor and Von Rosenberg 1974
- Ernst et al. 1979
- Smith and Farquharson 1980
- Zeliner and Wagner 1980
- Wagner and Zeuner 1981
- Schell 1980
- Kaufman and Del Greco 1981
- Del Greco and Kaufman 1982
- Wise et al. 1984
- Westenberg and Deloaches 1985
- Dixon-Lewis et al. 1986
- Wilson and O'Donovan 1987
- Breen and Glass 1970

---

**This Recommendation**
- (k1) 1989
- (k2 int) 1989
Baulch et al.

**OH + HO₂ → H₂O + O₂**

**Thermodynamic Data**
\[ \Delta H_{f298} = -291 \text{ kJ mol}^{-1} \]
\[ \Delta S_{f298} = -18.8 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ K_p = 0.517 \ T^{-0.247} \exp(3500/T) \]

**Rate Coefficient Data**

<table>
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<tr>
<th>( k ) [cm³ molecule⁻¹ s⁻¹]</th>
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<td>Feser and Sutton (1972)²</td>
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<td>Hack, Hoyermann, and Wagner (1975)⁷</td>
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<td>Dixit-Lewis and Rhodes (1975)⁸</td>
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**Reviews and Evaluations**

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<td>Tsang and Hampson (1986)³¹</td>
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**Comments**

(a) Thermal decomposition of H₂O₂ in Ar behind reflected shock waves. [H₂O₂] by UV absorption at 290 nm. Total densities 10⁻⁵ - 2×10⁻⁴ cm⁻³ Ar.

(b) Flat premixed lean H₂O₂:N₂ flames; [H] measured by Li/LiOH method. \( k \) derived under the assumption of partial equilibrium for H + O₂ and OH + OH reactions.

(c) Flash photolysis of water vapour at atmospheric pressure. [OH] and [HO₂] monitored by absorption measurements. Rate parameter adjusted by numerical simulation of a reaction mechanism.

(d) Computer simulation of burning velocities of rich H₂/O₂/N₂ flames. No great accuracy.

(e) Lean and stoichiometric CH₄/O₂ flat flames at 40 Torr; molecular beam sampling and mass spectrometric analysis.

(f) Photolysis of O₂/H₂O mixtures at 184.9 nm until a steady-state was reached. Total pressure 700 Torr. [O₃] monitored by absorption at 253.7 nm. Relative measurements with O₂/H₂O and O₂/H₂O/CO mixtures. Given value for \( k \) based on \( k(\text{OH} + \text{O}_2) = 6\times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) and \( k(\text{HO}_2 + \text{O}_2) = 3.6\times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \).

(g) Discharge-flow reactor; [OH] by electron spin resonance. Total pressures around 2 Torr He. Computer modelling of the reaction system.

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

(i) Fast-flow study of OH + H₂O or H + H₂O₂ reaction at a few Torr. [OH] and [HO₂] monitored by laser magnetic resonance

(j) Discharge-flow reactor. [OH] and [HO₂] monitored by laser magnetic resonance. Total pressures around 250 Pa He. Original value 3.0×10⁻¹¹ cm³ molecule⁻¹ s⁻¹, corrected by Keyser due to a new value for \( k(\text{OH} + \text{H}_2\text{O}) \).

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(l) As in (f), but smaller reaction cell and absorption spectrum scanned over the range 180–200 nm to monitor also H2O2.

(m) Discharge-flow system [OH] and [HO2] monitored by laser magnetic resonance. Total pressure 2 Torr. Original value 5.1·10^(-11) cm^3 molecule^(-1) s^(-1), corrected by Keyser(27) due to a new value for k(Oh + H2O2)H4. Result based on k(Oh + H2O2) = 8·10^-13 cm^3 molecule^(-1) s^(-1).

(n) Pulse-irradiation of H2O/O2/Ar mixtures. Total pressures up to 1200 Torr. Absorption measurements of HO2 (230 nm) and OH (308.7 nm). Computer modelling of a 14 reaction mechanism and parameter fitting to experimental concentrations.


(P) Low-frequency square-wave modulated photolysis of O3/H2O mixtures monitoring the steady-state absorption of HO2 at 210 nm. Total pressure 1 atm. Experimental upper limit for k adjusted to a lower value by computer modelling of a 17 reaction mechanism.

(q) Modulated photolysis of O3/H2O/O2/N2 or O3/H2O/O2/He mixtures at atmospheric pressure. [HO2] monitored by absorption at 210 nm, [OH] by resonance absorption at 308.2 nm. Modelling of a 15 reaction mechanism. The time dependence of [HO2] could not be accurately described throughout a photolysis cycle by a single value of k.

(r) Discharge-flow system. [OH] by laser-induced fluorescence, [H] and [O] by VUV resonance fluorescence; [HO2] measured by rapid conversion to OH with excess NO. Total pressure near 3 Torr.

(s) Discharge-flow tube. [OH] and [HO2] by laser magnetic resonance. Given value of k based on k(HO2 + HO2) = 1.6·10^-12 cm^3 molecule^(-1) s^(-1).

(t) Discharge-flow system. [OH], [O], and [H] monitored by resonance fluorescence. Total pressure 1 Torr. Computer simulation of 9 reaction mechanism.

(u) VUV flash photolysis of small amounts of H2O diluted in N2 at atmospheric pressure under slow-flow conditions. [OH] by resonance absorption at 308.2 nm. Computer simulation of a 16 reaction mechanism.

(v) Photolysis of H2O at 184.9 nm in He or Ar diluent with trace amounts of O2. Total pressures 75–730 Torr. Steady-state concentration of OH monitored by laser induced fluorescence. Computer simulation of a 7 reaction mechanism with a given value of k for atmospheric pressure. The authors observed a decline of k at lower pressures and support the hypothesis of a pressure-dependent radical – radical association in addition to the abstraction path of the reaction.

(w) Discharge-flow reactor. Total pressures 2.13 – 6.34 mbar He. [OH], [HO2], and [O] by laser magnetic resonance. Computer simulation of a 15 reaction mechanism. The results of Hack et al.(28) are shown to be too low because of leaks in their apparatus; the former measurements were reproduced and the results were now consistent with new data.

(x) Discharge-flow system. Total pressures 8–10 Torr He. [OH] by electron paramagnetic resonance, [HO2] by laser magnetic resonance.

(y) Discharge-flow tube. [OH] monitored by laser induced fluorescence, [HO2] by rapid conversion to OH with excess NO. The authors suggest the formation of a bound H2O2 complex as pressure-dependent reaction component.

(z) Discharge-flow system; [OH] by resonance fluorescence, [HO2] by converting to OH with an excess of NO, NO2 used to remove O and H atoms. Total pressure 1 Torr. The author concludes little or no pressure dependence of k over the range 1–1000 Torr because of the good agreement with measurements at 1 atm.

Preferred Values

\[ k = 4.8·10^{-11} \exp(\frac{+250}{T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \] over range 300–2000 K

Reliability

\[ \Delta \log k = \pm 0.2 \text{ at } 300 \text{ K rising to } \pm 0.5 \text{ at } 2000 \text{ K.} \]

Comments on Preferred Values

The value of Keyser(27) is adopted as it is one of the few temperature dependent values and consistent with most of the low temperature material.

References

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ \text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 \]

\[ \text{T/K} \]

\[ \log(k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}) \]

\[ 10^3 T^{-1}/K^{-1} \]

- Experimental data
  - Troe 1969
  - Friswell and Sutton 1972
  - Hochanadel et al. 1972
  - Day et al. 1973
  - Peeters and Mahnen 1973
  - DeMore and Tschulow-Rex 1974
  - Hoch 1975
  - Dixon-Lewis and Rhodes 1975
  - Burrows et al. 1977
  - Hoch et al. 1978
  - Chang and Koilman 1978
  - DeMore 1979
  - Burrows et al. 1979
  - Lee et al. 1980
  - Hochanadel et al. 1980
  - Cox et al. 1981
  - Burrows et al. 1981
  - Kurylo et al. 1981
  - Sridharan et al. 1981
  - Thrush and Wilkinson 1981
  - Keyser 1981
  - Braden et al. 1982
  - DeMore et al. 1982
  - Temps and Wagner 1982
  - Rezemanov et al. 1985
  - Sridharan et al. 1984
  - Keyser 1988
  - Goodings and Hayhurst 1988

- This recommendation 1989

Rate Coefficient Data

<table>
<thead>
<tr>
<th>Rate Coefficient Measurements</th>
<th>T[K]</th>
<th>Reference</th>
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<tr>
<td>4.10^{-13} T^{0.8} exp(-604/T)</td>
<td>300-458</td>
<td>Greiner (1968)</td>
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<td>1.20^{-12}</td>
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<td>8.00^{-12} exp(-670/T)</td>
<td>298-670</td>
<td>Hack et al. (1974)</td>
<td>(c)</td>
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<td>6.80^{-13}</td>
<td>298</td>
<td>Harris and Pitts (1979)</td>
<td>(d)</td>
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<td>2.50^{-12} exp(-126/T)</td>
<td>245-423</td>
<td>Keyser (1980)</td>
<td>(e)</td>
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<td>3.00^{-12} exp(-164/T)</td>
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<td>Sridharan et al. (1980)</td>
<td>(f)</td>
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<td>1.40^{-12}</td>
<td>295</td>
<td>Nelson et al. (1981)</td>
<td>(g)</td>
</tr>
<tr>
<td>3.70^{-12} exp(-260/T)</td>
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<td>Wine et al. (1981)</td>
<td>(h)</td>
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<td>1.70^{-12}</td>
<td>296</td>
<td>Temps and Wagner (1982)</td>
<td>(i)</td>
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<tr>
<td>1.20^{-12}</td>
<td>298</td>
<td>Marinelli and Johnston (1982)</td>
<td>(i)</td>
</tr>
<tr>
<td>7.80^{-12} exp(-158/T)</td>
<td>250-370</td>
<td>Kurylo et al. (1982)</td>
<td>(k)</td>
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<tr>
<td>7.00^{-10} T^{2.1} exp(+838/T)</td>
<td>241-413</td>
<td>Lamb et al. (1983)</td>
<td>(l)</td>
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</tbody>
</table>

Reviews and Evaluations

1.70^{-11} exp(-907/T) | 300-800 | Baulch et al. (1972) | 13 |
7.60^{-12} exp(-674/T) | 200-700 | Baulch et al. (1980) | 14 |
1.20^{-11} exp(-722/T) | 300-1000 | Warnatz (1984) | 15 |
2.80^{-10} exp(-156/T) | 300-2500 | Tsang and Hampson (1986) | 16 |

Comments

(a) Flash photolysis of H$_2$O$_2$ [OH] by absorption at 306.4 nm. Total pressure 100 Torr Ar.
(b) Photolysis of H$_2$O$_2$ at 254 nm in the presence of CO and O$_2$; mass spectrometric analysis. Total pressures 10–40 Torr. $k/(k + CO) = 8.13$; given value of $k$ based on $k(\text{OH} + CO) = 1.5\times10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.
(c) Isothermal flow reactor; microwave discharge of H$_2$/He; OH produced by H + NO$_2$ reaction. [H] and [OH] monitored by ESR. $k$ probably underestimated; OH is more rapidly regenerated by HO$_2$ + NO $\rightarrow$ OH + NO$_2$.
(d) VUV flash photolysis of mixtures of H$_2$O$_2$ and H$_2$O; [OH] monitored by resonance fluorescence near 306 nm. Result is too low due to the formation of H by H$_2$O$_2$ photolysis and the fast back reaction H + HO$_2$ $\rightarrow$ 2 OH.
(e) Flow tube; microwave discharge of H$_2$/He and H + NO$_2$ reaction; [OH] by resonance fluorescence near 308 nm. No pressure dependence between 1 and 4 Torr.
(f) Flow tube; microwave discharge of H$_2$ or F$_2$/He mixtures. [OH] monitored by laser induced fluorescence at 308.6 nm, [H] and [O] by resonance fluorescence at 121.6 nm or 130.2 nm, [H$_2$O$_2$] by absorption measurements at 213.9 nm.
(g) Laser flash photolysis of HNO$_3$ at 249 nm under slow flow conditions. [OH] monitored by resonance fluorescence, [H$_2$O$_2$] by absorption at 200 nm. Total pressure 10 Torr Ar.
(h) Pulsed laser photolysis of H$_2$O$_2$ at 266 nm. [OH] monitored by resonance fluorescence, [H$_2$O$_2$] by absorption at 228.8 nm. Total pressure 100 Torr He or 40 Torr SF$_6$.
(i) Isothermal flow reactor; microwave discharge of F$_2$/He. [OH] and [HO$_2$] by laser magnetic resonance. Total pressures 2–6 mbar He.
(j) Laser flash photolysis of H$_2$O$_2$ at 248 nm. [OH] by resonance fluorescence, [H$_2$O$_2$] by absorption at 200 nm. Total pressure 10 Torr Ar.
(k) Flash photolysis of H$_2$O$_2$/H$_2$O/Ar mixtures over a wide pressure range. [H$_2$O$_2$] by absorption at 213.9 nm, [OH] by resonance fluorescence.
(l) Flash photolysis of H$_2$O$_2$. [OH] by resonance fluorescence near 308 nm, [H$_2$O$_2$] by absorption measurements in the 205–220 nm range and by Fourier transform infrared spectroscopy. Total pressure 760 Torr He.

Preferred Values

\[ k = 1.3\times10^{-11} \exp(-670/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range 300–1000 K} \]

Reliability

\[ \Delta \log k = \pm 0.2 \text{ over total range.} \]

Comments on Preferred Values

The preferred value is based on the activation energy recommended by Baulch et al.\textsuperscript{14}; the preexponential factor has been increased to represent new experimental data.

For clarity, rate data measured before 1972 are included in the Arrhenius plot (see Baulch et al.\textsuperscript{13} for reference).

References
\textsuperscript{1}N. R. Greiner, J. Chem. Phys. 72, 406 (1968).
\textsuperscript{2}R. A. Gorse and D. H. Volman, J. Photochem. 1, 1 (1972).
\textsuperscript{4}G. W. Harris and J. N. Pitts, J. Chem. Phys. 70, 2581 (1979).
\textsuperscript{5}L. F. Keyser, J. Phys. Chem. 84, 1659 (1980).
BAULCH ET AL.

OH + H$_2$O$_2$ $\rightarrow$ HO$_2$ + H$_2$O

$T/K$

EXPERIMENTAL DATA

- Gorse and Volman 1972
- Hack et al. 1974
- Meagher and Heidken 1974
- Hack et al. 1975
- Vardanyan et al. 1974
- Horia and Pitka 1979
- Baldwin and Walker 1979
- Keyser 1980
- Sridharan et al. 1980
- Hack et al. 1980
- Temps and Wagner 1982
- Kaufman 1981
- Wine et al. 1981
- Sridharan et al. 1981
- Keyser et al. 1981
- Marinelli and Johnston 1982
- Nelson et al. 1981
- Kurylo et al. 1982
- Motina et al. 1982
- Lamp et al. 1983
- Baldwin et al. 1970
- Frost and Oldenburg 1938
- Forst and Giguere 1958
- Baldwin and Meyer 1960
- Baldwin and Burrell 1962
- Foner and Hudson 1962
- Baldwin et al. 1965
- Greiner 1966
- Hoare 1966
- Baldwin et al. 1967
- Greiner 1968

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Log($k$/cm$^3$ molecule$^{-1}$ s$^{-1}$) vs. $10^3 T^{-1}$/K$^{-1}$

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ \text{OH} + \text{NH} \rightarrow \text{NO} + \text{H}_2 \quad (1) \]
\[ \rightarrow \text{N} + \text{H}_2\text{O} \quad (2) \]

**Thermodynamic Data** (See Comments on Preferred Values)

\[ \Delta H_{298} (1) = -305 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298} (1) = -23.5 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ K_p (1) = 1.52 \times 10^{-7} T^{-0.19} \text{exp}(36800/T) \]
\[ \Delta H_{298} (2) = -164 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298} (2) = -22.8 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ K_p (2) = 5.61 \times 10^{-7} T^{-0.18} \text{exp}(19890/T) \]

**Rate Coefficient Data** \((k = k_1 + k_2)\)

<table>
<thead>
<tr>
<th>(k) [cm³ molecule⁻¹ s⁻¹]</th>
<th>(T) [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.3 \times 10⁻¹¹</td>
<td>300</td>
<td>Hack and Kurzke (1985)¹</td>
<td>(a)</td>
</tr>
</tbody>
</table>

**Comments**

(a) Discharge-flow system; NH₂ generated by the sequence F + NH₃ → HF + NH₂O; added downstream. [NH₂], [NH], [OH] monitored by laser induced fluorescence. Measured concentration profiles simulated.

**Preferred Values**

\[ k = 8.0 \times 10^{-11} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} \text{over range} 300-1000 \text{ K} \]

Reliability

\[ \Delta \log k = \pm 0.5 \text{ over range} 300-1000 \text{ K} \]

**Thermodynamic Data** (See Comments on Preferred Values)

\[ \Delta H_{298} (1) = -26.1 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298} (1) = -24.6 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ K_p (1) = 2.09 \times 10^{-3} T^{0.405} \text{exp}(3420/T) \]
\[ \Delta H_{298} (2) = -115 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298} (2) = -8.3 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ K_p (2) = 0.591 T^{-0.072} \text{exp}(13800/T) \]

**Rate Coefficient Data**

<table>
<thead>
<tr>
<th>(k) [cm³ molecule⁻¹ s⁻¹]</th>
<th>(T) [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_1) (= 1.1 \times 10^{-13}) exp(−2500/T)</td>
<td>300–1000</td>
<td>Baulch et al. (1973)³</td>
<td>(a)</td>
</tr>
<tr>
<td>(k_1) (= 3.3 \times 10^{-14}) exp(−2500/T)</td>
<td>300–1000</td>
<td>Hamson (1980)²</td>
<td>(b)</td>
</tr>
<tr>
<td>(k_1) (= 1.1 \times 10^{-13})</td>
<td>–</td>
<td>CODATA (1982)⁵</td>
<td>(c)</td>
</tr>
</tbody>
</table>

**Comments**

(a) Calculated from \(k_{-1}\) and a value for the equilibrium constant now known to be incorrect.

(b) Calculated from Baulch et al.’s \(k_{-1}\) and revised equilibrium data.

(c) Review of low temperature data; no recommendation.

**Preferred Values**

\[ k_1 = 3.3 \times 10^{-14} T^{0.405} \text{exp}(−2500/T) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} \text{over range} 500-2500 \text{ K} \]

Reliability

\[ \Delta \log k_1 = \pm 0.5 \text{ over range} 500-2500 \text{ K} \]

**Comments on Preferred Values**

There are no experimental data for \(k\) or the branching ratio.

However, the reverse of reaction (1) has been extensively studied. We have evaluated the available data (Refs. 4–18) and obtain $k_{-1} = 1.6 \times 10^{-11} \exp(-3670/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$ over the range 500–2500 K. Combining this with the thermodynamic data gives the recommended value for $k_1$. There is no information on the relative importance of the two possible channels. There are significant uncertainties associated with the thermodynamic data on NH.

References


**Thermodynamic Data**

\[ \Delta H_{f,0} = -104 \text{ kJ mol}^{-1} \]

\[ \Delta S_{f,0} = -52.8 \text{ J K}^{-1} \text{ mol}^{-1} \]

\[ k_r = 4.24 \times 10^{-17} T^{1.18} \exp(13000/T) \]

**Rate Coefficient Data**

<table>
<thead>
<tr>
<th>( k \text{[cm}^3 \text{ molecule}^{-1} \text{s}^{-1}] )</th>
<th>( T \text{[K]} )</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.7 \times 10^{-13}</td>
<td>296</td>
<td>Cox, Derwent, and Holt (1976) (^{1})</td>
<td>(a)</td>
</tr>
<tr>
<td>1.5 \times 10^{-13}</td>
<td>299</td>
<td>Atkinson, Perry, and Pitts (1976,1977) (^{2,3})</td>
<td>(b)</td>
</tr>
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<td>3.0 \times 10^{-13}</td>
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<td>Chan et al. (1977) (^{4})</td>
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<td>Atri et al. (1977) (^{5})</td>
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<td>Overend and Paraksevopoulos (1977) (^{6})</td>
<td>(e)</td>
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<td>Butler, Solomon, and Snelson (1978) (^{7})</td>
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<td>( \approx 1.5 \times 10^{-13} )</td>
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<td>Clyne and Holt (1979) (^{9})</td>
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<td>Husain, Plane, and Slater (1981) (^{10})</td>
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<td>Ravishankara and Thompson (1983) (^{11})</td>
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<td>DeMore (1984) (^{13})</td>
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<td>Hofzumahaus and Stuhl (1984) (^{14})</td>
<td>(m)</td>
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<td>2.4 \times 10^{-13}</td>
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<td>Niki et al. (1984) (^{15})</td>
<td>(n)</td>
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<td>1.5 \times 10^{-13}</td>
<td>298</td>
<td>Smith and Williams (1985) (^{16})</td>
<td>(o)</td>
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</tbody>
</table>

**Reviews and Evaluations**

| \( 2.5 \times 10^{-17} T^{+1} \exp(+385/T) | 250-2000 | Baulch et al. (1976) \(^{17}\) | |
| 7.3 \times 10^{-18} T^{+1} \exp(+373/T) | 300-2000 | Warnatz (1979) \(^{18}\) |
| 1.2 \times 10^{-13} \exp(9.2 \times 10^{-4} T) | 300-2000 | Zellner (1979) \(^{19}\) |
| 1.5 \times 10^{-13} | 200-300 | Baulch et al. (1980) \(^{20}\) |
| 1.2 \times 10^{-13} \exp(9.2 \times 10^{-4} T) | 300-2500 | Tsang and Hampson (1986) \(^{21}\) |
EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

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Comments

(a) Flow tube: photolysis of gaseous nitrous acid (HONO) at atmospheric pressure. [HONO], [NO], and [NO2] by the ozone–NO chemiluminescence technique. k measured relative to

\[ k(\text{OH} + \text{HONO}) \rightarrow \text{H}_2 \text{O} + \text{NO}_2 \text{ and based on} \]

\[ k(\text{OH} + \text{H}_2 \rightarrow \text{H}_2 \text{O} + \text{H}) = 7.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}. \]

(b) Pulsed vacuum ultraviolet photolysis of H2O (λ > 105 nm); slow flow conditions. [OH] by time-resolved resonance fluorescence at 306.4 nm. No effect of total pressure in the range 25–654 Torr Ar; when SF6 is used as diluent gas, k rises from 1.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} at 25 Torr to 3.4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} at 604 Torr.

(c) Photolysis of dilute mixtures of HONO, CO, i-C4H10, and NOx in synthetic air; Fourier transform infrared spectroscopy. k measured relative to k(\text{OH} + i-C4H10). Given value of k for p = 700 Torr, reducing to 1.4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} at 100 Torr.

(d) Small amounts of CO added to slowly reacting H2O/NO2 mixtures; relative H2O and CO2 yields by gas chromatography. Numerical integration of 19 reaction mechanism.

\[ k(\text{CO} + \text{OH})/k(\text{OH} + \text{H}_2) = 0.235; \text{based on} \]

\[ k(\text{OH} + \text{H}_2) = 6.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}. \text{Total pressure 500 Torr}. \]

(e) VUV photolysis (λ < 160 nm) of H2O in the presence of CO; [OH] by time-resolved resonance absorption. Given value of k for p = 50 Torr He. k = 3.2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} for 200 and 350 Torr SF6.

(f) Photolysis of H2O in O2/NO or O2/NO2/i-butane mixtures; [CO] by gas chromatography. Rate of Ref. reaction k(\text{OH} + i-C4H10) = 1.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} at 100 Torr based on a low pressure value of k(\text{CO} + \text{OH}) = 1.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} and assumed to be pressure-independent. Given value of k is the high-pressure limit for p > 300 Torr; depends also on the rate of the H2O + OH reaction (set to 8.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}).

(g) Pulsed VUV photolysis of H2O in the presence of CO and N2 or He; [OH] by time-resolved absorption near 308 nm. Total pressures 25–750 Torr. No pressure effect of N2 at pressures below 1 atm, but a strong increasing effect of O2 at high N2 pressures; at high O2 concentrations constant value of k; at 0.28 Torr O2 linear dependence of k on N2 pressure. Observations explained by a complex reaction mechanism involving formation of an excited HOCO adduct decomposing to H + CO2 or reacting after stabilization with O2 to give H2O + CO2. The authors recommend a linear extrapolation 1.4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} near 0 Torr to 2.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} at 760 Torr.

(h) Flow system; microwave discharge of H2, OH from H + NO2; [OH] by resonance fluorescence near 307 nm. Total pressure 200–260 Pa.

(i) VUV photolysis of water vapour (λ > 105 nm); [OH] by time-resolved resonance fluorescence at 307 nm. Slow flow conditions: total pressure 3.2 kPa He.

(j) Flash photolysis of H2O (λ > 165 nm); [OH] by time-resolved resonance fluorescence. Slow flow conditions; total pressure 100 Torr Ar.

(k) VUV flash photolysis of H2O; [OH] by time-resolved resonance absorption at 308.2 nm. Given value of k for p = 600 Torr N2, reducing to k = 1.4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} at 20 Torr. Addition of small amounts of O2 (0.1–0.2 Torr) resulted in non-exponential and slower decays of [OH]. Relative efficiencies in the deactivation of HOHO+: H2O + SF6 + CF4 + N2 + He = 1.0 : 0.5 : 0.3 : 0.1 : 0.02.

(l) Photolysis of H2O/CO mixtures at 184.9 nm; [OH] by laser-induced fluorescence near 309 nm. Slow flow conditions. k given for total pressures of 200–730 Torr Ar; similar result at 200 Torr N2. With SF6 as diluent k increases reaching a factor of 2 at 730 Torr SF6. Within the experimental accuracies no dependence on Ar pressure, for N2 enhancement of 30–50%; results according to the normal third-body efficiencies of these gases. No influence of added O2 on the pressure enhancement. Recommendation for pressure dependence: k = 1.5 \times 10^{-13} (1 + 0.4 \rho_{[\text{[atm]}]} \text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1}.

(m) VUV photolysis of H2O in the presence of N2; [OH] by resonance absorption. Total pressure 980–1000 mbar. Reinterpretation of the data of Biermann, Zetzsch, and Stuhl; effects of O2 addition explained by radical – radical reactions not considered there.

(n) Photolysis of mixtures containing RONO (R = CH3, C2H5), NO, isotopic CO, and C3H8; Fourier transform infrared spectroscopy. Total pressure 700 Torr purified air. k(\text{OH} + \text{C3H8})/k(\text{OH} + \text{CO}) = 35.95 and 36.30 for 12CO and 13CO, respectively.

\[ k(\text{OH} + \text{CO}) \text{based on} k(\text{OH} + \text{C3H8}) = 8.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}. \]

(o) Pulsed photolysis of H2O or HNO3 (λ > 185 nm); [OH] by laser induced fluorescence. Total pressure 18 Torr Ar.

Preferred Values

\[ k = 1.05 \times 10^{-17} T^{1.5} \exp(250/T) \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \text{ over range 300–2000 K}. \]

Reliability

\[ \Delta \log k = \pm 0.2 \text{ at 300 K rising to} \pm 0.5 \text{ at 2000 K} \]

Comments on Preferred Values

The large scatter of the high temperature measurements does not allow exact assignment of a rate coefficient. Thus, a relatively high value has been chosen compatible with flame simulations which are very sensitive to the rate of this reaction.°

References

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

$\text{OH} + \text{CO} \rightarrow \text{H} + \text{CO}_2$

\[ T/K \]

\[ \log(k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}) \]

\[ 10^3T^{-1}/K \]

EXPERIMENTAL DATA

- Cox et al. 1976
- Atkinson et al. 1976
- Abl et al. 1977
- Overend and Paraskevopoulos 1977
- Duder et al. 1978
- Durrani et al. 1979
- Clyne and Hall 1979
- Hatain et al. 1981
- Rotrans and Thompson 1983
- Paraskevopoulos and Irwin 1984
- DeMore 1984
- Hotzumahaus and Stuhl 1984
- NCI et al. 1984
- Smith and Williams 1985
- Chan et al. 1977
- Dabbs et al. 1971
- Kijewski and Tres 1971
- Mezely and Smith 1971
- Singh and Sawyer 1971
- Dixon-Lewis 1972
- Stuhl and NCI 1972
- Bone and Wilson 1972
- Garlmer et al. 1973
- Peeters and Manthen 1973
- Smith and Zeller 1973
- Westenberg and DeHaas 1973
- Davies et al. 1974
- Hewerd and Dreson 1974
- Trainer and Von Rosenberg 1975
- Vondoren et al. 1975
- Hynes et al. 1988

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**Thermodynamic Data**

\[
\begin{align*}
\Delta H_{298}^0 (1) &= -386 \text{ kJ mol}^{-1} \\
\Delta S_{298} (1) &= -138 \text{ J K}^{-1}\text{mol}^{-1} \\
K_p(1) &= 1.26 \times 10^{-5} T^{-0.295} \exp(46700/T)
\end{align*}
\]

\[
\begin{align*}
\Delta H_{298}^0 (2) &= 16.1 \text{ kJ mol}^{-1} \\
\Delta S_{298} (2) &= -16.7 \text{ J K}^{-1}\text{mol}^{-1} \\
K_p(2) &= 1.50 \times 10^{-4} T^{0.975} \exp(-1570/T)
\end{align*}
\]

\[
\begin{align*}
\Delta H_{298}^0 (3) &= 49.6 \text{ kJ mol}^{-1} \\
\Delta S_{298} (3) &= -34.6 \text{ J K}^{-1}\text{mol}^{-1} \\
K_p(3) &= 3.79 \times 10^{-2} T^{0.798} \exp(-5470/T)
\end{align*}
\]

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

<table>
<thead>
<tr>
<th>(k[^c m^3 \text{ molecule}^{-1} \text{ s}^{-1}])</th>
<th>(T[K])</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_1 = 3.3 \times 10^{-8} \exp(-13800/T))</td>
<td>1700-2300</td>
<td>Bhaskaran, Frank, and Just (1979)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>(9.3 \times 10^{-11})</td>
<td>296</td>
<td>Sworski, Hochanadel, and Ogren (1980)(^2)</td>
<td>(b)</td>
</tr>
<tr>
<td>(k_3 = 1.5 \times 10^{-9} \exp(-7800/T))</td>
<td>1850-2500</td>
<td>Roth and Just (1984)(^3)</td>
<td>(c)</td>
</tr>
<tr>
<td>(k_4)</td>
<td></td>
<td>Tsang and Hampson (1986)(^4)</td>
<td>(d)</td>
</tr>
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</table>

**Comments**

(a) Shock-tube decomposition of \(C_2H_4/O_2\) mixtures with direct detection of \(H\) and \(O\) by atomic resonance absorption spectrometry. \(k_3\) derived from a computer simulation of the experimental [\(H\)] and [\(O\)] profiles. It was suggested that channel (3) proceeds via the sequence \(\text{OH} + \text{CH}_3 \rightarrow \text{H} + \text{CH}_2\text{O} \text{ and } \text{CH}_3\text{O} \rightarrow \text{CH}_2\text{O} + \text{H}\), i.e. overall reaction \(\text{OH} + \text{CH}_3 \rightarrow 2\text{H} + \text{CH}_2\text{O}\).

(b) Flash photolysis of \(H_2O\) in presence of \(CH_2\) and \(O_2\) monitored by absorption at 216 nm. Rate coefficient obtained from a computer simulation of \([CH_3]_2\) profiles, based on a mechanism of 11 elementary reactions.

(c) Similar study to that of Bhaskaran et al.\(^1\) (see comment (a)) with CH\(_4\)/O\(_2\) mixtures.

(d) The reaction channels (1), (2), and (3) were assumed and it was suggested that (2) would be more likely than (3) on thermochemical grounds. Hence \(k_1 + k_2\) is an estimated high-pressure limiting value. RRKM calculations were carried out to obtain a pressure dependence of \(k_1 + k_2\). Dean and Westmoreland\(^2\) have recently made theoretical calculations of the energized complex, \(CH_3OH^+\), by unimolecular reaction rate theory, in which they consider six possible reaction channels.

**Preferred Values**

\[k = 6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range } 300-2000 \text{ K}\]

**Reliability**

\[\Delta \log k = \pm 0.7 \text{ over range 300-2000 K}\]

**Comments on Preferred Values**

The rate coefficients obtained by Bhaskaran et al.\(^1\) and by Roth and Just\(^4\) are in excellent agreement at 2000 K, i.e. \(k_3 = 3.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) and, within the experimental errors, equal to that of the low temperature study of Sworski et al.\(^2\), \(k = 9.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\).

Accordingly, we have selected a temperature independent overall rate coefficient of \(k = 6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\).

So far there has been no direct evidence concerning the product channels of this reaction. Channel (3) is the pathway suggested in the shock tube studies.\(^1\)\(^2\). A recent report on the \(\text{CH}_3 + \text{H}_2\text{O} \text{ reaction}^5\) has confirmed that the major products are \(\text{CH}_3 + \text{OH}\) and consequently channel (4) needs to be considered here. More experimental work is required on this aspect of the reaction together with direct measurements of \(k\) and any branching ratios as a function of temperature.

**References**

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

OH + CH₄ → H₂O + CH₃

Thermodynamic Data
ΔH°₂₉₈ = -60.2 kJ mol⁻¹
ΔS°₂₉₈ = 13.11 K⁻¹ mol⁻¹
K° = 20.5 T⁻¹.041 exp( +7050/T)

Rate Coefficient Data

<table>
<thead>
<tr>
<th>k [cm³ molecule⁻¹ s⁻¹]</th>
<th>Temperature [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate Coefficient Measurements</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.610⁻¹⁵</td>
<td>296</td>
<td>Sworski et al. (1980)¹</td>
<td>(a)</td>
</tr>
<tr>
<td>1.3210⁻¹⁷ T⁻¹.⁸² exp(−1355/T)</td>
<td>298–1020</td>
<td>Tully and Ravishankara (1980)²</td>
<td>(b)</td>
</tr>
<tr>
<td>7.710⁻¹⁵</td>
<td>300</td>
<td>Husain et al. (1981)³</td>
<td>(c)</td>
</tr>
<tr>
<td>1.2810⁻²⁴ T⁻¹.⁸² exp(−455/T)</td>
<td>296–473</td>
<td>Jeong and Kaufman (1984)⁵</td>
<td>(d,e)</td>
</tr>
<tr>
<td>1.510⁻¹⁸ T⁻².³ exp(−1370/T)</td>
<td>300–2000</td>
<td>Cohen (1982)⁶</td>
<td>(f)</td>
</tr>
<tr>
<td>1.310⁻¹²</td>
<td>1030</td>
<td>Fairchild et al. (1982)⁷</td>
<td>(g)</td>
</tr>
<tr>
<td>2.5710⁻¹⁷ T⁻¹.⁸² exp(−1396/T)</td>
<td>298–1512</td>
<td>Madronich and Felder (1984)⁸</td>
<td>(h)</td>
</tr>
<tr>
<td>3.710⁻¹¹ exp(−2550/T)</td>
<td>340–1750</td>
<td>Jonas et al. (1984)⁹</td>
<td>(i)</td>
</tr>
<tr>
<td>(1.25, 225, 1.55)10⁻¹²</td>
<td>(830, 870, 930)</td>
<td>Smith et al. (1985)¹¹</td>
<td>(a)</td>
</tr>
<tr>
<td>(2.1, 1.33, 3.6)10⁻¹²</td>
<td>(975,1030,1120)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1.72,3.3,3)10⁻¹²</td>
<td>(1150,1176,1200)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2.9,4.4,4,2)10⁻¹²</td>
<td>(1240,1400,1412)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Reviews and Evaluations

<table>
<thead>
<tr>
<th>Preferred Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>k = 2.5710⁻¹⁷ T⁻¹.⁸³ exp(−1396/T) cm³ molecule⁻¹ s⁻¹</td>
</tr>
</tbody>
</table>

Reliability

Reliability

Comments on Preferred Values

The rate constant is now known with considerable reliability and precision between 240 and 1500 K with excellent agreement between a large number of techniques. The early data of Fenimore and Jones¹⁸ has been reinterpreted using k(OH + CO) given by Baulch et al.¹⁹. The

Comments

(a) Flash photolysis of N₂/CH₄/H₂O mixtures. [CH₃] monitored by absorption at 216 nm.
(b) Flash photolysis of Ar/CH₄/H₂O mixtures. [OH] monitored by resonance fluorescence. Static system, first-order decay of [OH].
(c) Flash photolysis of He/CH₄/H₂O mixtures. [OH] monitored by resonance fluorescence. Flow system, first-order decay of [OH].
(d) Discharge flow system. [OH] monitored by resonance fluorescence. Pseudo-first-order conditions with [RH] ≫ [OH].
(e) Correction to fitting procedures applied, same kinetic data as for comment (d).
(f) Theoretical expression derived from transition state theory and calibrated using experimental data.
(g) Pulsed infrared CO₂ laser production of OH from H₂O₂; [OH] monitored by laser induced fluorescence.
(h) Flash photolysis of Ar/CH₄/H₂O mixtures; [OH] monitored by resonance fluorescence; first-order decay of [OH].
(i) Microwave discharge of He/CH₄/H₂O mixtures. Pseudo-first-order kinetics; [OH] monitored by resonance absorbance.
(j) Shock tube measurement, reported in comment on results of Ref. 8.
(k) Recommended value, based on low temperature data.
(l) Evaluation specifically for atmospheric modelling.
(m) Evaluation based on experimental data between 240 and 1600 K; favour the data of Tully and Ravishankara's² in making the recommendation.
(n) Recommends Tully and Ravishankara's expression without comment.
(o) Based on experimental data considered reliable, some weighting of data.
(p) Accept the recommendation given by Cohen and Westberg¹⁴.

Preferred Values

Reliability

Comments on Preferred Values

preferred value of $k$ is that obtained experimentally by Madronich and Felder\textsuperscript{8} which predicts very precisely the data obtained between 240 and 2000 K. It is not clear why the data of Zellner and Steinert\textsuperscript{20}, and of Jonah, Mulac, and Zeglinski\textsuperscript{9} lie consistently above the preferred values. Details of pre-1980 data are given in Ref. 16.

References

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

OH + CH₄ → H₂O + CH₃

T/K

Log(k/cm³ molecule⁻¹ s⁻¹)

10⁻²T⁻¹/K⁻¹

EXPERIMENTAL DATA

Svensson et al 1980
Tully and Rowlandshala 1980
Hassan et al 1981
Jeong and Kaufman 1981
Jee et al 1984
Farcas 1982
Cohen 1982
Mady and Felder 1984
Jonas et al 1984
Gom 1984
Smith et al 1985
Baldwin et al 1970
Gruner 1970
Bakker et al 1981
Simonsen et al 1971
Approx 1977
Carder 1973
Svensson 1973
Petersen and Herhen 1974
Doval et al 1975
Marston et al 1974
Ellison 1975
Gardin and Mala 1975
Hocen 1975
Vander et al 1975
Stewart and Zeller 1975
Bradley et al 1976
Cox and Sher (two works) 1976
Howard and Eveson 1976
Zeller and Stenert 1978
Ernst et al 1978

This Recommendation 1989

**Thermodynamic Data**

\[ \Delta H^{\text{f}}_{298} = -435 \text{ kJ mol}^{-1} \]

\[ \Delta S^{\text{f}}_{298} = -21.9 \text{ J K}^{-1}\text{mol}^{-1} \]

\[ K_p = 1.29 T^{-0.425} \exp(5200/T) \]

**Rate Coefficient Data**

<table>
<thead>
<tr>
<th>( k [\text{cm}^3\text{ molecule}^{-1}\text{ s}^{-1}] )</th>
<th>( T [\text{K}] )</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0 \times 10^{-11}</td>
<td>1000–1700</td>
<td>Browne <em>et al.</em> (1969)<em>1</em></td>
<td></td>
</tr>
<tr>
<td>1.7 \times 10^{-10}</td>
<td>1700–2500</td>
<td>Bowman (1970)<em>2</em></td>
<td></td>
</tr>
<tr>
<td>1.8 \times 10^{-10}</td>
<td>296</td>
<td>Temps and Wagner (1984)<em>3</em></td>
<td></td>
</tr>
<tr>
<td>8.3 \times 10^{-11}</td>
<td>1000–2500</td>
<td>Warnatz (1984)<em>4</em></td>
<td></td>
</tr>
<tr>
<td>( = 5.0 \times 10^{-11} )</td>
<td>300–2500</td>
<td>Tsang and Hampson (1986)<em>5</em></td>
<td></td>
</tr>
</tbody>
</table>

**Comments**

(a) Modelling study of rich and lean acetylene flames at low pressures. Species profiles by gas chromatography, [OH], [CH], and [C2] by absorption measurements.

(b) Oxidation of methane and ethane in Ar behind incident or reflected shock waves; reaction monitored by infrared emission of CO2, CO, and H2O. Numerical modelling of 14 (11) reaction mechanism for CH4 (C2H6) reaction. Results only slightly sensitive to variations in \( k \).

(c) Discharge-flow reactor; [OH] and [CHO] from far infrared laser magnetic resonance spectroscopy. Total pressure \( = 1.5 \text{ mbar He} \).

**Preferred Values**

\[ k = 1.7 \times 10^{-10} \text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1} \text{ over range 300–2500 K} \]

**Reliability**

\[ \Delta \log k = \pm 0.3 \text{ over range 300–2500 K} \]

**Comments on Preferred Values**

The rate coefficient for this reaction is expected to have only a very small temperature coefficient. This is supported by the high values of \( k \) measured at 298 K and the few existing higher temperature measurements. The preferred values are based on all of the existing data*1,2,3.

**References**


EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ \text{OH} + \text{HCHO} \rightarrow \text{CHO} + \text{H}_2\text{O} \]

**Thermodynamic Data**

\[ \Delta H_{\text{f}}^{298} = -121 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{f}}^{298} = 11.0 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_p = 42.9 T^{-0.318} \exp (+14400/T) \]

**Rate Coefficient Data**

<table>
<thead>
<tr>
<th>( k ) [cm(^3) molecule(^{-1}) s(^{-1})]</th>
<th>( T ) [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.6 \times 10^{-11}</td>
<td>1600</td>
<td>Peeters and Mahnen (1973)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>1.7 \times 10^{-11}</td>
<td>485</td>
<td>Vandooren and Van Tiggelen (1977)(^2)</td>
<td>(b)</td>
</tr>
<tr>
<td>2.2 \times 10^{-11}</td>
<td>570</td>
<td>Van Tiggelen (1977)(^2)</td>
<td>(b)</td>
</tr>
<tr>
<td>1.25 \times 10^{-11} \exp (-90/T)</td>
<td>299-426</td>
<td>Atkinson and Pitts (1978)(^3)</td>
<td>(c)</td>
</tr>
<tr>
<td>1.25 \times 10^{-11} \exp (-84/T)</td>
<td>1600-3000</td>
<td>Dean et al. (1980)(^4)</td>
<td>(d)</td>
</tr>
<tr>
<td>1.05 \times 10^{-11}</td>
<td>228-360</td>
<td>Stief et al. (1984)(^5)</td>
<td>(f)</td>
</tr>
<tr>
<td>8.4 \times 10^{-12}</td>
<td>299</td>
<td>Temps and Wagner (1984)(^7)</td>
<td>(g)</td>
</tr>
<tr>
<td>1.66 \times 10^{-11} \exp (-170/T)</td>
<td>292-597</td>
<td>Zabarnick et al. (1988)(^8)</td>
<td>(h)</td>
</tr>
</tbody>
</table>

**Reviews and Evaluations**

<table>
<thead>
<tr>
<th>( k ) [cm(^3) molecule(^{-1}) s(^{-1})]</th>
<th>( T ) [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 \times 10^{-11}</td>
<td>200-425</td>
<td>Hampson (1980)(^9)</td>
<td>(i)</td>
</tr>
<tr>
<td>5.0 \times 10^{-11} \exp (-600/T)</td>
<td>300-2500</td>
<td>Warnatz (1984)(^10)</td>
<td>(j)</td>
</tr>
<tr>
<td>1.1 \times 10^{-11}</td>
<td>200-425</td>
<td>CODATA (1984)(^11)</td>
<td>(k)</td>
</tr>
<tr>
<td>1.0 \times 10^{-11}</td>
<td>200-300</td>
<td>NASA (1985)(^12)</td>
<td>(k)</td>
</tr>
<tr>
<td>9.0 \times 10^{-12}</td>
<td>228-426</td>
<td>Atkinson (1986)(^13)</td>
<td>(l)</td>
</tr>
<tr>
<td>5.7 \times 10^{-15} T^{1.18} \exp (+225/T)</td>
<td>298-1600</td>
<td>Tsang and Hampson (1986)(^14)</td>
<td>(m)</td>
</tr>
</tbody>
</table>

**Preferred Values**

\[ k = 5.7 \times 10^{-15} T^{1.18} \exp (+225/T) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} \text{over range 300-3000 K} \]

**Reliability**

\[ \Delta \log k = \pm 0.7 \text{ at 3000 K reducing to } \pm 0.1 \text{ at 300 K} \]

**Comments on Preferred Values**

The low and intermediate temperature direct studies (200-600 K) are all in good agreement. The high temperature data of Dean et al.\(^4\) and Peeters and Mahnen\(^1\), and the intermediate temperature data of Vandooren and Van Tiggelen\(^2\) and Hoare\(^15\) are higher than expected by simple Arrhenius extrapolation. However, the earlier work is considered less reliable due to the complex systems used and the dependence of the derived \( k \) values on other rate constants in the models. We consider that the available data is best fitted by the expression of Tsang and Hampson\(^14\), which we recommend here.

**References**

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BAULCH ET AL.

4A. M. Dean, R. L. Johnson, and D. C. Steiner, Comb. Flame 37, 41 (1980).
12NASA evaluation No. 8, JPL Publication 87-41, September 1987.
EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

OH + HCHO → CHO + H₂O

T/K

EXPERIMENTAL DATA
Peeters and Mohnen 1973
Vandooren and Von Tiggelen 1977
Atkinson and Pits 1978
Deon et al. 1980
Stief et al. 1980
Nikl et al. 1984
Temps and Wagner 1984
Zobarnick et al. 1987
This Recommendation 1989

Thermodynamic Data

\[ \Delta H_{298}^\circ (1) = -89.8 \text{ kJ mol}^{-1} \]

\[ \Delta S_{298}^\circ (1) = -23.5 \text{ J K}^{-1}\text{mol}^{-1} \]

\[ K_p(1) = 2.99 \times 10^{-4} \exp \left( \frac{11100}{T} \right) \]

\[ \Delta H_{298}^\circ (2) = -96.8 \text{ kJ mol}^{-1} \]

\[ \Delta S_{298}^\circ (2) = -39.4 \text{ J K}^{-1}\text{mol}^{-1} \]

\[ K_p(2) = 1.14 \times 10^{-6} \exp \left( \frac{12100}{T} \right) \]

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

<table>
<thead>
<tr>
<th>(k) [(\text{cm}^3) molecule(^{-1}) s(^{-1})]</th>
<th>(T) [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1.0 \times 10^{-10})</td>
<td>2300–2600</td>
<td>Morley (1976)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>(9.5 \times 10^{-11})</td>
<td>1950–2380</td>
<td>Haynes (1977)(^2)</td>
<td>(b)</td>
</tr>
<tr>
<td>(8.3 \times 10^{-12})</td>
<td>1200–2600</td>
<td>Shaub and Bauer (1978)(^3)</td>
<td>(c)</td>
</tr>
<tr>
<td>(&lt; 1.85 \times 10^{-10})</td>
<td>2460–2840</td>
<td>Szekely, Hanson, and Bowman (1984)(^4)</td>
<td>(d)</td>
</tr>
</tbody>
</table>

Comments

(a) Hydrocarbon/O\(_2\) flames with additions of CH\(_3\)CN and pyridine. Product profiles (HCN, NH\(_3\), NO) determined by quadrupole mass spectrometry. \(k\) calculated from HCN profile. Equilibrium between CN and HCN assumed.

(b) Premixed hydrocarbon/O\(_2\) flames with additions of NH\(_3\), NO, or pyridine. Samples removed by water cooled silica probe for analysis by infrared spectrophotometry (NO), absorption in NaOH and determination of CN and NH species using ion-selective electrodes. [H] monitored by Li/LiOH technique.

(c) Single pulse shock tube study of Ar/O\(_2\)/hydrocarbon/NO mixtures. Products (CH\(_2\), C\(_2\)H\(_4\), C\(_2\)H\(_2\), CO, CO\(_2\), NO, N\(_2\), Ar) determined by gas chromatography. Yields fitted using large reaction mechanism. Results only slightly sensitive to value of \(k\).

(d) Shock tube study of C\(_2\)N\(_2\)/H\(_2\)O/Ar mixtures. [CN] monitored by broad band absorption at 388 nm, [OH] by laser absorption at 306.67 nm. Profiles fitted to reaction mechanism. Upper limit only to \(k\) obtained.

Preferred Values

\[ k = 1.0 \times 10^{-10} \text{ cm}^3\text{ molecule}^{-1}\text{s}^{-1} \text{ over range 1500–3000 K} \]

Reliability

\[ \Delta \log k = \pm 0.5 \text{ over range 1500–3000 K} \]

Comments on Preferred Values

All of the determinations of \(k\) involve computer modelling of substantial reaction mechanisms. The most direct determinations are those of Haynes\(^2\) and Morley\(^1\) which are the basis of our recommended values but with substantial error limits reflecting the lack of good quality direct measurements.

References

**Rate Coefficient Measurements**

<table>
<thead>
<tr>
<th>( k ) ( \text{[cm}^3 \text{molecule}^{-1} \text{s}^{-1}] )</th>
<th>( T ) ( \text{[K]} )</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 = 3.31 \times 10^{-11} \exp (-7554/T) )</td>
<td>1666–2300</td>
<td>Kanamura and Daito (1977)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>( k_3 = 3.32 \times 10^{-13} )</td>
<td>1950–2380</td>
<td>Haynes (1977)(^2)</td>
<td>(b)</td>
</tr>
<tr>
<td>( k_3 = 1.60 \times 10^{-11} \exp (-1860/T) )</td>
<td>298–563</td>
<td>Phillips (1979)(^3)</td>
<td>(c)</td>
</tr>
<tr>
<td>( k_1 = 1.0 \times 10^{-12} )</td>
<td>1800–2500</td>
<td>Roth, Lühr, and Hermann (1980)(^4)</td>
<td>(d)</td>
</tr>
<tr>
<td>( k_1 = 1.2 \times 10^{-12} )</td>
<td>2650</td>
<td>( k_1 ) and ( k_3 ) found and fitted to Troe expression to give quoted ( k_0 ) and ( k_{int} ). Relatively long lived adduct HCNOH observed. At temperatures above 500 K there is an increase in the activation energy interpreted as due to the onset of either channel (1) or (2).</td>
<td></td>
</tr>
<tr>
<td>( k_{\text{cm}} = 1.16 \times 10^{-13} \exp (-400/T) )</td>
<td>298–500</td>
<td>Brasseur et al. (1985)(^6)</td>
<td>(e)</td>
</tr>
<tr>
<td>( k_0 = 1.5 \times 10^{-31} \exp (-875/T) )</td>
<td>518–1027</td>
<td>Jacobs et al. (1988)(^11)</td>
<td>(g)</td>
</tr>
</tbody>
</table>

**Reviews and Evaluations**

| 1.2 \times 10^{-13} \exp (-400/T) | 296–433 | CODATA (1984)\(^12\) | (h) |

**Comments**

(a) Shock tube study, no experimental details.

(b) Flame study. Hydrocarbon/O\(_2\) flames with small additions of NH\(_3\), NO, or pyridine. Samples withdrawn via watercooled silica probe and analysed for NO (infrared absorption), HCN and NH species (by absorption in NaOH solution and use of ion-selective electrodes). [II] in post-flame gases determined by Li/LiOH technique.

(c) Discharge-flow study. OH generated by H + NO\(_2\) reaction: [OH] monitored by resonance fluorescence at 306 nm. CN produced by channel (1) scavenged by added H\(_2\). Results suggest pressure dependent \( k \); quoted \( k \) measured at pressures exceeding 10 Torr.

(d) Shock tube study of Ar/HCN/N\(_2\)/O\(_2\) mixtures. [H] and [O] monitored by resonance absorption at 121.6 nm and 130.5 nm respectively. Results fitted to 8 reaction mechanism but fit not very sensitive to assumed value of \( k \).

(e) Shock tube study of H\(_2\)/O\(_2\)/N\(_2\)/Ar mixtures. [CN] monitored by absorption at 288 nm and [OH] by absorption at 306 nm. Data fitted to 6 reaction mechanism to yield \( k_{-1} \). \( k_1 \) calculated using \( K(1) = 0.97 \) at 2650 K gives 2.9 \times 10^{-12} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}. Use of more recent thermodynamic data gives values of \( k \) tabulated.

(f) Flash photolysis study in flowing system. Decay of [OH] monitored by resonance absorption. Pressure dependent \( k \) found and fitted to Troe expression to give quoted \( k_0 \) and \( k_{int} \). Relatively long lived adduct HCNOH observed.

At temperatures above 500 K there is an increase in the activation energy interpreted as due to the onset of either channel (1) or (2).

(g) Derived from measurements of \( k_{-1} \) and thermodynamic data. Measurements of \( k_1 \) by laser photolysis with time resolved monitoring of [CN] and [OH] by laser induced fluorescence. Using our thermodynamic data we obtain \( k_1 = 2.7 \times 10^{-9} T^{-0.867} \exp (-6770/T) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} \).

(h) Review of low temperature data. Accepts value of Fritz et al.\(^6\).

**Preferred Values**

\( k_1 = 1.5 \times 10^{-11} \exp (-5400/T) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} \) over range 1500–2500 K

**Reliability**

\( \Delta \log k_1 = \pm 0.5 \) over range 1500–2500 K

**Comments on Preferred Values**

At high temperatures (1600–2500 K) the results of flame\(^5\) and shock tube studies\(^{52,31}\) are in reasonable agreement despite the fact that all of the techniques are indirect and values of \( k \) derived from computer fitting of substantial reaction mechanisms to the observed quanti
ties. At high temperatures it is most likely that channel (1) is dominant as discussed by Miller et al. and as suggested by the work of Jacobs et al. on the reaction of \( \text{CN} + \text{H}_2\text{O} \rightarrow \text{HCN} + \text{OH} \).

At lower temperatures (\(< 500 \text{ K}\)) the data of Phillips and of Brasseur et al. differ significantly. In both of these studies the rate constant was reported to be pressure dependent. No recommendation is made for this regime; further studies are required.

At high temperatures there are reliable data for \( k_1 \); our recommendation is derived from this and the thermodynamic data about which there is some uncertainty and hence large error limits must be assigned.

References

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

OH + HCN → H_2O + CN
   → HOCN + H
   → HNCO + H

T/K

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

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

EXPERIMENTAL DATA
Haynes (k3) 1977
Kanamuro and Datio (k1) 1977
Phillips (k1) 1979
Roth et al (k1) 1980
Fritz et al (k1) 1982
Szepesy et al (k1) 1984
Brosseur et al 1985
Jacobs et al (k1) 1986
This Recommendation (k1) 1989

**Thermodynamic Data**

\[ \Delta H_{298}^{\text{f}} (1) = -132.0 \text{ kJ mol}^{-1} \]

\[ \Delta H_{298}^{\text{f}} (2) = -85.8 \text{ kJ mol}^{-1} \]

**Rate Coefficient Data \( (k = k_1 + k_2) \)**

<table>
<thead>
<tr>
<th>( k ) [cm(^3) molecule(^{-1}) s(^{-1})]</th>
<th>( T ) [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 1.0 \times 10^{-11} )</td>
<td>300</td>
<td>Niki et al. (1983)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>( 2.93 \times 10^{-12} \exp (+190/T) )</td>
<td>203-423</td>
<td>Vaghjiani and Ravishankara (1989)(^2)</td>
<td>(b)</td>
</tr>
<tr>
<td>( k_2 = 1.78 \times 10^{-12} \exp (+220/T) )</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Comments**

(a) FTIR spectroscopic study of photolysis of \( \text{C}_2\text{H}_5\text{ONO} / \text{CH}_3\text{OOH}/\text{air} \) mixtures. \( k \) relative to rate constants for \( \text{OH} + \text{C}_2\text{H}_4 \) and \( \text{OH} + \text{CH}_3\text{CHO} \):

\[ k(\text{CH}_3\text{OOH})/k(\text{C}_2\text{H}_4) = 1.2 \pm 0.09; \]

\[ k(\text{CH}_3\text{OOH})/k(\text{CH}_3\text{CHO}) = 0.68 \pm 0.07 \text{ at 1 atm pressure. Product yields were consistent with branching ratio } k_1/k_2 = 0.77 (\pm 20 \%) \).

(b) Pulsed photolysis – laser induced fluorescence detection of OH. First order decay of OH used to determine \( k_2 \). Because OH is regenerated rapidly from the \( \text{CH}_3\text{OOH} \) product in the first channel, the overall rate coefficient was determined from \( ^{16}\text{OH} \) loss and from OH production from the reaction of \( ^{16}\text{OH} \) or \( ^{17}\text{OH} + \text{CH}_3\text{OOH} \). A thorough investigation of the mechanism and error sources is given.

**Preferred Values**

\[ k_1 = 1.2 \times 10^{-12} \exp (+130/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range 250–1000 K} \]

\[ k_2 = 1.8 \times 10^{-12} \exp (+220/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range 250–1000 K} \]

**Reliability**

\[ \Delta \log k_1 = \pm 0.4 \text{ at 1000 K reducing to } \pm 0.2 \text{ at 300 K} \]

\[ \Delta \log k_2 = \pm 0.3 \text{ at 1000 K reducing to } \pm 0.1 \text{ at 300 K} \]

**Comments on Preferred Values**

The preferred values are based on the comprehensive and thorough study of Vaghjiani and Ravishankara\(^2\). Considering the uncertainties in the earlier study of Niki et al.\(^1\), the agreement is satisfactory.

**References**

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ \text{OH} + \text{C}_2\text{H}_2 \rightarrow \text{C}_2\text{H} + \text{H}_2\text{O} \hspace{1cm} (1) \]
\[ \rightarrow \text{H} + \text{CH}_2\text{CO} \hspace{1cm} (2) \]
\[ \text{OH} + \text{C}_2\text{H}_2 \text{ (} + \text{M} \text{) } \rightarrow \text{C}_2\text{H}_2\text{OH} \text{ (} + \text{M} \text{) } \hspace{1cm} (3) \]

**Thermodynamic Data**

\[ \Delta H_{\text{f}}^\circ (1) = 53.1 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{f}}^\circ (1) = 11.6 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ K_r (1) = 817 \exp(-6650/T) \]

\[ \Delta H_{\text{f}}^\circ (2) = -99.6 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{f}}^\circ (2) = -28.1 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ K_r (2) = 5.64 \times 10^{-11} \exp(+12240/T) \]

No thermodynamic data available for channel (3). See text for estimate of \( \Delta H(3) \).

**Rate Coefficient Measurements**

<table>
<thead>
<tr>
<th>Rate Coefficient Measurements</th>
<th>( T ) [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 3 \times 10^{-13} )</td>
<td>1700-2000</td>
<td>Exaimore and Jones (1964) (^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>( 1.9 \times 10^{-11} \exp(-3500/T) )</td>
<td>1000-1700</td>
<td>Browne et al. (1969) (^2)</td>
<td>(b)</td>
</tr>
<tr>
<td>( 5.3 \times 10^{-13} \exp(-100/T) )</td>
<td>570-850</td>
<td>Vandooren and Van Tiggelen (1977) (^3)</td>
<td>(c)</td>
</tr>
<tr>
<td>( 5.8 \times 10^{-12} \exp(-4500/T) )</td>
<td>~ 2650</td>
<td>Bar Nun and Dove (1980) (^4)</td>
<td>(d)</td>
</tr>
<tr>
<td>( 3.0 \times 10^{-11} \exp(-3500/T) )</td>
<td>2000</td>
<td>Warnatz et al. (1982) (^5)</td>
<td>(e)</td>
</tr>
<tr>
<td>( 2.7 \times 10^{-13} )</td>
<td>1100</td>
<td>Smith, Fairchild, and Crosley (1984) (^6)</td>
<td>(f)</td>
</tr>
<tr>
<td>( 5.8 \times 10^{-13} )</td>
<td>1300</td>
<td>Liu, Mulac, and Jonah (1988) (^7)</td>
<td>(g)</td>
</tr>
<tr>
<td>( 4.5 \times 10^{-11} \exp(-5300/T) )</td>
<td>1100-1273</td>
<td>Liu, Mulac, and Jonah (1988) (^7)</td>
<td>(h)</td>
</tr>
<tr>
<td>( 1.0 \times 10^{-11} \exp(-3500/T) )</td>
<td>1000-2000</td>
<td>Warnatz (1984) (^8)</td>
<td>(i)</td>
</tr>
<tr>
<td>( 2.4 \times 10^{-26} T^{2/6} \exp(-6060/T) )</td>
<td></td>
<td>Tsang and Hampson (1986) (^9)</td>
<td></td>
</tr>
</tbody>
</table>

**Comments**

(a) Acetylene/oxygen atmospheric flames, mass spectrometric sampling of the burned gas.
(b) Acetylene flame, concentration profiles by absorption and emission spectroscopy. Computer simulation.
(c) Acetylene/oxygen low pressure flame, molecular beam/mass spectrometric sampling. Suggest the reaction product is ketene.
(d) Shock tube study with mass spectrometric sampling.
(e) Burner stabilised laminar flat \( \text{C}_2\text{H}_2/\text{O}_2/\text{Ar} \) flame. Sampling nozzle with mass spectrometric detection. Studied the formation of \( \text{C}_2\text{H}_3 \).
(f) \( \text{CO}_2 \) pulsed laser photolysis (\( \text{SF}_6, \text{H}_2\text{O}_2, \text{N}_2, \text{C}_2\text{H}_2 \)). \( \text{OH} \) detected by laser induced fluorescence. At 900 K the reaction shows a pressure dependence, but this is lost at 1100 and 1300 K, suggesting that the low temperature addition channel no longer operates.
(g) Pulse radiolysis, resonance absorption spectroscopy. The rate constant shows a complex \( (\rho, T) \) dependence below 1100 K as the addition channel becomes important.
(h) Evaluation, based on the value of Browne et al. \(^2\).
(i) Calculated BEBO value.

**Reliability**

\[ \Delta \log k = \pm 1.0 \]

**Comments on Preferred Values**

In the absence of contrary evidence, an abstraction mechanism has been assumed at high temperatures. Even exothermic \( H \) abstractions have a small activation barrier and they show pronounced positive Arrhenius curvature. Accordingly, a large temperature dependence, compatible with the data of Smith et al. \(^5\) and Fenimore and Jones \(^1\) and with the endothermicity, has been chosen, together with a large A factor, by comparison with the \( \text{OH} + \text{C}_2\text{H}_4 \) reaction. This dependence is somewhat stronger than that obtained by Liu et al. \(^7\) because their analysis does not make full allowance for the addition channel.

At temperatures below \( \approx 1100 \text{ K} \) and at atmospheric pressure, the addition channel (3) becomes important and shows a strong pressure dependence \(^10-12\). More recent and more complete measurements have been made at 298 K \(^\text{13,14} \), on the basis of which Atkinson \(^15\) proposes the parameters \( k_3 = 4 \times 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \), \( k_3^* = 8.7 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \), and \( F_2 = 0.6 \) in air at room temperature, with a \( T \) dependence of the form \( k_3^* = 1.9 \times 10^{-12} \exp(-230/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \).

The following parameters give a reasonable representation of the high temperature data for \( k_3 \) and are also compatible with Atkinson's analysis at low temperatures: \( k_3^* = 2 \times 10^{-12} \exp(-230/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \), \( k_3^* = 5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-2} \text{ s}^{-1} \), \( F_2 = 0.6 \).

Preferred Values

\[ k_1 = 1.0 \times 10^{-10} \exp(-6500/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range 1000-2000 K} \]
with $\Delta \log k_3 = \pm 1.0$. These parameters should be employed to assess the importance of the addition channel at temperatures below $= 1100$ K. Smith et al. estimated the dissociation energy, $\Delta E_0$, for the adduct to be $\approx 140$ kJ mol$^{-1}$.

References

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ \text{OH} + \text{C}_2\text{H}_2 \rightarrow \text{C}_2\text{H} + \text{H}_2\text{O} \]
\[ \rightarrow \text{H} + \text{CH}_2\text{CO} \]
\[ \rightarrow \text{C}_2\text{H}_2\text{OH} \]

T/K

Log(\text{k}, \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1})

\( 10^3 T^{-1} / K^{-1} \)

EXPERIMENTAL DATA
- Fenimore and Jones (k1) 1964
- Graeme et al (k1) 1969
- Vandooren & Van Tiggelen (k1) 1977
- Bar-Nun and Dawe (k1) 1980
- Smith et al (k1) 1984
- Liu et al 1988
- Wernitz et al (k1) 1982
- Green and Glass (k3) 1970
- Wohner and Zetisch (k3) 1985
- Schmidt et al (k3) 1985
- Schmitt et al (k3) 1982
- Hatakeyama et al (k2) 1986
- Atkinson et al (k3) 1984
- Perry et al (k3) 1982
- Michael et al (k3) 1980
- Perry et al (k3) 1977

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**Rate Coefficient Measurements**

<table>
<thead>
<tr>
<th>$k$ [cm$^3$ molecule$^{-1}$ s$^{-1}$]</th>
<th>$T$ [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5.7 \times 10^{-13}$</td>
<td>2.5-10</td>
<td>Baldwin (1972)</td>
<td>(g)</td>
</tr>
<tr>
<td>$4.0 \times 10^{-11}$ exp$(-2104/T)$</td>
<td>773</td>
<td>Baldwin (1972)</td>
<td>(g)</td>
</tr>
<tr>
<td>$3.9 \times 10^{-11}$ exp$(-5413/T)$</td>
<td>813</td>
<td>Baldwin et al. (1984)</td>
<td>(g)</td>
</tr>
<tr>
<td>$3.7 \times 10^{-11}$ exp$(-3870/T)$</td>
<td>748</td>
<td>Liu et al. (1987)</td>
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<tr>
<td>$3.4 \times 10^{-11}$ exp$(-2992/T)$</td>
<td>773</td>
<td>Baldwin (1972)</td>
<td>(g)</td>
</tr>
<tr>
<td>$3.1 \times 10^{-11}$ exp$(-1980/T)$</td>
<td>651</td>
<td>Wang (1984)</td>
<td>(g)</td>
</tr>
<tr>
<td>$2.8 \times 10^{-11}$ exp$(-1500/T)$</td>
<td>500-2000</td>
<td>Warnatz (1984)</td>
<td>(g)</td>
</tr>
</tbody>
</table>

**Comments**

(a) Flame study of C$_2$H$_2$/O$_2$ flames, H and O profiles measured by e.s.r. and C$_2$H$_4$, CO, and CO$_2$ by mass spectrometry. Concentration profile of OH is calculated using $k$(CO + OH → CO$_2$ + H) = $1.2 \times 10^{-11}$ exp$(-3870/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and [CO$_2$] and hence quoted value of $k$.

This is recalculated by Wilson$^9$ giving $k = 5.3 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 1240 K, $k = 8.3 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 1368 K, $k = 2.6 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 1447 K and $k = 1.0 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 1491 K.

(b) Inhibition of H$_2$O$_2$ reaction by addition of ethene. Ratio $k/k$(H$_2$ + OH) is obtained and use of $k$(H$_2$ + OH) = $1.2 \times 10^{-14}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 813 K gives the quoted value.

This is recalculated by Wilson$^9$ giving $k = 1.0 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 813 K.

(c) Shock tube study, analysis by UV absorption for [OH]; quoted value of $k$ obtained by computer modelling of a 28 reaction mechanism (proved to be sensitive to this reaction) and optimization.

(d) Flash photolysis of C$_2$H$_4$/He, N$_2$/O/He, H$_2$O/He gas streams using an excimer laser. [OH] monitored by resonance fluorescence at $T > 500$ K. [OH] decay is not exponential.

(e) Addition of C$_2$H$_2$ to slowly reacting H$_2$/O$_2$ mixtures. Pressure change and product yields (C$_2$H$_4$, HCHO, CH$_2$, C$_2$H$_4$, CO, CH$_3$CHO) in early stages of reaction were measured. $k$ sensitive to NO and CO yields. Difficult to distinguish between abstraction and OH + C$_2$H$_4$ → C$_2$H$_2$OH + O → 2HCHO + OH.

(f) Pulse radiolysis of H$_2$O/C$_2$H$_4$ mixtures in 1 atm Ar. [OH] monitored by resonance absorption. In temperature range 343-563 K addition of OH to C$_2$H$_4$ is dominant; 563-748 K addition, adduct decomposition, and abstraction occur concurrently; above 748 K abstraction is dominant.

(g) Infrared laser pyrolysis of flowing mixtures of H$_2$O$_2$/C$_2$H$_4$/SF$_6$/C$_2$H$_4$. [OH] monitored by laser induced fluorescence. Temperatures determined from population of OH rotational states.

(h) Laser photolysis of N$_2$/O$_2$/H$_2$/C$_2$H$_4$/He mixtures at 193 nm or H$_2$O/C$_2$H$_4$/Ar mixtures. [OH] monitored by laser induced fluorescence. Rate constant independent of nature or pressure of diluent gas.

(i) Review of results up to 1974, recalculation where necessary, separate incompatible values for $k$ at high and at low temperatures recommended.

(j) Review of Refs. up to 1980. Expression for $k$ at high temperatures which is compatible with low temperature results recommended.

**Preferred Values**

$$k = 3.4 \times 10^{-11} \exp(-2992/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range 650-1500 K}$$

**Reliability**

$\Delta \log k = \pm 0.5$ over range 650-1500 K

**Comments on Preferred Values**

The experimental studies on this reaction show that the abstraction channel predominates over addition at temperatures above approximately 650 K. The measured values of $k$ are in poor agreement at such temperatures. The most recent study of Tully$^9$ gives values much lower than those found in most other studies but compatible...
EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

with the work of Smith\textsuperscript{7} and the most recent work of Baldwin \textit{et al.}\textsuperscript{5}. We accept Tully's expression as the one preferred.

\textbf{References}

\textsuperscript{1}A. A. Westenberg and R. H. Fristrom, 10th Symp. (Int.) Combust., 473 (1965).
OH + C₂H₄ → C₂H₃ + H₂O

$T/K$

EXPERIMENTAL DATA
Westenberg and Fristrom 1965
Baldwin et al. 1966
Bradley et al. 1976
Tully 1983
Greiner 1970
Wilson and Westenberg 1967
Morris et al. 1971
Smith 1987
Tully 1988
Schmidt et al. 1985
This Recommendation 1980

Log($k$/cm³ molecule⁻¹ s⁻¹)

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

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

OH + C₂H₆ → H₂O + C₂H₅

**Thermodynamic Data**

\[ \Delta H_{298}^\circ = -79.7 \text{ kJ} \text{ mol}^{-1} \]

\[ \Delta S_{298}^\circ = 27.8 \text{ J} \text{ K}^{-1} \text{ mol}^{-1} \]

\[ K_p = 3.20 \times 10^3 \exp(-9340/T) \]

**Rate Coefficient Measurements**

<table>
<thead>
<tr>
<th>( k ) [cm³ molecule⁻¹ s⁻¹]</th>
<th>Temperature [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.32 \times 10^{-13}</td>
<td>295</td>
<td>Lee and Tang (1982)²</td>
<td>(a)</td>
</tr>
<tr>
<td>7.13 \times 10^{-14}</td>
<td>238</td>
<td>Margitan and Watson (1982)³</td>
<td>(b)</td>
</tr>
<tr>
<td>(see Ref. 1)</td>
<td>403-683</td>
<td>Baulch et al. (1983)⁴</td>
<td>(c)</td>
</tr>
<tr>
<td>1.43 \times 10^{-14} T^{-0.85}\exp(-911/T)</td>
<td>297-800</td>
<td>Tully et al. (1983)⁵</td>
<td>(d)</td>
</tr>
<tr>
<td>3.9 \times 10^{-21} T^{-0.86}\exp(+169/T)</td>
<td>248-472</td>
<td>Kautman et al. (1984)⁶</td>
<td>(a)</td>
</tr>
<tr>
<td>1.8 \times 10^{-11} \exp(-1240/T)</td>
<td>240-295</td>
<td>Molina et al. (1984)⁷</td>
<td>(e)</td>
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<td>2.68 \times 10^{-13}</td>
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<td>Baulch et al. (1985)⁸</td>
<td>(f)</td>
</tr>
<tr>
<td>2.2 \times 10^{-13}</td>
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<td>Schmidt et al. (1985)⁹</td>
<td>(g)</td>
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<td>1.26 \times 10^{-13}</td>
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<td>Molina et al. (1986)¹⁰</td>
<td>(h)</td>
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<td>2.51 \times 10^{-13}</td>
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<td>Nielsen et al. (1986)¹¹</td>
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<tr>
<td>2.98 \times 10^{-13}</td>
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<td>Tully et al. (1986)¹²</td>
<td>(k, j)</td>
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<tr>
<td>8.51 \times 10^{-19} T^{-0.86}\exp(-430/T)</td>
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<td>Anderson and Stephens (1986)¹³</td>
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<td>2.07 \times 10^{-15} \exp(-1299/T)</td>
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<td>Bournada, Lafage, and Denvold (1987)¹⁴</td>
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<td>2.74 \times 10^{-13}</td>
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<td>Tully et al. (1986)¹⁵</td>
<td>(k, j)</td>
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<tr>
<td>8.4 \times 10^{-12} \exp(-1050/T)</td>
<td>234-438</td>
<td>Wallington, Neuman, and Kurylo (1987)¹⁶</td>
<td>(d)</td>
</tr>
</tbody>
</table>

**Reviews and Evaluations**

1.29 \times 10^{-15} T^{0.92}\exp(-430/T) | 300-2000 | Cohen (1982)¹⁷ | (k)      |
| 3.6 \times 10^{-17} T^{-0.8}\exp(-570/T) | 200-300  | Cohen and Wadlys (1983)¹⁸ | (l)      |
| 1.05 \times 10^{-17} T^{-0.9}\exp(-325/T) | 200-300  | Warnatz (1984)¹⁹ | (m)      |
| 1.47 \times 10^{-14} T^{-1.04}\exp(-913/T) | 297-800 | Tully et al. (1986)²⁰ | (n)      |
| 2.3 \times 10^{-11} \exp(-1340/T) | 250-1200 | Baulch et al. (1986)¹ | (o)      |
| 1.37 \times 10^{-17} T^{0.9}\exp(-444/T) | 240-900  | Atkinson (1986)²¹ | (p)      |

**Comments**

(a) Fast flow discharge, [OH] monitored by resonance fluorescence.
(b) Flash photolysis of HNO₃/C₂H₆/He mixtures; [OH] monitored by resonance fluorescence.
(c) Static photolysis of H₂O/CO/C₂H₄ mixtures; competitive studies with GLC measurement of CO₂.
(d) Flash photolysis of H₂O/C₂H₆/Ar mixtures in static vessel. [C₂H₆] >> [OH] with [OH] monitored by resonance fluorescence.
(e) Flash photolysis of HNO₃/C₂H₆/He mixtures; [OH] monitored by resonance fluorescence.
(f) Discharge flow, OH generated from H + NO₂ with [OH] monitored by resonance fluorescence.
(g) Laser photolysis of H₂O₂ or HNO₃; [OH] monitored by pulsed dye laser fluorescence.
(h) Laser flash photolysis of HNO₃/C₂H₆/inert gas mixtures; [OH] monitored by resonance fluorescence.
(i) Pulse radiolysis of H₂O/C₂H₆/Ar mixtures; [OH] monitored by adsorption at about 309 nm.
(k) Calculated values based on transition state theory.
(l) Wide temperature evaluation of experimental data.
(m) Recommended without comment.
(n) Recommend expression given by Tully et al. (1983)³.
(o) Recommend Arrhenius expression between 250 and 1200 K, based on comprehensive assessment of experimental data.
(p) Critical review of data between 240 and 900 K.

**Preferred Values**

\[ k = 1.20 \times 10^{-17} T^{0.9}\exp(-435/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range } 250-2000 \text{ K} \]

**Reliability**

\[ \Delta \log k = \pm 0.07 \text{ between } 250 \text{ K and } 1000 \text{ K rising to } \pm 0.15 \text{ at } 2000 \text{ K} \]

**Comments on Preferred Values**

The rate constant is now known with considerable reliability and precision between 250 and 2000 K, with excellent agreement between a large number of techniques. The early data of Fenimore and Jones²² have been re-interpreted using \( k(\text{OH} + \text{CO}) \) given by Baulch et al.²². The preferred value of \( k \) is almost indistinguishable from the value obtained by Cohen¹⁶ from transition state calculations carried out for temperatures between 300
and 2000 K. This agreement between theory and experiment may be coincidental, but suggests that extrapolations to at least 3000 K may be carried out reasonably reliably with $\Delta \log k = \pm 0.3$ at 3000 K.

References

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ \text{OH} + \text{C}_2\text{H}_6 \rightarrow \text{H}_2\text{O} + \text{C}_2\text{H}_5 \]

\[ \frac{T}{K} \]

EXPERIMENTAL DATA

- Lee and Tang 1982
- Tully 1983
- Morgan and Watson 1982
- Baulch et al. 1983
- Tully et al. 1983
- Jeong et al. 1984
- Smith et al. 1984
- Baulch et al. 1985
- Schmidt et al. 1985
- Stochnik et al. 1986
- Nielsen et al. 1986
- Tully et al. 1986
- Andersen and Steven 1986
- Barmento et al. 1987
- Wallington et al. 1987
- Fenimore and Jones 1983
- This Recommendation 1989
**Thermodynamic Data**

\[
\begin{align*}
\Delta H_{298}^0 (1) & = -115 \text{ kJ mol}^{-1} \\
\Delta S_{298}^0 (1) & = 18.5 \text{ J K}^{-1} \text{mol}^{-1} \\
K_p (1) & = 210 \, T^{-0.48} \exp(+13700/T) \\
\Delta H_{298}^0 (2) & = -59.5 \text{ kJ mol}^{-1} \\
\Delta S_{298}^0 (2) & = 17.7 \text{ J K}^{-1} \text{mol}^{-1} \\
K_p (2) & = 969 \, T^{-0.38} \exp(+7070/T)
\end{align*}
\]

**Rate Coefficient Data** \( k = k_1 + k_2 \)

<table>
<thead>
<tr>
<th>( k [\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}] )</th>
<th>( T [\text{K}] )</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 4.65 \times 10^{-11} )</td>
<td>480-1000</td>
<td>Vandooren and Van Tiggelen (1977)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>( &gt; 1.7 \times 10^{-12} )</td>
<td>295</td>
<td>Faubel, Wagner, and Witack (1977)(^2)</td>
<td>(b)</td>
</tr>
<tr>
<td>( 1.8 \times 10^{-11} )</td>
<td>299</td>
<td>Hatakeyama et al. (1985)(^3)</td>
<td>(c)</td>
</tr>
</tbody>
</table>

**Comments**

(a) Study of \( \text{C}_2\text{H}_4\text{O}_2 \) flames. Analysis for \( \text{CO}_2, \text{CO}, \text{C}_2\text{H}_2, \text{H}_2, \text{H}_2\text{O}, \text{Ar}, \text{H}, \text{O}, \) and \( \text{OH} \) by molecular beam sampling mass spectrometry.

(b) Flow reactor, OH radicals produced by the reaction \( \text{H} + \text{NO}_2 \rightarrow \text{OH} + \text{NO} \). Product analysis by mass spectrometry; \( \text{C}_2\text{H}_4, \text{H}_2\text{CO}, \) and \( \text{CH}_3\text{OH} \) found in products. Quoted lower limit for \( k \) obtained by comparison with the rate constant for the reaction \( \text{C}_3\text{O}_2 + \text{OH} \rightarrow \text{H}_2\text{C}_2\text{O} + \text{CO}_2 \) \( (k(\text{C}_3\text{O}_2 + \text{OH}) = 1.2 \times 10^{-11} \exp(-620/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) \) also measured in this study.

(c) OH generated by photolysis of \( \text{CH}_3\text{ONO} \) in air at 1 atm. Analysis for \( \text{CH}_3\text{CO} \) by long path Fourier-transform infrared spectroscopy at 2164 cm\(^{-1}\). Ratio \( k/k(\text{OH} + \text{C}_2\text{H}_4) = 2.3 \) obtained. \( k(\text{OH} + \text{C}_2\text{H}_4) = 7.95 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) used\(^4\) to obtain \( k \). Main product observed was HCHO.

**Preferred Values**

\[ k = 1.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range 300-2000 K} \]

**Reliability**

\[ \Delta \log k = \pm 1.0 \text{ over range 300-2000 K} \]

---

**References**

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

**OH + CH₃CHO → H₂O + CH₂CO**  \(1\)

→ H₂O + CH₂CHO  \(2\)

**Thermodynamic Data**

\[\Delta H_{\text{fm}} (1) = -138 \text{ kJ mol}^{-1}\]
\[\Delta S_{\text{fm}} (1) = 8.0 \text{ J K}^{-1}\text{mol}^{-1}\]
\[K_p (1) = 136 T^{-0.957} \exp (+1640/T)\]

\[\Delta H_{\text{fm}} (2) = -90.4 \text{ kJ mol}^{-1}\]
\[\Delta S_{\text{fm}} (2) = 9.1 \text{ J K}^{-1}\text{mol}^{-1}\]
\[K_p (2) = 60 T^{0.398} \exp (+10650/T)\]

**Rate Coefficient Data**

<table>
<thead>
<tr>
<th>(k) [cm³ molecule⁻¹ s⁻¹]</th>
<th>(T) [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.87×10⁻¹² exp (+260/T)</td>
<td>299-426</td>
<td>Atkinson and Pitts (1978)¹</td>
<td>(a)</td>
</tr>
<tr>
<td>5.52×10⁻¹² exp (+307/T)</td>
<td>244-528</td>
<td>Michael, Keil, and Klemm (1985)²</td>
<td>(b)</td>
</tr>
<tr>
<td>7.1×10⁻¹² exp (+165/T)</td>
<td>253-424</td>
<td>Semmes et al. (1985)³</td>
<td>(c)</td>
</tr>
<tr>
<td>6.9×10⁻¹² exp (+260/T)</td>
<td>298-450</td>
<td>CODATA (1984)⁴</td>
<td>(d)</td>
</tr>
<tr>
<td>1.67×10⁻¹¹</td>
<td>300-2000</td>
<td>Warnatz (1984)⁵</td>
<td>(e)</td>
</tr>
<tr>
<td>6.87×10⁻¹² exp (+256/T)</td>
<td>200-500</td>
<td>Atkinson (1986)⁶</td>
<td>(f)</td>
</tr>
</tbody>
</table>

**Comments**

(a) Pulsed VUV flash photolysis of H₂O; resonance fluorescence detection of OH.
(b) Discharge flow; resonance fluorescence detection of OH; CH₂CO shown to be most probable product up to 530 K.
(c) Flash photolysis of H₂O; resonance fluorescence detection of OH; some difficulty encountered in defining CH₃CHO concentration.
(d) Based on Ref. 1 and earlier room temperature data of Morris et al.,² Cox et al.,³ Niki et al.,⁴ and Kerr and Sheppard.⁵
(e) Recommendation based on mean of room temperature values and assumed independence of \(k\) on temperature over wide range.
(f) Based on Ref. 1. Data from Semmes et al. were not included because of reported difficulties in defining CH₃CHO concentration.

**Preferred Values**

\[k = 3.89×10^{-14} \ T^{0.72} \exp (+560/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\]

over range 250–1200 K

**Reliability**

\[\Delta \log k = ±0.3 \text{ at } 1000 \text{ K reducing to } ±0.1 \text{ at } 250 \text{ K}\]

**References**

BAULCH ET AL.

\[ \text{OH} + \text{CH}_3\text{CHO} \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{CO} \]
\[ \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{CHO} \]

\[ \log(k/\text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1}) \]

\[ \frac{10^3 T^{-1}}{K^{-1}} \]

EXPERIMENTAL DATA
- Albinson and Pitts 1976
- Michael, Keil and Klemm 1985
- Semmes et al 1985
- Nis et al 1978
- Auranenko and Lorenzo 1949
- Morris et al 1971
- Cox et al 1976
- Kerr and Sheppard 1981

This Recommendation 1989

**EVALUATED KINETIC DATA FOR COMBUSTION MODELLING**

\[
\text{OH} + \text{C}_2\text{H}_5\text{OOH} \rightarrow \text{H}_2\text{O} + \text{C}_2\text{H}_5\text{OO} \quad (1)
\]
\[
\rightarrow \text{H}_2\text{O} + \text{C}_2\text{H}_4\text{OOH} \quad (2)
\]

**Thermodynamic Data**
\[
\Delta H_{\text{f}0}^\circ (1) = -131 \text{ kJ mol}^{-1} \quad \Delta H_{\text{f}0}^\circ (2) = -91.2 \text{ kJ mol}^{-1}
\]

**Comment**
There are no experimental data for the reaction of OH with \( \text{C}_2\text{H}_5\text{OOH} \). The overall rate expression \( k = 3.0 \times 10^{-12} \exp(+190/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) with channels (1) and (2) occurring at equal rates, is recommended by analogy with the reaction of OH with \( \text{CH}_3\text{OOH} \). Temperature range 250–1000 K with \( \Delta \log k = \pm 0.3 \) at 250 K and \( \pm 0.7 \) at 1000 K.

\[
\text{OH} + \text{C}_6\text{H}_6 \rightarrow \text{H}_2\text{O} + \text{C}_6\text{H}_6 \quad (1)
\]
\[
\rightarrow \text{C}_6\text{H}_5\text{OH} + \text{H} \quad (2)
\]
\[
\text{OH} + \text{C}_6\text{H}_6 (+ \text{M}) \rightarrow \text{C}_6\text{H}_5\text{OH} (+ \text{M}) \quad (3)
\]

**Thermodynamic Data**
\[
\Delta H_{\text{f}0}^\circ (1) = -35.3 \text{ kJ mol}^{-1} \quad \Delta H_{\text{f}0}^\circ (2) = -0.3 \text{ kJ mol}^{-1}
\]
\[
\Delta S_{\text{f}0}^\circ (1) = 24.2 \text{ J K}^{-1} \text{mol}^{-1} \quad \Delta S_{\text{f}0}^\circ (2) = -23.5 \text{ J K}^{-1} \text{mol}^{-1}
\]
\[
K_p(1) = 8.1 \times 10^{-3} T^{0.86} \exp(+3880/T) \quad K_p(2) = 4.7 \times 10^{-5} T^{-0.1} \exp(+260/T)
\]

**Rate Coefficient Data** \( (k = k_1 + k_2 + k_3) \)

<table>
<thead>
<tr>
<th>( k ) [cm(^3) molecule(^{-1}) s(^{-1})]</th>
<th>( T ) [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_3 = 5.0 \times 10^{-12} \exp(-453/T) )</td>
<td>296–325</td>
<td>Perry, Atkinson and Pitts (1977)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>( k_1 = 4.0 \times 10^{-11} \exp(-2013/T) )</td>
<td>380–473</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( k_1 = 1.7 \times 10^{-11} \exp(-3019/T) )</td>
<td>1200–1900</td>
<td>Fuji and Asaba (1977)(^2)</td>
<td>(b)</td>
</tr>
<tr>
<td>( k_1 = 3.1 \times 10^{-12} \exp(-270/T) )</td>
<td>250–298</td>
<td>Tully et al. (1981)(^3)</td>
<td>(c)</td>
</tr>
<tr>
<td>( k_1 = 2.4 \times 10^{-11} \exp(-2260/T) )</td>
<td>450–1000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 8.8 \times 10^{-13} )</td>
<td>295</td>
<td>Wahner and Zetzsch (1983)(^4)</td>
<td>(d)</td>
</tr>
<tr>
<td>( k_5 = 6.3 \times 10^{-12} \exp(-500/T) )</td>
<td>244–330</td>
<td>Lorenzo and Zellner (1983)(^5)</td>
<td>(e)</td>
</tr>
<tr>
<td>( 1.5 \times 10^{-12} )</td>
<td>298</td>
<td>Ohta and Ohyama (1985)(^6)</td>
<td>(f)</td>
</tr>
<tr>
<td>( 3.5 \times 10^{-11} \exp(-2300/T) )</td>
<td>790–1410</td>
<td>Felder and Madronich (1985)(^7)</td>
<td>(g)</td>
</tr>
<tr>
<td>( 1.3 \times 10^{-12} )</td>
<td>294</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( k_5 = 2.3 \times 10^{-12} \exp(-190/T) )</td>
<td>239–354</td>
<td>Witte, Urbanik, and Zetzsch (1986)(^8)</td>
<td>(h)</td>
</tr>
<tr>
<td>( 2.5 \times 10^{-12} \exp(-2050/T) )</td>
<td>790–1410</td>
<td>Madronich and Felder (1986)(^9)</td>
<td>(i)</td>
</tr>
<tr>
<td>( 1.3 \times 10^{-12} )</td>
<td>296</td>
<td>Edney et al. (1986)(^9)</td>
<td>(j)</td>
</tr>
<tr>
<td>( 2.0 \times 10^{-12} )</td>
<td>298</td>
<td>Atkinson (1987)(^1)</td>
<td>(k)</td>
</tr>
<tr>
<td>( k_2 = 2.2 \times 10^{-11} \exp(-5330/T) )</td>
<td>1000–1150</td>
<td>He et al. (1988)(^1)</td>
<td>(l)</td>
</tr>
</tbody>
</table>

**Comments**

(a) Flash photolysis–resonance fluorescence of OH at total pressures between 20 and 200 Torr.
(b) Rate expression for the addition channel was determined by a semi-empirical method. The pyrolysis and oxidation of benzene were studied by various methods using the shock tube technique. Experimental data on the formation of biphenyl and CO were modelled by computer simulation.
(c) Observed total rate coefficient is derived from the FP-RF technique for \( 20 < p < 200 \) Torr. Discussion of the reaction mechanism is presented. A rate expression for the abstraction reaction (1) has been evaluated.
(d) VUV flash photolysis of water; detection of OH by resonance fluorescence at 309 nm.
(e) Laser photolysis–resonance fluorescence technique.
(f) Relative rate constant for the overall reaction. OH radicals were produced by photolyzing \( \text{H}_2\text{O}_2 \). Analysis of organic compounds was by GC. Reaction paths are discussed. Empirical relationships between structure and reactivity of aromatics towards OH radicals are derived.
(g) The high temperature photochemistry technique (HTPC) was applied. OH radicals were produced by standard flash photolysis. Time dependent resonance fluorescence detection of OH at 309 nm.
(h) Flash photolysis production of OH radicals. Monitoring of OH by resonance fluorescence at 309 nm.
(i) Same method as in (g).

(j) Observed total rate coefficient based on a procedure of “relative rate”. OH radicals were produced by irradiation of methylnitrite. Decay rates of benzene and of the test compound were monitored by GC.

(k) Rate coefficient for OH consumption was calculated from structure-activity relationship (SAR) at atmospheric pressure.

(l) Results are from study of H and OH attack on phenol under single pulse shock tube conditions. The rate coefficient \( k_2 \) was calculated from the equilibrium constant and from the measured rate of the reverse of reaction (2).

**Preferred Values**

\[
k_1 = 2.7 \times 10^{-16} T^{1.42} \exp(-732/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range } 400-1495 \text{ K}
\]

\[
k_2 = 2.2 \times 10^{-11} \exp(-5530/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range } 1000-1150 \text{ K}
\]

\[
k_3 = 3.8 \times 10^{-12} \exp(-341/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range } 240-340 \text{ K}
\]

**Reliability**

\[
\Delta \log k_1 = \pm 0.3 \text{ over range } 400-1500 \text{ K}
\]

\[
\Delta \log k_2 = \pm 0.3 \text{ over range } 1000-1150 \text{ K}
\]

\[
\Delta \log k_3 = \pm 0.2 \text{ over range } 240-340 \text{ K}
\]

**Comments on Preferred Values**

The present studies indicate that the dominant reaction pathway at and below room temperature is the addition of the OH radical (channel (3)). Abstraction of ring hydrogen seems to be dominant at temperatures above 500 K (channel (1)). The displacement reaction (2) is not expected to be an elementary process but to proceed via the hydrocyclohexadienyl channel (3) at elevated temperatures.

**References**

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

$\text{OH} + \text{C}_6\text{H}_6 \rightarrow \text{H}_2\text{O} + \text{C}_6\text{H}_5$
$\rightarrow \text{H} + \text{C}_6\text{H}_5\text{OH}$
$\rightarrow \text{C}_6\text{H}_6\text{OH}$
\[ \text{OH} + \text{C}_6\text{H}_5\text{OH} (+ \text{M}) \rightarrow \text{C}_6\text{H}_5(\text{OH})_2(+ \text{M}) \] (1)

\[ \text{OH} + \text{C}_6\text{H}_5\text{OH} \rightarrow \text{C}_6\text{H}_5\text{O} + \text{H}_2\text{O} \] (2)

\[ \rightarrow \text{C}_6\text{H}_5\text{OH} + \text{H}_2\text{O} \] (3)

**Thermodynamic Data**

\[ \Delta H_{\text{fus}} (2) = -136.7 \text{ kJ mol}^{-1} \]

\[ \Delta S_{\text{fus}} (2) = -1.9 \text{ J K}^{-1}\text{mol}^{-1} \]

\[ K_r (2) = 1.6 \times 10^6 \exp(+1636/T) \]

**Rate Coefficient Data** \( (k = k_1 + k_2 + k_3) \)

<table>
<thead>
<tr>
<th>( k ) [cm(^3) molecule(^{-1}) s(^{-1})]</th>
<th>( T ) [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 = 2.8 \times 10^{-11} )</td>
<td>296</td>
<td>Rinke and Zetzsch (1984)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>( k_2 = 1.0 \times 10^{-11} )</td>
<td>1000-1150</td>
<td>He et al. (1988)(^2)</td>
<td>(b)</td>
</tr>
</tbody>
</table>

**Comments**

(a) Direct measurement using flash photolysis with resonance fluorescence for OH, \( p = 5-733 \text{ mbar He} \). Low initial OH concentrations. Very good linearity of the decays.

(b) This is an extension of the phenol + H study of these authors (see data sheet: phenol + H). By using CO as an OH quencher, H atoms are formed and more benzene is produced. This process is in competition with phenol + OH. Thus rate data for phenol + OH may be deduced. However, very large amounts (= 30%) of CO are needed. The kinetic system is not simple and a further uncertainty is introduced from the Ref. reaction CO + OH.

**Preferred Values**

\[ k_1 = 2.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 296 K and } 733 \text{ mbar He} \]

\[ k_2 + k_3 = 1.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range } 1000-1150 \text{ K} \]

**Thermodynamic Data**

\[ \Delta H_{\text{fus}} (1) = -130.8 \text{ kJ mol}^{-1} \]

\[ \Delta S_{\text{fus}} (1) = 1.4 \text{ J K}^{-1}\text{mol}^{-1} \]

\[ K_r (1) = 3.2 \times 10^{-1} \exp(+15730/T) \]

**Rate Coefficient Data** \( (k = k_1 + k_2) \)

<table>
<thead>
<tr>
<th>( k ) [cm(^3) molecule(^{-1}) s(^{-1})]</th>
<th>( T ) [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 = 5.0 \times 10^{-12} \exp(-453/T) )</td>
<td>380-473</td>
<td>Perry, Atkinson, and Pitts (1977)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>( k_2 = 3.2 \times 10^{-12} \exp(+805/T) )</td>
<td>296-325</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( k_1 = 1.7 \times 10^{-11} \exp(-1510/T) )</td>
<td>1700-2800</td>
<td>McLain et al. (1979)(^2)</td>
<td>(b)</td>
</tr>
<tr>
<td>( k_2 = 2.1 \times 10^{-11} \exp(-1300/T) )</td>
<td>500-1000</td>
<td>Tully et al. (1981)(^3)</td>
<td>(c)</td>
</tr>
<tr>
<td>( k_2 = 3.8 \times 10^{-12} \exp(+190/T) )</td>
<td>213-298</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( k_2 = 6.4 \times 10^{-12} )</td>
<td>298</td>
<td>Ohta and Ohyama (1985)(^4)</td>
<td>(d)</td>
</tr>
<tr>
<td>( k_2 = 5.4 \times 10^{-12} )</td>
<td>298</td>
<td>Eydey et al. (1986)(^5)</td>
<td>(e)</td>
</tr>
<tr>
<td>( k_2 = 6.2 \times 10^{-12} )</td>
<td>298</td>
<td>Atkinson (1987)(^6)</td>
<td>(f)</td>
</tr>
<tr>
<td>( 4.8 \times 10^{-12} )</td>
<td>773</td>
<td>Baldwin et al. (1987)(^7)</td>
<td>(g)</td>
</tr>
</tbody>
</table>

References


EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

Comments

(a) Flash photolysis–resonance fluorescence technique at total pressures around 10 Torr. Addition channel (2) is the dominant reaction pathway for temperatures below 325 K. The H abstraction reaction (channel (1)) was found to be the dominant reaction pathway for temperatures above 380 K.

(b) Incident shock wave investigation of the oxidation mechanism of C,H/O/Ar and C,H,CH/ O,/Ar mixtures by monitoring UV and IR emission of CO, CO, and the product [O][CO]. Arrhenius expression for the products C,H,CH + H,O (channel (1)) was estimated by comparison with data for benzene.

(c) Flash photolysis–resonance fluorescence technique. OH reactions with benzene, toluene, and selectively deuterated toluenes were studied in the temperature range 213 to 1150 K. The results indicate that the addition channel (2) is the dominant reaction pathway below 300 K and that side-chain hydrogen abstraction channels such as pathway (1) are the dominant reaction routes at higher temperatures. The rate expression for the side-chain hydrogen abstraction (channel (1)) has been estimated.

(d) Hexane was used as Ref. compound. Photolysis of H,O was the source of OH. Rate coefficient for OH consumption (channel (2)) was evaluated at atmospheric pressure.

(e) Rate constant value for reaction (2) derived by using a relative rate data procedure. Photolysis of methyl nitrite was the source of OH.

(f) Flash photolysis–resonance fluorescence. Measurement of rate coefficient for the addition reaction (2). An estimation of the rate coefficient for the addition reaction (2) by applying a structure activity relationship gave 5.5·10^-12 cm^3 molecule^-1 s^-1 at 298 K.

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

Preferred Values

\[ k_1 = 8.6·10^{-15} \exp(-440/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range } 400-1200 \text{ K} \]

\[ k_2 = 3.8·10^{-12} \exp(+180/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range } 213-298 \text{ K} \]

Reliability

\[ \Delta \log k_1 = \pm 0.5 \text{ at } 400 \text{ K reducing to } \pm 0.3 \text{ at } 1200 \text{ K} \]

\[ \Delta \log k_2 = \pm 0.4 \text{ over the range } 213-298 \text{ K} \]

Comments on Preferred Values

The present studies indicate that the dominant reaction pathway at and below room temperature is the addition of the OH radical (channel (2)). Side-chain hydrogen abstraction reaction seems to be the reaction at higher temperatures (channel (1)). The present data are reliable, but owing to the pressure dependence of the reaction (2) only a rate expression can be recommended for temperatures below 300 K. For channel (1) the more indirect data of Ref. 2 have been not considered for the evaluation of the rate constant. The recommendation for channel (1) covers only an intermediate temperature range of about 800 degrees.

References

BAULCH ET AL.

\[
\text{OH + C}_6\text{H}_5\text{CH}_3 \rightarrow \text{H}_2\text{O} + \text{C}_6\text{H}_5\text{CH}_2 \\
\rightarrow \text{C}_6\text{H}_5\text{CH}_3\text{OH}
\]

**EXPERIMENTAL DATA**
- Perry et al. (k1) 1977
- Perry et al. (k2) 1977
- Tully et al. (k1) 1981
- Tully et al. (k2) 1981
- Ohta and Ohyama (k2) 1985
- Edney et al. (k2) 1986
- Atkinson (k2) 1987
- Baldwin et al. 1987
- This Recommendation (k1) 1989
- This Recommendation (k2) 1989

**Graph**
- Log(k, cm$^3$/molecule$^{-1}$s$^{-1}$) vs. $10^3 T^{-1}$ (1/K)
- Temperature range: 2000 K to 300 K
EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[
\begin{align*}
\text{OH} + p\cdot\text{C}_6\text{H}_4(\text{CH}_3)_2 &\rightarrow p\cdot\text{C}_6\text{H}_4\text{CH}_2\text{CH}_3 + \text{H}_2\text{O} \quad (1) \\
\text{OH} + p\cdot\text{C}_6\text{H}_4(\text{CH}_3)_2 (+ \text{M}) &\rightarrow p\cdot\text{C}_6\text{H}_4(\text{CH}_3)_2\text{OH} (+ \text{M}) \quad (2)
\end{align*}
\]

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

<table>
<thead>
<tr>
<th>( k_1 [\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}] )</th>
<th>( T [\text{K}] )</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate Coefficient Measurements</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( k_2 = 1.2\cdot10^{-11} )</td>
<td>298</td>
<td>Doyle et al. (1975)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>( k_2 = 1.2\cdot10^{-11} )</td>
<td>298</td>
<td>Hansen et al. (1975)(^2)</td>
<td>(b)</td>
</tr>
<tr>
<td>( k_2 = 1.5\cdot10^{-11} )</td>
<td>298</td>
<td>Perry et al. (1977)(^3)</td>
<td>(c)</td>
</tr>
<tr>
<td>( k_2 = 6.3\cdot10^{-11}\exp(300/T) )</td>
<td>296-325</td>
<td>Raveishankara et al. (1978)(^4)</td>
<td>(d)</td>
</tr>
<tr>
<td>( k_2 = 6.3\cdot10^{-11}\exp(-1200/T) )</td>
<td>380-473</td>
<td></td>
<td>(e)</td>
</tr>
<tr>
<td>( k_2 = 8.8\cdot10^{-12} )</td>
<td>298</td>
<td></td>
<td>(f)</td>
</tr>
<tr>
<td>( k_2 = 1.0\cdot10^{-11} )</td>
<td>298</td>
<td></td>
<td>(g)</td>
</tr>
<tr>
<td>( k_2 = 1.1\cdot10^{-11} )</td>
<td>298</td>
<td></td>
<td>(h)</td>
</tr>
<tr>
<td>( k_2 = 1.4\cdot10^{-11} )</td>
<td>298-320</td>
<td>Nicovich et al. (1981)(^5)</td>
<td>(i)</td>
</tr>
<tr>
<td>( k_2 = 6.4\cdot10^{-11}\exp(-1440/T) )</td>
<td>500-960</td>
<td>Ohta and Ohyama (1985)(^6)</td>
<td>(j)</td>
</tr>
<tr>
<td>( k_2 = 1.4\cdot10^{-11} )</td>
<td>298</td>
<td>Edney et al. (1986)(^7)</td>
<td>(k)</td>
</tr>
<tr>
<td>( k_2 = 1.4\cdot10^{-11} )</td>
<td>296</td>
<td></td>
<td>(l)</td>
</tr>
<tr>
<td>( k_2 = 1.5\cdot10^{-11} )</td>
<td>298</td>
<td>Atkinson (1987)(^8)</td>
<td>(m)</td>
</tr>
</tbody>
</table>

Comments

(a) Experimentally measured relative rate coefficient. \( p = 1 \text{ bar} \).
(b) to (e) Flash photolysis–resonance technique. OH radical concentrations monitored as a function of time. \( p = 133 \text{ mbar} \).
(f) Flash photolysis–resonance technique. \( p = 4 \text{ mbar} \) Ar.
(g) Flash photolysis–resonance technique. \( p = 27 \text{ mbar} \) He.
(h) Flash photolysis–resonance technique. \( p = 270 \text{ mbar} \) He.
(i) Flash photolysis–resonance technique.
(j) Same method as in comment (i).
(k) Experimentally measured relative rate coefficient. \( p = 1 \text{ bar} \). Reference compound was hexane. H$_2$O$_2$ was the source of OH.
(l) Experimentally measured relative rate coefficient. \( p = 1 \text{ bar} \). Reference compound was cyclohexane. Methyl nitrite was the source of OH.
(m) The source of the given experimental value is not cited. \( p = 1 \text{ bar} \).

Preferred Values

\[
\begin{align*}
\Delta \log k_1 &= \pm 0.1 \\
\Delta \log k_2 &= \pm 0.1
\end{align*}
\]

Reliability

Comments on Preferred Values

The preferred value for \( k_1 \) is based on the data of Nicovich et al.\(^5\). The recommended \( k_2 \) is close to the high pressure limit.

References

BAULCH ET AL.

$$\text{OH} + p\text{-C}_6\text{H}_4(\text{CH}_3)_2 \rightarrow p\text{-C}_6\text{H}_4\text{CH}_2\text{CH}_3 + \text{H}_2\text{O}$$

$$\rightarrow p\text{-C}_6\text{H}_4(\text{CH}_3)_2\text{OH}$$

**EXPERIMENTAL DATA**

- Doyle et al. (k2) 1975
- Hansen, Atkinson, and Pitts (k2) 1975
- Perry, Atkinson, and Pitts (k2) 1977
- Perry, Atkinson, and Pitts (k1) 1977
- Ravishankara et al. (k2) 20 Torr 1978
- Ravishankara et al. (k2) 200 Torr 1978
- Nicovich et al. (k2) 1981
- Nicovich et al. (k1) 1981
- Ohta and Ohshima (k2) 1985
- Edney et al. (k2) 1986
- Atkinson (k2) 1987

**This Recommendation** (k1) 1989

**This Recommendation** (k2) 1989
EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[
\begin{align*}
\text{OH} + \text{C}_6\text{H}_5\text{C}_2\text{H}_5 & \rightarrow \text{C}_6\text{H}_4\text{C}_2\text{H}_4 + \text{H}_2\text{O} & (1) \\
& \rightarrow \text{C}_6\text{H}_4\text{C}_2\text{H}_5 + \text{H}_2\text{O} & (2) \\
\text{OH} + \text{C}_6\text{H}_5\text{C}_2\text{H}_5 (+ M) & \rightarrow \text{C}_6\text{H}_6\text{OHC}_2\text{H}_5 (+ M) & (3)
\end{align*}
\]

Thermodynamic Data
\[
\begin{align*}
\Delta H_{\text{fio}} (1) &= -157.4 \text{ kJ mol}^{-1} \\
\Delta S_{\text{fio}} (1) &= 0.9 \text{ J K}^{-1}\text{mol}^{-1} \\
K_r (1) &= 3.4 \times 10^{-10} \exp(+18850/T)
\end{align*}
\]

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

<table>
<thead>
<tr>
<th>([\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}])</th>
<th>(T[\text{K}])</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(8.0 \times 10^{-12})</td>
<td>305</td>
<td>Lloyd et al. (1976)</td>
<td>(a)</td>
</tr>
<tr>
<td>(7.5 \times 10^{-12})</td>
<td>298</td>
<td>Ravishankara et al. (1978)</td>
<td>(b)</td>
</tr>
<tr>
<td>(7.1 \times 10^{-12})</td>
<td>298</td>
<td></td>
<td>(c)</td>
</tr>
<tr>
<td>(8.0 \times 10^{-12})</td>
<td>298</td>
<td></td>
<td>(d)</td>
</tr>
<tr>
<td>(6.8 \times 10^{-12})</td>
<td>298</td>
<td>Ohta and Ohyama (1985)</td>
<td>(e)</td>
</tr>
</tbody>
</table>

Comments

(a) Relative rates of disappearance of ethylbenzene in air, \(p = 1\) bar. Analysis by GC.
(b) Flash photolysis–resonance fluorescence technique at pressure 4 mbar He.
(c) Same as comment (b); pressure 27 mbar He.
(d) Same as comment (b); pressure 270 mbar He.
(e) Photolysis at atmospheric pressure. Analysis by GC.

Preferred Values

\(k = 7.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) at 298 K and \(p = 1\) bar

Reliability
\[
\begin{align*}
\Delta \log k &= \pm 0.1 \\
\Delta \log k_1 &= \pm 0.1
\end{align*}
\]

H₂O (+ M) → H + OH (+ M)

Thermodynamic Data
\[
\begin{align*}
\Delta H_{\text{fio}} &= 409 \text{ kJ mol}^{-1} \\
\Delta S_{\text{fio}} &= 109 \text{ J K}^{-1}\text{mol}^{-1} \\
K_p &= 2.78 \times 10^2 \exp(-59800/T) \text{ atm}
\end{align*}
\]

Rate Coefficient Data

<table>
<thead>
<tr>
<th>([\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}])</th>
<th>(T[\text{K}])</th>
<th>(M)</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(5.8 \times 10^{-9} \exp(-52920/T))</td>
<td>2000–6000</td>
<td>(\text{N}_2)</td>
<td>Baulch et al. (1972)</td>
<td></td>
</tr>
<tr>
<td>(2.2 \times 10^{-8} \exp(-52920/T))</td>
<td>2000–6000</td>
<td>(\text{Ar})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(3.7 \times 10^{-8} \exp(-52920/T))</td>
<td>2000–6000</td>
<td>(\text{H}_2\text{O})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(5.8 \times 10^{-8} \exp(-52900/T))</td>
<td>2000–6000</td>
<td>(\text{N}_2)</td>
<td>Tsang and Hampson (1986)</td>
<td></td>
</tr>
</tbody>
</table>

References


### Preferred Values

\[ k = 5.8 \times 10^{-9} \exp(-52920/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range } 2000-6000 \text{ K for } M = N_2 \]

**Reliability**

\[ \Delta \log k = \pm 0.5 \text{ for } M = N_2 \]

**Comments on Preferred Values**

The value preferred by Baulch et al.\(^1\) is recommended because no new experimental data are available.

\[
\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2
\]

### Thermodynamic Data

\[ \Delta H_\text{f}^{\text{298}} = -157 \text{ kJ mol}^{-1} \]
\[ \Delta S_\text{f}^{\text{298}} = -20.1 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_p = 8.1 \times 10^{-3} T^{0.363} \exp(+19000/T) \]

### Rate Coefficient Data

<table>
<thead>
<tr>
<th>(k[\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}])</th>
<th>(T[\text{K}])</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5-3.0 \times 10^{-12}</td>
<td>1000-1250</td>
<td>Troe (1960)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>1.0-1.4 \times 10^{-12} \exp(+1057/T)</td>
<td>276-400</td>
<td>Liu et al. (1979)(^2)</td>
<td>(b)</td>
</tr>
<tr>
<td>3.6 \times 10^{-14} \exp(+1250/T)</td>
<td>273-339</td>
<td>Cox and Burrows (1979)(^3)</td>
<td>(c)</td>
</tr>
<tr>
<td>4.1 \times 10^{-13} \exp(+630/T)</td>
<td>298-510</td>
<td>Patrick and Pilling (1982)(^4)</td>
<td>(d)</td>
</tr>
<tr>
<td>2.3 \times 10^{-13} \exp(+600/T)</td>
<td>230-420</td>
<td>Kircher and Sander (1984)(^5)</td>
<td>(e)</td>
</tr>
<tr>
<td>+ 8.4 \times 10^{-34} \exp(+1100/T) [Ar]</td>
<td>Lightfoot et al. (1988)(^6)</td>
<td>(f)</td>
<td></td>
</tr>
<tr>
<td>2.2 \times 10^{-13} \exp(+620/T)</td>
<td>298, 418, 577</td>
<td></td>
<td></td>
</tr>
<tr>
<td>+ 1.9 \times 10^{-39} \exp(+980/T) [N_2]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(3.4, 1.5, 0.97) \times 10^{-12}</td>
<td>623, 677, 723</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(9.2, 9.7, 9.2) \times 10^{-13}</td>
<td>777</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.1 \times 10^{-12}</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Reviews and Evaluations

\[ \begin{align*}
3.3 \times 10^{-12} & \quad 300 & \text{Baulch et al. (1972)\(^7\)} & (g) \\
2.3 \times 10^{-12} & \quad 300 & \text{Baulch et al. (1980)\(^8\)} & (h) \\
6.6 \times 10^{-14} \exp(+1155/T) & \quad 300-400 & \text{Kaufman and Sherwell (1983)\(^9\)} & (i) \\
3.3 \times 10^{-12} & \quad 300-1200 & \text{Warnatz (1984)\(^10\)} & (j) \\
3.0 \times 10^{-12} & \quad 300-1200 & \text{Tsang and Hampson (1986)\(^11\)} & (k) \\
5.0 \times 10^{-12} \exp(-698/T) & \quad 570-770 & \text{Baldwin et al. (1986)\(^12\)} & (l) \\
2.1 \times 10^{-10} \exp(-5050/T) & \quad 300-1200 & \text{Lightfoot et al. (1988)\(^6\)} & (m) \\
+ 1.8 \times 10^{-13} \exp(+885/T) & \quad | & | |
+ 5.7 \times 10^{-12} \exp(-2405/T) & \quad | & | |
+ 1.8 \times 10^{-12} \exp(+885/T) & \quad | & | |
\end{align*}
\]

### Comments

(a) Thermal decomposition of \(\text{H}_2\text{O}_2\) behind reflected shock waves in Ar carrier at total pressures between 0.6 and 12 atmospheres. Fitted \(k\) using complex mechanism. Value of \(k\) sensitive to \(k(\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2)\) and consequently value of \(k\) may be slightly too high.

(b) Pulse radiolysis of mixtures containing 1200 Torr of \(\text{H}_2\) and 5 Torr of \(\text{O}_2\) to produce H atoms rapidly converted to \(\text{HO}_2\). Decay of [\(\text{HO}_2\)] monitored by kinetic spectroscopy at 230 nm.

(c) Molecular modulation photolysis of \(\text{Cl}_2\) in the presence of excess \(\text{H}_2\) and \(\text{O}_2\) or at lower pressures in the presence of \(\text{HCHO}\) and \(\text{O}_2\). Total pressure varied between 3 and 760 Torr. [\(\text{HO}_2\)] measured by UV absorption at 230 nm. \(k\) found to be independent of pressure above 25 Torr.

(d) Flash photolysis of anhydrous \(\text{Cl}_2/\text{CH}_3\text{OH}/\text{O}_2\) mixtures in \(\text{N}_2\); total pressure of 700 Torr. [\(\text{HO}_2\)] measured by UV absorption at 227.5 nm.

(e) Flash photolysis of \(\text{Cl}_2/\text{CH}_3\text{OH}/\text{O}_2\) mixtures. [\(\text{HO}_2\)] measured by UV absorption at 227.5 nm. Total pressure between 100 to 700 Torr with Ar and \(\text{N}_2\). Authors observed both a zero-pressure bimolecular component and a termolecular component linearly dependent on pressure up to 700 Torr. Rate constants also determined when up to 10 Torr of \(\text{H}_2\text{O}\) added.

(f) Flash photolysis of \(\text{Cl}_2/\text{CH}_3\text{OH}/\text{excess air mixtures at atmospheric pressure. [HO}_2\] measured by UV absorption between 200 and 227.5 nm. Allow for varia-
EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

Reliability

<table>
<thead>
<tr>
<th>Comment Code</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>Systematic dependence of $k$ on experimental conditions other than temperature was observed, but pressure was not varied. Suggest a minimum value of $k$ at about 700 K.</td>
</tr>
<tr>
<td>(b)</td>
<td>Recommended based on limited data at room temperature.</td>
</tr>
<tr>
<td>(c)</td>
<td>Recommended for atmospheric pressure only.</td>
</tr>
<tr>
<td>(d)</td>
<td>Based on the results of Cox and Burrows and of Lii et al. Values recommended refer to atmospheric pressure in the absence of H$_2$O and NH$_3$.</td>
</tr>
<tr>
<td>(e)</td>
<td>Authors fitted a double Arrhenius expression to Troe's single value of $k$ at about 150 K and their values at 760 Torr obtained between 298 and 777 K.</td>
</tr>
<tr>
<td>(f)</td>
<td>An alternative fit to the above data based on the A factor recommended by Baldwin et al.; Troe's value is effectively ignored.</td>
</tr>
<tr>
<td>(g)</td>
<td>Recommended without comment.</td>
</tr>
<tr>
<td>(h)</td>
<td>Based on very limited data at room temperature.</td>
</tr>
<tr>
<td>(i)</td>
<td>A direct bimolecular abstraction reaction assumed at temperatures above 600 K. Troe's value of $k$ combined with a thermochemically-calculated A factor to give the activation energy quoted.</td>
</tr>
<tr>
<td>(j)</td>
<td>Authors fitted a double Arrhenius expression to Troe's single value of $k$ at about 1150 K and their values at 760 Torr obtained between 298 and 777 K.</td>
</tr>
<tr>
<td>(k)</td>
<td>Recommended as best value for a wide temperature range.</td>
</tr>
<tr>
<td>(l)</td>
<td>A direct bimolecular abstraction reaction assumed at temperatures above 600 K. Troe's value of $k$ combined with a thermochemically-calculated A factor to give the activation energy quoted.</td>
</tr>
<tr>
<td>(m)</td>
<td>Authors fitted a double Arrhenius expression to Troe's single value of $k$ at about 1150 K and their values at 760 Torr obtained between 298 and 777 K.</td>
</tr>
<tr>
<td>(n)</td>
<td>An alternative fit to the above data based on the A factor recommended by Baldwin et al.; Troe's value is effectively ignored.</td>
</tr>
</tbody>
</table>

Preferred Values

$$k = 3.1 \times 10^{-14} \exp(-775/T) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} \text{between 550 and 1250 K}$$

Reliability

$$\Delta \log k = \pm 0.15 \text{ between 550 and 800 K, rising to } \pm 0.3 \text{ at 1250 K}$$

Comments on Preferred Values

The reaction is very important in combustion chemistry over the range 600–1200 K. Fortunately, a single, reliable recommendation may be made over this range. The graph shows data obtained above room temperature at pressures near to atmospheric (see comments). Troe's single value of $k$ was obtained from a study between 0.6 and 12 atmospheres, and the Lii et al. data were obtained at 1200 mmHg. Also shown is a theoretical estimate of $k$ by Patrick, Golden, and Barker over a wide range of temperatures for 700 mmHg of N$_2$. Below about 500 K, the rate constant varies with pressure and is particularly sensitive to the presence of polar gases such as H$_2$O and NH$_3$. The existence of a negative temperature coefficient below 500 K is clearly established. Recommendation for the value of $k$ below 500 K have been made by the IUPAC group. Studies by Kircher and Sander, Lii et al., Lightfoot, Veyret, and Lesclaux all suggest that $k$ becomes independent of pressure above about 500 K, and this is supported by the theoretical study. Above 500 K, the recommendation is based on Troe's shock-tube data point, which is sensitive to $k$ (OH + H$_2$O) required in a complex interpretation, (ii) the slight evidence obtained by Lightfoot, Veyret, and Lesclaux for a minimum value for $k$ at about 700 K, (iii) the theoretical study which predicts a minimum at about 1000 K and then a steady increase in $k$ up to 3000 K. Full details of the low-temperature data are given in the CODATA compilation.

To give a complete picture of the state of the data all of experimental results are included on the graph irrespective of whether the data are referenced in the text.

References

HO$_2$ + HO$_2$ → H$_2$O$_2$ + O$_2$

$T$/K

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

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

EXPERIMENTAL DATA
- Tree 1969
- Hochanadel et al. 1972
- Li et al. 1979
- Takacs and Howard 1986
- Paukert and Johnston 1972
- Vardanyan et al. 1974
- Hamilton and Li 1977
- Graham et al. 1979
- Cox and Burrows 1979
- Burrows et al. 1979
- Hochanadel et al. 1980
- Thrush and Tyndall 1982
- Thrush and Tyndall 1982
- Patrick and Pilling 1982
- DesMar 1982
- Simonaitis and Heicklen 1982
- Sander et al. 1982
- Sander 1984
- Rozenekliven et al. 1985
- Tacon and Howard 1984
- Cottell and Cox 1986
- McAdam et al. 1987
- Baldwin et al. 1984
- Anderson et al. 1988
- Lightfoot et al. 1992

This Recommendation 1989

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ \text{HO}_2 + \text{NH}_2 \rightarrow \text{O}_2 + \text{NH}_3 \]  
\[ \rightarrow \text{HNO} + \text{H}_2\text{O} \]

**Thermodynamic Data**

\[ \Delta H_{298} (1) = -247 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298} (1) = -25.9 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_p (1) = 1.75 \times 10^{-2} T^{0.19} \exp (29800/T) \]

\[ \Delta H_{298} (2) = -345 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298} (2) = -14.3 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_p (2) = 0.472 T^{-0.19} \exp (41200/T) \]

**Rate Coefficient Data** \((k = k_1 + k_2)\)

<table>
<thead>
<tr>
<th>(k) [(\text{cm}^3) molecule(^{-1}) s(^{-1})]</th>
<th>(T) [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5 \times 10^{-11}</td>
<td>298</td>
<td>Cheskis and Sarkisov (1979)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>2.7 \times 10^{-11}</td>
<td>349</td>
<td>Pagsberg, Eriksen, and Christensen (1979)(^2)</td>
<td>(b)</td>
</tr>
<tr>
<td>3.4 \times 10^{-11}</td>
<td>298</td>
<td>CODATA (1984)(^3)</td>
<td>(c)</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>Lesclaux (1984)(^4)</td>
<td>(d)</td>
</tr>
</tbody>
</table>

**Comments**

(a) Flash photolysis of \(\text{NH}_3/\text{O}_2\) mixtures. \([\text{NH}_3]\) decay monitored by intracavity laser absorption spectrometry at 598 nm. Reported value is based on ratio \(k/k(\text{NH}_3 + \text{NH}_2) = 1.1\) at 570 Torr \(\text{N}_2\) and \(k(\text{NH}_3 + \text{NH}_2) = 2.5 \times 10^{-11} \text{ cm}^3\) molecule\(^{-1}\) s\(^{-1}\) \(^6\). Measurements at 100 Torr \(\text{N}_2\) give same value of \(k\).

(b) Pulse radiolysis of \(\text{NH}_3/\text{O}_2\) mixtures. \([\text{NH}_3]\) decay monitored by absorption spectrometry at 598 nm. Absence of any effect of \(\text{O}_2\) on the \([\text{NH}_3]\) decay interpreted to imply that \(k = k(\text{H} + \text{NH}_2)\). Value reported is value of \(k(\text{H} + \text{NH}_2)\) determined in same study.

(c) Evaluation of room temperature data.

(d) Comprehensive review; no recommendation.

**Preferred Values**

\[ k = 2.6 \times 10^{-11} \text{ cm}^3\) molecule\(^{-1}\) s\(^{-1}\) over range 300–400 K \]

**Reliability**

\[ \Delta \log k = \pm 0.4 \text{ over the range 300–400 K} \]

**Comments on Preferred Values**

There are no recent studies of this reaction; all previous Refs. have been reviewed\(^1\)\(^4\). There are two published studies\(^1\)\(^2\) both giving rate constant ratios using different Ref. reactions but leading to values of \(k\) in excellent agreement. The recommended value is based on these. There is also some unpublished work of Kurasawa and Lesclaux\(^x\) suggesting a value of \(k\) a factor of 2 higher. The recommended error limits encompass this value.

There are no measurements of branching ratios. Lesclaux, mainly on the basis of unpublished work, concludes that the most likely path is channel (2) but (1) probably occurs also.

**References**

\(^5\) H. Kurasawa and R. Lesclaux, results presented at 14th Informal Conference on Photochemistry, Newport Beach, CA, March 1980.
BAULCH ET AL.

\[
\begin{align*}
\text{HO}_2 + \text{CH}_3 & \rightarrow \text{OH} + \text{CH}_3\text{O} \quad (1) \\
& \rightarrow \text{O}_2 + \text{CH}_4 \quad (2)
\end{align*}
\]

**Thermodynamic Data**

\[
\begin{align*}
\Delta H_{\text{f,0}} (1) & = \ -101 \, \text{kJ mol}^{-1} \\
\Delta S_{\text{m,0}} (1) & = \ -11.0 \, \text{J K}^{-1}\text{mol}^{-1} \\
K_p (1) & = 9.33 \times 10^{-2} T \exp(12300/T)
\end{align*}
\]

\[
\begin{align*}
\Delta H_{\text{f,298}} (2) & = \ -231 \, \text{kJ mol}^{-1} \\
\Delta S_{\text{m,298}} (2) & = \ -31.9 \, \text{J K}^{-1}\text{mol}^{-1} \\
K_p (2) & = 2.53 \times 10^{-2} T^{-1.0} \exp(27900/T)
\end{align*}
\]

**Rate Coefficient Data**

<table>
<thead>
<tr>
<th>(k [\text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1}])</th>
<th>(T [\text{K}])</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate Coefficient Measurements</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(k_1 = 3 \times 10^{-11})</td>
<td>1030–1115</td>
<td>Colket, Naegeli, and Glassman (1977)</td>
<td>(a)</td>
</tr>
<tr>
<td>Reviews and Evaluations</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(k_1 = 3.3 \times 10^{-11})</td>
<td>300–2500</td>
<td>Tsang and Hampson (1986)</td>
<td>(b)</td>
</tr>
<tr>
<td>(k_2 = 6.0 \times 10^{-12})</td>
<td>300–2500</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Comments**

(a) Study of the oxidation of \(\text{CH}_3\text{CHO}\) in a turbulent flow reactor at atmospheric pressure with endproduct analysis by GC. Reaction (1) was proposed to account for the oxidation of \(\text{CH}_3\) and a value of \(k\) was selected to obtain rate coefficients for other reactions in the mechanism consistent with literature data.

(b) \(k_1\) taken from study of Colket et al. and \(k_2\) estimated from \(k_2 = k_1 \cdot k\). It should be noted that the value of \(k_1\) is very uncertain in this calculation.

**Preferred Values**

\(k_1 = 3 \times 10^{-11} \text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1}\) over range 600–1200 K

**Reliability**

\(\Delta \log k_1 = \pm 1.0\) over range 600–1200 K

**Comments on Preferred Values**

We have recommended the value of \(k_1\) determined indirectly by Colket et al. but with wide error limits to indicate the large uncertainty. Direct measurements of the rate coefficient and its temperature dependence are needed.

**References**


**HO_2 + CH_4 → H_2O_2 + CH_3**

**Thermodynamic Data**

\[
\begin{align*}
\Delta H_{\text{f,0}} & = 74.0 \, \text{kJ mol}^{-1} \\
\Delta S_{\text{m,0}} & = 11.9 \, \text{J K}^{-1}\text{mol}^{-1} \\
K_p & = 0.321 T^{0.468} \exp(-8950/T)
\end{align*}
\]

**Rate Coefficient Data**

<table>
<thead>
<tr>
<th>(k [\text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1}])</th>
<th>Temperature [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate Coefficient Measurements</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(4.2 \times 10^{-19})</td>
<td>716</td>
<td>Baldwin, Jones and Walker (1988)</td>
<td>(a)</td>
</tr>
<tr>
<td>Reviews and Evaluations</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(3.0 \times 10^{-13} \exp(-9350/T))</td>
<td>no range quoted</td>
<td>Tsang and Hampson (1986)</td>
<td>(b)</td>
</tr>
<tr>
<td>(1.5 \times 10^{-11} \exp(-12440/T))</td>
<td>625–1275</td>
<td>Baldwin, Jones, and Walker (1988)</td>
<td>(c)</td>
</tr>
</tbody>
</table>

**Comments**

(a) Decomposition of tetramethylbutane in presence of \(\text{O}_2\) as source of \(\text{HO}_2\) with GLC analysis for products. Competitive study giving \(k/k_1^{1/2}; k_1 = 3.1 \times 10^{-12}\) exp\((-775/T)\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) for \(\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2\) (see present recommended value).

(b) Estimate based on relation given by Walker\(^3\) for \(\text{HO}_2\) attack on alkane.

(c) Assumed A factor (per C—H bond) in Arrhenius expression is the same for HO₂ + CH₄ and HO₂ + C₂H₆, activation energy calculated from single temperature point.

**Preferred Values**

\[ k = 1.5 \times 10^{-11} \exp(-12440/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range } 600-1000 \text{ K} \]

**Reliability**

\[ \Delta \log k = \pm 0.1 \text{ at } 700 \text{ K rising to } \pm 0.2 \text{ at } 600 \text{ K and } \pm 0.3 \text{ at } 1000 \text{ K} \]

**Comments on Preferred Values**

The value at 716 K is the only experimental determination of \( k \). The value of \( k/k_1^{1/2} \) is reliable and any error in \( k_1 \) is reduced by 50% in calculating \( k \). The preferred value of \( k \) is based on the single determination and thermochemical considerations involving the reliable values of the rate constant for HO₂ + C₂H₆. The constants in the preferred value of \( k \) are reasonable for the reaction but if \( k \) is of the form \( A T^n \exp(E/RT) \) with \( n \) likely to be between 2 and 3, then extrapolation will lead to low values of \( k \) above 1000 K.

**References**


\[ \text{HO}_2 + \text{HCHO} \rightarrow \text{H}_2\text{O}_2 + \text{CHO} \]

**Rate Coefficient Data**

<table>
<thead>
<tr>
<th>( k [\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}] )</th>
<th>( T [\text{K}] )</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k/k(\text{HO}_2 + \text{CO}) = 340 )</td>
<td>798</td>
<td>Blundell et al. (1965)¹</td>
<td>(a)</td>
</tr>
<tr>
<td>( k/k(\text{HO}_2 + \text{CO}) = 280 )</td>
<td>798</td>
<td>Hoare et al. (1967)²</td>
<td>(b)</td>
</tr>
<tr>
<td>( k/k(\text{HO}_2 + \text{HO}_2) = 9.2 \times 10^{-10} )</td>
<td>773</td>
<td>Baldwin et al. (1972)³</td>
<td>(c)</td>
</tr>
<tr>
<td>( 1.9 \times 10^{-11} \exp(-5230/T) )</td>
<td>773–973</td>
<td>Vardanyan et al. (1971)⁴</td>
<td>(d)</td>
</tr>
</tbody>
</table>

**Reviews and Evaluations**

1.7 \times 10^{-12} \exp(-4030/T)

3.3 \times 10^{-12} \exp(-5870/T)

3.3 \times 10^{-12} \exp(-5870/T)

Lloyd (1974)⁵

Walker (1975)⁶

Tsang and Hampson (1986)⁷

<table>
<thead>
<tr>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Study of the combustion of CH₄ in HF washed vessel. Attack of HO₂ on intermediate HCHO and CO compared by measuring O₃, CH₄, CO, CO₂, HCHO, and H₂O₂. → ( k = 2.8 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} ) if Tsang and Hampson's ( k(\text{HO}_2 + \text{CO}) ) is used.</td>
</tr>
<tr>
<td>(b) Same as (a) with boric acid coated vessel. → ( k = 2.3 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} ) if Tsang and Hampson's ( k(\text{HO}_2 + \text{CO}) ) is used.</td>
</tr>
<tr>
<td>(c) Measurement of the effect of HCHO in reducing the induction times of H₂O₂/N₂ mixtures. → ( k = 1.6 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} ) if Tsang and Hampson's ( k(\text{HO}_2 + \text{HO}_2) ) is used.</td>
</tr>
<tr>
<td>(d) ESR detection of HO₂ during oxidation of HCHO. H₂O₂ and HCHO trapped to measure H₂O₂ accumulation and HCHO decay. ( k ) calculated assuming H₂O₂ concentrations governed only by the HO₂/HCHO reaction, i.e. HO₂ + HO₂ → H₂O₂ and H₂O₂ + M → 2 OH are assumed to have a negligible effect on measured H₂O₂.</td>
</tr>
<tr>
<td>(e) Arrhenius factor A estimated. Combination with reported values leads to temperature dependence. Absolute values from relative rate studies are different however from above because of different Ref. rate constants.</td>
</tr>
<tr>
<td>(f) Based on the result of Baldwin et al. Assumed A leads to temperature dependence. A factor assumption based on a value of 1.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ per C—H bond.}</td>
</tr>
<tr>
<td>(g) Recommend Walker's expression.</td>
</tr>
</tbody>
</table>

**Preferred Values**

\[ k = 5.0 \times 10^{-12} \exp(-6580/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range } 600-1000 \text{ K} \]

**Reliability**

\[ \Delta \log k = \pm 0.5 \text{ over range } 600-1000 \text{ K} \]

Comments on Preferred Values

The preferred value is based on the determination of Baldwin et al.\(^3\) at 773 K together with an assumed A factor of \(5.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\). The only temperature dependence study gives a value for \(k\) at 773 K which is a factor of 20 higher and is considered unreliable.

References


EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ \text{HO}_2 + \text{HCHO} \rightarrow \text{H}_2\text{O}_2 + \text{HCO} \]

\( T/K \)

\[
\begin{align*}
\text{Log}(k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}) &\quad 10^3T^{-1}/K^{-1} \\
\end{align*}
\]

EXPERIMENTAL DATA
Blundell et al 1965
Hoare et al 1976
Baldwin et al 1972
Vardanyan et al 1971
This Recommendation 1989

Rate Coefficient Data

<table>
<thead>
<tr>
<th>Rate Coefficient Measurements</th>
<th>Temperature [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6×10⁻¹⁷</td>
<td>773</td>
<td>Walker (1973)¹</td>
<td>(a)</td>
</tr>
<tr>
<td>4.8×10⁻¹⁷ exp(−9590/T)</td>
<td>773</td>
<td>Baldwin and Walker (1981)²</td>
<td>(b)</td>
</tr>
<tr>
<td>1.05×10⁻¹¹ exp(−8650/T)</td>
<td>673-773</td>
<td>Baldwin et al. (1984)³</td>
<td>(c)</td>
</tr>
<tr>
<td>3.7×10⁻¹² exp(−8650/T)</td>
<td>653-773</td>
<td>Baldwin et al. (1986)⁴</td>
<td>(d)</td>
</tr>
</tbody>
</table>

Reviews and Evaluations
No reliable reviews

Comments
(a) Thermal oxidation of HCHO used as source of H2O2. Measurement of relative yields of CO and oxirane gave k/k(H2O2 + HCHO) = 0.016 at 773 K. Use of k(H2O2 + HCHO) = 9.8×10⁻¹⁶ cm³ molecule⁻¹ s⁻¹ (based on k(H2O2 + H2O) = 3.1×10⁻¹² exp(−775/T) cm³ molecule⁻¹ s⁻¹) gives the absolute value of k.
(b) Addition of C2H4 to slowly reacting mixtures of H2 + O2, and measurement of yield of oxirane. Computer interpretation to determine [H2O2].
(c) Decomposition of tetramethylbutane in presence of O2 in KCl-coated vessels as source of HO2 radicals, with GLC analysis of products. Competitive studies give k/k1⁵.
   k1 = 3.1×10⁻¹² exp(−775/T) cm³ molecule⁻¹ s⁻¹ for reaction H2O2 + HO2 → H2O2 + O2. Later⁴ shown that values of k are slightly too high above 723 K.
(d) Similar study to that referred to in comment (c), but aged-boric-acid-coated vessels used. Lack of surface effects makes results more reliable.

Preferred Values

k = 3.7×10⁻¹² exp(−8650/T) cm³ molecule⁻¹ s⁻¹ over range 600–900 K

Reliability
Δlog k = ± 0.15 between 600 and 750 K, rising to ± 0.25 at 900 K

Comments on Preferred Values
No absolute determinations of k have been made, and all are based on measurements of oxirane. The values of k/k1⁵ in the Baldwin, Dean, and Walker study⁴ are reliable, and any error in k1 is reduced by 50% in calculating k. The preferred values for k form part of a consistent set of data for H2O2 addition to a number of alkenes⁷. On the basis of this it has been argued that the rate parameters do refer to the addition steps H2O2 + C2H4 → CH2=CH2OOH⁷. This reaction is unlikely to be important in combustion chemistry above 900 K.

The recommended values are preferred to those of a previous study⁵ which was carried out in KCl-coated vessels as it is possible that [H2O2] may be affected by a small amount of radical generation at the surface above 720 K.

References
⁶See recommendation for k(H2O2 + H2O2 → H2O2 + O2).
EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[
\text{HO}_2 + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_4\text{O} + \text{OH}
\]

EXPERIMENTAL DATA

- Walker 1973
- Baldwin and Walker 1981
- Baldwin et al 1984
- Baldwin et al 1986
- This Recommendation 1989


### Thermodynamic Data

\[ \Delta H_{\text{f}298} = 54.5 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{f}298} = 26.5 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_p = 51.8 \text{ } T^{-0.082} \exp(-6650/T) \]

### Rate Coefficient Data

<table>
<thead>
<tr>
<th>Rate Coefficient Measurements</th>
<th>Temperature [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(9.5 \times 10^{-18})</td>
<td>734</td>
<td>Hoare and Patel (1969)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>(2.0 \times 10^{-16})</td>
<td>773</td>
<td>Baldwin et al. (1986)(^2)</td>
<td>(b)</td>
</tr>
<tr>
<td>(2.22 \times 10^{-11} \exp(-1035/T))</td>
<td>673-773</td>
<td>Lloyd (1974)(^3)</td>
<td>(c)</td>
</tr>
</tbody>
</table>

### Comments

(a) Oxidation of CH\(_4\)/C\(_2\)H\(_6\) mixtures. Obtained \(k/\langle\text{HO}_2 + \text{CO}\rangle = 3.8 \pm 0.7\) and 0.4 at 773 K and 734 K, respectively. Authors consider values unreliable. Values of \(k\) obtained from \(k/\langle\text{HO}_2 + \text{CO}\rangle = 2.5 \times 10^{-10} \exp(-11870/T) \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}\) given by Baulch et al.\(^6\).

(b) Decomposition of tetramethylbutane in presence of O\(_2\) as source of HO\(_2\) radicals, with GLC analysis of products. Competitive studies giving \(k/k_1 = 1.0 \times 10^{-12} \exp(-775/T)\) \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}\) for HO\(_2\) + HO\(_2\) \rightarrow H\(_2\)O\(_2\) + O\(_2\) (see present recommended value).

(c) An upper limit for \(k\), based on early H\(_2\) + O\(_2\) addition studies by Baldwin et al.\(^3\).

(d) Estimate based on rate constant for HO\(_2\) attack on i-butane and 2,3-dimethylbutane.

(e) Recommended without comment, but based on an estimate by Baldwin and Walker\(^2\).

### Preferred Values

\[ k = 2.22 \times 10^{-11} \exp(-10353/T) \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}\] over range 500-1000 K

### Reliability

\[ \Delta \log k = \pm 0.1 \text{ between 670 K and 770 K rising to } \pm 0.2 \text{ at 500 K and } \pm 0.3 \text{ at 1000 K} \]

### Comments on Preferred Values

The only reliable experimental results are those of Baldwin et al. The values of \(k/k_1\) are reliable and any error in \(k_1\) is reduced by 50% in calculating \(k\). The constants in the preferred expression are reasonable, but if \(k\) is of the form \(A T^n \exp(E/RT)\) with \(n\) likely to be between 2 and 3, then extrapolation will lead to low values of \(k\) above 1000 K.

### References


### HO\(_2\) + CH\(_3\)CHO \rightarrow CH\(_3\)CO + H\(_2\)O\(_2\)

### Thermodynamic Data

\[ \Delta H_{\text{f}298} = -3.85 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{f}298} = 6.78 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_p = 2.13 \text{ } T^{0.024} \exp (+385/T) \]

### Rate Coefficient Data

<table>
<thead>
<tr>
<th>Rate Coefficient Measurements</th>
<th>Temperature [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2.8 \times 10^{-12} \exp(-5350/T))</td>
<td>1030-1115</td>
<td>Colket et al. (1975)(^1)</td>
<td>(a)</td>
</tr>
</tbody>
</table>
Comments

(a) High temperature oxidation of CH$_3$CHO (1030-1115 K). Turbulent flow - stable species determined by GC. The time dependence of [CH$_3$CHO], [H$_2$], [CO], [C$_2$H$_4$], and [HCHO] results modelled by a 25 reaction chemical scheme. Rate constants were derived for 4 reactions.

Preferred Values

\[ k = 5.0 \times 10^{-12} \exp(-6000/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range 900–1200 K} \]

Reliability

\[ \Delta \log k = \pm 0.7 \text{ over range 900–1200 K} \]

References


H$_2$O$_2$ (+ M) → OH + OH (+ M)

Thermodynamic Data

\[ \Delta H_{298} = 214 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298} = 134 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ K_p = 4.42 \times 10^7 T^{-0.093} \exp(-26000/T) \text{ atm} \]

Rate Coefficient Data

<table>
<thead>
<tr>
<th>$k$ [s$^{-1}$]</th>
<th>$T$ [K]</th>
<th>$[M]$ [molecule cm$^{-3}$]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Low Pressure Range</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[Ar] 3.0 \times 10^{-8} \exp(-21600/T)$</td>
<td>450-1450</td>
<td>(0.5-5) $\times 10^9$</td>
<td>Kijewski and Troe (1972)$^1$</td>
<td>(a)</td>
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<tr>
<td><strong>Intermediate Fall-off Range</strong></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>$2.0 \times 10^{12} \exp(-21600/T)$</td>
<td>1100-1300</td>
<td>1.2 $\times 10^{20}$ (Ar)</td>
<td>Meyer et al. (1969)$^2$</td>
<td>(b)</td>
</tr>
<tr>
<td><strong>Reviews and Evaluations</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_o = [N_2] 2.0 \times 10^{-7} \exp(-22900/T)$</td>
<td>700-1500</td>
<td></td>
<td>Bauleh et al. (1972)$^3$</td>
<td>(c)</td>
</tr>
<tr>
<td>$k_o = [N_2] 3.6 \times 10^{-10} T^{-4.5} \exp(-26795/T)$</td>
<td>500-1500</td>
<td></td>
<td>Tsang and Hampson (1986)$^4$</td>
<td>(d)</td>
</tr>
<tr>
<td>$k_o = [Ar] 10^{-73} \exp(-21640/T)$</td>
<td>1000-1400</td>
<td></td>
<td>Brouwer et al. (1987)$^5$</td>
<td>(e)</td>
</tr>
<tr>
<td>$k_o = 10^{44.5} \exp(-24374/T)$</td>
<td>1000-1500</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$F_r(\text{Ar}) = 0.5$</td>
<td>500-1500</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Preferred Values</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_o = [Ar] 3.0 \times 10^{-8} \exp(-21600/T)$ s$^{-1}$ over range 1000-1500 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_o = [N_2] 2.0 \times 10^{-7} \exp(-22900/T)$ s$^{-1}$ over range 700-1500 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_o = 3.0 \times 10^{14} \exp(-24400/T)$ s$^{-1}$ over range 1000-1500 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$F_r = 0.5$ for M = Ar over range 700–1500 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Reliability

\[ \Delta \log k_o = \pm 0.2 \text{ over range 700–1500 K} \]
\[ \Delta \log k_\cdot = \pm 0.5 \text{ over range 700–1500 K} \]
\[ \Delta F_r = \pm 0.1 \text{ over range 700–1500 K} \]

Comments on Preferred Values

The preferred values represent the experimental results in satisfactory comparison with theoretical modelling.
The high pressure data are from a single experiment only and, therefore, require independent confirmation. However, they are consistent with non-thermal dissociation results.

References


N + CN → N₂ + C

Thermodynamic Data

\[ \Delta H_{298} = -191 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298} = -6.22 \text{ J K}^{-1} \text{ mol}^{-1} \]
\[ K_p = 0.937 \exp \left( \frac{-22900}{T} \right) \]

Rate Coefficient Data

<table>
<thead>
<tr>
<th>Rate Coefficient Measurements</th>
<th>1.0 \times 10^{-10}</th>
<th>300</th>
<th>Whyte and Phillips (1983)\textsuperscript{1}</th>
</tr>
</thead>
</table>

Comments

(a) Fast flow system, CN generated by pulsed laser photolysis of C₂N₂ at 193 nm. N generated by electrical discharge in N₂ and [N] measured by titration with NO. [CN] decay in excess N monitored by laser induced fluorescence. Total pressures 1.5–3.5 Torr.

Preferred Values

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

Reliability

\[ \Delta \log k = \pm 1.0 \text{ over range 300–2500 K} \]

Comments on Preferred Values

Results up to 1980 have been reviewed\textsuperscript{2}. Only more recent results are tabulated.

The mechanism of the reaction of CN radicals with N atoms is not well understood. It is not clear whether N₂ molecules are formed directly by the reaction CN + N → C + N₂ or by the sequence N + CN → CN₂ + M, N + CN₂ → CN + N₃. The only data at high temperatures comes from Slack and Fishburne\textsuperscript{3}. These data have been re-evaluated by Slack\textsuperscript{4,5}. Confirmatory studies are required before they can be recommended.

At low temperatures the measurements scatter over four orders of magnitude. The most recent study gives a value of \( k \) at 300 K comparable with the only high temperature data.

The recommended value together with the substantial error limits encompass the high temperature and recent low temperature data.

References

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ \text{N + NCO} \rightarrow \text{NO + CN} \quad (1) \]
\[ \rightarrow \text{N}_2 + \text{CO} \quad (2) \]

**Thermodynamic Data**

\[ \Delta H_{\text{f298}}^{\text{m}} (1) = -107 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{f298}}^{\text{m}} (1) = -2.79 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_p (1) = 2.68\times10^6 \ T^{-0.995} \exp (+12500/T) \]
\[ \Delta H_{\text{f298}}^{\text{m}} (2) = -743 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{f298}}^{\text{m}} (2) = -3.73 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_p (2) = 5.20\times10^7 \ T^{-1.94} \exp (+88900/T) \]

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

<table>
<thead>
<tr>
<th>(k [\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}])</th>
<th>(T[\text{K}])</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_1 = 1.7\times10^{-12})</td>
<td>1700</td>
<td>Lifshitz and Frenklach (1980)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>(k_2 = 3.3\times10^{-11})</td>
<td>1700</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Comments**

(a) Measurement of the induction time for ignition behind reflected shocks in \(\text{C}_2\text{N}_2\text{O}_2/\text{Ar}\) mixtures. Values of \(k\) obtained by computer fitting to assumed reaction mechanism. Fitting reasonably sensitive to value of \(k_2\) but not to \(k_1\).

**Preferred Values**

\(k_2 = 3.3\times10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) at 1700 K

**Reliability**

\[ \Delta \log k_2 = \pm 0.5 \text{ at 1700 K} \]

**Comments on Preferred Values**

There have been no direct measurements of the rate coefficients of this reaction. The two channels have been assumed to be of similar importance\(^1\) but there is no experimental confirmation.

Louge and Hanson\(^2\) have calculated values of \(k_1\) from the equilibrium constant and the only measured values of \(k_{-1}\) by Colket\(^4\). They obtain

\[ k_1 = 7.6\times10^{-10} \exp(-5580/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the range 2150-2400 K. Using Colket's expression for } k_{-1} \text{ and more recent thermodynamic data, we obtain} \]

\[ k_1 = 4.6\times10^{-6} \ T^{-0.995} \exp(-8690/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the same temperature range. This gives a value close to that assigned to } k_1 \text{ at 1700 K by Lifshitz and Frenklach}\(^1\) confirming the predominance of channel (2). \]

We accept the only experimental data available for \(k_2\) as our recommended value but with large error limits.

**References**


\[ \text{NH} + \text{O}_2 \rightarrow \text{NO} + \text{OH} \quad (1) \]
\[ \rightarrow \text{NO}_2 + \text{H} \quad (2) \]
\[ \rightarrow \text{HNO} + \text{O} \quad (3) \]

**Thermodynamic Data (See Comments on Preferred Values)**

\[ \Delta H_{\text{f298}}^{\text{m}} (1) = -227 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{f298}}^{\text{m}} (1) = 8.05 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_p (1) = 8.27 \ T^{-4.15} \exp (+27200/T) \]
\[ \Delta H_{\text{f298}}^{\text{m}} (2) = -105 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{f298}}^{\text{m}} (2) = -31.7 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_p (2) = 2.22\times10^{-4} \ T^{-6.65} \exp (+12900/T) \]
\[ \Delta H_{\text{f298}}^{\text{m}} (3) = -7.73 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{f298}}^{\text{m}} (3) = 4.65 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_p (3) = 9.64\times10^{-7} \ T^{-0.237} \exp (+1060/T) \]

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

<table>
<thead>
<tr>
<th>(k [\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}])</th>
<th>(T[\text{K}])</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_1 = 8.5\times10^{-15})</td>
<td>296</td>
<td>Zetsch and Hansen (1978)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>(&lt; 3.32\times10^{-14})</td>
<td>300</td>
<td>Pagsberg et al. (1979)(^2)</td>
<td>(b)</td>
</tr>
<tr>
<td>(1.26\times10^{-13} \exp(-770/T))</td>
<td>268-543</td>
<td>Hack, Kurzke, and Wagner (1985)(^3)</td>
<td>(c)</td>
</tr>
</tbody>
</table>

**Reviews and Evaluations**

Hanson and Salimian (1984)\(^4\)

Comments

(a) Flash photolysis study. NH generated by photolysis of NH3/O2/He mixtures. [NH] monitored by resonance fluorescence. No effect of changes in total pressure observed.


(c) Discharge flow system. NH produced by the sequence F + NH3 → NH2 + HF, NH2 + F → NH + HF. [O] and [H] monitored by resonance fluorescence and [NH] and [OH] by laser induced fluorescence. Reaction NH + O2 → products also studied; \( k \leq (1 \pm 2) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) obtained for it.

(d) Review of all data to 1984; theoretical expression due to Miller et al.5 suggested but no expression recommended.

Preferred Values

\[
k = 1.26 \times 10^{-13} \exp(-770/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range 270–550 K}
\]

Reliability

\[\Delta \log k = \pm 0.2 \text{ at 270 K rising to } \pm 0.5 \text{ at 550 K}\]

Comments on Preferred Values

The preferred rate expression is that of Hack et al.3 with which the \( k \) value of Zetzsch and Hansen1 at 296 K is in close agreement, but wide error limits are assigned reflecting the lack of confirmatory data over the temperature range. There is only one experimental measurement of the temperature coefficient of \( k \) and, in view of the low values of the pre-exponential factor and \( E/R \), there may be appreciable upward curvature of the Arrhenius plot. Extrapolation to higher temperature is thus very uncertain.

Hansen and Salimian4 quote an expression derived by Miller et al.5 \( (k = 1.66 \times 10^{-11} \exp(-6000/T)) \) but this gives values much lower than the sparse experimental data available.

The only experimental information on the branching ratios comes from the work of Hack et al.3 who observed no H atom production in their study at 268–543 K. They favour channel (1) as the predominant channel.

Theoretical calculations by Melius and Binkley6 favour channels (1) and (2) as the most likely low temperature paths with channel (3) becoming dominant at higher temperatures.

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

References

5. A. Miller, M. D. Smooke, R. M. Green, and R. J. Kee, Fall Meeting Western Sec. Comb. lnst. (1982).

\[
\begin{align*}
\text{NH} + \text{NO} & \rightarrow \text{H} + \text{N}_2\text{O} \quad (1) \\
& \rightarrow \text{HN}_2 + \text{O} \quad (2) \\
& \rightarrow \text{N}_2 + \text{OH} \quad (3)
\end{align*}
\]

**Thermodynamic Data (See Comments on Preferred Values)**

\[
\begin{align*}
\Delta H_{298}^\circ (1) &= -147 \text{ kJ mol}^{-1} \\
\Delta S_{298}^\circ (1) &= -57.3 \text{ J K}^{-1}\text{mol}^{-1} \\
K_p(1) &= 4.64 \times 10^{-7} T^{1.36} \exp(+18100/T) \\
\Delta H_{298}^\circ (2) &= 47.5 \text{ kJ mol}^{-1} \\
\Delta S_{298}^\circ (2) &= -6.48 \text{ J K}^{-1}\text{mol}^{-1} \\
K_p(2) &= 3.58 \times 10^{-2} T^{0.36} \exp(-5530/T) \\
\Delta H_{298}^\circ (3) &= -408 \text{ kJ mol}^{-1} \\
\Delta S_{298}^\circ (3) &= -16.7 \text{ J K}^{-1}\text{mol}^{-1} \\
K_p(3) &= 0.484 T^{0.16} \exp(+49000/T)
\end{align*}
\]

**Rate Coefficient Data \((k = k_1 + k_2 + k_3)\)**

<table>
<thead>
<tr>
<th>(k [\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}])</th>
<th>(T[\text{K}])</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate Coefficient Measurements</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(4.8 \times 10^{-11})</td>
<td>300</td>
<td>Cox, Nelson, and McDonald (1985)1</td>
<td>(a)</td>
</tr>
<tr>
<td>(5.78 \times 10^{-11})</td>
<td>269–373</td>
<td>Harrison, Whyte, and Phillips (1986)2</td>
<td>(b)</td>
</tr>
<tr>
<td>Reviews and Evaluations</td>
<td></td>
<td>Hanson and Salimian (1985)4</td>
<td>(c)</td>
</tr>
</tbody>
</table>

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

Comments

(a) Pulsed laser photolysis of N₂H/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 N₂H/Ar/NO mixtures at 248 nm in flowing system. [NH] decay monitored by laser induced fluorescence at 336 nm. He, N₂, and N₂O also used as carrier gases give same results.
(c) Review of data to 1985; no recommendation.

Preferred Values

\[ k = 5.0 \times 10^{-11} \text{ over range 269–373 K} \]

Reliability

\[ \Delta \log k = \pm 0.2 \text{ over range 269–373 K} \]

Comments on Preferred Values

Studies up to 1985 have been reviewed¹. Only more recent measurements are tabulated here.

At low temperatures there is excellent agreement between all of the available studies. Our recommendation is based on all of them¹,²,⁴,⁵.

At higher temperatures there are three studies⁶,⁷,⁸ covering the range 670–2850 K. They are extremely divergent both in absolute values of \( k \) and their temperature coefficients of \( k \). All are nearly an order of magnitude or more lower than the values measured at temperatures close to 300 K. Further high temperature studies are required before any recommendation can be made for this temperature regime.

There are no experimental data on the relative importance of the various channels. Calculations⁹ suggest that, of the bimolecular routes, channel (1) is likely to predominate since channel (2) is highly endothermic and channel (3), although exothermic, is likely to have a substantial activation energy as a result of the 1–3 hydrogen shift required to produce N₂ and OH from the initially formed HNNO.

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

References

⁶W. S. Nip, Ph. D. Thesis, University of Toronto (1974), reported in Ref. 3.
⁷R. C. Petersen, Ph. D. Thesis, Purdue University (1981), reported in Ref. 3.
NH + NO → H + N₂O  
→ HN₂ + O  
→ N₂ + OH

EXPERIMENTAL DATA
Harrison et al 1985  
Cox et al 1985  
Gordon et al 1971  
Hansen et al 1976  
Nip 1974  
Rosas et al 1981  
Peterson 1981  
This Recommendation 1989
EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ \text{NH}_2 + \text{O}_2 \rightarrow \text{NO} + \text{H}_2\text{O} \quad (1) \]
\[ \rightarrow \text{NO}_2 + \text{H}_2 \quad (2) \]
\[ \rightarrow \text{HNO} + \text{OH} \quad (3) \]
\[ \rightarrow \text{HNO}_2 + \text{H} \quad (4) \]
\[ \rightarrow \text{H}_2\text{NO} + \text{O} \quad (5) \]
\[ \text{NH}_2 + \text{O}_2 + \text{M} \rightarrow \text{NH}_2\text{O}_2 + \text{M} \quad (6) \]

Thermodynamic Data
\[ \Delta H_{f98} (1) = -342 \text{ kJ mol}^{-1} \]
\[ \Delta S_{f98} (1) = 0.281 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_P (1) = 4.89 \times 10^{-6} \text{ exp} \left( \frac{41000}{T} \right) \]
\[ \Delta H_{f98} (2) = -157 \text{ kJ mol}^{-1} \]
\[ \Delta S_{f98} (2) = -29.1 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_P (2) = 1.16 \times 10^{-3} \text{ exp} \left( \frac{19000}{T} \right) \]
\[ \Delta H_{f98} (3) = -51.8 \text{ kJ mol}^{-1} \]
\[ \Delta S_{f8} (3) = 4.56 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_P (3) = 0.914 \times 10^{10} \text{ exp} \left( \frac{62400}{T} \right) \]
\[ \Delta H_{f98} (4) = -49.1 \text{ kJ mol}^{-1} \]
\[ \Delta S_{f8} (4) = -35.7 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_P (4) = 1.43 \times 10^{-6} \text{ exp} \left( \frac{63700}{T} \right) \]

There are no thermodynamic data available for channels (5) and (6).

Rate coefficient data \((k = k_1 + k_2 + k_3 + k_4 + k_5 + k_6)\)

<table>
<thead>
<tr>
<th>(k [\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}])</th>
<th>(T[K])</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(&lt; 4.6 \times 10^{-17})</td>
<td>1245</td>
<td>Michael et al. (1985) (^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>(&lt; 7.7 \times 10^{-18})</td>
<td>298</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(&lt; 5.6 \times 10^{-18})</td>
<td>459</td>
<td>Losovsky, Ioffe, and Sarkisov (1984) (^2)</td>
<td>(b)</td>
</tr>
<tr>
<td>(&lt; 3 \times 10^{-18})</td>
<td>298</td>
<td>CODATA (1984) (^3)</td>
<td>(c)</td>
</tr>
<tr>
<td>(</td>
<td>)</td>
<td></td>
<td>Lesclaux (1984) (^4)</td>
</tr>
<tr>
<td>(</td>
<td>)</td>
<td></td>
<td>Hanson and Salimian (1985) (^5)</td>
</tr>
</tbody>
</table>

Comments

(a) Flash photolysis of \(\text{NH}_3/\text{O}_2/\text{He}\) mixtures. [\(\text{NH}_2\)] monitored by laser induced fluorescence at 578 nm. Total pressure 25 Torr He. Flash energy varied 1.5 - 16.8 J. No effect of \(\text{O}_2\) at low flash energies.

(b) Flash photolysis of \(\text{NH}_3/\text{O}_2/\text{N}_2\) mixtures at total pressures \(< 30\) Torr. [\(\text{NH}_2\)] monitored by intracavity laser absorption spectroscopy at 598 nm. Decay rate of \(\text{NH}_2\) observed to be independent of \(\text{O}_2\) pressure above 1 Torr. Observed decay attributed to \(\text{NH}_2 + \text{O}_2\) reaction.

(c) Evaluation of low temperature data only.

(d) Comprehensive review, no recommendation.

(e) Comprehensive review, no recommendation.

Preferred Values

\(k < 3 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) at 298 K

Comments on Preferred Values

Studies up to 1984 have been tabulated and reviewed. \(^9\)

There has been considerable interest in this reaction because of its likely importance in ammonia oxidation but at low temperatures it is so slow that it is difficult to study by the usual fast reaction techniques. Furthermore, the measurements are very sensitive to the presence of \(\text{H}\) atoms which initiate \(\text{NH}_2\) oxidation by \(\text{HO}_2\) formation in \(\text{NH}_3/\text{O}_2\) systems which have been used frequently in these studies. At low temperatures only upper limits to \(k\) are available, mostly determined by flash photolysis. Our preferred value for \(k\) is that of Lesclaux and Demissy \(^6\). The only discharge-flow study \(^2\) suggests a pressure dependent rate coefficient, interpreted as due to the formation of \(\text{NH}_2\text{O}_2\) as a relatively stable intermediate, but this is not supported by the flash photolysis studies and theoretical calculations \(^1\).\(^5\)\(^7\).

At high temperatures the only available data are from a shock tube study \(^3\) and one in which \(\text{NH}_3/\text{O}_2\) mixtures were passed through a hot tubular reactor \(^4\). Interpretation of the results required computer fitting using large reaction schemes and values obtained differ substantially. We do not consider these results to be certain enough to make a recommendation without further studies.

There is no conclusive experimental evidence on the relative importance of the various possible reaction channels. Recent theoretical calculations \(^1\) suggest the \(\text{NH}_2\text{O}_2\) is stable only to the extent of \(\approx 20 \text{ kJ mol}^{-1}\) and hence is very short-lived, even at 300 K. As suggested by Benson \(^7\), these calculations favour channel (5) as the preferred route despite its estimated endothermicity of \(\approx 125 \text{ kJ mol}^{-1}\). The exothermic channels proceed via \(\text{NH}_2\text{O}_2\) which must surmount a large energy barrier to
before going on to form products [channels (1), (2), (3), (4)]. Channel (3) has been widely accepted in many modelling studies and despite the theoretical evidence against it, the possibility of it making a contribution at high temperatures should not be ruled out.

In contrast to the reaction of ground state O₂, the rate of reaction between NH₂ and O₂ (Δₐ) has been measured by discharge flow methods. A value of 1.0×10⁻¹⁴ cm³ molecule⁻¹ s⁻¹ over the range 295–353 K was obtained⁴.

References


\[
\text{NH}_2 + \text{NO} \rightarrow \text{N}_2 + \text{H}_2\text{O} \quad (1)
\]
\[
\rightarrow \text{N}_2 + \text{H} + \text{OH} \quad (2)
\]
\[
\rightarrow \text{NH} + \text{HNO} \quad (3)
\]
\[
\rightarrow \text{NH}_2\text{NO} \quad (4)
\]
\[
\rightarrow \text{N}_2\text{H} + \text{OH} \quad (5)
\]
\[
\rightarrow \text{N}_2\text{O} + \text{H}_2 \quad (6)
\]

**Thermodynamic Data**

\[\Delta H_{\text{f}0}^{\circ} (1) = -523 \text{ kJ mol}^{-1}\]
\[\Delta S_{\text{f}0}^{\circ} (1) = -250 \text{ J K}^{-1}\text{mol}^{-1}\]
\[K_p (1) = 0.286 \text{ T}^{0.522} \exp (+62700/T)\]

\[\Delta H_{\text{f}0}^{\circ} (2) = -23.7 \text{ kJ mol}^{-1}\]
\[\Delta S_{\text{f}0}^{\circ} (2) = 84.5 \text{ J K}^{-1}\text{mol}^{-1}\]
\[K_p (2) = 79.6 \text{ T}^{0.405} \exp (+2960/T)\]

\[\Delta H_{\text{f}0}^{\circ} (3) = 175 \text{ kJ mol}^{-1}\]
\[\Delta S_{\text{f}0}^{\circ} (3) = -3.49 \text{ J K}^{-1}\text{mol}^{-1}\]
\[K_p (3) = 0.110 \text{ T}^{-0.343} \exp (-2100/T)\]

\[\Delta H_{\text{f}0}^{\circ} (5) = 3.37 \text{ kJ mol}^{-1}\]
\[\Delta S_{\text{f}0}^{\circ} (5) = 2.73 \text{ J K}^{-1}\text{mol}^{-1}\]
\[K_p (5) = 0.339 \text{ T}^{-0.118} \exp (-357/T)\]

\[\Delta H_{\text{f}0}^{\circ} (6) = -199 \text{ kJ mol}^{-1}\]
\[\Delta S_{\text{f}0}^{\circ} (6) = -54.8 \text{ J K}^{-1}\text{mol}^{-1}\]
\[K_p (6) = 2.43×10^{-4} \text{ T}^{0.405} \exp (+24200/T)\]

**Rate Coefficient Data** \((k = k_1 + k_2 + k_3 + k_4 + k_5 + k_6)\)

<table>
<thead>
<tr>
<th>(k[\text{cm}^3\text{ molecule}^{-1}\text{ s}^{-1}])</th>
<th>(T[\text{K}])</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4×10⁻¹¹</td>
<td>298</td>
<td>Gericke et al. (1984)¹</td>
<td>(a)</td>
</tr>
<tr>
<td>2.17×10⁻¹¹</td>
<td>297</td>
<td>Stephens et al. (1984)²</td>
<td>(b)</td>
</tr>
<tr>
<td>5×10⁻¹²</td>
<td>298</td>
<td>Dreier and Wolfrum (1985)³</td>
<td>(c)</td>
</tr>
<tr>
<td>1.7×10⁻¹¹</td>
<td>298</td>
<td>Hall et al. (1986)⁴</td>
<td>(d)</td>
</tr>
<tr>
<td>1.3×10⁻¹¹</td>
<td>298</td>
<td>Dobson (1986)⁵</td>
<td>(e)</td>
</tr>
<tr>
<td>1.6×10⁻¹¹</td>
<td>300</td>
<td>Silver and Kolbe (1987)⁶</td>
<td>(f)</td>
</tr>
<tr>
<td>(k_1 = 1.06×10⁻¹¹)</td>
<td>298</td>
<td>Atakan et al. (1989)⁷</td>
<td>(g)</td>
</tr>
<tr>
<td>(k_2 = 1.36×10⁻¹¹)</td>
<td>294–1027</td>
<td>Lesclaux (1984)⁸</td>
<td>(h)</td>
</tr>
<tr>
<td>(k_3 = 2.98×10⁻¹²)</td>
<td>210–500</td>
<td>CODATA (1989)⁹</td>
<td>(i)</td>
</tr>
<tr>
<td>(k_4 = 2.73×10⁻¹¹)</td>
<td>⁴</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(k_5 = 8.9×10⁻¹³)</td>
<td>⁵</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Comments

(a) NH₂ generated by multiphoton dissociation of N₂H₄ or CH₃NH₂ [NH₂] monitored by laser induced fluorescence.

(b) Discharge flow study of OH + NH₃ reaction. [OH] monitored by resonance fluorescence. Secondary chemistry modelled to give quoted k value.

(c) Flow reactor. Laser flash photolysis of NH₃ at 193 nm. NH₂ radicals and product N₂ monitored by CARS. Independent value of k obtained by monitoring vibrationally excited H₂O by time resolved infrared fluorescence.

(d) Infrared kinetic spectroscopy detection of products in range 2.3-3.2 μm following NH₃ production by laser photolysis of NH₃. Detection of vibrationally excited H₂O as product.

(e) Fast-flow tube reactor with modulated beam mass spectrometry detection. [OH] / [H₂O] product ratio measured.

(f) Re-evaluation of branching ratio from data reported in earlier paper.

(g) Laser photolysis of NH₃. Laser induced fluorescence monitoring of [NH₃] and [OH]. It is concluded that OH is a direct product of the reaction. [OH]/[NH₃] = 0.1 at 300 K rising to 0.19 at 1000 K.

(h) Comprehensive review of all studies up to 1984.

(i) Based mainly on sparse low temperature data.

Preferred Values

\[ k = 1.8 \times 10^{-12} \exp (+650/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range } 220-2000 \text{ K} \]

Reliability

Δlog k = ± 0.5 over range 220–2000 K

Comments on Preferred Values

The major studies prior to 1984 have been reviewed and are not tabulated here.

The data close to room temperature range over a factor of 3 there being a significant discrepancy between those from flash photolysis studies (≈ 20×10⁻¹² cm³ molecule⁻¹ s⁻¹) and those from discharge flow measurements (≈ 9×10⁻¹² cm³ molecule⁻¹ s⁻¹). We take a mean value of 1.6×10⁻¹¹ cm³ molecule⁻¹ s⁻¹ based on Refs. 3, 10–19.

It is clear that the rate coefficient has a significant negative temperature dependence. Our recommendations are based on all of these studies on the temperature dependence which are in reasonable agreement.

The relative importance of the various reaction channels has been the subject of considerable experimental work and theoretical calculations. The negative temperature dependence suggests formation and subsequent rearrangement and dissociation of the addition product NH₃NO.

At high temperatures little information about the branching ratios is available. Channels (1), (2) and (5) are likely to be important but N₂O production has also been observed at high temperatures. The energetics of the reaction pathways have been the subject of several theoretical studies.

References

BAULCH ET AL.

\[ \text{NH}_2 + \text{NO} \rightarrow \text{N}_2 + \text{H}_2\text{O} \]
\[ \rightarrow \text{N}_2 + \text{H} + \text{OH} \]
\[ \rightarrow \text{N}_2\text{H} + \text{OH} \]
\[ \rightarrow \text{N}_2\text{O} + \text{H}_2 \]

\[ T/K \]

**EXPERIMENTAL DATA**
- Gordon et al. 1971
- Gehring et al. 1973
- Kaskan and Hughes 1973
- Duxbury and Pratt 1974
- Lasriou et al. 1975
- Hancox et al. 1975
- Fenimore 1976
- Sarkar et al. 1978
- Kurosawa 1979
- Böttcher 1979
- Hocking et al. 1979
- Kurosawa and Lasriou 1979
- Morgan 1981
- Roux et al. 1981
- Sief et al. 1982
- Silber and Kolbe 1982
- Andrews et al. 1982
- Whyte and Phillips 1983
- Duncan et al. 1983
- Dörr and Wollum 1985
- Gärtsch et al. 1984
- Stephens (k2) 1984
- Hall et al. 1985
- Stephens 1984
- Hocking et al. (k1) 1985
- Hall et al. (k2) 1986
- Hall et al. (k3) 1986
- Dobson (k1) 1986
- Dobson (k3) 1986
- Atkinson et al. 1989

This Recommendation 1989

\[ \log(k/\text{cm}^3\text{ molecule}^{-1}\text{s}^{-1}) \]
\[ 10^3T^{-1}/K^{-1} \]
## Reactions of C₂ Species

<table>
<thead>
<tr>
<th>$k$ [cm$^3$ molecule$^{-1}$ s$^{-1}$]</th>
<th>$T$ [K]</th>
<th>Reference</th>
<th>Comments</th>
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<td>$2.8 \times 10^{-12}$</td>
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<td>Pasternack and McDonald (1979)$^4$</td>
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<td>$C_2 (X^1Σ_g^+) + O_2 \rightarrow$ Products</td>
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<td>Donnelly and Pasternack (1979)$^1$</td>
<td>(f)</td>
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<td></td>
<td>300-600</td>
<td>Pasternack et al. (1981)$^9$</td>
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<td>Pasternack et al. (1981)$^9$</td>
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<td>Pasternack et al. (1981)$^9$</td>
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EVALUATED KINETIC DATA FOR COMBUSTION MODELLING


### Reactions of C₂ Species – Continued

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<td>Reister et al. (1980)⁶</td>
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<td>$5.5 \times 10^{-12}$ exp( +24/T)</td>
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<td>Pasternack et al. (1981)⁹</td>
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<td>Pitts et al. (1982)¹⁰</td>
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### Comments

(a) $C_2(X^1Σ^+)$ produced by multiphoton UV excimer laser photodissociation of hexafluorobutyne-2; monitored by laser induced fluorescence at 691 nm. The authors explain the faster reaction rates of $C_2(X^1Σ^+)$ with H₂ and hydrocarbons by a hydrogen atom exchange reaction to form ground state $C_2H$ which is forbidden for $C_2(a^3Π_u)$. Considerable intersystem crossing with heavy collision partners or with non-singlet partners.

(b) IR multiple photon dissociation of $C_2H_3CN$. Radical depletion monitored by laser induced fluorescence, CO formation by chemiluminescence. Total pressures 1-4 Torr Ar. The authors conclude that CO in highly excited triplet states is the primary product.

(c) IR multiple photon dissociation of $C_2H_3CN$ or $C_2HCl_3$. $C_2$ monitored by laser induced fluorescence. Total pressures 1-4 Torr Ar or He. Measurements of intersystem crossing rates with $C_2Cl_4$ as scavenger.

(d) Production of $C_2(X^1Σ^+)$ by photolysis of hexafluorobutyne-2 in 10 Torr He. $C_2$ monitored by time resolved laser induced fluorescence, in the cases of $O_2$ as reactant only at low temperatures (at high temperature $[^3]C_2$ from chemiluminescence of excited CO from $C_2 + O_2$ reaction). Propose insertion mechanism for reaction of $C_2(X^1Σ^+)$ with $H-H$ and $C-H$ bonds. Very fast equilibration between $C_2(X^1Σ^+)$ and $C_2(a^3Π_u)$ in the presence of $O_2$. Different sets of Arrhenius parameters for $C_2 + O_2$ under the assumptions that (1) $k \left(^3C_2 + O_2\right) \approx k \left(^3C_2 + O_3\right)$, and (2) $k \left(^3C_2 + O_2\right) > k \left(^3C_2 + O_3\right)$.

(e) $C_2$ produced by 193 nm excimer laser photolysis of hexafluorobutyne-2 and monitored by laser induced fluorescence. Total pressure 10-170 Torr CH₄.
(f) \( \text{C}_2(\text{a}^3\Pi_L) \) formed by multiphoton UV photolysis of \( \text{C}_2\text{H}_2 \) or \( \text{C}_2\text{H}_4 \) at 193 nm; monitored by laser induced fluorescence. Total pressures 0–300 Torr.

(g) \( \text{C}_2(\text{a}^3\Pi_L) \) produced by multiphoton UV excimer laser photodissociation of hexafluorobutyne-2 or benzene. \( \text{C}_2 \) depletion measured by laser induced fluorescence. Authors suggest that the reactions of \( \text{C}_2 \) with \( \text{H}_2 \) and saturated hydrocarbons proceed via H atom abstraction (supported by BEBO techniques, linear free energy correlations, and Evans-Polanyi plots) whereas with unsaturated hydrocarbons faster insertion reactions take place.

(h) \( \text{C}_2(\text{a}^3\Pi_L) \) by IR multiple photon dissociation of either vinylcyanide or ethylene in the presence of NO or Ar. Decay of \( \text{C}_2(\text{a}^3\Pi_L) \) monitored by laser induced fluorescence; slow flow conditions. CN formation observed by chemiluminescence.

(i) IR multiple photon dissociation of acrylonitrile \( \text{C}_2\text{H}_3\text{CN} \), laser induced fluorescence of \( \text{C}_2(\text{a}^3\Pi_L) \); total pressures up to 50 Torr. A VUV chemiluminescence signal was observed when \( \text{O}_2 \) was present in the mixture; electronically excited \( \text{CO}(\text{A}^3\Pi) \) proposed.

(j) IR-MPD of vinylcyanide or trichloroethylene. \( \text{C}_2(\text{a}^3\Pi_L) \) and \( \text{C}_2(\text{A}^3\Sigma^+) \) observed by laser induced fluorescence. The intersystem crossing rates were obtained by increasing the concentration of \( \text{O}_2 \) in the sample and comparing the removal rates of \( \text{C}_2 \) and \( ^3\text{C}_2 \). At 300 K the intersystem crossing is much faster than chemical reactions; therefore it is impossible to measure distinct reaction rates of \( ^1\text{C}_2 \) and \( ^3\text{C}_2 \), only the rate of equilibrated \( ^1\text{C}_2/ ^3\text{C}_2 \) mixtures.

References


\[
\text{CH} + \text{O}_2 \rightarrow \text{CHO} + \text{O} \quad (1) \\
\rightarrow \text{CO} + \text{OH} \quad (2)
\]

**Thermodynamic Data**

\[
\Delta H_{\text{f}}(1) = -301 \text{ kJ mol}^{-1} \\
\Delta S_{\text{f}}(1) = -2.5 \text{ J K}^{-1} \text{mol}^{-1} \\
K_p(1) = 0.487 \exp(-36300/T)
\]

\[
\Delta H_{\text{f}}(2) = -666 \text{ kJ mol}^{-1} \\
\Delta S_{\text{f}}(2) = -6.82 \text{ J K}^{-1} \text{mol}^{-1} \\
K_p(2) = 10.1 \exp(-7990/T)
\]

**Rate Coefficient Data**

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<th>( T ) [K]</th>
<th>Reference</th>
<th>Comments</th>
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<tr>
<td>1.7-10⁻¹¹</td>
<td>298</td>
<td>Bosnialli and Perner (1971)¹</td>
<td>(a)</td>
</tr>
<tr>
<td>3.9-10⁻¹¹</td>
<td>298</td>
<td>Jachimowski (1977)²</td>
<td>(b)</td>
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<td>298</td>
<td>Messing, Sadowsky, and Filseth (1979)³</td>
<td>(c)</td>
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<tr>
<td>2.3-10⁻¹¹</td>
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<td>Butler et al. (1980,1981)⁴</td>
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<td>Berman et al. (1982)⁵</td>
<td>(e)</td>
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<td>Duncanson and Guillory (1983)⁶</td>
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<td>( k_2 ) = 8.10⁻¹¹</td>
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<td>Lichtin, Berman, and Lin (1984)⁷</td>
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<td>2.3-10⁻¹¹</td>
<td>290</td>
<td>Anderson, Freedman, and Kolb (1987)⁸</td>
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**Comments**

(a) Pulse radiolysis of 15 Torr \( \text{CH}_4 \) with various amounts of \( \text{O}_2 \) added; \([\text{CH}]\) by absorption spectroscopy at 314.4 nm.

(b) Oxidation of \( \text{C}_2\text{H}_2 \) and \( \text{C}_2\text{H}_4 \) behind incident shock waves. Emission monitored at 370 nm (\( \text{CO} + \text{O} \rightarrow \text{CO}_2 + h\nu \)), at 5.0 μm (\( \text{CO} \)), and at 4.3 μm (\( \text{CO}_2 \)). Total pressure 1.1–1.7 atm Ar. Numerical modelling of 38 reaction mechanism. \( k(\text{CH} + \text{O}_2) \) arbitrarily set.

(c) Multiphoton dissociation of methylamine at 1047 cm⁻¹; \([\text{CH}]\) by laser induced fluorescence at 431.4 nm, \([\text{OH}(\text{A}^3\Sigma^+)]\) by chemiluminescence. Total pressure 10–30 Torr Ar. No pressure dependence reported.

(d) Multiphoton dissociation of \( \text{CHBr}_3 \) at 193 nm; \([\text{CH}]\) by laser induced fluorescence near 430 nm. Total pressure 100 Torr Ar.

(e) Multiphoton dissociation of \( \text{CHBr}_3 \) at 266 nm; \([\text{CH}]\) by laser induced fluorescence at 429.8 nm. Total pressure 100 Torr Ar. No significant temperature dependence.

(f) IR-multiphoton dissociation of \( \text{CH}_3\text{OH} \); \([\text{CH}(\text{A}^3\Pi), \nu = 0 \text{ and } \nu = 1]\) by laser induced fluorescence at 430.0 nm and 487.3 nm. Total pressure 10 Torr Ar.
Given value of \( k \) for \( v = 0 \). \( k(v = 1) = 4.3 \times 10^{-12} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) including vibrational relaxation.

(g) Multiphoton dissociation of CHBr\(_3\) at 266 nm; \([\text{OH} (A^2\Sigma^+)]\) by chemiluminescence. Total pressure 21 Torr, mainly Ar.

(h) Fast flow reactor; CH formation by sequential Br atom abstraction from CHBr\(_3\) with excess alkali-metal atoms (Na or K); [CH] and [OH] by laser induced fluorescence. Total pressure 2 Torr He/Ar mixture.

Preferred Values

\[ k = 5.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range } 300-2000 \text{ K} \]

Reliability

\[ \Delta \log k = \pm 0.3 \text{ at } 300 \text{ K rising to } \pm 0.5 \text{ at } 2000 \text{ K} \]

Comments on Preferred Values

The recommendation is based on the study of Berman et al.\(^6\) because it covers a large temperature range and is in reasonable agreement with other recent studies.

References

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

CH + O₂ → CHO + O
→ CO + OH

T/K

Log(k/cm³ molecule⁻¹ s⁻¹)

10⁻¹¹ to 10⁻¹⁰

10⁻¹⁰.0

0.5 1.0 1.5 2.0 2.5 3.0 3.5

10³ T⁻¹/K⁻¹

EXPERIMENTAL DATA
Ruseck and Desser 1971
Jochimsen 1977
Massing et al 1979
Butler et al 1983
Berman et al 1984
Duncan and Guilford 1983
Anderson et al 1987
Lichten et al (2 works) (x2) 1984
This Recommendation 1989

Thermodynamic Data

\[ \Delta H^{\circ} (1) = 10.8 \text{ kJ mol}^{-1} \]
\[ \Delta S^{\circ} (1) = -3.44 \text{ J K}^{-1} \text{ mol}^{-1} \]
\[ K_p (1) = 0.275 T^{100} \exp(-1220/T) \]

\[ \Delta H^{\circ} (2) = -448 \text{ kJ mol}^{-1} \]
\[ \Delta S^{\circ} (2) = -119 \text{ J K}^{-1} \text{ mol}^{-1} \]
\[ K_p (2) = 1.71 \times 10^{-5} T^{-0.108} \exp(54000/T) \text{ atm}^{-1} \]

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

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<td>Berman and Lin (1984)(^4)</td>
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<td>Zabarnick, Fleming, and Lin (1986)(^6)</td>
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Comments

(a) VUV flash photolysis of CH\(_4\) with added H\(_2\); [CH] by absorption spectroscopy at 314.3 nm. Total pressures 1–10 Torr.
(b) Pulse radiolysis of 15 Torr CH\(_4\) with added H\(_2\); [CH] by absorption spectroscopy at 314.3 nm.
(c) Multiphoton dissociation of CHBr\(_3\) at 193 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressures 30–100 Torr Ar.
(d) Multiphoton dissociation of CHBr\(_3\) at 266 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 100 Torr Ar. Pressure dependence of \( k \) studied at 297 K over range 25–600 Torr; \( k \) increasing from 7.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) at 25 Torr to 4.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) at 600 Torr. Temperature and pressure dependence of \( k \), isotopic effects and a transition-state model support an addition mechanism.
(e) Multiphoton dissociation of CHBr\(_3\) at 266 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 100 Torr Ar. \( k_1 \) determined by measuring total rate at higher temperatures and subtracting \( k_2 \) from Ref. 5. Rate coefficient over range 300–2500 K from transition-state theory.

Preferred Values

\[ k_1 = 2.4 \times 10^{-10} \exp(-1760/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \] over range 300–1000 K

Reliability

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

Comments on Preferred Values

The most recent value of Lin and coworkers has been taken as the recommendation which is in reasonable agreement with the other data at higher temperatures. At lower temperatures there is evidence for channel (2) becoming significant.

References

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ \text{CH} + \text{H}_2 \rightarrow \text{CH}_2 + \text{H} \]
\[ \rightarrow \text{CH}_3 \]

\[ T/K \]

\[ \log(k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}) \]

\[ 10^3 T^{-1}/K^{-1} \]

EXPERIMENTAL DATA

- Berman and Lin (k1) 1984
- Zabarnick et al (k1) 1986
- Braun et al 1997
- Braendell and Perner 1971
- Butler et al (2 works) 1980
- Zabarnick et al (k2) 1988
- Berman and Lin (k2) 1984
- This Recommendation 1989

### CH + H₂O → Products

#### Rate Coefficient Data

<table>
<thead>
<tr>
<th>$k$ [cm³ molecule⁻¹ s⁻¹]</th>
<th>$T$ [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$4.5 \times 10^{-11}$</td>
<td>298</td>
<td>Bosnali and Perner (1971)¹</td>
<td>(a)</td>
</tr>
<tr>
<td>$9.5 \times 10^{-12} \exp(380/T)$</td>
<td>298–669</td>
<td>Zabarnick, Fleming, and Lin (1988)²</td>
<td>(b)</td>
</tr>
</tbody>
</table>

**Comments**

(a) Pulse radiolysis of 15 Torr CH₄ [OH] by absorption at 314.4 nm.

(b) Multiphoton dissociation of CHBr₃ at 266 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 100 Torr Ar. $k$ independent of pressure over range 20–300 Torr at room temperature.

#### Preferred Values

$k = 9.5 \times 10^{-12} \exp(380/T)$ cm³ molecule⁻¹ s⁻¹ over range 300–1000 K

**Reliability**

$\Delta \log k = \pm 1.0$ over range 300–1000 K

**Comments on Preferred Values**

The rate coefficient given by Zabarnick, Fleming, and Lin is recommended but with wide error limits.

**References**


### CH + CO → Products

#### Rate Coefficient Data

<table>
<thead>
<tr>
<th>$k$ [cm³ molecule⁻¹ s⁻¹]</th>
<th>$T$ [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
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<tbody>
<tr>
<td>$4.8 \times 10^{-12}$</td>
<td>298</td>
<td>Bosnali and Perner (1971)¹</td>
<td>(a)</td>
</tr>
<tr>
<td>$2.1 \times 10^{-11}$</td>
<td>298</td>
<td>Butler et al. (1980, 1981)²³</td>
<td>(b)</td>
</tr>
<tr>
<td>$4.6 \times 10^{-13} \exp(861/T)$</td>
<td>297–676</td>
<td>Berman et al. (1982)⁴</td>
<td>(c)</td>
</tr>
</tbody>
</table>

**Comments**

(a) Pulse radiolysis of 15 Torr CH₄ [OH] by absorption at 314.4 nm.

(b) Multiphoton dissociation of CHBr₃ at 193 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 100 Torr Ar. $k$ probably pressure dependent; suggest an addition mechanism similar to the CH₂ + N₂ reaction.

(c) Multiphoton dissociation of CHBr₃ at 266 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 100 Torr Ar. $k$ (CH + CO) increases by a factor of 3 over range 50–640 Torr Ar. Possible products of CH + CO₂ either CHO + CO or H + 2 CO.

#### Preferred Values

$k = 4.6 \times 10^{-13} \exp(861/T)$ cm³ molecule⁻¹ s⁻¹ over range 300–1000 K

**Reliability**

$\Delta \log k = \pm 1.0$ over range 300–1000 K

**Comments on Preferred Values**

The rate coefficient of Berman et al.⁴ (which is consistent with the room temperature value of Butler et al.²³) is taken as the recommendation but with wide error limits.

**References**

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

CH + CO₂ → Products

Rate Coefficient Data

<table>
<thead>
<tr>
<th>Rate Coefficient Measurements</th>
<th>T[K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.9×10⁻¹²</td>
<td>298</td>
<td>Butler et al. (1980,81)¹,²</td>
<td>(a)</td>
</tr>
<tr>
<td>5.7×10⁻¹² exp(-345/T)</td>
<td>297-676</td>
<td>Berman et al. (1982)³</td>
<td>(b)</td>
</tr>
</tbody>
</table>

Comments

(a) Multiphoton dissociation of CHBr₃ at 193 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 100 Torr Ar. k probably pressure dependent; suggest an addition mechanism similar to the CH + N₂ reaction.

(b) Multiphoton dissociation of CHBr₃ at 266 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 100 Torr Ar. k(CH + CO) increases by a factor of 3 over range 50–640 Torr Ar. Possible products of CH + CO₂ either HCO + CO or H + 2 CO.

Preferred Values

\[ k = 5.7 \times 10^{-12} \exp(-345/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range 300–1000 K} \]

Reliability

\[ \Delta \log k = \pm 1.0 \text{ over range 300–1000 K} \]

Comments on Preferred Values

The value of Berman et al.³ is recommended but with wide error limits.

References

CH + CH₄ → Products

Rate Coefficient Data

<table>
<thead>
<tr>
<th>k [cm³ molecule⁻¹ s⁻¹]</th>
<th>T[K]</th>
<th>Reference</th>
<th>Comments</th>
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<td>Braun, McNesby, and Bass (1967)¹</td>
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<td>3.3×10⁻¹¹</td>
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<td>Bosnali and Perner (1971)²</td>
<td>(b)</td>
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<tr>
<td>2.9×10⁻¹⁰</td>
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<td>Butler et al. (1979)³</td>
<td>(c)</td>
</tr>
<tr>
<td>3.0×10⁻¹⁰</td>
<td>298</td>
<td>Butler et al. (1981)⁴</td>
<td>(d)</td>
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<tr>
<td>5.0×10⁻¹¹ exp(+200/T)</td>
<td>167-652</td>
<td>Berman and Lin (1983)⁵</td>
<td>(e)</td>
</tr>
<tr>
<td>5.4×10⁻¹¹</td>
<td>290</td>
<td>Anderson, Freedman, and Kolb (1987)⁶</td>
<td>(f)</td>
</tr>
</tbody>
</table>

Comments

(a) VUV flash photolysis of pure CH₄; [CH] by absorption measurement at 314.3 nm. Addition of a diluent gas (Ar) resulted in decreasing [CH] to a limiting value of 0.6 times [CH] (pure CH₄) at 10 Torr of Ar and a rate coefficient of 3.3×10⁻¹² cm³ molecule⁻¹ s⁻¹; this effect is also influenced by the flash intensity and probably due to quenching of an excited species otherwise leading to CH.

(b) Pulse radiolysis of 15 Torr CH₄; [OH] by absorption at 314.4 nm.

(c) Multiphoton dissociation of CHBr₃ at 193 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 30–100 Torr Ar.

(d) Multiphoton dissociation of CHBr₃ at 193 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 100 Torr Ar.

(e) Multiphoton dissociation of CHBr₃ at 266 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 100 Torr Ar. k(CH + C₃H₄) estimated, based on the observed linear dependence of k on the number of C–H bonds. k(CH + CH₄) pressure-independent between 25 Torr and 200 Torr. Formation of an excited insertion intermediate C₂HJ leading to C₂H₂ + H confirmed by transition-state and RRKM theory.

(f) Fast flow reactor. CH formation by sequential Br atom abstraction from CHBr₃ with excess alkali-metal atoms (Na or K); [CH] by laser induced fluorescence. Total pressure 2 Torr He/Ar mixture.

Preferred Values

\[ k = 5.0 \times 10^{-11} \exp(+200/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range 200–700 K} \]

Reliability

\[ \Delta \log k = \pm 1 \text{ over range 200–700 K} \]

Comments on Preferred Values

The available data shows considerable scatter. The preferred values are those of Berman et al.² but wide error limits are suggested.

References


CH + C₂H₂ → Products

Rate Coefficient Data

<table>
<thead>
<tr>
<th>k [cm³ molecule⁻¹ s⁻¹]</th>
<th>T[K]</th>
<th>Reference</th>
<th>Comments</th>
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</thead>
<tbody>
<tr>
<td>8.1×10⁻¹¹</td>
<td>298</td>
<td>Bosnali and Perner (1971)³</td>
<td>(a)</td>
</tr>
<tr>
<td>2.2×10⁻¹⁰</td>
<td>298</td>
<td>Butler et al. (1981)⁴</td>
<td>(b)</td>
</tr>
<tr>
<td>3.5×10⁻¹⁰ exp(+61/T)</td>
<td>171-657</td>
<td>Berman et al. (1982)⁶</td>
<td>(c)</td>
</tr>
</tbody>
</table>

Comments

(a) Pulse radiolysis of 15 Torr CH₄; [OH] by absorption at 314.4 nm.

(b) Multiphoton dissociation of CHBr₃ at 193 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 100 Torr Ar.

(c) Multiphoton dissociation of CHBr₃ at 266 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 100 Torr Ar. Discrepancies with Butler's results⁴ probably due to photolysis of reactants (C₂H₂, C₂H₄) at 193 nm. Suggest an addition mechanism of CH to the C–C double or triple bond leading to a three-membered ring followed by rapid ring opening.
EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

Preferred Values

\[ k = 3.5 \cdot 10^{-10} \exp(+61/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range 200-700 K} \]

Reliability

\[ \Delta \log k = \pm 0.7 \text{ over range 200-700 K} \]

Comments on Preferred Values

The most recent study is in reasonable agreement with the similar earlier study by Butler et al.\(^2\) and is adopted as our recommendation but with wide error limits.

CH + C\(_2\)H\(_4\) → Products

Rate Coefficient Data

<table>
<thead>
<tr>
<th>( k ) [cm(^3) molecule(^{-1}) s(^{-1})]</th>
<th>( T ) [K]</th>
<th>( \Delta \log k = \pm 0.7 \text{ over range 200-700 K} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate Coefficient Measurements</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.2 \cdot 10^{-10}</td>
<td>298</td>
<td>Bosnali and Perner (1971)(^1)</td>
</tr>
<tr>
<td>2.1 \cdot 10^{-10}</td>
<td>298</td>
<td>Butler et al. (1981)(^2)</td>
</tr>
<tr>
<td>2.2 \cdot 10^{-10} \exp(+173/T)</td>
<td>160-652</td>
<td>Berman et al. (1982)(^3)</td>
</tr>
</tbody>
</table>

Comments

(a) Pulse radiolysis of 15 Torr CH\(_4\); [OH] by absorption at 314.4 nm.
(b) Multiphoton dissociation of CHBr\(_3\) at 193 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 100 Torr Ar.
(c) Multiphoton dissociation of CHBr\(_3\) at 266 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 100 Torr Ar. Discrepancies with Butler’s results\(^4\) probably due to photolysis of reactants (C\(_2\)H\(_4\), C\(_2\)H\(_2\)) at 193 nm. Suggest an addition mechanism of CH to the C–C double or triple bond leading to a three-membered ring followed by rapid ring opening.

Preferred Values

\[ k = 2.2 \cdot 10^{-10} \exp(+173/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range 200-700 K} \]

References


**CH + C₂H₆ → Products**

**Rate Coefficient Data**

<table>
<thead>
<tr>
<th>$k$ [cm$^3$ molecule$^{-1}$ s$^{-1}$]</th>
<th>$T$ [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
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<tbody>
<tr>
<td><strong>Rate Coefficient Measurements</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.0·10$^{-10}$</td>
<td>298</td>
<td>Butler et al. (1981)$^1$</td>
<td>(a)</td>
</tr>
<tr>
<td>1.8·10$^{-10}$ exp(+132/T)</td>
<td>162–650</td>
<td>Berman and Lin (1983)$^2$</td>
<td>(b)</td>
</tr>
</tbody>
</table>

**Comments**

(a) Multiphoton dissociation of CHBr$_3$ at 193 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 100 Torr Ar.

(b) Multiphoton dissociation of CHBr$_3$ at 266 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 100 Torr Ar. $k$ (CH + C$_3$H$_6$) estimated, based on the observed linear dependence of $k$ on the number of C–H bonds.

**Preferred Values**

$k = 1.8·10^{-10}$ exp$(+132/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$ over range 200–700 K

**Reliability**

$\Delta \log k = \pm 0.7$ over range 200–700 K

**Comments on Preferred Values**

The available data are in reasonable agreement but until they are confirmed wide error limits are suggested.

**References**


---

**CH + C₃H₆ → Products**

**Rate Coefficient Data**

<table>
<thead>
<tr>
<th>$k$ [cm$^3$ molecule$^{-1}$ s$^{-1}$]</th>
<th>$T$ [K]</th>
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<td><strong>Rate Coefficient Measurements</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>1.4·10$^{-10}$</td>
<td>298</td>
<td>Bosnali and Perner (1971)$^1$</td>
<td>(a)</td>
</tr>
<tr>
<td>3.7·10$^{-10}$</td>
<td>298</td>
<td>Berman and Lin (1983)$^2$</td>
<td>(b)</td>
</tr>
<tr>
<td>1.9·10$^{-10}$ exp(+240/T)</td>
<td>298–689</td>
<td>Zabarnick, Fleming, and Lin (1987)$^3$</td>
<td>(c)</td>
</tr>
</tbody>
</table>

**Comments**

(a) Pulse radiolysis of 15 Torr CH$_4$ [OH] by absorption at 314.4 nm.

(b) Multiphoton dissociation of CHBr$_3$ at 266 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 100 Torr Ar. $k$ (CH + C$_3$H$_6$) estimated, based on the observed linear dependence of $k$ on the number of C–H bonds.

(c) Multiphoton dissociation of CHBr$_3$ at 266 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 20–300 Torr Ar. Rates independent of total pressure.

**Preferred Values**

$k = 1.9·10^{-10}$ exp$(+240/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$ over range 300–700 K

**Reliability**

$\Delta \log k = \pm 0.7$ over range 300–700 K

**Comments on Preferred Values**

The preferred values are based on the two most recent studies$^3$ which are in good agreement but wide error limits are suggested.

**References**

# EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

## CH + n-C4H10 → Products

### Rate Coefficient Data

<table>
<thead>
<tr>
<th>Rate Coefficient Measurements</th>
<th>T[K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.3 \times 10^{-10}$</td>
<td>298</td>
<td>Bosnali and Perner (1971)$^1$</td>
<td>(a)</td>
</tr>
<tr>
<td>$5.8 \times 10^{-10}$</td>
<td>298</td>
<td>Butler et al. (1981)$^2$</td>
<td>(b)</td>
</tr>
<tr>
<td>$4.4 \times 10^{-10} \exp(+28/T)$</td>
<td>257-653</td>
<td>Berman and Lin (1983)$^3$</td>
<td>(c)</td>
</tr>
</tbody>
</table>

### Comments

(a) Pulse radiolysis of 15 Torr CH$_4$ [OH] by absorption at 314.4 nm.

(b) Multiphoton dissociation of CHBr$_3$ at 193 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 100 Torr Ar.

(c) Multiphoton dissociation of CHBr$_3$ at 266 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 100 Torr Ar. $k$ (CH + C$_4$H$_6$) estimated, based on the observed linear dependence of $k$ on the number of C–H bonds.

### Preferred Values

$k = 4.4 \times 10^{-10} \exp(+28/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$ over range 250–700 K

## CH + i-C4H10 → Products

### Rate Coefficient Data

<table>
<thead>
<tr>
<th>Rate Coefficient Measurements</th>
<th>T[K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2.0 \times 10^{-10} \exp(+240/T)$</td>
<td>298-689</td>
<td>Zabarnick, Fleming, and Lin (1988) $^1$</td>
<td>(a)</td>
</tr>
</tbody>
</table>

### Comments

(a) Multiphoton dissociation of CHBr$_3$ at 266 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 20–300 Torr Ar. Rates independent of total pressure.

### Preferred Values

$k = 2.0 \times 10^{-10} \exp(+240/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$ over range 300–700 K

Reference

Rate Coefficient Measurements

\[ k = 1.6 \times 10^{-10} \exp\left(\frac{+340}{T}\right) \text{cm}^3\text{molecule}^{-1}\text{s}^{-1} \text{ over range } 300-700 \text{ K} \]

Comments

(a) Multiphoton dissociation of CHBr₃ at 266 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 20–300 Torr Ar. Rates independent of total pressure.

Preferred Values

\[ k = 1.6 \times 10^{-10} \exp\left(\frac{+340}{T}\right) \text{cm}^3\text{molecule}^{-1}\text{s}^{-1} \text{ over range } 300-700 \text{ K} \]

References


CH + neo-C₅H₁₂ → Products

Rate Coefficient Data

<table>
<thead>
<tr>
<th>( k [\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}] )</th>
<th>( T [\text{K}] )</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 4.6 \times 10^{-10} )</td>
<td>298</td>
<td>Butler et al. (1981)</td>
<td>(a)</td>
</tr>
</tbody>
</table>

Comments

(a) Multiphoton dissociation of CHBr₃ at 193 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 100 Torr Ar.

Preferred Values

No recommendation.
EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

CH + CH₂O → Products

Rate Coefficient Data

<table>
<thead>
<tr>
<th>$k$ [cm³ molecule⁻¹ s⁻¹]</th>
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<th>Comments</th>
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<tr>
<td>Rate Coefficient Measurements</td>
<td>2.0-10⁻¹² $exp(+260/T)$</td>
<td>297-670</td>
<td>Zabarnick, Fleming, and Lin (1988)¹</td>
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</table>

Comments

(a) Multiphoton dissociation of CHBr₃ at 266 nm; [CH] by laser induced fluorescence at 429.8 nm. Total pressure 20-300 Torr Ar. Rates independent of total pressure.

Preferred Values

$k = 1.6·10^{-10} \ exp(+260/T)$ cm³ molecule⁻¹ s⁻¹ over range 300-700 K

Reliability

$\Delta \log k = \pm 1$ over range 300-700 K

Comments on Preferred Values

The only available experimental measurement is adopted but with wide error limits.

$\Delta H_{298}^\circ (1) = -241$ kJ mol⁻¹

$\Delta S_{298}^\circ (1) = 95.2$ J K⁻¹ mol⁻¹

$K_p(1) = 1.15·10^{-7} T^{0.74} exp(+29000/T)$ atm

$\Delta H_{298}^\circ (3) = -739$ kJ mol⁻¹

$\Delta S_{298}^\circ (3) = -14.3$ J K⁻¹ mol⁻¹

$K_p(3) = 4.14 T^{-0.46} exp(+88800/T)$ atm

$\Delta H_{298}^\circ (5) = -345$ kJ mol⁻¹

$\Delta S_{298}^\circ (5) = 42.4$ J K⁻¹ mol⁻¹

$K_p(5) = 4.87·10^{-4} T^{-0.92} exp(+42000/T)$ atm

$\Delta H_{298}^\circ (2) = -781$ kJ mol⁻¹

$\Delta S_{298}^\circ (2) = -56.2$ J K⁻¹ mol⁻¹

$K_p(2) = 1.55·10^{-5} T^{0.67} exp(+94100/T)$

$\Delta H_{298}^\circ (4) = -254$ kJ mol⁻¹

$\Delta S_{298}^\circ (4) = -21.0$ J K⁻¹ mol⁻¹

$K_p(4) = 4.66·10^{-3} T^{0.14} exp(+30800/T)$

Rate Coefficient Data ($k = k_1 + k_2 + k_3 + k_4 + k_5$)

<table>
<thead>
<tr>
<th>$k$ [cm³ molecule⁻¹ s⁻¹]</th>
<th>$T$ [K]</th>
<th>Reference</th>
<th>Comments</th>
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<tr>
<td>Rate Coefficient Measurements</td>
<td>1.5·10⁻¹²</td>
<td>298</td>
<td>Laufer and Bass (1974)¹</td>
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<tr>
<td>1.2·10⁻¹²</td>
<td>298</td>
<td>Pilling and Robertson (1977)²</td>
<td>(a)</td>
</tr>
<tr>
<td>1.7·10⁻¹²</td>
<td>298</td>
<td>Vinckier and DeBruyn (1978)³</td>
<td>(b)</td>
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<tr>
<td>2.2·10⁻¹¹ $exp(-750/T)$</td>
<td>290-600</td>
<td>Vinckier and DeBruyn (1979)⁴</td>
<td>(b)</td>
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<td>$k_5 = 6.7·10^{-11} \ exp(-1100/T)$</td>
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<td>Warnatz (1981)⁵</td>
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<tr>
<td>3.3·10⁻¹²</td>
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<td>Böhland et al. (1984)⁶</td>
<td>(d)</td>
</tr>
</tbody>
</table>

Reviews and Evaluations

1.4·10⁻¹² | 298 | Tsang and Hampson (1986)⁷ | (e) |

Comments

(a) Flash photolysis of ketene in helium and argon. Products analysed by GC and simulated by numerical integration. Rate coefficient determined primarily relative to that for \(3\text{CH}_2 + 3\text{CH}_2\) which was taken as \(5.3 \times 10^{-11}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\).

(b) Discharge flow study of O + C\(_2\)H\(_2\) with molecular beam sampling and mass spectrometric analysis. Rate coefficient obtained from the effect of [O\(_2\)] on the steady-state [C\(_2\)H\(_2\)] signal.

(c) Modelling acetylene/O\(_2\) laminar flames. Channel and rate coefficient correctly predict the mole fractions and temperature profiles in lean flames.

(d) Discharge flow with LMR detection of \(3\text{CH}_2\); the methylene was generated either from discharging ketene or from O + CH\(_2\)CO.

(e) Based on an earlier evaluation by Laufer\(^4\) which relied on the data from Refs. 1 and 2.

Preferred Values

\[
k = 4.1 \times 10^{-11} \exp(-750/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range } 300-1000 \text{ K}
\]

Reliability

\[
\Delta \log k = \pm 0.5 \text{ at } 1000 \text{ K reducing to } \pm 0.3 \text{ at } 300 \text{ K}
\]

Thermodynamic Data

\[
\begin{align*}
\Delta H_{298}^\circ (1) &= -547.2 \text{ kJ mol}^{-1} \\
\Delta S_{298}^\circ (1) &= -59.5 \text{ J K}^{-1}\text{mol}^{-1} \\
K_p(1) &= 1.66 \times 10^{-7} T^{1.16} \exp(+66240/T)
\end{align*}
\]

\[
\begin{align*}
\Delta H_{298}^\circ (3) &= -269.7 \text{ kJ mol}^{-1} \\
\Delta S_{298}^\circ (3) &= -44.8 \text{ J K}^{-1}\text{mol}^{-1} \\
K_p(3) &= 2.15 \times 10^{-10} T^{1.10} \exp(+33010/T)
\end{align*}
\]

Rate Coefficient Data

<table>
<thead>
<tr>
<th>(k) [cm(^3) molecule(^{-1}) s(^{-1})]</th>
<th>(T) [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.3 \times 10^{-11}</td>
<td>298</td>
<td>Braun et al. (1970)(^1)</td>
<td>(a)</td>
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<tr>
<td>(k_3/k \gg 0.9)</td>
<td>298</td>
<td>Becerra et al. (1987)(^2)</td>
<td>(b)</td>
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<tr>
<td>(k_3 = 1.7 \times 10^{-10})</td>
<td>2000-2800</td>
<td>Frank, Bhaskaran, and Just (1987)(^3)</td>
<td>(c)</td>
</tr>
<tr>
<td>5.3 \times 10^{-11}</td>
<td>298</td>
<td>Laufer (1981)(^4)</td>
<td>(d)</td>
</tr>
</tbody>
</table>

References

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

(a) VUV flash photolysis of ketene, time-dependence of \(^3\)CH\(_2\) and of \(\text{C}_2\text{H}_2\) monitored by absorption spectroscopy.

(b) Reanalysis of earlier work based on excimer laser flash photolysis of ketene (308 nm). Source of molecular hydrogen now identified as \(^3\)CH\(_2\) + H, leaving atomic products as the more likely for \(^3\)CH\(_2\) + \(^3\)CH\(_3\). Their analysis allowed up to 10% of the reaction to occur via channel (1).

(c) Absorption spectroscopy study of H and CO in thermal decomposition of dilute ketene mixtures in argon behind reflected shock waves.

(d) Evaluation based on Ref. 1.

Preferred Values

\[ k = 2.0 \times 10^{-10} \exp(-400/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range 300–3000 K} \]

\[ k_{ij} / k = 0.9 \text{ over range 300–3000 K} \]

\[^3\text{CH}_2 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_4 + \text{H} \]

Thermodynamic Data

\[ \Delta H^\circ_{298} = -262 \text{ kJ mol}^{-1} \]

\[ \Delta S^\circ_{298} = -55.7 \text{ J K}^{-1} \text{mol}^{-1} \]

\[ K_p = 2.36 \times 10^{-7} T^{1.0} \exp(32200/T) \]

Rate Coefficient Data

<table>
<thead>
<tr>
<th>(k) [cm(^3) molecule(^{-1}) s(^{-1})]</th>
<th>(T) [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
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<tr>
<td>(5 \times 10^{-11})</td>
<td>298</td>
<td>Pilling and Robertson (1975)(^1)</td>
<td>(a)</td>
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<tr>
<td>(1 \times 10^{-10})</td>
<td>298</td>
<td>Laufner and Bass (1975)(^2)</td>
<td>(b)</td>
</tr>
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<td>(3 \times 10^{-11})</td>
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<td>Olson and Gardner (1978)(^3)</td>
<td>(c)</td>
</tr>
<tr>
<td>(3 \times 10^{-11})</td>
<td>1700–2200</td>
<td>Bhaskaran, Frank, and Just (1979)(^4)</td>
<td>(d)</td>
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<td>(7 \times 10^{-11})</td>
<td>1320–2300</td>
<td>Frank and Braun-Unkhoff (1987)(^5)</td>
<td>(e)</td>
</tr>
<tr>
<td>(7 \times 10^{-11})</td>
<td>298</td>
<td>Laufner (1981)(^6)</td>
<td>(f)</td>
</tr>
<tr>
<td>(7 \times 10^{-11})</td>
<td>300–2500</td>
<td>Warnatz (1984)(^7)</td>
<td>(g)</td>
</tr>
</tbody>
</table>

Comments

(a) Flash photolysis of mixtures of ketene and azomethane, end product analysis by GC. Products simulated by numerical integration. Rate coefficient sensitive to value chosen for CH\(_3\) + CH\(_3\) (4.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}).

(b) Flash photolysis of mixtures of ketene and azomethane, end product analysis by GC. Products simulated by numerical integration. Rate coefficient sensitive to value chosen for CH\(_3\) + CH\(_3\) (9.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}).

(c) IR absorption study of fuel rich CH\(_4\)/O\(_2\)/Ar mixtures behind incident shock waves. Product yields by numerical integration.

(d) Atomic resonance absorption study of H in reflected shock waves.

(e) Atomic resonance absorption study of H in reflected shock waves using a range of CH\(_3\) precursors (CH\(_3\)N\(_2\), CH\(_3\)S, C\(_2\)H\(_6\)) to obtain data over a wide range of temperatures.

(f) Evaluation based on a reanalysis of Refs. 1 and 2.

(g) Evaluation based on both low and high temperature data (Refs. 1–4).

Preferred Values

\[ k = 7.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range 300–3000 K} \]

References


Reliability
\[ \Delta \log k = \pm 0.3 \text{ at } 300 \text{ K rising to } \pm 0.5 \text{ at } 3000 \text{ K} \]

Comments on Preferred Values
The rate data of Refs. 1 and 2 need correction for the methyl recombination rate coefficients used in the simulations. Taking \( k(CH_3 + CH_3) = 6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) (Ref. 8) at 298 K at the pressures employed, increases the rate coefficient in Ref. 1 to \( 6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) and decreases that in Ref. 2 to \( 8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \).

The reaction presumably proceeds via an ethyl radical adduct. A significant temperature dependence is not, therefore, expected and is confirmed by the results of Refs. 3-5.

\[ 3\text{CH}_2 + \text{C}_2\text{H}_2 \rightarrow \text{CH}_2\text{CCH}_2 \quad (1) \]
\[ \rightarrow \text{CH}_3\text{CCH} \quad (2) \]

Thermodynamic Data
\[ \Delta H_{298} (1) = -424 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298} (1) = -1.27 \times 10^{-2} \text{ J K}^{-1} \text{ mol}^{-1} \]
\[ K_p(1) = 9.37 \times 10^{-11} \exp(-51500/T) \text{ atm}^{-1} \]
\[ \Delta H_{298} (2) = -430 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298} (2) = -189 \text{ J K}^{-1} \text{ mol}^{-1} \]
\[ K_p(2) = 1.27 \times 10^{-11} \exp(-52080/T) \text{ atm}^{-1} \]

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

<table>
<thead>
<tr>
<th>( k [\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}] )</th>
<th>( T ) [K]</th>
<th>Reference</th>
<th>Comments</th>
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</thead>
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<tr>
<td>( 7.5 \times 10^{-12} )</td>
<td>298</td>
<td>Laufer and Bass (1974)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>( 4.9 \times 10^{-12} )</td>
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<td>Pilling and Robertson (1977)(^2)</td>
<td>(a)</td>
</tr>
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<td>( 1.3 \times 10^{-12} )</td>
<td>295</td>
<td>Vinckier and Debruyne (1979)(^3)</td>
<td>(b)</td>
</tr>
<tr>
<td>( 3.1 \times 10^{-12} )</td>
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<td>Homann and Schweinfurth (1981)(^4)</td>
<td>(c)</td>
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<tr>
<td>(&lt;10^{-15})</td>
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<td>Canosa-Mas, Frey, and Walsh (1984)(^5)</td>
<td>(d)</td>
</tr>
<tr>
<td>(&lt;2.6 \times 10^{-15})</td>
<td>298</td>
<td>Canosa-Mas, Frey, and Walsh (1985)(^6)</td>
<td>(d)</td>
</tr>
<tr>
<td>( 2.0 \times 10^{-11} \exp(-3330/T))</td>
<td>296-700</td>
<td>Böhlund, Temps, and Wagner (1986)(^7)</td>
<td>(e)</td>
</tr>
</tbody>
</table>

Comments
(a) Flash photolysis of ketene, end product analysis by GC. Rate related to production of allene and propyne in presence of inert gas.
(b) Fast flow reactor study of O + C\(_2\)H\(_2\). Products and intermediates detected by molecular beam sampling and mass spectrometry. Reaction attributed to production of C\(_3\)H\(_2\) + H.
(c) Discharge flow study of O + C\(_2\)H\(_2\), C\(_2\)H\(_4\) detected by mass spectrometry. Reaction attributed to formation of C\(_3\)H\(_2\) + H and C\(_3\)H\(_2\) + H\(_2\). Pressure = 1-6 Torr.
(d) Laser flash photolysis of ketene (308 nm) in presence of Ar and C\(_2\)H\(_2\). Products detected by GC. High rate coefficients in Refs. 1 and 2 attributed to failure to account properly for reactions of \(^1\)CH\(_2\). Suggest rate is probably less than \( 2.6 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \).
(e) Flow tube study, \(^3\)CH\(_2\) generated from discharge or laser flash photolysis of CH\(_2\)CO (308 nm). \(^1\)CH\(_2\) detected by LMR.

Preferred Values
\[ k = 2.0 \times 10^{-11} \exp(-3330/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range 300-1000 K} \]

Reliability
\[ \Delta \log k = \pm 0.3 \]

Comments on Preferred Values
The recent careful work of Canosa-Mas \textit{et al.}\(^5\) has revealed the deficiencies in the mechanistic interpretations of Refs. 1-4. Canosa-Mas \textit{et al.} employed a full reaction scheme using predominantly available literature data. The observed yields of C\(_3\)H\(_4\) were fully explained by the reactions of \(^3\)CH\(_2\) with C\(_2\)H\(_2\). Their conclusions have recently been fully endorsed by the direct measurements of Böhlund \textit{et al.}\(^7\).
EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

References


\[
\begin{align*}
\text{CH}_2 + \text{C}_2\text{H}_4 & \rightarrow \text{C}_3\text{H}_6 & (1)
\rightarrow \text{c-C}_3\text{H}_6 & (2)
\rightarrow \text{C}_3\text{H}_6 + \text{H} & (3)
\end{align*}
\]

Thermodynamic Data

\[
\begin{align*}
\Delta H^\circ_m (1) & = -419 \text{ kJ mol}^{-1} \\
\Delta S^\circ_m (1) & = -157 \text{ J K}^{-1} \text{mol}^{-1} \\
K_r(1) & = 5.68 \times 10^{-11} \text{T}^{0.562} \exp(50900/T) \text{atm}^{-1}
\end{align*}
\]

\[
\begin{align*}
\Delta H^\circ_m (3) & = -87.3 \text{ kJ mol}^{-1} \\
\Delta S^\circ_m (3) & = -42.9 \text{ J K}^{-1} \text{mol}^{-1} \\
K_r(3) & = 3.03 \times 10^{-9} \text{T}^{20} \exp(11300/T)
\end{align*}
\]

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

<table>
<thead>
<tr>
<th>(k[\text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1}])</th>
<th>(T [\text{K}])</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\leq 3 \times 10^{-14})</td>
<td>298</td>
<td>Laufer and Bass (1975)</td>
<td>(a)</td>
</tr>
<tr>
<td>(&lt; 5 \times 10^{-16})</td>
<td>298</td>
<td>Canosa-Mas, Frey, and Walsh (1985)</td>
<td>(b)</td>
</tr>
<tr>
<td>(5.3 \times 10^{-12} \exp(-2660/T))</td>
<td>206-728</td>
<td>Bohland, Temps, and Wagner (1986)</td>
<td>(c)</td>
</tr>
</tbody>
</table>

Comments

(a) Flash photolysis of ketene + \text{C}_2\text{H}_4 + 700 \text{ Torr He}. End product analysis by GC. Rate measured relative to \text{C}_2\text{H}_2 + \text{C}_2\text{H}_4.
(b) Excimer laser flash photolysis (308 nm) of ketene + \text{C}_2\text{H}_4 + 400 \text{ Torr Ar}. End product analysis by GC. Product yields simulated by numerical integration.
(c) Discharge flow, \text{CH}_2 monitored by LMR and generated from O + \text{CH}_2\text{CO} and by laser flash photolysis (308 nm) of \text{CH}_2\text{CO}. Correction made for reaction proceeding via activation to singlet.

Comments on Preferred Values

The rate coefficients were measured over the pressure range 0.4–5.7 Torr and were found to be independent of pressure. RRKM calculations demonstrate that the most likely fate of the energised triplet adduct, under these conditions, is decomposition to generate H + \text{C}_3\text{H}_5. At higher pressures propene is formed and cyclopropane is the major product in the high pressure limit. Propene is the major product for reaction in excess \text{C}_2\text{H}_4 in the range 10–175 Torr and cyclopropane predominates at higher pressures, although the yields of propene and cyclopropane will decrease with increasing temperature.

Preferred Values

\(k = 5.3 \times 10^{-12} \exp(-2660/T) \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}\) over range 300–1000 K

Reliability

\(\Delta \log k = \pm 0.3\) at 1000 K reducing to \(\pm 0.2\) at 300–700 K

References

Thermodynamic Data

\[
\Delta H_{298}^\circ = -37.7 \text{ kJ mol}^{-1} \text{ (see comment (a))}
\]

\[
\Delta S_{298}^\circ = 6.8 \text{ J K}^{-1} \text{ mol}^{-1}
\]

\[
K_p = 2.17 \times 10^{0.016} \exp(4520/T)
\]

Rate Coefficient Data (Preferred Values)

<table>
<thead>
<tr>
<th>[M]</th>
<th>(k) [cm(^3) molecule(^{-1}) s(^{-1})]</th>
<th>(T) [K]</th>
<th>Comments</th>
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</thead>
<tbody>
<tr>
<td>Ar</td>
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<td>(b), (c)</td>
</tr>
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<td>N(_2)</td>
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<td>CH(_4)</td>
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<td>(b), (c), (d)</td>
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<td>C(_2)H(_2)</td>
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<td>C(_2)H(_4)</td>
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<td>(e), (d)</td>
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<tr>
<td>C(_2)H(_6)</td>
<td>(3.6 \times 10^{-11})</td>
<td>298</td>
<td>(e), (d)</td>
</tr>
</tbody>
</table>

Comments

(a) Based on an analysis of spectroscopic data from a variety of sources [including LMR and diode laser spectroscopy of CH\(_2(X^3\Sigma \_1^+)\)], and photoelectron spectroscopy of CH\(_2(X^3\Sigma \_1^+)\). The value for \(\Delta H_{298}^\circ\) is calculated from the quoted value for \(\Delta H_{298}^\circ\) given in Ref. 1, using recent spectroscopic and theoretical data to calculate \(\Delta C_p(T)\).

(b) Room temperature laser pump and probe experiments, using IRMPD of acetic anhydride to generate \(^1\)CH\(_2\) and LIF to detect it. Total removal rate (reaction + deactivation) measured.

(c) Room temperature excimer laser flash photolysis of ketene (308 nm) and time-resolved cw dye laser absorption spectroscopy of \(^1\)CH\(_2\). Total removal rate (reaction + deactivation) measured.

(d) Room temperature LMR measurements of the fractional yield of \(^3\)CH\(_2\) following photolysis of ketene at 308 nm. The quantum yield, \(\phi\), for the production of \(^3\)CH\(_2\) in the photolysis was assumed zero. The absolute deactivation rate coefficients were calculated from the fractional yield and the rate coefficients for total removal from refs. 2 and 3. Since \(\phi\) was assumed zero, these rate coefficients represent upper limits.

(e) Room temperature laser flash photolysis of ketene at 308 nm. \(^1\)CH\(_2\) detected by LIF. Production of \(^3\)CH\(_2\) detected by LMR.

Reliability

\(\Delta \log k = \pm 0.3\) for Ar and N\(_2\) over range 300–2000 K

\(\Delta \log k = \pm 0.4\) for hydrocarbons over range 300–2000 K

Comments on Preferred Values

There is excellent agreement between the overall removal rate coefficients reported in Refs. 2 and 3. For Ar and N\(_2\) at room temperatures, these represent exclusively the deactivation channel, although reactive channels probably become available for N\(_2\) at higher temperatures and association at higher pressures. The deactivation channel efficiencies, required to determine \(k\) for the hydrocarbons, are less precisely known. The rate coefficients may be assumed temperature independent, although a slight decrease with increasing temperatures may occur.

References

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ ^1\text{CH}_2 + \text{O}_2 \rightarrow \text{H} + \text{CO} + \text{OH} \quad (1) \]
\[ \rightarrow \text{H}_2 + \text{CO}_2 \quad (2) \]
\[ \rightarrow \text{CO} + \text{H}_2\text{O} \quad (3) \]
\[ \rightarrow ^3\text{CH}_2 + \text{O}_2 \quad (4) \]

### Thermodynamic Data

\[ \Delta H_{298}^\circ (1) = -278 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298}^\circ (1) = 102 \text{ JK}^{-1}\text{mol}^{-1} \]
\[ K_p(1) = 2.49 \times 10^3 \ T^{0.707} \exp( +33500/T) \text{ atm} \]
\[ \Delta H_{298}^\circ (2) = -818 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298}^\circ (2) = -49.4 \text{ JK}^{-1}\text{mol}^{-1} \]
\[ K_p(2) = 3.37 \times 10^{-3} \ T^{0.803} \exp( +98600/T) \]
\[ \Delta H_{298}^\circ (3) = -777 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298}^\circ (3) = -7.49 \text{ JK}^{-1}\text{mol}^{-1} \]
\[ K_p(3) = 8.96 \times 10^{-6} \ T^{-0.44} \exp( +93300/T) \]
\[ \Delta H_{298}^\circ (4) = -37.7 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298}^\circ (4) = 6.8 \text{ JK}^{-1}\text{mol}^{-1} \]
\[ K_p(4) = 2.17 \ T^{0.536} \exp( +4520/T) \]

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

<table>
<thead>
<tr>
<th>(k ) [cm(^3) molecule(^{-1}) s(^{-1})]</th>
<th>(T ) [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
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<tr>
<td>3.0 \times 10^{-11}</td>
<td>298</td>
<td>Ashfold et al. (1981) (^1)</td>
<td>(a)</td>
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<td>7.4 \times 10^{-11}</td>
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<td>Langford, Petek, and Moore (1983) (^2)</td>
<td>(b)</td>
</tr>
<tr>
<td>(&lt; 3.0 \times 10^{-10})</td>
<td>298</td>
<td>Laufer (1981) (^3)</td>
<td>(c)</td>
</tr>
<tr>
<td>5.2 \times 10^{-11}</td>
<td>298</td>
<td>Tsang and Hampson (1986) (^4)</td>
<td>(d)</td>
</tr>
</tbody>
</table>

**Comments**

(a) Pump and probe experiments, with \(^1\text{CH}_2\) produced by IRMPD of acetic anhydride and detected by LIF. Measured total rate of removal of \(^1\text{CH}_2\).

(b) Excimer laser flash photolysis of ketene at 308 nm and time-resolved dye laser absorption spectroscopy of \(^1\text{CH}_2\). Measured total rate of removal of \(^1\text{CH}_2\).

(c) Based on flash photolysis - gas chromatography study of ketene\(^5\). Rate coefficient determined relative to a value of 3.4\times10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} for deactivation of \(^1\text{CH}_2\) by He. More recent measurements give the latter as 3.3\times10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, requiring a tenfold increase in the upper estimate for \(^1\text{CH}_2 + \text{O}_2\) to \(< 3\times10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\).

(d) Based on Refs. 1 and 2.

**Preferred Values**

\[ k = 5.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range 300-1000 K} \]

**Reliability**

\[ \Delta \log k = \pm 0.5 \text{ at 1000 K reducing to } \pm 0.3 \text{ at 300 K} \]

**Comments on Preferred Values**

The agreement between the measured values of rate coefficients in Refs. 1 and 2 was significantly worse for this reaction than for any others. It was suggested that there may be a precursor dependence, which might be connected with a vibrational energy dependence of the reaction and incomplete vibrational relaxation before reaction. The rate coefficient refers to total removal, but Ashfold et al.\(^1\) argue that \(k\) is three times greater than the value expected for deactivation and that a chemical mechanism predominates. In \(^1\text{CH}_2\text{CO}\) tracer studies, Rowland et al.\(^6\) found similar relative product yields for both \(^1\text{CH}_2\) and \(^3\text{CH}_2\) + \text{O}_2. They suggested that this might indicate that the main mechanism of reaction of \(^1\text{CH}_2\) with \text{O}_2 is deactivation to \(^3\text{CH}_3\), in contrast with the conclusions of Ashfold et al.\(^1\).

**References**

Thermodynamic Data

\[ \Delta H_{298} = -61.0 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298} = -10.7 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_p = 4.22 \times 10^{-1} T^{0.51} \exp(+7640/T) \]

Rate Coefficient Data

<table>
<thead>
<tr>
<th>( k [\text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1}] )</th>
<th>( T [\text{K}] )</th>
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<th>Comments</th>
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<td>Ashfold et al. (1981)</td>
<td>(a)</td>
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<td>1.05 \times 10^{-10}</td>
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<td>Langford, Petek, and Moore (1983)</td>
<td>(b)</td>
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<td>1.2 \times 10^{-10}</td>
<td>298</td>
<td>Tsang and Hampson (1986)</td>
<td>(c)</td>
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</tbody>
</table>

Comments

(a) Pump and probe experiments, with \(^1\text{CH}_2\) produced by IRMPD of acetic anhydride and detected by LIF. Measure total rate of removal of \(^1\text{CH}_2\).
(b) Excimer laser flash photolysis of ketene at 308 nm and time-resolved dye laser absorption spectroscopy of \(^1\text{CH}_2\). Measure total rate of removal of \(^1\text{CH}_2\).
(c) Based on Refs. 1 and 2.

Preferred Values

\[ k = 1.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \] over range 300–1000 K

Reliability

\[ \Delta \log k = \pm 0.3 \text{ at } 1000 \text{ K reducing to } \pm 0.1 \text{ at } 300 \text{ K} \]

Comments on Preferred Values

Both measurements refer to the total rate of removal of \(^1\text{CH}_2\) and could include a contribution from the deactivation to \(^2\text{CH}_2\). Ashfold et al. argue against such a contribution from a comparison of the magnitude of the rate coefficient with those for deactivation of \(^1\text{CH}_2\) to \(^3\text{CH}_2\) by inert gases. In addition, Braun et al. detected the \(\text{CH}_3\) product and demonstrated that more than 80% of the overall \(^1\text{CH}_2\) removal led to methyl radical production.

References


\(^1\text{CH}_2 + \text{C}_2\text{H}_2 \rightarrow \text{CH}_2\text{CCH}_2 \quad (1)\]
\[ \rightarrow \text{CH}_2\text{CCH} \quad (2) \]
\[ \rightarrow \text{C}_2\text{H}_3 + \text{H} \quad (3) \]
\[ \rightarrow \text{C}_2\text{H}_2 + \text{C}_2\text{H}_2 \quad (4) \]

Thermodynamic Data

\[ \Delta H_{298} (1) = -462 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298} (1) = -160 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_p (1) = 2.03 \times 10^{-10} T^{0.51} \exp(+56020/T) \text{ atm}^{-1} \]
\[ \Delta H_{298} (3) = -113 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298} (3) = -24.4 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_p (3) = 4.76 \times 10^{-3} T^{0.18} \exp(+14020/T) \]

\[ \Delta H_{298} (2) = -467 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298} (2) = -183 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_p (2) = 2.75 \times 10^{-11} T^{0.21} \exp(+56600/T) \text{ atm}^{-1} \]
\[ \Delta H_{298} (4) = -37.7 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298} (4) = 6.8 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_p (4) = 2.17 T^{0.06} \exp(+4520/T) \text{ atm}^{-1} \]

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

<table>
<thead>
<tr>
<th>( k [\text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1}] )</th>
<th>( T [\text{K}] )</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1 \times 10^{-10}</td>
<td>295</td>
<td>Canosa-Mas, Frey, and Walsh (1983)</td>
<td>(a)</td>
</tr>
<tr>
<td>3.7 \times 10^{-10}</td>
<td>298</td>
<td>Hack et al. (1988)</td>
<td>(b)</td>
</tr>
</tbody>
</table>
(a) Excimer laser flash photolysis of ketene (308 nm) in the presence of Ar and C₂H₂. Products detected by GC. Pressure = 400 Torr. Product distribution simulated by numerical integration. Partial decomposition of the adduct occurred at the pressure employed. An RRKM calculation gives a decomposition rate for C₃H₆ of 4.5·10⁹ s⁻¹, and an effective stabilization rate constant in argon of 2.1·10⁻¹¹ cm³ molecule⁻¹ s⁻¹. The complexity of the system suggests a greater uncertainty than the ± 25% proposed by the authors. The relative rates of reactions (1) and (2) are given as 1:1.6.

(b) Laser flash photolysis of ketene (308 nm), C₁H₂ detected by LIF. Production of C₂H₂ (channel (4)) detected by LMR.

Preferred Values

\[ k = 3.7·10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range 300-1000 K} \]

\[ k_d/k = 0.22 \]

\[ 1\text{CH}_2 + C_2H_4 \rightarrow C_3H_6 \quad (1) \]

\[ \rightarrow C_2H_2 + C_2H_4 \quad (2) \]

Thermodynamic Data

\[ \Delta H_{298} (1) = -457 \text{ kJ mol}^{-1} \]

\[ \Delta S_{298} (1) = -150 \text{ J K}^{-1} \text{ mol}^{-1} \]

\[ K_p (1) = 25.7 T^{0.78} \exp(55400/T) \text{ atm}^{-1} \]

\[ \Delta H_{298} (2) = -37.7 \text{ kJ mol}^{-1} \]

\[ \Delta S_{298} (2) = 6.8 \text{ J K}^{-1} \text{ mol}^{-1} \]

\[ K_p (2) = 2.17 T^{0.104} \exp(4520/T) \]

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

<table>
<thead>
<tr>
<th>Rate Coefficient Measurements</th>
<th>T [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5·10⁻¹⁰</td>
<td>295</td>
<td>Langford, Petek, and Moore (1983)¹</td>
<td>(a)</td>
</tr>
<tr>
<td>2.1·10⁻¹⁰</td>
<td>295</td>
<td>Canosa-Mas, Frey, and Walsh (1985)²</td>
<td>(b)</td>
</tr>
<tr>
<td>0.15</td>
<td>295</td>
<td>Bohland, Temps, and Wagner (1985)²</td>
<td>(c)</td>
</tr>
</tbody>
</table>

Comments

(a) Excimer laser flash photolysis of ketene (308 nm) followed by time-resolved detection of \(^1\text{CH}_2\) by cw dye laser absorption.

(b) Excimer laser flash photolysis of ketene (308 nm) in the presence of Ar and C₂H₂. Products detected by GC. Pressure approximately 400 Torr. Product distribution simulated by numerical integration. Assumed same rate coefficient for \(^1\text{CH}_2 + C_2H_4\) and \(^1\text{CH}_2 + C_2H_4\). 

(c) Excimer laser flash photolysis of ketene (308 nm), LMR detection of \(^1\text{CH}_2\). Assumed triplet quantum yield at 308 nm = 0.0. The \(k_d/k_i\) value represents an upper limit.

Reliability

\[ \Delta \log k = \pm 0.7 \text{ at 1000 K reducing to } \pm 0.3 \text{ at 300 K} \]

\[ \Delta k_d/k = \pm 0.1 \]

Comments on Preferred Values

(a) Excimer laser flash photolysis of ketene (308 nm) in the presence of Ar and C₂H₂. Products detected by GC. Pressure = 400 Torr. Product distribution simulated by numerical integration. Assumed same rate coefficient for \(^1\text{CH}_2 + C_2H_4\) and \(^1\text{CH}_2 + C_2H_4\). Assumed triplet quantum yield at 308 nm = 0.0. The \(k_d/k_i\) value represents an upper limit.

References

icant yields of cyclopropane and, especially at higher temperatures, the product can be taken as propene. A general discussion of $^1$CH$_2$ $\rightarrow$ $^3$CH$_2$ deactivation may be found on p644. $k_1$ may decrease slightly with temperature.

**References**


**CH$_3$ + M $\rightarrow$ CH$_2$ + H + M**

**Thermodynamic Data**

$\Delta H_{298}^\circ = 459$ kJ mol$^{-1}$

$\Delta S_{298}^\circ = 116$ J K$^{-1}$mol$^{-1}$

$k_p = 1.61 \times 10^{7}$ T$^{-0.721}$ $\times$ exp$(-55200/T)$ atm

**Rate Coefficient Data**

<table>
<thead>
<tr>
<th>$k$ [cm$^3$ molecule$^{-1}$ s$^{-1}$]</th>
<th>$T$ [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.0 \times 10^{-4}$ exp$(-44900/T)$</td>
<td>1700-2300</td>
<td>Bhaskaran, Frank, and Just (1979)$^1$</td>
<td>(a)</td>
</tr>
<tr>
<td>$3.23 \times 10^{-4}$ exp$(-46100/T)$</td>
<td>2150-2850</td>
<td>Roth, Barner, and Löh (1979)$^2$</td>
<td>(b)</td>
</tr>
<tr>
<td>$1.7 \times 10^{-5}$ exp$(-45600/T)$</td>
<td>1500-3000</td>
<td>Warnatz (1984)$^3$</td>
<td>(c)</td>
</tr>
</tbody>
</table>

**Comments**

(a) Shock-tube decomposition of C$_2$H$_6$/O$_2$ mixtures with direct detection of H and O by atomic resonance absorption spectrometry.
(b) Shock-tube study of the decomposition of C$_2$H$_6$ in Ar with direct measurement of time dependent [H].
(c) Based on data of Bhaskaran et al.$^1$ and Roth et al.$^2$.

**Preferred Values**

$k = 1.7 \times 10^{-8}$ exp$(-45600/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$ over range 1500-3000 K

**Reliability**

$\Delta \log k = \pm 0.5$ over range 1500-3000 K

**Comments on Preferred Values**

We have adopted the recommendation of Warnatz$^3$ which is based on the experimental data of Bhaskaran et al.$^1$ and of Roth et al.$^2$.

**References**

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ \text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{O} + \text{O} \quad (1) \]
\[ \rightarrow \text{CH}_2\text{O} + \text{OH} \quad (2) \]

**Thermodynamic Data**

\[ \Delta H_{298}^{(1)} = -120 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298}^{(1)} = -96.6 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ k_p(1) = 1.13 \times 10^{-2} \ T^{0.44} \text{ exp}(-14100/T) \]
\[ \Delta H_{298}^{(2)} = -223 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298}^{(2)} = 3.1 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ k_p(2) = 4.32 \ T^{6.17} \text{ exp}(26800/T) \]

**Rate Coefficient Data**

<table>
<thead>
<tr>
<th>Rate Coefficient Measurements</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k ) [{cm}^3 molecule^{-1} s^{-1}]</td>
<td>( T ) [K]</td>
<td></td>
</tr>
<tr>
<td>( &lt; 5 \times 10^{-17} )</td>
<td>1000-1220</td>
<td>Baldwin and Golden (1978)</td>
</tr>
<tr>
<td>( k_1 = 1.2 \times 10^{-11} \text{ exp}(-12900/T) )</td>
<td>1700-2300</td>
<td>Bhaskaran, Frank, (b)</td>
</tr>
<tr>
<td>( k_2 = 8.6 \times 10^{-11} \text{ exp}(-17400/T) )</td>
<td>1700-2300</td>
<td>and Just (1979)</td>
</tr>
<tr>
<td>( k_3 = 1.07 \times 10^{-10} \text{ exp}(-15500/T) )</td>
<td>1150-1560</td>
<td>Hsu et al. (1983)</td>
</tr>
<tr>
<td>( k_4 = 3.7 \times 10^{-10} \text{ exp}(-17000/T) )</td>
<td>1430-2150</td>
<td>Saito et al. (1986)</td>
</tr>
<tr>
<td>( k_5 = 5.3 \times 10^{-10} \text{ exp}(-4500/T) )</td>
<td>1430-2150</td>
<td>Fraak and Zellner</td>
</tr>
<tr>
<td>( k_6 = 5.6 \times 10^{-10} \text{ exp}(-4500/T) )</td>
<td>1100-1600</td>
<td></td>
</tr>
<tr>
<td>( k_7 = 2.5 \times 10^{-11} \text{ exp}(-14400/T) )</td>
<td>1000-2300</td>
<td>Warnatz (1984)</td>
</tr>
<tr>
<td>( k_8 = 3.3 \times 10^{-6} \ T^{0.57} \text{ exp}(-14710/T) )</td>
<td>300-2500</td>
<td>Tsang and Hampson (1986)</td>
</tr>
</tbody>
</table>

**Comments**

(a) Very low pressure pyrolysis of (CH₃)₂N₂ in the presence of O₂, with mass spectrometric detection of CH₃. With [O₂] in excess of (CH₃)₂N₂ by a factor of 100, no detectable change in CH₃ mass peak was observed. Upper limit rate coefficient deduced from estimated limit of detection of change in CH₃ peak.

(b) Shock-tube decomposition of CH₃O₂ mixtures with direct detection of H and O by atomic resonance absorption spectrometry. Rate coefficients derived from a computer simulation of the [H] and [O] profiles.

(c) Shock-tube study of the decomposition of dilute mixtures of (CH₃)₂N₂ in O₂ with detection of time-resolved profiles of CO product formation. Rate data derived from kinetic modelling of CO formation.

(d) Shock-tube study of the decompositions of mixtures of C₂H₆/O₂/Ar and CH₃I/O₂/Ar with time-resolved monitoring of O, H, and OH. Rate coefficients derived from kinetic modelling of experimental profiles based on a mechanism of 18 elementary reactions.

(e) Shock-tube study of the decompositions of mixture of (CH₃)₂N₂ in presence of O₂ and Ar with time-resolved measurements of [CH₃] and [OH] at 216 and 308 nm respectively. Derived rate coefficients are comparable with above tabulated Arrhenius equation obtained from an RRKM calculation for \( k_3 \).

(f) Based on data of Brabbs and Brokaw and of Bhaskaran et al.

(g) Based on data of Bhaskaran et al. and of Hsu et al. and assuming that the reaction proceeds via CH₂O₂.

**Preferred Values**

\[ k_1 = 2.2 \times 10^{-10} \text{ exp}(-15800/T) \text{ over range } 300-2500 \text{ K} \]
\[ k_2 = 5.5 \times 10^{-10} \text{ exp}(-4500/T) \text{ over range } 1000-2500 \text{ K} \]

**Reliability**

\[ \Delta \log k_1 = \pm 0.5 \]
\[ \Delta \log k_2 = \pm 0.5 \]

**Comments on Preferred Values**

The rate coefficients reported for channel (1) fall into two groups, i.e. the data of (i) Brabbs and Brokaw and of Bhaskaran et al. and the data of (ii) Hsu et al. and of Saito et al. At 1669 K these two sets of results yield values of \( k \), which differ by about a factor of 2.5. We have derived the preferred rate expression from an analysis of the data of Hsu et al. and of Saito et al. mainly on the grounds that they involved more comprehensive experimental data than the other two studies. Reitelboim et al., Dean and Westmoreland, and Zellner and Ewig have calculated values of \( k \) from RRKM theory involving a CH₂O intermediate. In all cases the calculated rate coefficients are lower than the above recommended value of \( k_1 \). The recent studies of Saito et al. and of Fraak and Zellner have confirmed that channel (2) is the favoured route in the reaction between CH₃ and O₂. The above recommended value of \( k_2 \) is a mean of the sets of results, which are in excellent agreement. In this case the calculated rate coefficients (\( k_2 \)) based on RRKM theory are totally consistent with the experimental data.
References

5 W. Fraak and R. Zellner, unpublished data.

Thermodynamic Data

\[ \Delta H_{\text{fus}} = -135 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{fus}} = -126 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ K_p = 9.45 \times 10^{-5} \frac{T}{\exp(-15930/T)} \text{ atm}^{-1} \]

Rate Coefficient Data

<table>
<thead>
<tr>
<th>( k [\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}] )</th>
<th>( T [\text{K}] )</th>
<th>([M] [\text{molecule cm}^{-3}] )</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low Pressure Range</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(3.4 \times 10^{-31} ) [He]</td>
<td>(295)</td>
<td>((0.2-2.2) \times 10^{-7}) (He)</td>
<td>Plumb and Ryan (1982)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>(8.0 \times 10^{-32} \exp(+560/T) ) [Ar]</td>
<td>(230-568)</td>
<td>((6-30) \times 10^{-8}) (Ar)</td>
<td>Pratt and Wood (1984)(^2)</td>
<td>(b)</td>
</tr>
<tr>
<td>(4.8 \times 10^{-31} ) [Ar]</td>
<td>(298)</td>
<td>((1.7-19) \times 10^{-8}) (Ar)</td>
<td>Seitzer and Bayes (1983)(^3)</td>
<td>(c)</td>
</tr>
<tr>
<td>(7.0 \times 10^{-31} ) [Ar]</td>
<td>(298)</td>
<td>((6.0-3600) \times 10^{-8}) (Ar)</td>
<td>Pilling and Smith (1985)(^4)</td>
<td>(d)</td>
</tr>
<tr>
<td>(8.0 \times 10^{-31} [N_2])</td>
<td>(1.5 \times 10^{-22} T^{-1.3} ) [Ar]</td>
<td>(334-582)</td>
<td>((0.5-15) \times 10^{-8}) (Ar)</td>
<td>Keiffer, Pilling, and Smith (1987)(^6)</td>
</tr>
<tr>
<td>High Pressure Range</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1.1 \times 10^{-12})</td>
<td>(298)</td>
<td>((1.0-15) \times 10^{-8}) (Ar)</td>
<td>Pilling and Smith (1985)(^4)</td>
<td>(d)</td>
</tr>
<tr>
<td>(2.2 \times 10^{-12})</td>
<td>(298)</td>
<td>((6.0-3600) \times 10^{-8}) (N(_2)Ar)</td>
<td>Cobos et al. (1985)(^5)</td>
<td>(e)</td>
</tr>
<tr>
<td>(1.3 \times 10^{-15} T^{1.2})</td>
<td>(334-582)</td>
<td>((0.5-15) \times 10^{-8}) (Ar)</td>
<td>Keiffer, Pilling, and Smith (1987)(^6)</td>
<td>(f)</td>
</tr>
<tr>
<td>(1.2 \times 10^{-12})</td>
<td>(298)</td>
<td>((3.3-450) \times 10^{-7}) (He)</td>
<td>Caldwell, Parent, and Nelson (1989)(^7)</td>
<td>(g)</td>
</tr>
</tbody>
</table>

Reviews and Evaluations

\( k_o = 7.9 \times 10^{-16} T^{-0.5} \) [N\(_2\)] | 260-300 | Baulch et al. (1982)\(^8\) | (h) |
\( k_o = 2.0 \times 10^{-12}\) | 260-400 | | |
\( F_c(N\(_2\)) = \exp(-7/360) + \exp(-1440/T)\) | | | |
\( k_o = 4.1 \times 10^{-20} T^{-2.5} \) [N\(_2\)] | 200-300 | DeMore et al. (1987)\(^9\) | (i) |
\( k_o = 2.9 \times 10^{-8} T^{-1.7}\) | | | |
\( F_c = 0.6\) | | | |

Comments

(a) Discharge flow, mass spectrometry. CH\(_3\) generated from \( F + CH\(_4\) \). \( k_o \) obtained by extrapolation using \( k_e = 2 \times 10^{-12} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\), \( F_c = 0.51\).
(b) Discharge flow, analysis by gas chromatography. CH\(_3\) generated by \( H + C\(_2\)H\(_4\) \). \( k_o \) obtained by fits using same parameters as Plumb and Ryan\(^1\).
(c) Laser flash photolysis, photoionisation mass spectrometry. CH\(_3\) generated by 193 nm photolysis of nitromethane. Relative collisional efficiencies \( \text{Ar} : N\(_2\) \text{ : O}_2 \text{ : He} \) determined as \( 1.0 : 1.1 : 1.1 : 1.9\).
(d) Laser flash photolysis, absorption spectroscopy. CH\(_3\) generated by 193 nm photolysis of azomethane. Demonstrated that earlier flash photolysis/absorption spectroscopy experiments were in error because of neglect of CH\(_3\) + CH\(_2\)O. Technique devised to eliminate contributions from this reaction.
(e) Laser flash photolysis, absorption spectroscopy in high pressure cell. CH\(_3\) generated by 193 nm photolysis of azomethane.
(f) Laser flash photolysis, absorption spectroscopy. CH\(_3\) from 193 nm photolysis of acetone.

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

(g) Laser flash photolysis, resonance enhanced multi-photon ionisation detection of CH₃. CH₃ generated from 266 nm photolysis of CH₃I.

(h) Based mainly on earlier flash photolysis studies at high radical densities, where radical-radical reactions play a significant role.

(i) Based on Ref. 5 ($k_w$) and on the low pressure results of Refs. 1 and 3.

Preferred Values

\[
\begin{align*}
  k_0 &= 1.5 \times 10^{-22} T^{-3.3} \ [\text{Ar}] \ \text{cm}^3 \ \text{molecule}^{-1} \ \text{s}^{-1} \ \text{over range} \ 300-800 \ \text{K} \\
  k_0 &= 1.6 \times 10^{-22} T^{-3.3} \ [\text{N}_2] \ \text{cm}^3 \ \text{molecule}^{-1} \ \text{s}^{-1} \ \text{over range} \ 300-800 \ \text{K} \\
  k_w &= 1.3 \times 10^{-15} T^{1.2} \ \text{cm}^3 \ \text{molecule}^{-1} \ \text{s}^{-1} \ \text{over range} \ 300-800 \ \text{K} \\
  F_e &= 0.466-1.30 \times 10^{-4} T
\end{align*}
\]

Reliability

\[\Delta \log k = \pm 0.3 \ \text{over the temperature range} \ 300-800 \ \text{K} \ \text{and the pressure range} \ 0.5-1500 \ \text{Torr}\]

Comments on Preferred Values

The rate parameters are determined from the data of Refs. 3, 4, and 6 but they are in good agreement with the data of Refs. 2 and 7. The fits do not reproduce the high pressure data of Cobos et al., suggesting that this representation is unsatisfactory at higher pressures.

References

BAULCH ET AL.

\[ \text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{O} \]
\[ \rightarrow \text{HCHO} + \text{OH} \]
\[ \rightarrow \text{CH}_3\text{O}_2 \]

TEMPERATURE (T/K)

EXPERIMENTAL DATA

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

CH$_3$ + H$_2$ → CH$_4$ + H

**Thermodynamic Data**

$\Delta H_{298} = -2.6 \text{ kJ mol}^{-1}$

$\Delta S_{298} = -24.0 \text{ J K}^{-1} \text{mol}^{-1}$

$k_p = 5.5 \times 10^{-3} \ T^{1.25} \exp(+638/T)$

**Rate Coefficient Data**

<table>
<thead>
<tr>
<th>$k$ [cm$^3$ molecule$^{-1}$ s$^{-1}$]</th>
<th>$T$ [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.32 \times 10^{-18} \ T^{-2} \exp(-4810/T)$</td>
<td>372–1370</td>
<td>Kobriniskiy and Pacey (1974)$^1$</td>
<td>(a)</td>
</tr>
<tr>
<td>$8.3 \times 10^{-13} \exp(-5290/T)$</td>
<td>584–671</td>
<td>Marshall and Shahkar (1981)$^2$</td>
<td>(b)</td>
</tr>
<tr>
<td>$3.3 \times 10^{-11} \exp(-7200/T)$</td>
<td>1066–2166</td>
<td>Möller, Mozhukhin, and Wagner (1986)$^3$</td>
<td>(c)</td>
</tr>
<tr>
<td>$2.57 \times 10^{-11} \exp(-7801/T)$</td>
<td>1200–2000</td>
<td>Clark and Dove (1973)$^4$</td>
<td>(d)</td>
</tr>
<tr>
<td>$1.4 \times 10^{-12} \exp(-5490/T)$</td>
<td>370–700</td>
<td>Kerr and Parsonage (1976)$^5$</td>
<td>(e)</td>
</tr>
<tr>
<td>$1.1 \times 10^{-21} \ T^{3.0} \exp(-3900/T)$</td>
<td>300–2500</td>
<td>Warnatz (1984)$^6$</td>
<td>(f)</td>
</tr>
<tr>
<td>$4.8 \times 10^{-22} \ T^{3.12} \exp(-4384/T)$</td>
<td>300–2500</td>
<td>Tsang and Hampson (1986)$^7$</td>
<td>(g)</td>
</tr>
</tbody>
</table>

**Comments**

(a) Pyrolysis of neo-C$_4$H$_2$ in the presence of H$_2$ in a flow system over the temperature range 826–968 K. End-product analysis for CH$_4$ and C$_2$H$_6$. Rate equation for temperature range 372–1370 K includes earlier data.

(b) Pyrolysis of (CH$_3$N)$_2$ in the presence of H$_2$ in a flow system. End-product analysis for CH$_4$ and C$_2$H$_6$. Kinetic treatment of data gives $k$ (CH$_3$ + H$_2$) directly without involving $k$ (CH$_3$ + CH$_3$).

(c) Shock-tube study with time resolved measurement of [CH$_3$] by absorption at 216.5 nm. CH$_3$ produced from decomposition of (CH$_3$)$_2$Sn, (CH$_3$)$_2$N$_2$ or (CH$_3$)$_2$Hg.

(d) Shock-tube study of the pyrolysis of (CH$_3$N)$_2$ in the presence of H$_2$ over the temperature range 1272–1370 K. Rate coefficient at 1340 K derived from a computer simulation of the experimental concentration-time profiles of CH$_4$ and C$_2$H$_6$. Rate equation for temperature range 1200–2000 K includes earlier literature data.

(e) Linear least-mean squares fit of literature experimental rate coefficients.

(f) Fit of three parameter rate equation to data analysed in comment (d).

(g) Rate equation obtained from re-analysis of available experimental data.

**Preferred Values**

$k = 1.14 \times 10^{-20} \ T^{2.74} \exp(-4740/T) \ \text{cm}^3 \ \text{molecule}^{-1} \ \text{s}^{-1}$

over range 300–2500 K

Reliability

$\Delta \log k = \pm 0.15$ over range 300–700 K

$= \pm 0.3$ over range 700–2500 K

**Comments on Preferred Values**

The above recommendation is from a re-analysis of the data base used by Tsang and Hampson$^7$ together with the more recent high temperature measurements of Möller et al.$^3$. This latter study, which involved direct monitoring of [CH$_3$], provides a firmer base concerning the curvature of the Arrhenius plot and the reliability of the rate coefficients at higher temperatures.

It has already been pointed out$^5$ that there is a discrepancy between the ratio of rate coefficients for this reaction and the reverse reaction and the equilibrium constant calculated from thermochemical data.

**References**

CH$_3$ + H$_2$ → CH$_4$ + H

**EXPERIMENTAL DATA**
- Gowenlock et al 1953
- Gesser and Steacie 1956
- Benson and Join 1959
- Shapiro and Weston 1972
- Clark and Dave 1973
- Kibrinsky and Pacey 1974
- Marshall and Shakir 1981
- Moller et al 1986
- This Recommendation 1989

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

CH$_3$ + CH$_3$ $\rightarrow$ H + C$_2$H$_5$ \hspace{1cm} (1)

CH$_3$ + CH$_3$ (+ M) $\rightarrow$ C$_2$H$_6$ (+ M) \hspace{1cm} (3)

**Thermodynamic Data**

\[ \Delta H_{\text{th}} (1) = 43.8 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{th}} (1) = -21.9 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ k_{p}(1) = 2.21 \times 10^{-4} T^{3.24} \exp(-4790/T) \]

\[ \Delta H_{\text{th}} (2) = -239 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{th}} (2) = -38.3 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ k_{p}(2) = 1.21 \times 10^{-4} T^{6.26} \exp(+2950/T) \]

\[ \Delta H_{\text{th}} (3) = -375 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{th}} (3) = -159 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ k_{p}(3) = 2.41 \times 10^{-10} T^{2.26} \exp(+45700/T) \text{ atm}^{-1} \]

**Rate Coefficient Data**

<table>
<thead>
<tr>
<th>$k$ [cm$^3$ molecule$^{-1}$ s$^{-1}$]</th>
<th>$T$ [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1 = 1.0 \times 10^{-7} \exp(-21600/T)$</td>
<td>2000-2700</td>
<td>Gardiner et al. (1975)$^1$</td>
<td>(a)</td>
</tr>
<tr>
<td>$k_2 = 1.6 \times 10^{-8} \exp(-15400/T)$</td>
<td>1700-2000</td>
<td>Tsuibo (1978)$^2$</td>
<td>(b)</td>
</tr>
<tr>
<td>$k_3 = 5.1 \times 10^{-8} \exp(-3400/T)$</td>
<td>1650-2100</td>
<td>Roth and Just (1979)$^3$</td>
<td>(c)</td>
</tr>
<tr>
<td>$k_4 = 1.7 \times 10^{-8} \exp(-16100/T)$</td>
<td>1700</td>
<td>Chiang and Skinner (1981)$^4$</td>
<td>(d)</td>
</tr>
<tr>
<td>$k_5 = 2.5 \times 10^{-13}$</td>
<td>1600-2500</td>
<td>Kiefer and Budach (1984)$^5$</td>
<td>(e)</td>
</tr>
<tr>
<td>$k_6 = 1.3 \times 10^{-11} \exp(-6562/T)$</td>
<td>1320-2300</td>
<td>Frank and Braun-Unkhoff (1987)$^6$</td>
<td>(f)</td>
</tr>
</tbody>
</table>

**Comments**

(a) Methane pyrolysis in shock wave; time of flight mass spectrometry, IR laser absorption and laser schlieren. Numerical integration of complex scheme. 
(b) Shock tube study of C$_2$H$_6$, C$_2$H$_4$O$_2$. Monitored CH$_3$ by absorption, decay second order in methyl, suggested contribution from (k$_1$ + k$_2$). 
(c) Reflected shock wave study of dilute C$_2$H$_6$ in Ar; II detected by atomic resonance absorption spectroscopy. 
(d) Study of shock heated C$_2$H$_6$, C$_2$D$_6$ mixtures by atomic resonance absorption spectroscopy of H. Need additional source of H at higher temperatures when H $+$ C$_2$H$_6$ $\rightarrow$ C$_2$H$_2$ $\rightarrow$ C$_2$H$_4$ + H becomes unimportant on the monitoring time scale. 
(e) Argue that previous estimates are too high. Shock wave study of C$_2$H$_3$/Kr mixtures by laser schlieren. 
(f) Shock tube/atomic resonance absorption study of H with a variety of CH$_3$ precursors (CH$_3$N$_2$, CH$_3$I, C$_2$H$_4$, all in Ar) to cover a wide range of temperatures. Numerical integration. 
(g) Evaluation. Adopted the values of Roth and Just$^3$. 
(h) Based on $k_1$ and $k_p$. 

**Preferred Values**

$k_1 = 5.1 \times 10^{-11} \exp(-6800/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$ over range 1300-2500 K

$k_2$ no recommendation

Reliability

$\Delta \log k_1 = \pm 0.6$

**Comments on Preferred Values**

Considering the indirect nature of most of the experiments, they give remarkably consistent results, although Kiefer and Budach's$^2$ values seem too low. The preferred value is based on the recent, more direct data of Frank and Braun-Unkhoff$^6$. It should be noted, however, that extrapolation of values based on the low temperature $k_1$ values and the equilibrium constant gives $k_1 = 7 \times 10^{-12}$ exp(-6300/T) cm$^3$ molecule$^{-1}$ s$^{-1}$ over the range 1300-2500 K.

There are insufficient data to make a recommendation on $k_2$.

**References**

Thermodynamic Data

\[ \Delta H_{298} = -375 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298} = -159 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ K_p = 2.41 \times 10^{-10} T^{0.245} \exp(+45700/T) \text{ atm}^{-1} \]

Rate Coefficient Data

<table>
<thead>
<tr>
<th>Rate Coefficient Measurements</th>
<th>T[K]</th>
<th>[M] [molecule cm(^{-2})]</th>
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<th>Comments</th>
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<td>4.0 \times 10^{-11}</td>
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<td>(3.2-29.4)\times10^{18} (N(_2))</td>
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<td>1.6\times10^{19} (N(_2)) , Callear and Metcalfe (1976)(^\text{j})</td>
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<td>Zaslavko and Smirnov (1979)(^\text{n})</td>
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<td>Adachi et al. (1980)(^\text{p})</td>
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<tr>
<td>3.8 \times 10^{-11}</td>
<td>1.3\times10^{17} (N(_2))</td>
<td>Arthur (1986)(^\text{r})</td>
<td>(l)</td>
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<td>4.0 \times 10^{-11}</td>
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<td>Arthur and Biordi (1986)(^\text{s})</td>
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<td>4.4 \times 10^{-11}</td>
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<td>Slagie et al. (1988)(^\text{t})</td>
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<td>4.0\times10^{18} (Ar)</td>
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<td>High Pressure Range</td>
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<td>(2.5-523)\times10^{19} (Ar)</td>
<td>Hippler et al. (1984)(^\text{t})</td>
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</table>

Reviews and Evaluations

<p>| k = 5.1 \times 10^{-11} | 300 | Quack and Troe (1977)(^\text{u}) | (o) |
| k = 4.8 \times 10^{-11} | 1300 | Baulch and Duxbury (1980)(^\text{v}) | (p) |
| k = 4.0 \times 10^{-11} | 250-420 | Baur and Wardlaw (1988)(^\text{w}) | (q) |
| k = 4.1 \times 10^{-10} T^{-0.4} | 300-1200 | | (r) |
| k = 1.7 \times 10^{-9} T^{-0.64} | 250-1400 | | (s) |
| k = 1.5 \times 10^{-7} T^{-1.18} \exp(-329/T) | 300-2000 | | |
| k = [Ar] 8.8 \times 10^{-7} T^{-7} \exp(-1390/T) | 300-1400 | | |
| F_{c} = 0.38 \exp(-T/73) + 0.62 \exp(-7/1180) | 250-1400 | | |
| k = 6.0 \times 10^{-11} | 300-1400 | Troe (1989)(^\text{y}) | (t) |
| k = 1.7 \times 10^{-9} T^{-0.64} | 250-1400 | Tsang (1989)(^\text{z}) | (u) |</p>
<table>
<thead>
<tr>
<th>Comments</th>
<th>Preferred Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Molecular modulation spectroscopy, CH$_3$ detection at 216 nm.</td>
<td>$k_a = 6.0 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ over range 300–2000 K</td>
</tr>
<tr>
<td>(b) Flash photolysis of HgMe$_2$, $k = 4.9 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for 2 CD$_3$ + M $\rightarrow$ C$_2$D$_6$ + M; CH$_3$ detection at 216 nm.</td>
<td>$k_0 = [\text{Ar}] 3.5 \times 10^{-7} T^{-2} \exp(-1390/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$ over range 300–2000 K</td>
</tr>
<tr>
<td>(c) Flash photolysis of HgMe$_2$, CH$_3$ detection at 216 nm, pressure dependence between 3 and 30 Torr.</td>
<td>$F_c = 0.38 \exp(-(T/73) + 0.62 \exp(-T/1180))$ over range 300–2000 K</td>
</tr>
<tr>
<td>(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$_2$D$_6$ + Ar identical to those for methyl recombination.</td>
<td>Reliability</td>
</tr>
<tr>
<td>(e) Flash photolysis of azomethane, CH$_3$ detection at 216 nm.</td>
<td>$\Delta \log k_a = \pm 0.05$ at 300 K</td>
</tr>
<tr>
<td>(f) Discharge-flow study of the reaction H + CH$_4$, modelling of the mechanism.</td>
<td>$\Delta \log k_a = \pm 0.3$ at 2000 K</td>
</tr>
<tr>
<td>(g) Shock wave pyrolysis study of tetramethyl tin, CH$_3$ detection at 216 nm.</td>
<td>$\Delta \log k_0 = \pm 0.3$ over range 300–2000 K</td>
</tr>
<tr>
<td>(h) Flash photolysis of azomethane, CH$_3$ detection at 216 nm.</td>
<td>$\Delta F_c = \pm 0.1$ over range 300–2000 K</td>
</tr>
<tr>
<td>(i) Flow pyrolysis of neo-pentane, study of the induction period.</td>
<td>Comments on Preferred Values</td>
</tr>
<tr>
<td>(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.</td>
<td>The recent work from Refs. 4, 10, 11, and 14 has provided extensive data on the pressure and temperature dependence of this reaction for temperatures below 1000 K. At $T &gt; 1000$ K, data are still scarce and reliable extrapolations to the limiting rate coefficients are difficult to make. Fig. 1 summarizes these experimental results. Theoretical modelling helps to extend the range of conditions. The modelling of $k_a$ from Ref. 15 here is preferred, since it appears to give a better fit to the high temperature data$^{24}$ and is in better accord with weak temperature coefficients found for a series of bimolecular capture rate constants. The expressions for $k_0$ and $F_c$ are based on the modelling of Ref. 20, however, the values for $k_0$ had to be scaled by a temperature-independent factor in order to accommodate the chosen $k_a$ value.</td>
</tr>
<tr>
<td>(k) Excimer laser flash photolysis of azomethane at 193 nm, CH$_3$ detection at 216 nm, temperature dependence between 296 and 577 K.</td>
<td>References</td>
</tr>
<tr>
<td>(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.</td>
<td>$^{3}$H. E. Van den Bergh, Chem. Phys. Lett. 43, 201 (1976).</td>
</tr>
<tr>
<td>(t) Modelling of experimental data form refs. 4, 10, 11, and 14 with constant $k_{rec,s}$ such as suggested by statistical adiabatic channel model from Ref. 15.</td>
<td>$^{9}$P. D. Pacey and J. H. Wimalasena, J. Phys. Chem. 84, 2221 (1980).</td>
</tr>
</tbody>
</table>

$^{22}$W. Tsang, Comb. Flame 78, 71 (1989).
CH$_3$ + CH$_3$ → H + C$_2$H$_2$
→ H$_2$ + C$_2$H$_4$
→ C$_2$H$_6$

T/K

EXPERIMENTAL DATA
- Gardiner et al. (k2) 1975
- Tsuji 1978
- Roth and Just (k1) 1979
- Chiang and Skinner (k1) 1981
- Kaiser and Buda (k1) 1984
- Frank and Braun-Unkoff (k1) 1987
- Roth and Just (k2) 1979
- Parkes et al. (k3) (N$_2$) 1976
- Collier and Metcalf (k3) (N$_2$) 1976
- Hachmold et al. (k2) (N$_2$) 1977
- Adachi et al. (k3) (n-sentane) 1980
- Hippler et al. (k3) (Ar) 1984
- Hippler et al. (k3) (N$_2$) 1984
- Macpherson et al. (k3) (Ar) 1985
- Arthur et al. (k3) (N$_2$) 1986
- Slagle et al. (k3) (Ar) 1988
- This Recommendation (k1) 1989
- This Recommendation (k3 (inf)) 1989
EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[
\text{CH}_3 + \text{HCHO} \rightarrow \text{CH}_4 + \text{CHO}
\]

**Thermodynamic Data**

\[
\Delta H_{298} = -61.2 \text{ kJ mol}^{-1} \\
\Delta S_{298} = -20.7 \text{ JK}^{-1}\text{mol}^{-1} \\
K_p = 2.1 \times 10^{-0.176} \exp(+7360/T)
\]

**Rate Coefficient Data**

<table>
<thead>
<tr>
<th>(k[\text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1}])</th>
<th>(T[\text{K}])</th>
<th>Reference</th>
<th>Comments</th>
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<tr>
<td>5.33 \times 10^{-14}</td>
<td>1005</td>
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<tr>
<td>2.1 \times 10^{-11} \exp(-5415/T)</td>
<td>788–935</td>
<td>Manthorne and Pacey (1978)²</td>
<td>(b)</td>
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<tr>
<td>1.66 \times 10^{-12} \exp(-3887/T)</td>
<td>399–434</td>
<td>Selby (1978)³</td>
<td>(c)</td>
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<td>1.4 \times 10^{-12} \exp(-3502/T)</td>
<td>500–603</td>
<td>Anastasi (1983)⁴</td>
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<td>1.75 \times 10^{-13} \exp(-30BO/T)</td>
<td>9.2 \times 10^{-21} \exp(-2950/T)</td>
<td>Kerr and Parsonage (1976)⁵</td>
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<td>1.75 \times 10^{-13} \exp(-30BO/T)</td>
<td>9.2 \times 10^{-21} \exp(-2950/T)</td>
<td>Warnatz (1984)⁶</td>
<td>(e)</td>
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<tr>
<td>9.2 \times 10^{-21} \exp(-2950/T)</td>
<td>300–2500</td>
<td>Tsang and Hampson (1986)⁷</td>
<td>(f)</td>
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</table>

**Comments**

(a) Flow pyrolysis of dimethyl ether to generate \(\text{CH}_3\) and HCHO. [\(\text{CH}_3\)] measured by UV absorption, CO, \(\text{CH}_4\), and \(\text{C}_2\text{H}_6\) by gas chromatography. Independent values of \(k\) and \(k(\text{CH}_3 + \text{CH}_3)\) reported.

(b) Flow pyrolysis of dimethyl ether; CO, \(\text{CH}_4\), and \(\text{C}_2\text{H}_6\) measured by gas chromatography. \(k\) relative to \(k(\text{CH}_3 + \text{CH}_3) = 4.03 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}\).

(c) Pyrolysis of di-\(\text{t}\)-butylperoxide; product analysis by gas chromatography.

(d) Molecular modulation-UV absorption detection of \(\text{CH}_3\) at 216 nm in presence of excess HCHO; \(\text{CH}_3\) produced by photolysis of acetone; first order rate constants corrected for contribution (up to 30%) due to \(\text{CH}_3 + \text{CH}_3\text{CHO}\) reaction. Contribution due to radical + radical reactions estimated from measurements of \(\text{CH}_4\) and other products by gas chromatography.

(e) Based on data of Blake and Kutske⁸ and Toby and Kutske⁹ obtained from pyrolysis of di-\(\text{t}\)-butylperoxide and photolysis of \(\text{CH}_3\text{NNCH}_3\) respectively.

(f) Accepts the recommendation of Kerr and Parsonage⁷.

(g) Based on data in Refs. 1, 2, and 4 and the low temperature data evaluation of Kerr and Parsonage⁵.

**Preferred Values**

\[
k = 6.8 \times 10^{-12} \exp(-4450/T) \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \text{ over range 300–1000 K}
\]

**Reliability**

\[
\text{Alog} k = \pm 0.3 \text{ over range 300–1000 K}
\]

**Comments on Preferred Values**

The only direct study of this reaction is that of Anastasi, the other values being relative to methyl radical recombination. The direct measurements which cover an intermediate temperature range are higher than predicted from the expression given by Manthorne et al. from non-linear least squares analysis of the high (800–1000 K) and low (350–420 K) temperature data. The evidence for non-Arrhenius behaviour is less clear cut than in the case of \(\text{CH}_3 + \text{CH}_3\text{CHO}\), in the absence of reliable data at \(T > 1000\) K. The preferred Arrhenius expression is based on a best fit to the data of Selby³, Anastasi⁴, and Manthorne et al.².

**References**

CH₃ + HCHO → CH₄ + HCO

*Experimental Data*
- Kutaka et al. 1959
- Held et al. 1977
- Morthorne and Pacey 1978
- Selby 1978
- Anastasi 1983
- This Recommendation 1989

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[
CH_3 + C_2H_2 \rightarrow CH_3CH=CH \quad (1) \\
\rightarrow CH_4 + C_2H_2 \quad (2)
\]

**Thermodynamic Data**

\[\Delta H_{298} (1) = -238 \text{ kJ mol}^{-1}\]
\[\Delta S_{298} (1) = -138 \text{ J K}^{-1}\text{mol}^{-1}\]
\[K_p(1) = 1.37 \times 10^{-10} T^{-0.789} \exp(29300/T)\]
\[\Delta H_{298} (2) = 113 \text{ kJ mol}^{-1}\]
\[\Delta S_{298} (2) = -1.5 \text{ J K}^{-1}\text{mol}^{-1}\]
\[K_p(2) = 39.9 \times 10^{-64} \exp(-13700/T)\]

**Rate Coefficient Data**

<table>
<thead>
<tr>
<th>(k \text{[cm}^3 \text{molecule}^{-1} \text{s}^{-1}] )</th>
<th>(T[K] )</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_1 = 1.3 \times 10^{-13} \exp(-2760/T) )</td>
<td>417-514</td>
<td>Mandelcorn and Steacie (1954)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>(k_1 = 4.2 \times 10^{-13} \exp(-3900/T) )</td>
<td>371-479</td>
<td>Garcia-Dominguez and Trotman-Dickenson (1962)(^2)</td>
<td>(b)</td>
</tr>
<tr>
<td>(k_1 = 1.0 \times 10^{-12} \exp(-3900/T) )</td>
<td>397-487</td>
<td>Holt and Kerr (1977)(^3)</td>
<td>(c)</td>
</tr>
<tr>
<td>(k_1 = 4.2 \times 10^{-13} \exp(-3900/T) )</td>
<td>371-514</td>
<td>Kerr and Parsonage (1972)(^4)</td>
<td>(d)</td>
</tr>
</tbody>
</table>

**Comments**

(a) Steady-state photolysis of \(CH_3COCH_3\) in presence of \(C_2H_2\). End-product analysis for \(CH_4, C_2H_6\) and CO. \(k\) derived from a kinetic analysis based on a mass balance, and a calculated relative to \(k(CH_3 + CH_3) = 3.6 \times 10^{-11} \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}\).

(b) Steady-state photolysis of \(CH_3CHO\) in presence of \(C_2H_2\) with end-product analysis for adduct products and radical dimer. \(k\) derived from rate of formation of adduct produced and calculated relative to \(k(CH_3 + CH_3) = 3.6 \times 10^{-11} \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}\).

(c) Steady-state photolysis of \((CH_3CO)_2\) in the presence of \(C_2H_2\) and \(i-C_4H_{10}\) with end-product analysis for \(CH_4\) and CO. \(k\) derived from a kinetic analysis based on a mass balance and calculated relative to \(k(CH_3 + i-C_4H_{10}) = 1.38 \times 10^{-13} \exp(-4030/T) \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}\).

(d) Based on data of Garcia-Dominguez and Trotman-Dickenson\(^2\).

**Preferred Values**

\(k_1 = 1 \times 10^{-12} \exp(-3900/T)\) over range 300-600 K

**Reliability**

\(\Delta \log k = \pm 0.5\) over range 300-600 K

**Comments on Preferred Values**

As pointed out by Holt and Kerr\(^5\) the agreement between the three determinations of the rate coefficient \(k_1\) is poor. The largest discrepancy is between the values of \(k_1\) reported by Mandelcorn and Steacie\(^1\) and by Garcia-Dominguez and Trotman-Dickenson\(^2\). Here we have recommended the rate expression determined by Holt and Kerr\(^5\) which represents a median position, but this has been assigned larger error limits. What is required in this case is a direct study of the rate of this reaction. Use of the preferred rate equation at temperatures above 600 K should involve error limits of \(\Delta \log k \pm 1.0\). There appears to be no published data\(^5\) on the rate coefficient \(k_2\), but in view of its endothermic nature this must be a considerably slower reaction than reaction (1). We estimate a rate coefficient of \(k_2 < 10^{-20} \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}\) at 600 K, based on the enthalpy change \(\Delta H^\circ = 113 \text{ kJ mol}^{-1}\) and an assumed value of \(A_2 < 1 \times 10^{-10} \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}\).

**References**

BAULCH ET AL.

\[ \text{CH}_3 + \text{C}_2\text{H}_2 \rightarrow \text{C}_3\text{H}_6 \]
\[ \rightarrow \text{CH}_4 + \text{C}_2\text{H} \]

\( T/K \)

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

\( 10^3 T^{-1}/K^{-1} \)

EXPERIMENTAL DATA

- Mandelcorn and Sleacle \((k1)\) 1954
- Garcia-Dominguez et al \((k1)\) 1962
- Holt and Kerr \((k1)\) 1977
- This Recommendation \((k1)\) 1989

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ \text{CH}_3 + \text{C}_2\text{H}_4 \rightarrow \text{n-C}_3\text{H}_7 \quad (1) \]
\[ \rightarrow \text{CH}_4 + \text{C}_2\text{H}_3 \quad (2) \]

**Thermodynamic Data**

\[ \Delta H_{\text{sw}} (1) = -104 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{sw}} (1) = -145 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_p (1) = 1.38 \times 10^{-10} \exp ( + 12800/T) \]
\[ \Delta H_{\text{sw}} (2) = 13.2 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{sw}} (2) = 4.4 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_p (2) = 25.7 \exp (-1630/T) \]

**Rate Coefficient Data**

<table>
<thead>
<tr>
<th>( k [\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}] )</th>
<th>( T [\text{K}] )</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 ) = 1.7 \times 10^{-15} \exp (-3700/T)</td>
<td>1038</td>
<td>Chen, Back, and Back (1976)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>( k_1 ) = 3.5 \times 10^{-13} \exp (-3700/T)</td>
<td>305-503</td>
<td>Holt and Kerr (1977)(^2)</td>
<td>(b)</td>
</tr>
<tr>
<td>( k_2 ) = 3.5 \times 10^{-12} \exp (-5500/T)</td>
<td>305-503</td>
<td>Tabayashi and Bauer (1979)(^4)</td>
<td>(c)</td>
</tr>
<tr>
<td>( k_3 ) = 6.9 \times 10^{-12} \exp (-5500/T)</td>
<td>460-650</td>
<td>Kerr and Parsonage (1972)(^5)</td>
<td>(d)</td>
</tr>
</tbody>
</table>

**Comments**

(a) Pyrolysis of \( \text{CH}_4 \) in a static reaction vessel with end-product analysis by GC. Value of \( k_2 \) derived from measured ratio \( k_1 k_2/k_3 \) (obtained from yields of propene and acetylene) where \( k_3 \) refers to the reaction \( n-\text{C}_3\text{H}_7 \rightarrow \text{C}_3\text{H}_4 + \text{M} \) (3) and \( k_4 \) to the equilibrium \( \text{CH}_3 + \text{C}_2\text{H}_4 \rightleftharpoons n-\text{C}_3\text{H}_7 \) (4).

(b) Steady-state photoanalysis of \( (\text{CH}_3\text{CO})_2 \) in the presence of \( \text{C}_2\text{H}_4 \) and \( i-\text{C}_3\text{H}_10 \) with end-product analysis for \( \text{CH}_4 \) and \( \text{CO} \). \( k \) derived from a kinetic analysis based on a mass balance and calculated relative to \( k(\text{CH}_3 + i-\text{C}_3\text{H}_10) = 1.38 \times 10^{-13} \exp (-4030/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \). Data incorporated into an updated evaluation of previous data considered by Kerr and Parsonage\(^5\).

(c) Shock-tube study of the early stages of the pyrolysis of \( \text{CH}_4 \). Rate expression derived from a computer analysis to fit predicted to observed profiles of density gradients. Mechanism of twelve elementary reactions considered.

(d) Evaluation based on data of Brinton\(^6\), Hogg and Kebbarle\(^7\), Endrenyi and Le Roy\(^8\), and Cvetanovic and Irwin\(^9\).

(e) Evaluation based on data of Trotman-Dickenson and Steacie\(^10\).

**Preferred Values**

\[ k_1 = 3.5 \times 10^{-13} \exp (-3700/T) \text{ over range } 300-600 \text{ K} \]
\[ k_2 = 6.9 \times 10^{-12} \exp (-5600/T) \text{ over range } 400-3000 \text{ K} \]

**Reliability**

\[ \Delta \log k_1 = \pm 0.3 \text{ over range } 300-500 \text{ K} \]
\[ \Delta \log k_2 = \pm 1.0 \text{ over range } 400-3000 \text{ K} \]

**Comments on Preferred Values**

There is agreement among the steady-state photolysis measurements of \( k_1 \) over the temperature range 300-500 K. Here we have selected the updated evaluation of Holt and Kerr\(^2\) which includes several earlier studies\(^6\)\(^-\)\(^9\). The use of this rate expression at temperatures above 500 K should certainly involve larger error limits and we suggest \( \Delta \log k_1 = \pm 0.5 \) up to 2500 K. The preferred rate expression for \( k_2 \) is from the evaluation of Kerr and Parsonage\(^5\) which is derived from the low-temperature steady-state experiments of Trotman-Dickenson and Steacie\(^10\). This expression is in good agreement with the indirect rate coefficients reported by Tabayashi and Bauer\(^4\) from high-temperature shock-tube measurements but not in such good agreement with the rate coefficient reported by Chen et al.\(^1\) at 1038 K. More definitive measurements are required at the higher end of the temperature range. The existing results indicate no curvature in the Arrhenius plot for \( k_2 \) and it has been suggested\(^1\) that this could be due to a mechanism involving an addition complex rather than a simple H-transfer process.

**References**

\(^3\) K. Tabayashi and S. H. Bauer, Comb. Flame, 34, 63 (1979).
BAULCH ET AL.

\[ \text{CH}_3 + \text{C}_2\text{H}_4 \rightarrow n\text{-C}_3\text{H}_7 \]
\[ \rightarrow \text{CH}_4 + \text{C}_2\text{H}_3 \]

\[ T/\text{K} \]

\[ \log(k/\text{cm}^3\text{ molecule}^{-1}\text{s}^{-1}) \]

\[ 10^3T^{-1}/\text{K}^{-1} \]

EXPERIMENTAL DATA
- Chen et al. (k2) 1976
- Tribrovich and Bauer (k2) 1979
- Trotman-Dickenson et al. (k2) 1951
- Holt and Kerr (k1) 1977

This Recommendation (k1) 1989
This Recommendation (k2) 1989

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ \text{CH}_3 + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4 \quad (1) \]
\[ \rightarrow \text{CH}_4 + \text{C}_2\text{H}_4 \quad (2) \]

Thermodynamic Data
\[ \Delta H_{\text{fam}} \text{(1)} = -367 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{fam}} \text{(1)} = -175 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ k_n(1) = 4.40 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \exp(44700/T) \]
\[ \Delta H_{\text{fam}} \text{(2)} = -285 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{fam}} \text{(2)} = -40.5 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ k_n(2) = 3.01 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \exp(34500/T) \]

Rate Coefficient Data

<table>
<thead>
<tr>
<th>( k ) [cm(^3) molecule(^{-1}) s(^{-1})]</th>
<th>( T ) [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 ) = 4.2 \times 10^{-12}</td>
<td>1050-1700</td>
<td>Lifshitz and Frenklach (1975)(^{(a)} )</td>
<td></td>
</tr>
<tr>
<td>( k_1 ) = 1.2 \times 10^{-11}</td>
<td>1300-1700</td>
<td>Koike and Gardiner (1980)(^{(b)} )</td>
<td></td>
</tr>
<tr>
<td>( k_1 ) = 1.3 \times 10^{-10} \exp(5700/T)</td>
<td>1300-1700</td>
<td>Simmie, Gardiner, and Eubank (1982)(^{(c)} )</td>
<td></td>
</tr>
<tr>
<td>( k_1 ) = 1.5 \times 10^{-16} \exp(14700/T)</td>
<td>1500-1650</td>
<td>Arthur and Anastasi (1983)(^{(d)} )</td>
<td></td>
</tr>
<tr>
<td>( k_1 ) = 4.5 \times 10^{-11}</td>
<td>308</td>
<td>Kanani, Parnell, and Smith (1983)(^{(e)} )</td>
<td></td>
</tr>
<tr>
<td>( k_1 ) = 1.46 \times 10^{-11} \exp(856/T)</td>
<td>773-793</td>
<td>Anastasi and Arthur (1987)(^{(e)} )</td>
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<tr>
<td>( k_1 ) = 4.73 \times 10^{-11}</td>
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<td></td>
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<tr>
<td>( k_1/k_1 ) = 0.036</td>
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<tr>
<td>( k_1^{*} ) = 4.7 \times 10^{-11} (300/T)^{0.5}</td>
<td>300-2500</td>
<td>Tsang and Hampson (1986)(^{(b)} )</td>
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</tr>
<tr>
<td>( k_2/k_1 ) = 0.04</td>
<td>300-2500</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Comments

(a) Estimated from \( k_1 = k_{-1}K \).
(b) Pyrolysis of \( \text{C}_3\text{H}_8 \) in Ar behind reflected shock waves at pressures near 760 Torr, with IR laser absorption kinetic spectroscopy. \( k \) derived from a computer fit of the absorption profiles based on a mechanism of 44 elementary reactions.
(c) Re-analysis of data of Koike and Gardiner\(^{2} \) for experiments with 4.3\% \( \text{C}_3\text{H}_8 \) in Ar.
(d) Same experimental procedure as in (b) but at pressures of \( \sim 1400 \) Torr and with a mixture of 5\% \( \text{C}_3\text{H}_8 \) in Ar.
(e) Molecular modulation spectroscopy. \( \text{CH}_3 \) and \( \text{C}_2\text{H}_5 \) produced from photolysis of \( \text{C}_4 \) at 350 nm. [\( \text{CH}_3 \)] and [\( \text{C}_2\text{H}_5 \)] monitored by UV absorption. \( k \) obtained from computer simulation of concentration profiles.
(f) Study of the pyrolysis of \( \text{C}_3\text{H}_8 \) in a static reaction vessel in the presence of \( \text{C}_3\text{H}_6 \). \( k_1 \) calculated from \( k_{-1}K \).
(g) Based on results of Koike and Gardiner\(^{2} \).
(h) Calculated from \( k(\text{CH}_3 + \text{CH}_2) \) and \( k(\text{C}_2\text{H}_5 + \text{C}_2\text{H}_4) \) and and combination/cross-combination ratio. Tabulated data also presented to allow for pressure dependence.

Preferred Values

\( k_1^{*} = 4.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \) over range 300-800 K
\( k_2/k_1 = 0.04 \)

Reliability

\( \Delta \log k_1 = \pm 0.3 \text{ over range 300-800 K} \)
\( \Delta k_2/k = \pm 0.005 \)

Comments on Preferred Values

The preferred value of \( k_1 \) is from the work of Anastasi and Arthur\(^{4} \) at 308 K, which is the most direct study so far reported. This recommendation is in excellent agreement with the value of \( k_1 \) derived from a study\(^{4} \) of the pyrolysis of \( \text{C}_3\text{H}_8 \) at temperatures near 800 K, and based on a calculated equilibrium constant for the reaction. From these two determinations the temperature coefficient of \( k_1 \) would appear to be negligible. At the same time the preferred value of \( k_1 \) is in reasonable agreement with the value of \( k_1 \) derived by Tsang and Hampson\(^{3} \) on the basis of the values of \( k(\text{CH}_3 + \text{CH}_2) \) and \( k(\text{C}_2\text{H}_5 + \text{C}_2\text{H}_4) \) and the cross-combination/combination ratio of rate coefficients. The preferred value of \( k_2/k_1 \) is from the recommended value of the ratio \( k_2/k_1 = 0.04 \) which has been established from low temperature studies\(^{5} \). In keeping with other disproportionation/combination ratios of rate coefficients, this value of \( k_2/k_1 \) would not be expected to show any marked temperature dependence.

Tsang and Hampson\(^{3} \) have made calculations of the dependence of the value of \( k_1 \) upon concentration and temperature. These become important at temperatures above 1000 K.

References

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ \text{CH}_3 + \text{C}_2\text{H}_5 \rightarrow \text{CH}_4 + \text{C}_2\text{H}_4 \]
\[ \rightarrow \text{C}_2\text{H}_6 \]

\[ \text{T/K} \]

\[ \text{Log}(k/\text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1}) \]

\[ 10^3 \text{T}^{-1}/\text{K}^{-1} \]

EXPERIMENTAL DATA

- Lifshitz and Frenklach (k2) 1975
- Kols and Gardiner (k2) 1980
- Simmie et al (k2) 1980
- Arthur and Anastasi (k2) 1983
- Kanas et al (k2) 1983
- Anastasi and Arthur (k2) 1987
- Anastasi and Arthur (k1) 1987
- Simmie et al (k1) 1980

This Recommendation (k1) 1989
This Recommendation (k2) 1989

**Thermodynamic Data**

\[
\Delta H_{298} = -19.5 \text{ kJ mol}^{-1}
\]

\[
\Delta S_{298} = 14.7 \text{ J K}^{-1} \text{mol}^{-1}
\]

\[
K_p = 1.61 \times 10^{12} T^{-14} \exp(2300/T)
\]

---

**Rate Coefficient Data**

<table>
<thead>
<tr>
<th>[k \text{[cm}^3 \text{molecule}^{-1} \text{s}^{-1}]]</th>
<th>Temperature [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>[3.3 \times 10^{-13} \exp(-5250/T)]</td>
<td>389-567</td>
<td>Trotman-Dickenson et al. (1951)</td>
<td>(a)</td>
</tr>
<tr>
<td>[7.1 \times 10^{-13} \exp(-5710/T)]</td>
<td>435-614</td>
<td>Wijnen (1955)</td>
<td>(b)</td>
</tr>
<tr>
<td>[1.52 \times 10^{-12} \exp(-5810/T)]</td>
<td>519-797</td>
<td>McNesby and Gordon (1955)</td>
<td>(c)</td>
</tr>
<tr>
<td>[5.9 \times 10^{-13}]</td>
<td>1330</td>
<td>Clark et al. (1971)</td>
<td>(d)</td>
</tr>
<tr>
<td>[3.3 \times 10^{-9} \exp(-10800/T)]</td>
<td>1055-1325</td>
<td>Pacey and Purnell (1977)</td>
<td>(e)</td>
</tr>
<tr>
<td>[7.4 \times 10^{-11} \exp(-8770/T)]</td>
<td>980-1130</td>
<td>Yampolskii and Rybin (1974)</td>
<td>(f)</td>
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<tr>
<td>[5.4 \times 10^{-11} \exp(-9060/T)]</td>
<td>1055-1325</td>
<td>Bradley and West (1976)</td>
<td>(g)</td>
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<td>[6.0 \times 10^{-15}]</td>
<td>880</td>
<td>Chen, Back, and Back (1976)</td>
<td>(h)</td>
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<td>[7.8 \times 10^{-15}]</td>
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<td>[19.8 \times 10^{-15}]</td>
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<td>[1.1 \times 10^{-13}]</td>
<td>1206</td>
<td>Lee and Yeh (1979)</td>
<td>(i)</td>
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<td>[6.8 \times 10^{-15}]</td>
<td>902</td>
<td>Pacey and Wimalasena (1984)</td>
<td>(j)</td>
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<tr>
<td>[3.3 \times 10^{-11} \exp(-6800/T)]</td>
<td>1100-1400</td>
<td>Möller et al. (1987)</td>
<td>(k)</td>
</tr>
</tbody>
</table>

**Reviews and Evaluations**

\[1.1 \times 10^{-15} \exp(-12200/T) + 4.2 \times 10^{-15} \exp(-4580/T)\]

\[9.15 \times 10^{-20} T^4 \exp(-4167/T)\]

\[9.3 \times 10^{-13} \exp(-5840/T)\]

\[9.15 \times 10^{-20} T^4 \exp(-4167/T)\]

\[9.15 \times 10^{-20} T^4 \exp(-4167/T)\]

\[4.2 \times 10^{-15} \exp(-4580/T)\]

\[9.15 \times 10^{-20} T^4 \exp(-4167/T)\]

\[9.15 \times 10^{-20} T^4 \exp(-4167/T)\]

\[9.15 \times 10^{-20} T^4 \exp(-4167/T)\]

\[9.15 \times 10^{-20} T^4 \exp(-4167/T)\]

\[9.15 \times 10^{-20} T^4 \exp(-4167/T)\]

**Comments**

(a) Competitive photolysis of acetone-\(d_6\), \(k\) for \(C\text{D}_2\) reaction, relative to \(k(\text{CD}_3 + \text{CD}_3) = 4.15 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\).

(b) Competitive photolysis of acetone-\(d_6\), \(k\) for \(C\text{D}_2\) reaction, relative to \(k(\text{CD}_3 + \text{CD}_3, \text{COCD}_3) = 8.0 \times 10^{-13} \exp(-5760/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\).

(c) Competitive photolysis of acetone-\(d_6\), \(k\) for \(C\text{D}_2\) reaction, relative to \(k(\text{CD}_3 + \text{CD}_3, \text{COCD}_3)\) as in (b). Values of \(k_1\) extrapolated from \(T\) data. If log \(k_1-T\) plot shows upward curvature, values of \(k\) may be too low (see graph).

(d) Shock tube, time-of-flight mass spectrometry, complex system.

(e) Pyrolysis, computer fit of products. Complex system, \(k\) values quoted with considerable error limits, \(\log A = -9.1 \pm 1.0, E = 90 \pm 20 \text{ kJ} \text{ mol}^{-1}\).

(f) Pyrolysis of \(\text{C}_3\text{H}_6 + \text{D}_2\) mixture; competitive technique. Obtained \(k/\langle\text{CH}_3 + \text{D}_2\rangle\). Original values corrected by use of high temperature value of \(k(\text{CH}_3 + \text{D}_2) = 2.3 \times 10^{-11} \exp(-8120/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) based on Tsang and Hampson's recommended value for \(k(\text{CH}_3 + \text{H}_2)\).

(g) Shock tube, computer simulation of reaction products. Value of \(k\) dependent on a number of rate constants.

(h) Thermal decomposition of \(\text{C}_2\text{H}_6\), product analysis, complex system. Value of \(k\) dependent on a number of rate constants.

(i) Ethane pyrolysis, computer simulation of products, complex system. Value of \(k\) dependent on a number of rate constants.

(j) Pyrolysis in flow system giving \(k/\langle\text{CH}_3 + \text{CH}_2\rangle\). \(k\) calculated from \(k(\text{CH}_3 + \text{CH}_2) = 4.15 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\).

(k) Fit to experimental points between 300 and 1350 K.

(l) Simplified BEBO calculation of \(k\) values.

(m) Detailed review of low temperature data.

(n) Recommended without comment.

(o) Recommend the Clark and Dove BEBO calculations in order to relate the high and low temperature data.

(p) Shock-tube determination with UV detection of \(\text{CH}_3\).

**Preferred Values**

\[k = 2.45 \times 10^{-31} T^6 \exp(-3043/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range } 300-1500 \text{ K}\]

**Reliability**

\[\Delta \log k = \pm 0.1 \text{ at } 300 \text{ K rising to } \pm 0.15 \text{ at } 1000 \text{ K and to } \pm 0.2 \text{ at } 1500 \text{ K}\]
Comments on Preferred Values

A sharply curved non-Arrhenius dependence is required to account for the low and high temperature results. The Clark and Dove expression lies above the experimental values at low temperatures, but does give a good fit above 800 K. The preferred value of \( k \) fits at high and low temperature, but lies above the McNesby and Gordon values between 650 and 800 K. However, as pointed out in comment (c), these values of \( k \) may have been seriously underestimated. A \( T^6 \) term is required to explain the curvature observed, although Furue and Pacey suggest a \( T^{2.5} \) expression gives a good fit if tunnelling is considered. For high temperature values (1500-2500 K) Clark and Dove’s expression is recommended (9.15 \times 10^{-25} T^4 \exp(-4167/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}). Non-allowance for fall-off in \( k(CH_3 + CH_3) \) may be responsible for higher than expected values of \( k \) at high temperatures.

References

BAULCH ET AL.

\[ \text{CH}_3 + \text{C}_2\text{H}_6 \rightarrow \text{CH}_4 + \text{C}_2\text{H}_5 \]

T/K

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

10\(^3\)T\(^{-1}\)/K\(^{-1}\)

EXPERIMENTAL DATA
- Yamposkii and Rybin 1974
- Clark et al. 1971
- Tretman-Dickenson et al. 1951
- Wijnen 1933
- McNeaby and Gordon 1955
- Pacey and Purnell 1972
- Bradley and West 1976
- Chen et al. 1976
- Lee and Teh 1979
- Pacey and Wimalasena 1984
- Moller et al. 1987

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EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ \text{CH}_3 + \text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CH}_3\text{CO} \quad (1) \]
\[ \rightarrow \text{CH}_4 + \text{CH}_2\text{CHO} \quad (2) \]

**Thermodynamic Data**

\[ \Delta H_{\text{m}0} (1) = -77.9 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{m}0} (1) = -5.09 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_p (1) = 66.5 T^{-0.416} \exp(+9330/T) \]

\[ \Delta H_{\text{m}0} (2) = -30.2 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{m}0} (2) = -4.0 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_p (2) = 2.93 T^{-0.297} \exp(+3600/T) \]

**Rate Coefficient Data**

<table>
<thead>
<tr>
<th>( k [\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}] )</th>
<th>( T [\text{K}] )</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 2.64 \times 10^{-12} \exp(-4240/T) )</td>
<td>753-813</td>
<td>Liu and Laidler (1968)¹</td>
<td>(a)</td>
</tr>
<tr>
<td>( 3.3 \times 10^{-31} T^{0.9} \exp(-860/T) )</td>
<td>1051-1225</td>
<td>Colket <em>al</em> (1975)²</td>
<td>(b)</td>
</tr>
<tr>
<td>( 6.2 \times 10^{-12} \exp(-3020/T) )</td>
<td>300-525</td>
<td>Kerr and Parsonage (1976)³</td>
<td>(c)</td>
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<tr>
<td>( 6.2 \times 10^{-12} \exp(-3020/T) )</td>
<td>300-525</td>
<td>Warnatz (1984)⁴</td>
<td>(d)</td>
</tr>
</tbody>
</table>

**Comments**

(a) Pyrolysis of CH₃CHO; \( k \) relative to \( k(\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_4) = 3.67 \times 10^{-11} \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1} \)
(b) Pyrolysis of CH₃CHO in 1 atm N₂; \( k \) relative to \( k(\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_4) \)
(c) Based on low temperature relative rate data of Kerr and Calvert, Brinton and Volman, Dodd, Calvert *et al*., Buchanan and McRae, and Birrel and Trotman-Dickenson.
(d) Accepts recommendation of Kerr and Parsonage.

**Preferred Values**

\[ k = 3.3 \times 10^{-30} T^{0.64} \exp(-1240/T) \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1} \text{ over range 300–1250 K} \]

Reliability
\[ \Delta \log k = \pm 0.3 \text{ over range 300–1250 K} \]

**Comments on Preferred Values**

There are no direct studies of the kinetics of this reaction and all of the \( k \) values are relative to methyl recombination. The results of Colket *et al* at \( T > 1000 \text{ K} \) show a significantly greater activation energy than the data from lower temperature and taken with the intermediate temperature data of Liu and Laidler, the rate coefficient clearly shows non-Arrhenius temperature dependence. The large amount of low temperature data is broadly self consistent, although there is a spread of approximately a factor of 2 in the values near 400 K. The preferred values are based on a line constructed through the mean of the low temperature data and the data of Liu and Laidler and Colket *et al*., both of which appear to be reliable relative rate studies. There is no experimental data on the contribution of the second channel. Assuming \( k_2 = 1/2 \) \( k(\text{CH}_3 + \text{C}_2\text{H}_4) \), this channel contributes 1% and 7.8% of the total rate at 500 K and 1000 K respectively.

**References**

BAULCH ET AL.

CH$_3$ + CH$_2$CHO $\rightarrow$ CH$_4$ + CH$_3$CO

$T/K$

Experimantal Data:
- Dodd 1955
- Birneg et al. 1960
- Kerr and Calvert 1965
- Liu and Laidler 1968
- Colket et al. 1975
- This Recommendation 1989

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ \text{CH}_4(+\text{M}) \rightarrow \text{CH}_3 + \text{H}(+\text{M}) \]

**Thermodynamic Data**

\[
\Delta H_{298} = 439 \text{ kJ mol}^{-1} \\
\Delta S_{298} = 123 \text{ J K}^{-1} \text{mol}^{-1} \\
K_p = 5.68 \times 10^5 T^{1.66} \exp\left(-52700/T\right) \text{ atm}
\]

**Rate Coefficient Data**

<table>
<thead>
<tr>
<th>$k$ [s$^{-1}$]</th>
<th>$T$ [K]</th>
<th>$[M]$ [molecule cm$^{-3}$]</th>
<th>Reference</th>
<th>Comments</th>
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<tr>
<td><strong>Thermal Data</strong></td>
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</table>

**Rate Coefficient Measurements**

**Low Pressure Range**

\[
[\text{Ar}] \quad 3.3 \times 10^{-7} \exp(-44800/T) \\
1850-2500 \quad (3.3-90.0) \times 10^{19} \text{ (Ar)} \\
\]

**Intermediate Fall-off Range**

\[
2.5 \times 10^{12} \exp(-48300/T) \\
1850-2500 \quad 3.3 \times 10^{19} \text{ (Ar)} \\
\]

<table>
<thead>
<tr>
<th>$k$ [s$^{-1}$]</th>
<th>$T$ [K]</th>
<th>$[M]$ [molecule cm$^{-3}$]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Rate Coefficient Data</strong></td>
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</table>

**Reference**

Hartig et al. (1971)$^1$
Hartig et al. (1971)$^1$
Dean and Kistiakowsky (1971)$^2$
Napier and Subrahmanyan (1972)$^3$
Vompe (1973)$^4$
Roth and Just (1975)$^5$
Gardiner et al. (1975)$^6$
Chen et al. (1975)$^7$
Bowman (1975)$^8$
Hefington et al. (1977)$^9$
Tabayashi and Bauer (1979)$^10$
Barnes, Pratt, and Wood (1989)$^11$

### Rate Coefficient Data

<table>
<thead>
<tr>
<th>Rate Coefficient Measurements</th>
<th>T[K]</th>
<th>[M] [molecule cm(^{-3})]</th>
<th>Reference</th>
<th>Comments</th>
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<tr>
<td><strong>High Pressure Range</strong></td>
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<tr>
<td>(1.3 \times 10^{15} \exp(-52300/T))</td>
<td>1850-2500</td>
<td>(3.3-90.0) \times 10^{16} (Ar)</td>
<td>Hartig et al. (1971)(^{(a)})</td>
<td></td>
</tr>
<tr>
<td>(2.8 \times 10^{16} \exp(-54100/T))</td>
<td>995-1103</td>
<td>(0.43-7.2) \times 10^{16} (CH(_4))</td>
<td>Chen et al. (1975)(^{(g)})</td>
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<tr>
<td>(1.75 \times 10^{16} \exp(-53000/T))</td>
<td>1073-1148</td>
<td>(3.2-33.4) \times 10^{16} (CH(_4))</td>
<td>Barnes, Pratt, and Wood (1989)(^{(k)})</td>
<td></td>
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<tr>
<td><strong>Reviews and Evaluations</strong></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>(k_\omega = 2.9 \times 10^{15} \exp(-52200/T))</td>
<td>-</td>
<td></td>
<td>Benson and Orq Neal (1970)(^{(I)})</td>
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<tr>
<td>(k_\omega = 1.0 \times 10^{15} \exp(-50500/T))</td>
<td>1000-3000</td>
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<td>Warnatz (1984)(^{(m)})</td>
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<tr>
<td>(k_\omega = 3.7 \times 10^{15} \exp(-52200/T))</td>
<td>300-2500</td>
<td></td>
<td>Tsang and Hampson (1986)(^{(n)})</td>
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<tr>
<td>(k_\omega = 3.7 \times 10^{17} \exp(-52782/T))</td>
<td>300-2500</td>
<td></td>
<td>Stewart et al. (1989)(^{(o)})</td>
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<tr>
<td>(k_0 = [\text{Ar}] 1.2 \times 10^{16} \exp(-47000/T))</td>
<td>1000-3000</td>
<td></td>
<td>Cobos and Troe (1990)(^{(p)})</td>
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<tr>
<td>(k_\omega = 2.4 \times 10^{16} \exp(-52800/T))</td>
<td>1000-3000</td>
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<tr>
<td>(F_\omega(\text{Ar}) = \exp(-0.45-T/3231))</td>
<td>1000-3000</td>
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</tbody>
</table>

### Comments

(a) Shock wave study of CH\(_4\)/Ar mixtures. The reaction was followed by infrared emission of CH\(_4\) and by infrared emission and ultraviolet absorption of the formed species.
(b) Shock wave study of CH\(_4\)/O\(_2\)/CO/Ar mixtures. The reaction was followed by measuring infrared emissions from CO and O\(_2\).
(c) The CH\(_4\) pyrolysis was investigated by a shock waves technique.
(d) Shock wave study of CH\(_4\)/Ne mixtures. The reaction was analysed by time-of-flight mass spectrometry.
(e) Direct measurements of the time dependent H atom concentration during the pyrolysis of CH\(_4\)/Ar mixtures using shock waves technique.
(f) Pyrolysis of CH\(_4\) in shock waves. The reaction was followed by time-of-flight mass spectrometry, infrared laser absorption, and laser schlieren technique.
(g) Pyrolysis of CH\(_4\) in a static system. Initial rates based on analysis of H\(_2\), C\(_2\)H\(_6\), and C\(_2\)H\(_4\). \(k_\omega\) values extrapolated with RRKM theory.
(h) Shock waves study of CH\(_4\)/O\(_2\)/Ar mixtures. Reaction followed by absorption measurements of OH and by emission from the chemiluminescent reaction O + CO.
(i) Shock waves study of CH\(_3\) pyrolysis. The reaction was followed monitoring the CH\(_4\) emission and absorption at 3.392 μm.
(j) Shock waves measurements of CH\(_4\)/Ar mixtures. Modelling of 12 reactions.
(k) Pyrolysis of CH\(_4\) at very early stages (0.003-0.05% reaction) in a quartz-lived flow reactor. Reactant and products (ethyne, ethylene, acetylene, and propylene) detected by gas chromatography.
(l) Review of literature previous to 1966.
(m) Review of literature previous to 1980.

(n) The \(k_\omega\) recommended is based on the Hartig et al.\(^{(a)}\) results scaled up by a factor 3.
(o) Single-channel hindered Gorin model RRKM calculations of the CH\(_4\) decomposition with a fit to experimental results.
(p) The experiments by Hartig et al.\(^{(a)}\) have been re-evaluated taking into account the increasing amount of IR emissions from species other than CH\(_4\) such as documented in Ref. 1. These corrections become most pronounced in the high pressure experiments. The theoretical calculations were done using the \(k_0\) formalism from Ref. 16, fall-off expression from Ref. 17, and SACM-modified PST calculations from Ref. 18 which lead to a nearly temperature independent value of \(k_\omega\) for the reverse recombination H + CH\(_3\) → CH\(_4\) of 3.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.

### Preferred Values

\[
k_0 = [\text{Ar}] 1.2 \times 10^{-6} \exp(-47000/T) \text{ s}^{-1} \text{ over range } 1000-3000 \text{ K}
\]

\[
k_0 = [\text{CH}_4] 1.4 \times 10^{-5} \exp(-48100/T) \text{ s}^{-1} \text{ over range } 1000-2000 \text{ K}
\]

\[
k_\omega = 2.4 \times 10^{16} \exp(-52800/T) \text{ s}^{-1} \text{ over range } 1000-3000 \text{ K}
\]

\[
F_\omega = \exp(-0.45-T/3231) \text{ for } M = \text{Ar}
\]

\[
F_\omega = \exp(-0.37-T/2210) \text{ for } M = \text{CH}_4
\]

### Reliability

\[
\Delta \log k_0 = \pm 0.3 \text{ over range } 1000-3000 \text{ K}
\]

\[
\Delta \log k_\omega = \pm 0.5 \text{ over range } 1000-3000 \text{ K}
\]

\[
\Delta F_\omega = \pm 0.1 \text{ over range } 1000-3000 \text{ K}
\]

### Comments on Preferred Values

The preferred values for \(k_0\) are taken from the comparison of the experimental data from Refs. 1, 5, 7, 8-10 with the theoretical modelling from Ref. 16. This is based on the assumption of nearly temperature independent
EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ \beta_c = 0.11 \text{ for } M = \text{CH}_4 \text{ and } \beta_c = 0.03 \text{ for } M = \text{Ar} \] which was rationalized by very inefficient energy transfer and a positive temperature coefficient of \( <\Delta E> \) at low temperatures. The preferred values of \( k_\alpha \) are consistent with a nearly temperature independent \( k_\alpha \) of \( 3.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) for the reverse recombination \( \text{H} + \text{CH}_3 \rightarrow \text{CH}_4 \). Since the evaluation of the high pressure data from Ref. 1 there appears to be no experimental evidence for a stronger negative temperature coefficient of \( k_\alpha \) for the recombination such as was suggested in Ref. 15. Recent theoretical models based on realistic potential energy surfaces have all predicted temperature coefficients consistent with the presently preferred values (see e.g. Cobos$^{16}$).

References

BAULCH ET AL.

CH$_4$ + Ar $\rightarrow$ CH$_3$ + H + Ar

EXPERIMENTAL DATA

- Heffington et al. (1977)
- Bowman (1975)
- Roth and Just (1975)
- Tabayerki and Bauer (1979)
- Hartig et al. (1971)
- Re-evaluated: Cobos and Troe (1989)

T = 2200

This Recommendation 1989

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

CHO + O₂ → HO₂ + CO  (1)
→ OH + CO₂  (2)
→ HCO₂  (3)

Thermodynamic Data

\[ \Delta H_{298}^{\circ} (1) = -144 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298}^{\circ} (1) = -3.03 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ K_p(1) = 2.5 \times 10^{-178} \exp (+17200/T) \]

\[ \Delta H_{298}^{\circ} (2) = -398 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298}^{\circ} (2) = -32.2 \text{ JK}^{-1} \text{mol}^{-1} \]
\[ K_p(2) = 2.65 \times 10^{11} \times 10^{-58} \exp (+47960/T) \]

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

<table>
<thead>
<tr>
<th>( k ) [cm³ molecule⁻¹ s⁻¹]</th>
<th>( T ) [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 5.0 \times 10^{-11} )</td>
<td>1400-1800</td>
<td>Peeters and Mahnken (1973)⁵</td>
<td>(a)</td>
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<tr>
<td>( 5.7 \times 10^{-12} )</td>
<td>297</td>
<td>Washida, Martins, and Buyca (1974)⁶</td>
<td>(b)</td>
</tr>
<tr>
<td>( 1.3 \times 10^{-11} )</td>
<td>2000</td>
<td>Tsuboi (1976)⁷</td>
<td>(c)</td>
</tr>
<tr>
<td>( k_2/k_1 = 5 )</td>
<td>266-298</td>
<td>Osif and Heicklen (1976)⁸</td>
<td>(d)</td>
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<tr>
<td>( k_2/k_1 &lt; 0.19 )</td>
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<tr>
<td>( 5.6 \times 10^{-17} )</td>
<td>296</td>
<td>Shibuya et al. (1977)⁹</td>
<td>(e)</td>
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<tr>
<td>( 5.5 \times 10^{-12} \exp (-3522/T) )</td>
<td>1000-1350</td>
<td>Westbrook et al. (1977)¹⁰</td>
<td>(f)</td>
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<tr>
<td>( 4.0 \times 10^{-12} )</td>
<td>296</td>
<td>Reilly et al. (1978)¹¹</td>
<td>(g)</td>
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<tr>
<td>( k_3 = 1.2 \times 10^{-30} [M] )</td>
<td>298</td>
<td>Horowitz, Su, and Calvert (1978)¹²</td>
<td>(h)</td>
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<tr>
<td>( 4.0 \times 10^{-12} )</td>
<td>298</td>
<td>Nadroshenko et al. (1979)¹³</td>
<td>(i)</td>
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<tr>
<td>( 5.5 \times 10^{-11} \exp (-\text{4}) )</td>
<td>298-503</td>
<td>Veyret and Lesclaux (1981)¹⁴</td>
<td>(j)</td>
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<tr>
<td>( 5.8 \times 10^{-12} )</td>
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<td>Cherian et al. (1981)¹⁵</td>
<td>(k)</td>
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<td>( 5.2 \times 10^{-12} )</td>
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<td>Temp and Wagner (1984)¹⁶</td>
<td>(l)</td>
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<tr>
<td>( k_2/k_\text{gas} &lt; 4 \times 10^{-3} )</td>
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<td>( k_2/k_\text{gas} &lt; 0.07 )</td>
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<td>Langford and Moore (1984)¹⁷</td>
<td>(m)</td>
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<td>Vandooreen et al. (1986)¹⁸</td>
<td>(n)</td>
</tr>
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<td>( 4.5 \times 10^{-11} \exp (-600/T) )</td>
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<tr>
<td>( 1.3 \times 10^{-11} \exp (-205/T) )</td>
<td>295-713</td>
<td>Timonen et al. (1988)¹⁹</td>
<td>(o)</td>
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</tbody>
</table>

Comments

(a) Investigation of lean and stoichiometric CH₄/O₂/Ar flames burning at 40 Torr; concentration measurements by molecular beam sampling - mass spectrometry. O₂ considered as the only reaction partner of CHO.

(b) Discharge-flow system; total pressure near 4 Torr. [CHO] measured during the reaction of CH₄ with O atoms by photoionization mass spectrometry. Addition of O₂ resulted in a decrease of the steady-state concentration of CHO.

\( k(\text{CHO} + \text{O}_2)/k(\text{CHO} + \text{O}) = 2.7 \times 10^{-2} \). Given value of \( k \) based on \( k(\text{CHO} + \text{O}) = 2.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \).

(c) Computer simulation of a 39 reaction mechanism and comparison with experimental induction periods and concentration profiles.

(d) Photolysis of C₆H₅CH₂O₃/Ar mixtures. [CO] and [CO₂] by gas chromatography, [HCOOH] by IR spectroscopy. Total pressures 62-704 Torr (298 K) and 344-688 Torr (266 K). Reaction (3) was found to be in the second-order region. No indication of a total pressure effect in [HCOOH].

(e) Flash photolysis of acetaldehyde in He with small amounts of O₂ (\( \lambda > 200 \text{ nm} \)). [CHO] monitored by absorption around 613.8 nm. Total pressures in the range 10-530 Torr; no pressure dependence of \( k \) within the experimental limits.

(f) Computer modelling of 56 reaction mechanism for the reaction of dilute moist CO in air and of dilute CH₄ in air at atmospheric pressure. Comparison with experimental concentration profiles of stable species obtained by gas chromatography of quenched samples.

(g) Near-UV laser photolysis of CH₃O₂ mixtures; intracavity laser spectroscopy of CHO absorbance near 614 nm. Total pressure near 10 Torr.

(h) Photolysis of CH₃O at 313 nm in the presence of O₂. Gas chromatographic analysis of products. Total pressure 7-8 Torr CH₃O. Computer simulation of a 20 reaction mechanism.

(i) Photolysis of CH₃O or CH₃CHO in the presence of O₂. Intracavity laser spectroscopy of CHO ab-
sorbance. No pressure dependence observed between 13 and 100 Torr.

(j) Flash photolysis of CH₂O or CH₃CHO; total pressures 45 and 500 Torr. [CHO] by resonance absorption at 614.5 nm.

(k) Computer modelling of 27 reaction mechanism and comparison of burning velocities of premixed CH₄/air flames.

(l) Discharge-flow reactor; [CHO], [HO₂], and [OH] monitored by laser magnetic resonance. Total pressures 1.3–4.1 mbar. Channel (1) was found to be predominant.

(m) Laser photolysis of formaldehyde or glyoxal; total pressures up to 1000 Torr N₂. [CHO] by resonance absorption. No pressure dependence observed. k increased for reaction of DCA indicating that the reaction occurs via formation of a HCOO₂ adduct and not by simple hydrogen abstraction.

(n) Study of lean CH₂O/O₂ flames burning at 22.5 Torr by molecular beam sampling coupled with mass spectrometric analysis. Combination of their experimental results with the low temperature value \( k(300 \text{ K}) = 5.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) gave the temperature dependent rate parameters.

(o) Flash photolysis of CH₃CHO, photoionisation mass spectrometry.

Preferred Values

\[ k = 5.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range 300–2500 K} \]

Reliability

\[ \Delta \log k = \pm 0.3 \text{ over range 300–2500 K} \]

Comments on Preferred Values

A temperature independent recommendation is given because the temperature dependent measurements give no or only a very weak dependence.¹ⁱ,¹⁶

References


CHO + O₂ → HO₂ + CO
→ OH + CO₂
→ HCO₃

**EVALUATED KINETIC DATA FOR COMBUSTION MODELLING**

\[
\text{Log}(k/\text{cm}^3\text{molecule}^{-1}\text{~s}^{-1})
\]

\[
10^3T^{-1}/K^{-1}
\]

**EXPERIMENTAL DATA**
- Bosevich et al. 1971
- Peeters and Mahnen 1973
- Vondyayn et al. 1974
- Mannan et al. 1974
- Teubl 1976
- Shibuya et al. 1977
- Westbrook et al. 1977
- Reilly et al. 1978
- Clark et al. 1978
- Hristovnev et al. 1978
- Veyss et Leclaus 1981
- Cherlon et al. 1981
- Temps and Wagner 1984
- Longford and Moore 1984
- Vandooren et al. 1986
- Timonen et al. 1988
- Vandooren et al. 1986
- Temps and Wagner (k2) 1984
- Temps and Wagner (k3) 1984
- This Recommendation 1989

Thermodynamic Data

\[
\Delta H_{\text{fus}}(1) = -329 \text{ kJ mol}^{-1} \\
\Delta S_{\text{fus}}(1) = -32.9 \text{ J K}^{-1} \text{mol}^{-1} \\
K_c(1) = 2.98 \times 10^{-2} T^{-0.167} \exp(\frac{37773}{T})
\]

Rate Coefficient Data

<table>
<thead>
<tr>
<th>(k [\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}])</th>
<th>(T [\text{K}])</th>
<th>Reference</th>
<th>Comments</th>
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<td>(3-10) \times 10^{-11}</td>
<td>298</td>
<td>Reilly \textit{et al.} (1978)</td>
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<td>Hochanadel, Sworsky, and Ogren (1980)</td>
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<td>Veyret, Lesclaux, and Roussel (1984)</td>
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<td>Temps and Wagner (1984)</td>
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<td>Baggott \textit{et al.} (1986)</td>
<td>(f)</td>
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</table>

Comments

(a) Near-UV pulsed photolysis of formaldehyde; intracavity dye laser spectroscopy of CHO absorption at 613.8 nm or 614.5 nm. Total pressure 10 Torr pure formaldehyde. Fitting of a kinetic scheme. Large error limits due to non-uniform distribution of CHO in the reaction cell.

(b) Pulse photolysis of acetaldehyde in Ar; total pressures 10-200 Torr. Intracavity dye laser spectroscopy of CHO.

(c) Flash photolysis of H2O in the presence of CO; total pressures 1-3 atm CO, [CHO] and [CH3] monitored by UV absorption. Modelling of a 17 reaction mechanism.

(d) Flash photolysis of CH2O; [CHO] monitored by resonance absorption at 614.5 nm. Total pressures 10-20 Torr. No temperature dependence observed. The initial absolute concentrations of radicals were determined by measuring the yields of molecular hydrogen using mass spectrometry in the presence and in the absence of hydrogen atom scavengers.

(e) Isothermal discharge-flow reactor; total pressures 1.4-4.5 mbar. [CHO], [HO2], and [OH] monitored by far-infrared laser magnetic resonance.

(f) Laser flash photolysis of glyoxal or formaldehyde at 308 nm; time-resolved dye laser absorption of CHO at 614.6 nm. Pressure range 10-30 Torr. Discrepancies with other results ascribed to differences in the measured absorption cross section of CHO.

Preferred Values

\[k = 5.0 \times 10^{-11} \text{ at 300 K} \]

Reliability

\[\Delta \log k = \pm 0.3 \text{ at 300 K} \]

Comments on Preferred Values

The recommended value and error limits cover scattered data available.

References

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

HCHO(+M) → CHO + H(+M) (1)
→ CO + H₂(+M) (2)

Thermodynamic Data

\[ \Delta H_{298}^\circ (1) = 377 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298}^\circ (1) = 121 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_p(1) = 1.19 \times 10^9 T^{-10.5} \exp(-45400/T) \text{ atm} \]
\[ \Delta H_{298}^\circ (2) = 5.3 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298}^\circ (2) = 109.3 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_p(2) = 1.36 \times 10^5 T^{0.37} \exp(-895/T) \text{ atm} \]

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

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<tr>
<td>8.0 \times 10^{-8} \exp(-36300/T) [M]</td>
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<td>Schechter and Jost (1969)¹</td>
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<tr>
<td>3.5 \times 10^{-8} \exp(-17700/T) [M]</td>
<td>1350–1900</td>
<td>Peeters and Mahnen (1973)²</td>
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<tr>
<td>1.7 \times 10^{-10} \exp(-43800/T) [M]</td>
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<td>2.2 \times 10^{-8} \exp(-35600/T) [M]</td>
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<td>Bhaskaran et al. (1979)⁴</td>
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<tr>
<td>6.0 \times 10^{-7} \exp(-4380/T) [M]</td>
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<td>Dean et al. (1979)⁴</td>
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<tr>
<td>5.5 \times 10^{-4} \exp(-4800/T) [M]</td>
<td>1600–3000</td>
<td>Dean et al. (1980)⁶</td>
<td>(f)</td>
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<td>4.2 \times 10^{-11} \exp(-14600/T) [M]</td>
<td>1400–2000</td>
<td>Vandooren and Van Tiggelen (1981)⁷</td>
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<tr>
<td>5.25 \times 10^{-5} \exp(-37700/T) [M]</td>
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<td>Saito et al. (1985)⁸</td>
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<tr>
<td>( k_1 = 2.08 \times 10^{-8} \exp(-39171/T) [M] )</td>
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<td>Rimpel and Just (1988)⁹</td>
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<td>( k_2 = 5.18 \times 10^{-16} \exp(-28100/T) [M] )</td>
<td>1900–2400</td>
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</table>

Reviews and Evaluations

| \( 8.3 \times 10^{-8} \exp(-38500/T) [M] \) | 1000–3000 | Warnatz (1984)¹⁰ | (j) |
| 2.0 \times 10^{17} T^{-4.6} \exp(-48500/T) [M] | 1000–3000 | Tsang and Hampson (1986)¹¹ | (k) |

Comments

(a) Shock tube study of thermal decomposition of HCHO. Analysis by UV and IR absorption.
(b) Thermal decomposition of HCHO in a flame. Mass spectrometric analysis.
(c) Thermal decomposition of HCHO in a flow reactor. Gas chromatographic analysis.
(d) Shock tube study of HCHO decomposition. Analysis by resonance absorption.
(e) HCHO decay behind reflected shock wave monitored by IR emission.
(f) HCHO/O₂/Ar and HCHO/N₂/Ar mixtures investigated behind reflected shock waves; HCHO detected by IR emission. M = Ar.
(g) Thermal decomposition of HCHO in a flame. Mass spectrometric analysis.
(h) Thermal decomposition of HCHO behind reflected shock waves. HCHO decay and CO production determined by IR emission. H atom production measured by ARAS. M = Ar. Channel (2) appeared to have a smaller rate under the experimental conditions.
(i) Thermal decomposition of HCHO behind reflected shock wave. H atom production measured by ARAS. M = Ar.
(j) Based on the shock tube data of Schechter and Jost¹, Bhaskaran et al.⁴, and Dean et al.⁵,⁶.
(k) Theoretical calculation of \( k_1 \) in Ar using RRKM theory.

Preferred Values

\( k_0(1) = 2.1 \times 10^{-8} \exp(-39200/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) over range 1500–2500 K

Reliability

\( \Delta \log k_0(1) = \pm 0.3 \) over range 1500–2500 K

Comments on Preferred Values

The more recent shock tube data are in reasonable agreement near 2000 K and both Saito et al.⁵ and Rimpel and Just⁹ quote expressions for \( k_0(1) \). Rimpel and Just give an expression for \( k_0(2) \) for the molecular channel, which gives rates faster than obtained for \( k_0(1) \) at temperatures near 2000 K, while Saito et al.⁵ suggest that channel (2) is slower. The situation regarding channel (2) is therefore unclear and we are unable to recommend values for \( k_0(2) \). The preferred expression for \( k_0(1) \) is that of Rimpel and Just which gives values consistent with the other recent studies over the temperature range specified. The reaction is second order under all conditions where it has been studied and there is no information on fall-off.

References

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BAULCH ET AL.

6A. M. Dean, R. L. Johnson, and D. C. Steiner, Comb. Flame 37, 41 (1980).
EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

HCHO + M → HCO + H + M
→ H₂ + CO + M

EXPERIMENTAL DATA

- Schecker and Jestl 1969
- Peeters and Mohren 1973
- Aronowitz et al. 1977
- Shapivan et al. 1979
- Dean et al. 1979
- Dean et al. 1980
- Vanders and van Tiggelen 1981
- Sato et al. 1985
- Rempel and Juul (V2) 1989
- Rempel and Juul (P1) 1989

This Recommendation (K1) 1989
Rate Coefficient Measurements

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<td>453</td>
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<td>Westbrook and Dryer (1979) (^2)</td>
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<td>Pagsberg et al. (1989) (^13)</td>
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Comments

(a) The rate coefficient for \( \text{CH}_3\text{OH} + \text{O} \) was measured between 350–800 K in a discharge flow reactor under very large \((=10^{15} \text{molecule cm}^{-3})\) concentrations of both reactants. The residence time was poorly defined. \( k \) was derived by simulating the stable endproduct profiles as measured at 453 K. Therefore, the value on \( k \) is probably unreliable. It is quoted again in Ref. 2.

(b) The quoted expression has been used to simulate the profiles of stable endproducts, as measured for methanol oxidation in a turbulent flow reactor.

(c) Discharge flow reactor with \( \text{CH}_3\text{OH} + \text{Cl} \) as \( \text{CH}_3\text{OH} \) source. Title reaction was isolated. \( k \) was obtained from relative \( \text{HO}_2 \) measurements (LMR) by varying the \( \text{O}_2 \) concentration for a fixed residence time. This actually yields \( k \) relative to the wall loss rate coefficient. This may introduce a considerable error. Radford was the first to show that this reaction is much faster than the corresponding \( \text{CH}_3\text{O} + \text{O}_2 \). Since then \( \text{CH}_3\text{OH}/\text{Cl}/\text{O}_2 \) has been widely used as \( \text{HO}_2 \) source.

(d) Mass spectrometric investigation of three low pressure \((53 \text{ mbar})\) methanol flames \((\phi = 0.89, 0.36, 0.21)\). Aside from other labile species, \( \text{CH}_2\text{OH}/\text{CH}_3\text{O} \) has been detected. Unfortunately, the latter two species could not be discriminated and their calibration seems somewhat unclear.

(e) Shock tube at densities between \(6 \times 10^{18}\) and \(1.2 \times 10^{20} \text{ molecules cm}^{-3}\), Ar. Highly diluted methanol oxygen mixtures \((\phi = 0.2 \text{ to } 2.0)\). Profiles for \( \text{CH}_3\text{OH}, \text{H}_2\text{O}, \text{CO}_2, \text{CO}, \text{and} \text{CH}_3\text{O} \) were measured by IR emission. \( k \) was obtained by simulating the system.

(f) Calculation study of the burning velocity of methanol/air mixtures. Title reaction is one of the 40 reaction set. This expression for \( k \) is also recommended in Ref. 8.

(g) Discharge flow reactor. Method very similar to Ref. 4 with the exception that \( \text{HO}_2 \) was monitored by \( \text{OH} (A^2\Sigma \rightarrow X^2\Pi) \) photofragment emission. See comment (c) for disadvantages of the method. Further problems might have been introduced by the use of very high \((=10^{14} \text{ molecules cm}^{-3})\) initial \( \text{Cl}_2 \) concentrations, so that subsequent reactions like \( \text{CH}_3\text{OH} + \text{Cl} \) and \( \text{CH}_2\text{OH} + \text{CH}_3\text{O} \) might have played a role which was not accounted for.

(h) Discharge flow reactor. Source: \( \text{CH}_3\text{OH} + \text{Cl} \). Title reaction was isolated. \( k \) from \( \text{CH}_3\text{OII} \) profiles, measured by a mass spectrometer. From absolute \( \text{CH}_3\text{O} \) measurements, it was concluded that this channel is major.

(i) Method as above (h), however \( \text{CH}_3\text{OH} \) monitored by LMR. From \( \text{HO}_2 \) built-up rates, it was concluded, that the \( \text{HO}_2 + \text{CH}_3\text{O} \) channel is major. No pressure dependence for \( k \) in the range 0.7 to 6.5 mbar. This led to the suggestion that the reaction proceeds via an excited state of a bound intermediate.

(j) Method as above. Mass spectrometric \( \text{CH}_3\text{OII} \) detection.

(k) Method as above. Significant non-Arrhenius behaviour of \( k \) in the temperature range used. This led...
EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

(1) Method as above. Extension to temperatures below ambient. Large intercepts in the $k^1$ vs. $[O_2]$ plots may indicate a wall problem, particularly at lower temperatures.

(m) Static reactor, 1000 mbar, Ar. CH$_3$OH source was CH$_3$OH + F. F atoms were produced from pulse radiolysis of SF$_6$. CH$_2$OH detection by UV absorption.

Preferred Values

$$k_1 = 2.6 \times 10^{-9} \ T^{-1} + 1.2 \times 10^{-10} \ \exp(-1800/T) \ \text{cm}^3 \ \text{molecule}^{-1} \ \text{s}^{-1} \ \text{over range 300-1200 K}$$

Reliability

$\Delta \log k_1 = \pm 0.1$ at 300 K increasing to $\pm 0.3$ at 1000 K

Comments on Preferred Values

For the six most recent studies there is an excellent agreement at ambient temperature. The low temperature branch of Ref. 13 has been slightly adjusted to yield the mean of these studies.

For the abstraction channel a common fit for the measurements of Ref. 5 and Ref. 13 has been used.

For temperature below ambient, no recommendation is possible.

References

CH$_2$OH + O$_2$ → CH$_2$O + HO$_2$

**Experimental Data**

- Baulch et al. 1975
- Westbrook and Dryer 1979
- Radford 1980
- Vandooren and van Tiggelen 1980
- Taubal and Hashimoto 1981
- Dove and Warnatz 1983
- Wang et al. 1984
- Grotheer et al. 1985
- Dobe et al. 1985
- Payne et al. 1988
- Grotheer et al. 1988
- Nesbitt et al. 1988
- Anastasi et al. 1988
- Avromenko and Kolesnikova 1981
- Avromenko and Kolesnikova 1981
- This Recommendation 1989

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\( \text{CH}_3\text{O}(+\text{M}) \rightarrow \text{HCHO} + \text{H}(+\text{M}) \)

**Thermodynamic Data**

\[ \Delta H_{298} = 85.8 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298} = 105 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ k_c = 6.67 \times 10^9 \text{ T}^{0.57} \exp(-10300/T) \text{ atm} \]

**Rate Coefficient Data**

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<tr>
<th>( k ) [s(^{-1})]</th>
<th>( T ) [K]</th>
<th>Reference</th>
<th>Comments</th>
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<td>N/A Batt (1987) (^3)</td>
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<td>1.7 \times 10^{-16} \exp(-12640/T), ([\text{M}] = \text{N}_2)</td>
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<td>300–2000 Tsang and Hampson (1986) (^5)</td>
<td>(d)</td>
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</tbody>
</table>

**Comments**

(a) Based on the thermochemistry and estimated \( A \) factor.
(b) Theoretical prediction using RRKM theory and taking into account fall-off effects. Similar treatment for \( \text{CH}_3\text{OH} \) decomposition.
(c) Based on the interpretation of complex mechanisms in shock tube studies of Bowman \(^6\), Brabbs and Brokaw \(^6\), and Tsuboi and Hashimoto \(^8\), and flow system studies of Westbrook and Dryer \(^7\).
(d) Based on \( k_c \) from Ref. 1 and RRKM calculations. Strong collision value given, as well as collision efficiency effects in tabular form.

**Preferred Values**

\[ k_0 = 3.16 \times 10^5 \text{ T}^{-2.7} \exp(-15400/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

over range 300–1000 K

**Reliability**

\( \Delta \log k = \pm 1.0 \)

**Comments on Preferred Values**

There are no direct measurement on this reaction. The reaction is under practically all conditions in combustion systems in the second-order region. The recent estimates of Greenhill \textit{et al.} \(^2\) and Tsang and Hampson \(^5\) are in moderately good agreement and give values of \( k_0 \) which are considerably higher than earlier estimates. The recommendation of Tsang and Hampson is accepted. The recommended expression is the strong collision rate coefficient. For collision efficiency effects refer to Tsang and Hampson \(^5\).

**References**

\(^1\) L. Batt, Int. J. Chem. Kin. 11, 977 (1979)
Thermodynamic Data

\[ \Delta H_{\text{fus}} = -122 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{fus}} = 14.1 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_p = 4.63 T^{-0.28} \exp(+14500/T) \]

Rate Coefficient Data

<table>
<thead>
<tr>
<th>Rate Coefficient Measurements</th>
<th>T [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.05 \times 10^{-13} \exp(-1310/T)</td>
<td>413–628</td>
<td>Gutman, Sanders, and Butler (1982)</td>
<td>(a)</td>
</tr>
<tr>
<td>5.5 \times 10^{-14} \exp(-1000/T)</td>
<td>298–450</td>
<td>Lorenz et al. (1985)</td>
<td>(b)</td>
</tr>
</tbody>
</table>

Reviews and Evaluations

<table>
<thead>
<tr>
<th>Rate Coefficient Measurements</th>
<th>T [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1 \times 10^{-12} \exp(-1310/T)</td>
<td>298–630</td>
<td>CODATA (1984)</td>
<td>(c)</td>
</tr>
<tr>
<td>1.66 \times 10^{-11} \exp(-3610/T)</td>
<td>300–3000</td>
<td>Wamatz (1984)</td>
<td>(d)</td>
</tr>
<tr>
<td>1.1 \times 10^{-13} \exp(-1310/T)</td>
<td>413–608</td>
<td>Tsang and Hampson (1986)</td>
<td>(e)</td>
</tr>
<tr>
<td>3.9 \times 10^{-14} \exp(-900/T)</td>
<td>200–300</td>
<td>NASA (1987)</td>
<td>(f)</td>
</tr>
</tbody>
</table>

Comments

(a) Laser photolysis of CH3ONO at 266 nm; CH3O monitored by LIF. Pseudo first order conditions with excess O2.
(b) Laser photolysis of CH3ONO at 248 nm; CH3O decay in excess O2 monitored by LIF. k independent of pressure between 100 and 200 mbar.
(c) Based on data of Gutman et al. and earlier relative rate studies.
(d) Based on earlier relative rate studies and estimates of k from shock tube and other high temperature studies.
(e) Accepts the recommendation from CODATA.
(f) Based on data of Lorenz et al.

Preferred Values

\[ k = 6.7 \times 10^{-14} \exp(-1070/T) \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \text{ over range } 300-1000 \text{ K} \]

Reliability

\[ \Delta \log k = \pm 0.2 \text{ at } 500 \text{ K increasing to } \pm 0.3 \text{ at } 300 \text{ K and } 1000 \text{ K} \]

Comments on Preferred Values

The new data from Lorenz et al. extend the temperature range for which direct measurements of k are available down to room temperature. The agreement with earlier relative rate measurements at 298 K is reasonable and both sets of direct measurements agree well near 450 K. The temperature dependence in the new study is lower than that found by Gutman et al., which may indicate non-Arrhenius behaviour; however, in view of the limited range covered by the data and the uncertainties, we recommend an Arrhenius expression obtained by least squares fit to the data of Gutman et al. and Lorenz et al., applicable up to 1000 K.

References

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[
\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2
\]

\[\log(k/\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1})\]

\[10^3T^{-1}/K^{-1}\]

EXPERIMENTAL DATA
- Gutman et al 1982
- Lorenz et al 1985
- Batt and Robinson 1979
- Cox et al 1980
- Alcock and Milne 1975
- Weaver et al 1975
- Barker et al 1977
- Kirsch and Parkes 1977
- Selby and Waddington 1977
- This Recommendation 1989
### Thermodynamic Data

CH$_3$OOH($+\text{M}$) $\rightarrow$ CH$_3$O + OH($+\text{M}$)

\[ \Delta H_{298}^\circ = 180 \text{ kJ mol}^{-1} \]

### Rate Coefficient Data

<table>
<thead>
<tr>
<th>$k$ [s$^{-1}$]</th>
<th>$T$ [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Rate Coefficient Measurements</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_\infty$ = 1.0$\times$10$^{11}$ exp($-16360/T$)</td>
<td>565–651</td>
<td>Kirk (1965)$^1$</td>
<td>(a)</td>
</tr>
<tr>
<td>$k_\infty$ $\ll$ 0.0085</td>
<td>553</td>
<td>Kaiser et al. (1986)$^2$</td>
<td>(b)</td>
</tr>
<tr>
<td><strong>Reviews and Evaluations</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_\infty$ = 4$\times$10$^{14}$ exp($-21640/T$)</td>
<td>N/A</td>
<td>Benson (1981)$^3$</td>
<td>(c)</td>
</tr>
</tbody>
</table>

### Comments

(a) Pyrolysis of CH$_3$OOH in gas phase by toluene carrier method.

(b) Static pyrolysis of CH$_3$OOH; mass spectrometric detection of parent ion. Upper limit value. Recommended expression based on estimate by Benson$^4$ of activation energy of 190 kJ mol$^{-1}$ was 6.5$\times$10$^{14}$ exp($-21640/T$) s$^{-1}$.

(c) Based on thermochemistry together with an assumed temperature independent value for the reverse reaction.

### Preferred Values

$k_\infty$ = 4$\times$10$^{12}$ exp($-21600/T$) s$^{-1}$ over range 400–1000 K

### Reliability

\[ \Delta \log k_\infty = \pm 0.5 \text{ at } 600 \text{ K increasing to } \pm 1.0 \text{ at the end of range} \]

### Comments on Preferred Values

The earlier experimental data of Kirk give low values of both the activation energy and the $A$ factor compared with those expected from thermochemical kinetic considerations$^4$. The author reported problems with heterogeneous reactions and these also are a potential problem in the work of Kaiser et al.$^7$. The preferred values are based on experimentally derived Arrhenius expressions for decomposition of C$_7$-hydroperoxides$^4$, which agrees, within the stated uncertainty, with the value of $k_\infty$ estimated from thermodynamic considerations. The main uncertainty arises from the unknown effects of fall-off on the rate at the temperatures where this reaction is important (500–700 K), which are almost certainly quite substantial, but not enough to account for the very low values of $A$ and $E_a$ reported by Kirk$^1$.

### References

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

CN + O₂ → NCO + O

**Thermodynamic Data**

\[ \Delta H_{\text{rev}} = -26.0 \text{kJ mol}^{-1} \]

\[ \Delta S_{\text{rev}} = -14.5 \text{ J K}^{-1} \text{mol}^{-1} \]

\[ K_p = 3.44 \times 10^{-4} T^{0.95} \exp( + 3500/T) \]

**Rate Coefficient Data**

<table>
<thead>
<tr>
<th>( k ) [cm³ molecule⁻¹ s⁻¹]</th>
<th>( T ) [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.35 × 10⁻¹¹</td>
<td>300</td>
<td>Whyte and Phillips (1983)¹</td>
<td>(a)</td>
</tr>
<tr>
<td>1.25 × 10⁻¹¹ ( (\nu = 1) )</td>
<td>2400</td>
<td>Louge and Hanson (1984)²</td>
<td>(b)</td>
</tr>
<tr>
<td>2.0 × 10⁻¹¹</td>
<td>300</td>
<td>Li, SAYAH, and Jackson (1984)³</td>
<td>(c)</td>
</tr>
<tr>
<td>2.4 × 10⁻¹¹ ( (\nu = 1) )</td>
<td>204</td>
<td>Lichtin and Lin (1985)⁴</td>
<td>(d)</td>
</tr>
<tr>
<td>8.1 × 10⁻¹²</td>
<td>2195–3390</td>
<td>Thielen and Roth (1987)⁵</td>
<td>(e)</td>
</tr>
<tr>
<td>1.86 × 10⁻¹¹</td>
<td>295</td>
<td>deJuan, Smith, and Veyret (1987)⁶</td>
<td>(f)</td>
</tr>
<tr>
<td>1.82 × 10⁻¹¹</td>
<td>205</td>
<td>Anastasi and Hancoke (1988)⁷</td>
<td>(g)</td>
</tr>
<tr>
<td>1.25 × 10⁻¹¹ ( \exp( + 205/T) )</td>
<td>294–761</td>
<td>Sims and Smith (1988)⁸</td>
<td>(h)</td>
</tr>
<tr>
<td>4.0 × 10⁻¹⁰ ( \exp(- 450/T) )</td>
<td>290–400</td>
<td>Roulch et al. (1981)⁹</td>
<td>(i)</td>
</tr>
<tr>
<td>1.1 × 10⁻¹¹ ( \exp( + 205/T) )</td>
<td>290–760</td>
<td>CODATA (1989)¹⁰</td>
<td>(j)</td>
</tr>
</tbody>
</table>

**Comments**

(a) Fast flow system. CN radicals generated from (CN)₂ by ArF laser pulses. Decay of [CN, \( \nu = 0, \nu = 1 \)] in excess O₂ monitored by laser induced fluorescence.
(b) Shock tube study on O₂/(CN)₂/Ar mixtures. [CN] monitored by absorption at 388 nm. Data of [CN] analysed numerically in terms of 27 reaction mechanism. Fitting gives \( k \). Sensitivity to assumed rate coefficient checked.
(c) Pulsed laser photolysis of (CN)₂/Ar/O₂ mixtures. [CN, \( \nu = 0, \nu = 1 \)] monitored as a function of time by laser induced fluorescence.
(d) Pulsed laser photolysis of ICN/O₂/Ar mixtures in flowing system. [CN] monitored as a function of time at both 388 nm and 619 nm, the latter giving the less precise of the two values of \( k \) tabulated.
(e) Shock wave study using reflected shocks in HCN/O₂ mixtures in Ar at 1.5–1.9 atm total pressure. [H], [O], [N] monitored by resonance absorption. [H], [O], [N] profiles computed from large reaction mechanism and fitted to experimental results. Sensitivity of fit to \( k \) checked.
(f) Laser pulsed photolysis of ICN in flow system with laser induced fluorescence determination of [CN]. Total pressure 10–30 Torr.
(g) Flash photolysis of (CN)₂ in Ar in flow system with laser induced fluorescence determination of [CN].
(h) Pulsed laser photolysis of flowing NCNO/Ar mixtures at 532 nm. [CN] monitored by laser induced fluorescence.
(i) Based on limited low temperature data.
(j) Accepts temperature coefficient of Sims and Smith⁸.

**Preferred Values**

\[ k = 1.1 \times 10^{-11} \exp( + 205/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range 298–2500 K} \]

**Reliability**

\[ \Delta \log k = \pm 0.25 \text{ at 298 K rising to } \pm 0.5 \text{ at 2500 K} \]

**Comments on Preferred Values**

Measurements up to 1981 have been reviewed⁶. Only more recent values are tabulated here.

At temperatures close to 300 K the available data range over a factor of 3.1.3.6.7.8.11.23.31.32.33.35.36.38. The techniques used have been very similar and it has been suggested that the lower results might arise from population of the monitored \( \nu \) levels by quenching of higher \( \nu \) levels. The most recent studies²,6,12 are in reasonable agreement giving a mean value of 2.1 × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹.

The measurements at higher temperatures are fewer and less precise but suggest that \( k \) has little or no temperature dependence²,5,7. This is in accord with the temperature dependence of \( k \) recently measured by Sims and Smith⁸ which value we accept as the basis for the recommended expression.

The reaction has an alternative, highly exothermic channel giving CO + NO (\( \Delta H = -455 \text{ kJ mol}^{-1} \)). The experimental evidence suggests that it is unimportant both at high and low temperatures²,18.

**References**

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

CN + O₂ → NCO + O

T/K

Log(k, cm³/ mol· s⁻¹)

10⁻¹²

10⁻¹¹

10⁻¹⁰

10⁻⁹

10⁻⁸

10⁻⁷

10⁻⁶

10⁻⁵

T / K

10³ T⁻¹ / K⁻¹

EXPERIMENTAL DATA
Paul and Dolby 1962
Bosco 1965
Boden and Thrush 1968
Bullock and Cooper 1972
Schacke and Wolfrum 1972
Schnake et al 1973
Albers et al 1975
Mulvihill and Phillips 1975
Whyte and Phillips 1983
Lunze and Hansen 1984
Li et al 1984
Lichten and Lin 1985
de Juan et al 1987
Thielen and Roth 1987
Anastasi and Hancock 1988
Sims and Smith 1988
This Recommendation 1989

CN + H₂O → HCN + OH  \hspace{1cm} (1)
→ HOCN + H  \hspace{1cm} (2)

Thermodynamic Data

\[ \Delta H_{298}^0 (1) = -19.2 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298}^0 (1) = -5.91 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ k_p (1) = 4.79 \times 10^{-3} \text{T}^{0.98} \exp(2520/T) \]
\[ \Delta H_{298}^0 (2) = 15.1 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298}^0 (2) = -28.78 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ k_p (2) = 4.97 \times 10^{-5} \text{T}^{-0.94} \exp(-1493/T) \]

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

<table>
<thead>
<tr>
<th>(k [\text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1}])</th>
<th>(T [\text{K}])</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_1 = 3.8 \times 10^{-11} \exp(-6700/T))</td>
<td>850–2600</td>
<td>Szekely, Hanson, and Bowman (1984)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>(k_1 = 1.3 \times 10^{-11} \exp(-3750/T))</td>
<td>518–1027</td>
<td>Jacobs et al. (1988)(^2)</td>
<td>(b)</td>
</tr>
</tbody>
</table>

Reviews and Evaluations

- Baulch et al. (1981)\(^3\)

Comments

(a) Shock tube studies of C₂N₂/H₂O/Ar mixtures. [CN] and [OH] monitored by broad band absorption spectroscopy at 388 nm and narrow-line laser absorption at 306.67 nm respectively. Computer fit of data to assumed reaction mechanism shown to be sensitive to \(k_1\). Values of \(k_1\) from this study combined by authors with data of Fritz et al.\(^4\) on the reverse reaction and with the equilibrium constant to obtain quoted expression for \(k_1\).

(b) Laser photolysis at 193 nm of flowing C₂N₂/N₂ mixtures. [CN] in the \(v = 0\) and \(v = 1\) states and [OH] were monitored as function of time by laser induced fluorescence.

(c) Quotes early work of Paul and Dalby\(^5\) which appears to give too high a value of \(k_1\). No recommendation made.

Preferred Values

\[ k_1 = 1.3 \times 10^{-11} \exp(-3750/T) \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \text{ over range 500–3000 K} \]

Reliability

\[ \Delta \log k_1 = \pm 0.3 \text{ at 500 K rising to } \pm 0.5 \text{ at 3000 K} \]

Comments on Preferred Values

The recommended expression is that of Jacobs et al.\(^2\). If it is extrapolated to high temperatures it gives values of \(k_1\) in good agreement with measured values of Szekely et al.\(^1\). The measurements of \(k_1\) by Szekely et al. are likely to be valid but by combining them with data on the reverse reaction at lower temperatures and equilibrium data, they obtain an erroneous rate expression for \(k_1\).

The other channel, (2) has been invoked to explain some features of nitrogen containing flames\(^6\) but there is no direct evidence for its occurrence.

References

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

CN + CH₄ → HCN + CH₃

**Thermodynamic Data**

\[ \Delta H_{298}^o = -79.4 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298}^o = 7.18 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_p = 9.79 \times 10^{-2} \ T^{1.026} \exp(+9570/T) \]

**Rate Coefficient Data**

<table>
<thead>
<tr>
<th>( k ) [cm³ molecule⁻¹ s⁻¹]</th>
<th>( T ) [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0 \times 10^{-13}</td>
<td>293</td>
<td>Schacke, Wagner, and Wolfrum (1973)¹</td>
<td>(a)</td>
</tr>
<tr>
<td>1.1 \times 10^{-12}, CN⁻_1</td>
<td>300</td>
<td>Li, Sayah, and Jackson (1984)²</td>
<td>(b)</td>
</tr>
<tr>
<td>5.6 \times 10^{-13}</td>
<td>294</td>
<td>Lichtin and Lin (1985)³</td>
<td>(c)</td>
</tr>
<tr>
<td>8.3 \times 10^{-13}, CN⁻_1</td>
<td>298</td>
<td>Balla and Pasternack (1987)⁴</td>
<td>(d)</td>
</tr>
</tbody>
</table>

**Comments**

(a) Flash photolysis of CH₄(0.037–0.4 Torr)/C₂N₂(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 C₂N₂/Ar/CH₄ mixtures. [CN(v = 0, v = 1)] monitored as a function of time by laser induced fluorescence.

(c) Pulsed laser photolysis of ICN/CH₄/Ar mixtures in flowing system. [CN] monitored as a function of time at 388 nm by laser induced fluorescence.

(d) Laser photolysis of C₂N₂(0.05–0.3 Torr)/CH₃(0–0.15 Torr) mixtures with He, N₂, or Ar bath gas. Total pressures 1–200 Torr. [CN] decay and HCN formation monitored by diode laser absorption spectroscopy at 2015.22 cm⁻¹ and 3280.987 cm⁻¹ respectively.

(e) Review of all data up to 1980; no recommendation.

**Preferred Values**

\[ k = 1.5 \times 10^{-11} \exp(-940/T) \text{ cm}^{3} \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range 260–400 K} \]

**Reliability**

\[ \Delta \log k = \pm 0.3 \text{ over range 260–400 K} \]

**Comments on Preferred Values**

Experimental work on this reaction is largely confined to \( T < 400 \) K. The only higher temperature study by Boden and Thrush⁶ yielded only an upper limit which does not correlate well with the lower temperature studies.

The results at 300 K range over a factor of 2 but the two studies of the temperature coefficient of \( k \) are in good agreement. The recommended values are based mainly on the work of Schacke et al.⁷ and Bullock and Cooper⁸.

The rate of the reaction is increased by vibrational excitation of the CN and several of the rate coefficients for CN(v = 1) have been determined²⁻⁹.

**References**

CN + CH₄ → CH₃ + HCN

T/K

Log(k/cm³ molecule⁻¹ s⁻¹)

10³T⁻¹/K⁻¹

EXPERIMENTAL DATA
- Bullock and Cooper 1971
- Bullock and Cooper 1972
- Schocke et al 1973
- Li et al 1984
- Lichtin and Lin 1985
- Bolla and Pasternack 1987

This Recommendation 1989

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

NCO(+ M) → N + CO(+M)

**Thermodynamic Data**

\[ \Delta H_{\text{f}}^{\text{uo}} = 203 \text{ kJ mol}^{-1} \]

\[ \Delta S_{\text{f}}^{\text{uo}} = 119 \text{ J K}^{-1} \text{mol}^{-1} \]

\[ K_p = 5.49 \times 10^9 T^{-0.114} \exp(-24560/T) \text{ atm} \]

**Rate Coefficient Data**

<table>
<thead>
<tr>
<th>( k [\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}] )</th>
<th>( T [\text{K}] )</th>
<th>( \text{M} )</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1 \times 10^{-20}</td>
<td>1700</td>
<td>Ar</td>
<td>Lifshitz and Frenklach (1980)</td>
<td>(a)</td>
</tr>
<tr>
<td>1.7 \times 10^{-9} \exp(-23450/T)</td>
<td>1450–2600</td>
<td>Ar</td>
<td>Higashihara et al. (1983)</td>
<td>(b)</td>
</tr>
<tr>
<td>1.7 \times 10^{-11} T^{0.5} \exp(-20600/T)</td>
<td>2240–2955</td>
<td>Ar</td>
<td>Colket (1984)</td>
<td>(c)</td>
</tr>
<tr>
<td>8.1 \times 10^{-11} \exp(-31800/T)</td>
<td>2150–2400</td>
<td>Ar</td>
<td>Louge and Hanson (1984)</td>
<td>(d)</td>
</tr>
<tr>
<td>8.8 \times 10^{-11} T^{0.5} \exp(-24000/T)</td>
<td>2150–2400</td>
<td>Ar</td>
<td>Louge and Hanson (1984)</td>
<td>(e)</td>
</tr>
</tbody>
</table>

**Comments**

(a) Shock tube study on \( \text{C}_2\text{N}_2\text{O}_2/\text{Ar} \) mixtures. Computer simulations indicated induction period sensitive to this and 3 other reactions in 15 reaction mechanism. Only moderate agreement obtained between simulation and experiment.

(b) Shock tube study on \( \text{HCN/O}_2/\text{Ar} \) and \( \text{HCN/O}_2/\text{NO}/\text{Ar} \) mixtures. Detailed induction time data simulated using large reaction mechanisms in which title reaction and \( \text{NCO} + \text{O} \rightarrow \text{CO} + \text{NO} \) are key reactions.

(c) Shock tube study on \( \text{C}_2\text{N}_2\text{O}_2/\text{Ar} \) mixtures. Experimental [NO] profiles simulated using 8 reaction mechanism. Adjusting title \( k \) by factor of 3 hardly affected [CN] profile.

(d) Shock tube study of \( \text{C}_2\text{N}_2\text{O}_2/\text{Ar} \) and \( \text{C}_2\text{N}_2\text{O}_2/\text{Ar} \) mixtures. Analysis of [NO] profile in former and [CN] in latter gave \( k(\text{NCO} + \text{O})/k(\text{NCO} + \text{Ar}) = 10^{-3.45} \exp(+31800/T) \). Quoted expression calculated using \( k(\text{NCO} + \text{O}) = 7.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) (this review).

(e) Shock tube study of \( \text{C}_2\text{N}_2\text{N}_2\text{O}/\text{Ar} \) mixtures. Analysis of [NCO], in conjunction with own earlier results (see (d)) gave \( k(\text{NCO} + \text{O})/k(\text{NCO} + \text{Ar}) = 10^{-3.1} T^{0.5} \exp(+24000/T) \). Quoted expression calculated using \( k(\text{NCO} + \text{O}) = 7.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) (this review).

**Preferred Values**

\[ k = 1.7 \times 10^{-9} \exp(-23500/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ for } M=\text{Ar} \text{ over the range 1450–2600 K} \]

**Reliability**

\[ \Delta \log k = \pm 0.4 \text{ over the range 1450–2600 K} \]

**Comments on Preferred Values**

We recommend the expression obtained by Higashihara et al.\(^2\) from analysis of a fairly detailed induction period data set over a wide temperature range, and subsequently corroborated by Louge and Hanson\(^4,5\). The result of Lifshitz and Frenklach\(^1\) can be considered as a preliminary value and the experimental data of Colket\(^3\) were hardly sensitive to the rate of this reaction.

**References**

NCO + NO $\rightarrow$ N$_2$O + CO \hspace{1cm} (1)  
$\rightarrow$ N$_2$ + CO$_2$ \hspace{1cm} (2)  
$\rightarrow$ N$_2$ + CO + O \hspace{1cm} (3)

**Thermodynamic Data**

$\Delta H_{298}^\circ$ (1) = $-278$ kJ mol$^{-1}$  
$\Delta S_{298}^\circ$ (1) = $-25.4$ J K$^{-1}$ mol$^{-1}$  
$K_p$(1) = $0.164$ $T^{-0.190}$ exp$(+33400/T)$  

$\Delta H_{298}^\circ$ (2) = $-643$ kJ mol$^{-1}$  
$\Delta S_{298}^\circ$ (2) = $-37.5$ J K$^{-1}$ mol$^{-1}$  
$K_p$(2) = $7.22 \times 10^{-2}$ $T^{-0.295}$ exp$(+77300/T)$

$\Delta H_{298}^\circ$ (3) = $-111$ kJ mol$^{-1}$  
$\Delta S_{298}^\circ$ (3) = $107$ J K$^{-1}$ mol$^{-1}$  
$K_p$(3) = $2.96 \times 10^6$ $T^{-0.219}$ atm

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

<table>
<thead>
<tr>
<th>$k$ [cm$^3$ molecule$^{-1}$ s$^{-1}$]</th>
<th>$T$ [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.66 \times 10^{-12}$</td>
<td>1329-1846</td>
<td>Fifer and Homes (1982)$^1$</td>
<td>(a)</td>
</tr>
<tr>
<td>$1.69 \times 10^{-11}$ exp$(+197/T)$</td>
<td>294-338</td>
<td>Perry (1985)$^2$</td>
<td>(b)</td>
</tr>
<tr>
<td>$3.4 \times 10^{-11}$</td>
<td>295</td>
<td>Hancock and McKendrick (1986)$^3$</td>
<td>(c)</td>
</tr>
</tbody>
</table>

**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 reaction mechanism.

(b) Flowing system. NCO produced by pulsed laser photolysis of HCNO/Ar/NO mixtures. Decay of [NCO] monitored using laser induced fluorescence at 416.8 nm.

(c) NCO produced by infrared multiphoton dissociation of phenyl isocyanate. Decay of [NCO] in large excess of NO monitored by laser induced fluorescence at 438.48 nm. This work supersedes earlier similar studies$^4,5$ in which vibrational excitation of NCO may have influenced results.

**Preferred Values**

$k = 1.7 \times 10^{-11}$ exp$(+200/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$ over range 300–600 K

**Reliability**

$\Delta \log k = \pm 0.5$ over range 300–600 K

**Comments on Preferred Values**

The preferred expression is that of Perry$^2$ which is in good agreement with the results of Hancock and McKendrick$^3$ at ambient temperatures. These are the only direct measurements and therefore we assign fairly large error limits. The only available value of $k$ at higher temperatures is a very indirect determination which is an order of magnitude lower than that obtained by extrapolation of our recommended expression. We therefore limit our recommendation to the low temperature region.

There have been no studies of the branching ratios. Both Perry$^2$ and Hancock and McKendrick$^3$ have suggested that reaction (1) is the dominant channel as (2) and (3) are likely to have significant energy barriers, reaction (2) proceeding via a triplet surface and (3) requiring a 1,3 oxygen migration via a 4 centre transition state. Furthermore, Hancock and McKendrick$^3$ observe no NO + O recombination afterglow in their experiments, thus suggesting the absence of channel (3).

**References**

C₂H + O₂ → CH + CO₂  (1)  
→ H + 2 CO    (2)  
→ O + C₂H₂O    (3)  
→ CHO + CO    (4)  

**Thermodynamic Data**

\[ \Delta H_{298}^0 (1) = -360 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298}^0 (1) = 15.8 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ K_p (1) = 4.69 \times 10^5 T^{-0.196} \exp (43400/T) \]

\[ \Delta H_{298}^0 (2) = -564 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298}^0 (2) = 97.2 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ K_p (2) = 6.41 \times 10^6 T^{-0.130} \exp (67700/T) \]

\[ \Delta H_{298}^0 (3) = -134 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298}^0 (3) = 2.67 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ K_p (3) = 2.70 \times 10^{-17} T^{0.446} \exp (16200/T) \]

\[ \Delta H_{298}^0 (4) = -628 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298}^0 (4) = 9.65 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ K_p (4) = 1.79 \times 10^{-17} T^{0.936} \exp (15300/T) \]

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

<table>
<thead>
<tr>
<th>( k ) (cm³ molecule⁻¹ s⁻¹)</th>
<th>( T ) [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.7 \times 10^{-11} \exp (-5032/T)</td>
<td>320</td>
<td>Lange and Wagner (1975)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>2.1 \times 10^{-11}</td>
<td>1400-2600</td>
<td>Shaub and Bauer (1978)(^2)</td>
<td>(b)</td>
</tr>
<tr>
<td>( k_1 = 1.0 \times 10^{-12} )</td>
<td>300</td>
<td>Renlund et al. (1981, 1982)(^3,4)</td>
<td>(c)</td>
</tr>
<tr>
<td>( k_4 = 4.0 \times 10^{-12} )</td>
<td>295</td>
<td>Laufer and Lechleider (1984)(^5)</td>
<td>(d)</td>
</tr>
<tr>
<td>4.2 \times 10^{-11}</td>
<td>298</td>
<td>Stephens et al. (1987)(^6)</td>
<td>(e)</td>
</tr>
</tbody>
</table>

**Comments**

(a) Flow reactor; C₂H from microwave discharge of C₂HBr/He; mass spectrometric product analysis. Total pressure 4.1 Torr, [C₂H₂O] observed, no CHO or C₂O detected; (3) supposed to be the main reaction channel. Lower limit of \( k \).

(b) Shock heating of C₂H₂O/Ar mixtures. Final product concentrations by gas chromatography. Numerical modelling of 17 reaction mechanism.

(c) UV or IR photodissociation of C₂HCF₃, C₂HC₃H, C₂H₂, or C₂HBr. Observation of CH(\( \text{A}^2\Sigma^+ \rightarrow \text{X}^2\Pi \)) and CO(\( \text{A}^2\Sigma^+ \rightarrow \text{X}^2\Pi \)) chemiluminescence at 432.6 nm and 790 nm and of CO₂(\( \Delta v = 1 \)) emission at 2300 cm⁻¹. Total pressures 0.2-2.0 Torr He or Ar. CO and CH emissions independent of the nature of the buffer gas (He, Ar, N₂, or Xe) and of its pressure (0.6-100 Torr). They propose the formation of an intermediate peroxy species with enough vibrational energy to allow significant rearrangements of the nuclei during the course of the reaction.

(d) Flash photolysis of CF₂C₂H; gas chromatographic sampling; [CO] by absorption at 154.4 nm. Reaction rates independent of pressure in the range 50-600 Torr (He or N₂). Lack of CHO detection in Ref. 1 explained by low detection limit and fast consumption of CHO.

(e) Flash photolysis of CF₂C₂H at 193 nm; IR absorption of ground state C₂H at 3594.4 cm⁻¹. Total pressure 20 Torr He; SF₆ added to ensure rapid vibrational relaxation of C₂H.

**Preferred Values**

\( k = 3.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) at 300 K

Reliability
\[ \Delta \log k = \pm 0.5 \text{ at } 300 \text{ K} \]

**Comments on Preferred Values**

The larger rate coefficient based on Refs. 3, 4, 6 is taken as the recommendation due to the modern methods used. From the measurements of Laufer and Lechleider\(^7\) the product channel (4) seems to be the most important one which is similar to channel (2) at high temperature.

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References

Thermodynamic Data

\[ \Delta H_{298}^\circ = -116 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298}^\circ = -22.5 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_p = 1.38 \times 10^{-4} \exp (+14300/T) \]

Rate Coefficient Data

<table>
<thead>
<tr>
<th>Rate Coefficient Measurements</th>
<th>T[ K ]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1.7 \times 10^{-13})</td>
<td>320</td>
<td>Lange and Wagner (1975)¹</td>
<td>(a)</td>
</tr>
<tr>
<td>(5.1 \times 10^{-13})</td>
<td>298</td>
<td>Lauffer and Bass (1979)²</td>
<td>(b)</td>
</tr>
<tr>
<td>(9.3 \times 10^{-12})</td>
<td>625-3400</td>
<td>Tanzawa and Gardiner (1980)³</td>
<td>(c)</td>
</tr>
<tr>
<td>(1.2 \times 10^{-11})</td>
<td>300</td>
<td>Renlund et al. (1981)⁴</td>
<td>(d)</td>
</tr>
<tr>
<td>(1.3 \times 10^{-11})</td>
<td>1800-2500</td>
<td>Koike and Morinaga (1981)⁵; coor. by Gardiner et al. (1985)⁶</td>
<td>(e)</td>
</tr>
<tr>
<td>(3.9 \times 10^{-13})</td>
<td>298</td>
<td>Ohabe (1981)⁷</td>
<td>(f)</td>
</tr>
<tr>
<td>(1.2 \times 10^{-11})</td>
<td>2300-3200</td>
<td>Kiefer et al. (1983)⁸</td>
<td>(g)</td>
</tr>
<tr>
<td>(4.8 \times 10^{-13})</td>
<td>298</td>
<td>Stephens et al. (1987)⁹</td>
<td>(h)</td>
</tr>
</tbody>
</table>

Reviews and Evaluations

\[2.5 \times 10^{-11} \exp (-1564/T)\] | 300-3000 | Warnatz (1984)¹⁰ | |
\[1.9 \times 10^{-11} \exp (-1443/T)\] | 300-2800 | Gardiner et al. (1985)⁸ | |
\[1.8 \times 10^{-11} \exp (-1455/T)\] | 300-2500 | Tsang and Hampson (1986)¹¹ | |

Comments

(a) Flow reactor; C₂H from microwave discharge of C₂HBr/He. Mass spectrometric product analysis. Total pressure 4.2 Torr. Lower limit of k.

(b) VUV flash photolysis of C₂H with and without added H₂; [C₂H] by gas chromatographic sampling and VUV absorption at 144.6 nm. Total pressures 20 or 700 Torr He.

\[k(C₂H + H₂)/k(C₂H + C₂H₂) = 4.9 \times 10^{-3}\]. Given value based on \(k(C₂H + C₂H₂) = 3.1 \times 10^{-11}\) cm³ molecule⁻¹ s⁻¹.

(c) Modelling study of C₂H₂ pyrolysis in shock tubes, flow reactors, and bulb dissociation experiments. Wrong data transcription in the table; corrected in Ref. 6.

(d) UV or IR flash photolysis of C₂H₂, C₂HBr, or C₂HCHO. CH(\(A^2Δ\rightarrow X^3Σ^\text{II})\) and CO₂ chemiluminescence at 432.6 nm and 2300 cm⁻¹. Total pressures 200-800 mTorr Ar or He. k measured relative to reaction with O₂. The authors do not exclude the possibility of C₂H reacting from an excited state.

(e) Shock heating of C₂H₂, C₂H₃/He, or C₂H₄ in 0.5 atm Ar. Absorption measurements at 216 nm and 230 nm. Numerical modelling of 25 reaction mechanism, k adjusted to fit the absorption profile of C₂H₂. Wrong thermochemical data for C₂H; correction in Ref. 6.

(f) Photolysis of C₂H₂ at 147 nm. [C₂H₂], [C₂H₃], and [C₂H₄] by absorption measurements at = 165 nm, 174.4 nm, and 151.9 nm. Relative rate \(k(C₂H + H₂)/k(C₂H + C₂H₂) = 1/130\). Given value of k based on \(k(C₂H + C₂H₂) = 5 \times 10^{-11}\) cm³ molecule⁻¹ s⁻¹.

(g) Pyrolysis of C₂H₂/Kr mixtures behind incident shock waves; laser schlieren measurements. Total pressure 200-750 Torr. Numerical modelling of 29 reaction mechanism based on Ref. 3. k adjusted.

(h) Flash photolysis of CF₃C₂H at 193 nm. Ground state C₂H monitored by IR absorption at 3594.4 cm⁻¹. Total pressure 20 Torr He; SF₆ added to ensure rapid vibrational relaxation of C₂H₂.

Preferred Values

\[k = 2.5 \times 10^{-11} \exp (-1564/T)\] cm³ molecule⁻¹ s⁻¹ over range 300-2500 K

Reliability

\[\Delta \log k = \pm 0.3\] at 300 K rising to \(\pm 0.7\) at 2500 K

Comments on Preferred Values

The recommendation of Warnatz¹⁰ is adopted. It gives a good representation of the high and low temperature data available.

References

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ \text{C}_2\text{H} + \text{H}_2 \rightarrow \text{C}_2\text{H}_2 + \text{H} \]

\[ \log(k/\text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1}) \]

\[ T/K \]

\[ 2000 \quad 1000 \quad 500 \quad 400 \quad 300 \]

**EXPERIMENTAL DATA**
- Lange and Wagner 1975
- Laufer and Boss 1979
- Tanzawa and Gardiner 1980
- Rentund et al 1981
- Koike and Mariogga (Gardiner) 1981
- Okabe 1981
- Kiefer et al 1983
- Stephens et al 1987

This Recommendation 1989

### Thermodynamic Data

\[ \Delta H_\text{fus} = -102 \text{ kJ mol}^{-1} \]
\[ \Delta S_\text{fus} = -43.5 \text{ J K}^{-1} \text{ mol}^{-1} \]

\[ K_p = 4.46 \times 10^{-7} T^{1.43} \exp \left( \frac{-12600}{T} \right) \]

### Rate Coefficient Data

<table>
<thead>
<tr>
<th>( k [\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}] )</th>
<th>( T [\text{ K}] )</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 5 \times 10^{-11} )</td>
<td>320</td>
<td>Lange and Wagner (1975)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>( 3.1 \times 10^{-11} )</td>
<td>298</td>
<td>Laufer and Bass (1979)(^2)</td>
<td>(b)</td>
</tr>
<tr>
<td>( (5-6.6) \times 10^{-11} )</td>
<td>2300-2700</td>
<td>Frank and Just (1980)(^3)</td>
<td>(c)</td>
</tr>
<tr>
<td>( 1.5 \times 10^{-10} )</td>
<td>298</td>
<td>Stephens et al. (1987)(^4)</td>
<td>(d)</td>
</tr>
<tr>
<td>( 4.0 \times 10^{-11} )</td>
<td>300-2500</td>
<td>Tsang and Hampson (1986)(^5)</td>
<td></td>
</tr>
</tbody>
</table>

### Comments

(a) Flow reactor; mass spectrometric product analysis. \( \text{C}_2\text{H} \) from microwave discharge of \( \text{C}_2\text{HBr/He} \). Total pressure 4.1 Torr. \( \text{C}_4\text{H}_2 \) identified as main product. Lower limit of \( k \).

(b) VUV flash photolysis of \( \text{C}_2\text{H}_3 \). \( \text{C}_2\text{H}_2 \) formation observed by gas chromatographic sampling and absorption measurement at 144.6 nm. Total pressures 20 and 700 Torr He.

(c) Thermal decomposition of \( \text{C}_2\text{H}_3 \) and \( \text{C}_2\text{H}_2 \) behind reflected shock waves. \( [\text{H}] \) by atomic resonance absorption spectroscopy at 121.5 nm. Total pressures 1.5-4 bar Ar.

(d) Flash photolysis of \( \text{C}_2\text{H}_2 \) at 193 nm; \( [\text{C}_2\text{H}] \) monitored by IR absorption at 3594.4 cm\(^{-1} \). Total pressure 20 Torr He; \( \text{SF}_6 \) added to ensure rapid vibrational relaxation of \( \text{C}_2\text{H} \).

### Preferred Values

\( k = 5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) over range 300-2700 K.

### References


\(^3\)P. Frank and Th. Just, Comb. Flame 38, 231 (1980).


### C\(_2\)H + CH\(_4\) → Products

### Rate Coefficient Data

<table>
<thead>
<tr>
<th>( k [\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}] )</th>
<th>( T [\text{ K}] )</th>
<th>Reference</th>
<th>Comments</th>
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</thead>
<tbody>
<tr>
<td>( 4.8 \times 10^{-12} )</td>
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<td>Renlund et al. (1981)(^6)</td>
<td>(a)</td>
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<td>( 1.2 \times 10^{-12} )</td>
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<td>Laufer (1981)(^7)</td>
<td>(b)</td>
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<td>( 1.6 \times 10^{-12} )</td>
<td>298</td>
<td>Okabe (1981)(^8)</td>
<td>(c)</td>
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<tr>
<td>( 3.0 \times 10^{-12} \exp(-2500/T) )</td>
<td>300-2500</td>
<td>Tsang and Hampson (1986)(^4)</td>
<td></td>
</tr>
</tbody>
</table>

Comments

(a) Flash photolysis of $\text{C}_2\text{H}_2$, $\text{C}_2\text{HBr}$, or $\text{C}_2\text{HCO}$ at 193 nm, or of $\text{C}_2\text{HCO}$ at 953 cm$^{-1}$. CH($\text{A}^2\Delta$) from $\text{C}_2\text{H} + \text{O}_2$ reaction monitored by chemiluminescence at 432.6 nm, with and without added $\text{CH}_4$, $\text{[CO]}$ monitored by chemiluminescence at 2300 cm$^{-1}$. Total pressures 200–800 mTorr Ar or He.

(b) VUV flash photolysis of $\text{C}_2\text{HClF}_3$. Gas chromatographic sampling, $\text{[C}_2\text{H}_2]$ by absorption spectroscopy at 152 nm. $k$ independent of pressure between 20 and 700 Torr.

(c) Photolysis of $\text{C}_2\text{H}_2$ at 147 nm; $\text{[C}_2\text{H}_2]$, $\text{[C}_2\text{H}_4]$, and $\text{[C}_3\text{H}_2]$ by absorption spectroscopy at $\approx$ 165 nm, 174.4 nm, and 151.9 nm, respectively. Relative rates $k(\text{C}_2\text{H} + \text{CH}_4)/k(\text{C}_2\text{H} + \text{C}_2\text{H}_2) = 4.2/130$. $k$ based on $k(\text{C}_2\text{H} + \text{C}_2\text{H}_2) = 5 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.

Preferred Values

$k = 2.0 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K

C$_2$H + C$_2$H$_6$ → C$_2$H$_2$ + C$_2$H$_5$

Thermodynamic Data

$\Delta H_{298} = -133$ kJ mol$^{-1}$

$\Delta S_{298} = 16.2$ J K$^{-1}$mol$^{-1}$

$K_p = 4.04 \cdot 10^{-906} \exp(+12640/T)$

Rate Coefficient Data

<table>
<thead>
<tr>
<th>$k$ [cm$^3$ molecule$^{-1}$ s$^{-1}$]</th>
<th>$T$ [K]</th>
<th>Reference</th>
<th>Comments</th>
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<tr>
<td><strong>Rate Coefficient Measurements</strong></td>
<td></td>
<td></td>
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<tr>
<td>$6.5 \times 10^{-12}$</td>
<td>298</td>
<td>Laufer (1981)$^1$</td>
<td>(a)</td>
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<tr>
<td><strong>Reviews and Evaluations</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$6.0 \times 10^{-12}$</td>
<td>300–2500</td>
<td>Tsang and Hampson (1986)$^2$</td>
<td></td>
</tr>
</tbody>
</table>

Comments

(a) Photolysis of $\text{C}_2\text{H}_2$ at 147 nm; $\text{[C}_2\text{H}_2]$, $\text{[C}_2\text{H}_4]$, and $\text{[C}_3\text{H}_2]$ by absorption spectroscopy at $\approx$ 165 nm, 174.4 nm, and 151.9 nm, respectively. Relative rates $k(\text{C}_2\text{H} + \text{CH}_4)/k(\text{C}_2\text{H} + \text{C}_2\text{H}_2) = 4.2/130$. $k$ based on $k(\text{C}_2\text{H} + \text{C}_2\text{H}_2) = 5 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.

Preferred Values

No recommendation.

References


Thermodynamic Data
\[ \Delta H_{\text{fus}} = 158 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{fus}} = 171 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ k_e = 2.43 T^{1.5} \exp(-18900/T) \text{atm} \]

Rate Coefficient Data

<table>
<thead>
<tr>
<th>Rate Coefficient Measurements</th>
<th>( T ) [K]</th>
<th>([M]) [molecule cm(^{-3})]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intermediate Fall-off Range</td>
<td></td>
<td></td>
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<tr>
<td>( 3 \times 10^{-12} \text{[C}_2\text{H}_4] )</td>
<td>1500</td>
<td>5 \times 10^{14} (C(_2)H(_4))</td>
<td>Peeters and Mahnen (1973)(^3)</td>
<td>(c)</td>
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<tr>
<td>( 2.7 \times 10^{-9} \exp(-16100/T) \text{[C}_2\text{H}_4] )</td>
<td>1800-2400</td>
<td>5 \times 10^{14} (C(_2)H(_4))</td>
<td>Jachimowski (1977)(^4)</td>
<td>(d)</td>
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<tr>
<td>( 2.6 \times 10^{-7} \exp(-15800/T) \text{[Ar]} )</td>
<td>1300-2000</td>
<td>(1-9) \times 10^{13} (Ar)</td>
<td>Coats and Williams (1979)(^5)</td>
<td>(e)</td>
</tr>
</tbody>
</table>

Reviews and Evaluations

- \( k_0 = 5.0 \times 10^{-7} \exp(-16200/T) \) [Ar] 500-2500 (Ar) Benson and Haugen (1967)\(^1\) (a)
- \( k_\infty = 1.6 \times 10^{14} \exp(-19200/T) \) 500-2500 (Ar) Skinner, Sweet, and Davis (1971)\(^2\) (b)
- \( k_\infty = 6.9 \times 10^{17} T^{-7.5} \exp(-22900/T) \) \( > 600 \) (N\(_2\)) Tsang and Hampson (1986)\(^7\) (g)

Comments

(a) Analysis of available experimental data on the hydrogenation of C\(_2\)H\(_2\) and the pyrolysis of C\(_2\)H\(_4\).
(b) Pyrolysis of dilute mixtures of C\(_2\)H\(_4\), C\(_2\)H\(_4\)/C\(_2\)D\(_4\), C\(_2\)H\(_2\)/C\(_2\)D\(_2\) in Ar in a shock tube. No dependence of \( k \) on pressure observed, suggested that the reaction was in the high pressure range. Here represented as a pressure-proportional rate coefficient.
(c) Molecular beam sampling, mass spectrometric analysis of C\(_2\)H\(_2\) flames at 40 Torr.
(d) Oxidation of C\(_2\)H\(_2\) behind incident shock waves. Monitored IR emission from CO and CO\(_2\), and chemiluminescence from O + CO \( \rightarrow \) CO\(_2\) + h\(_v\). \( k \) mainly derived from induction time modelling of a 11 step mechanism.
(e) Study of n-heptane/O\(_2\)/Ar mixtures behind incident and reflected shock waves. Monitored IR emission from CO, CO\(_2\), and chemiluminescence from OH, CH, and C\(_2\).
(f) Evaluation of literature data.
(g) Evaluation of literature data. RRKM calculation of fall-off curve (misprinted table).

Preferred Values

\[ k_0 = 6.9 \times 10^{17} T^{-7.5} \exp(-22900/T) \text{cm}^{-3} \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range } 500-2500 \text{ K (in Ar and N}_2\)\]
\[ k_\infty = 2 \times 10^{14} \exp(-20000/T) \text{ s}^{-1} \text{ over range } 500-2500 \text{ K} \]
\[ F_c = 0.35 \text{ over range } 500-2500 \text{ K} \]

Reliability

\[ \Delta \log k_0 = \pm 0.5 \text{ over range } 500-2500 \text{ K} \]
\[ \Delta \log k_\infty = \pm 0.5 \text{ over range } 500-2500 \text{ K} \]
\[ \Delta F_c = \pm 0.1 \text{ over range } 500-2500 \text{ K} \]

Comments on Preferred Values

There are no sufficiently direct measurements for this reaction. The preferred value for \( k_0 \) follows the analysis by Tsang and Hampson\(^7\) based on a RRKM fit of the reverse reaction. The preferred value for \( k_\infty \) follows the evaluation by Warnatz\(^6\). An RRKM modelling of the reaction from this evaluation with the potential energy surface calculated by Harding et al.\(^8\) leads to \( k_\infty = 1.1 \times 10^{14} \exp(-20000/T) \text{ s}^{-1} \) which is sufficiently close to the recommended value. As long as no more direct measurement are available, more elaborate specification of the \( T \) dependence of \( F_c \) appears premature.

References

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ \text{C}_2\text{H}_3 + \text{O}_2 \rightarrow \text{C}_2\text{H}_2 + \text{HO}_2 \quad (1) \]
\[ \rightarrow \text{H}_2\text{CO} + \text{CHO} \quad (2) \]
\[ \rightarrow \text{C}_2\text{H}_3\text{O}_2 \quad (3) \]

**Thermodynamic Data**

\[ \Delta H_{\text{fm}} (1) = -49 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{fm}} (1) = -6.7 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_p(1) = 1.69 \times 10^{-2} \text{ } T^{0.35} \exp(+5940/T) \]
\[ \Delta H_{\text{fm}} (2) = -360 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{fm}} (2) = 6.6 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_p(2) = 23.1 \text{ } T^{-0.33} \exp(+43000/T) \]

No thermodynamic data available for channel (3)

**Rate Coefficient Data** \((k = k_1 + k_2 + k_3)\)

<table>
<thead>
<tr>
<th>(k) ([\text{cm}^3\text{ molecule}^{-1}\text{ s}^{-1}])</th>
<th>(T) ([\text{K}])</th>
<th>Reference</th>
<th>Comments</th>
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<tbody>
<tr>
<td>(k_1) = 1.7 \times 10^{-12})</td>
<td>1726</td>
<td>Cooke and Williams (1971)(^1)</td>
<td>(a)</td>
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<td>(k_2) = 6.6 \times 10^{-12}\exp(+125/T))</td>
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<td>Slagle et al. (1984)(^2)</td>
<td>(b)</td>
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<td>(k_3) = 1.0 \times 10^{-11})</td>
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<td>Krueger and Weitz (1988)(^3)</td>
<td>(c)</td>
</tr>
<tr>
<td>(k_4) = 2.5 \times 10^{-12})</td>
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<td>Munk et al. (1987)(^4)</td>
<td>(d)</td>
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</tbody>
</table>

**Reviews and Evaluations**

| \(k_1\) = 1.7 \times 10^{-12}\) | 1000-2000 | Warnatz (1984)\(^5\) | (e) |
| \(k_1\) = 2.0 \times 10^{-13}\) | \(-\) | Tsang and Hampson (1986)\(^6\) | (f) |
| \(k_3\) = 1.0 \times 10^{-11}\) | \(-\) | \(-\) | \(-\) |

**Comments**

(a) Shock tube study of \(\text{C}_2\text{H}_4, \text{CH}_4 + \text{O}_2\) mixtures. Based on simulation of reaction mechanism.

(b) Excimer laser flash photolysis (193 nm) – photoionisation mass spectrometry at 0.76–3.60 Torr. Monitored \(\text{C}_2\text{H}_3, \text{CHO}, \text{H}_2\text{CO}\). No signals corresponding to products of channel (1), therefore \(k_1 \approx k_2\). Similar conclusion by Baldwin and Walker\(^7\).

(c) Excimer laser flash photolysis (248 nm) – diode laser spectroscopy on \(\text{C}_2\text{H}_4\) in \(\text{C}_2\text{H}_3/\text{HCl}/\text{O}_2\) mixtures at \(7\) Torr.

(d) Pulse radiolysis with variety \(\text{C}_2\text{H}_3\) precursors, pressure \(= 1\) atm. Monitored disappearance of \(\text{C}_2\text{H}_3\) and the build-up of a long-lived product at 230 and 270 nm. Latter ascribed to a product \(X\) of \(\text{C}_2\text{H}_3 + \text{O}_2\); the rate coefficient was deduced from the product build-up.

(e) Based on the observation that \(\text{H}_2\text{O}_2\) forming reactions of \(\text{R} + \text{O}_2\) have small pre-exponential factors of \(\approx 2 \times 10^{-12}\) \text{cm}^3\text{ molecule}^{-1}\text{ s}^{-1}.

(f) Determined by analogy with \(\text{C}_2\text{H}_3\).

**Reliability**

\[ \Delta \log k_2 = \pm 0.3 \text{ over range } 300–600 \text{ K}; \pm 0.5 \text{ over range } 600–2000 \text{ K} \]

**Comments on Preferred Values**

There is no direct evidence for the involvement of channel (1). There is excellent agreement between the data of Slagle et al.\(^2\) and Krueger and Weitz\(^3\). It is curious that Munk et al.\(^4\) record a slower reaction at higher pressures; it is possible that they were not observing the formation of \(\text{C}_2\text{H}_3\text{O}_2\) but of a secondary product.

**References**

Thermodynamic Data

\[ \Delta H_{298}^\circ (1) = -54.3 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298}^\circ (1) = -8.5 \text{ J K}^{-1}\text{mol}^{-1} \]
\[ K_e(1) = 1.19 \times 10^{-1} \exp(6550/T) \]

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

<table>
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<th>(k) ([\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}])</th>
<th>(T) ([\text{K}])</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_1 = 2.1 \times 10^{-13})</td>
<td>295</td>
<td>Plumb and Ryan (1981)</td>
<td>(a)</td>
</tr>
<tr>
<td>(1.5 \times 10^{-14} \exp(+1660/T))</td>
<td>294-1002</td>
<td>Slagle, Feng, and Gutman (1984)</td>
<td>(b)</td>
</tr>
<tr>
<td>(k_1 = 1.8 \times 10^{-14} \exp(+760/T))</td>
<td>593-753</td>
<td>McAdam and Walker (1987)</td>
<td>(c)</td>
</tr>
<tr>
<td>(k_2 \leq 0.01)</td>
<td>298</td>
<td>Niki et al. (1982)</td>
<td>(d)</td>
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</table>

Reviews and Evaluations

| \(k_1 = 2 \times 10^{-13}\) | 298   | CODATA (1984) | (e) |
| \(k_1 = 3.3 \times 10^{-12} \exp(-2510/T)\) | 700-2000 | Warnatz (1984) | (f) |
| \(k_1 = 1.4 \times 10^{-12} \exp(-1950/T)\) | 300-2500 | Tsang and Hampson (1986) | (g) |

Comments

(a) Discharge-flow system with He carrier gas. \(C_2H_5\) produced from \(Cl + C_2H_5\) and \([C_2H_4]\) and \([C_2H_2]\) measured directly by mass spectrometry. Rate coefficient determined from yields of \(C_2H_4\) and shown to be independent of pressure over range 0.6-10 Torr.

(b) Slow-flow system, radicals produced by \(Cl + C_2H_6\) reaction with pulsed formation of CI from IR multiphoton induced decomposition of CFCl_3. Reactants and products monitored in real time using photolization mass spectrometry. Rate expression has been calculated here from high-pressure values of \(k\) for the overall reaction.

(c) Thermal oxidation of \(C_2H_4CHO\) in a static system. Yields of \(C_2H_4\) and \(C_2H_2\) were determined by GC analysis for the early stages of the reaction. Ratio of rate coefficients determined to be \(k_1/k(C_2H_5 + C_2H_4CHO) = 6.76 \times 10^{-2} \exp(4414/T)\). The above value of \(k_1\) is derived by taking \(k(C_2H_5 + C_2H_4CHO) = 2.7 \times 10^{-13} \exp(-3636/T)\) \(\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}\) as evaluated by McAdam and Walker from literature data.

(d) FTIR study of the photo-oxidation of \(C_2H_4\) initiated by \(Cl_2\) in the presence of \(O_2/N_2\) mixtures at total pressures of 760 Torr. Rate coefficient ratio derived from the analysis of \(CH_3CHO, C_2H_5OH\) and \(C_2H_2\) products.

(e) Based on data of Plumb and Ryan.

(f) Based on an analysis of data prior to study of Plumb and Ryan.

(g) Based on data of Baldwin et al.

Preferred Values

\[ k_1 = 1.7 \times 10^{-14} \exp(+1100/T) \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1} \text{ over range 600-1200 K} \]

Reliability

\[ \Delta \log k_1 = \pm 0.3 \text{ over range 600-1200 K} \]

Comments on Preferred Values

For temperatures about 600 K we have chosen to represent \(k_1\), by a compromise between the results reported by McAdam and Walker and those we have derived from the data of Slagle et al.

Over the wider temperature range 300-1000 K a recent experimental and theoretical study by Wagner et al. recommends a mechanism involving activated \(C_2H_3O_2\) radicals and its isomerization to \(C_2H_3O_2^+\) radicals, followed by decomposition of this radical to the products \(C_2H_4\) and \(HO_2\). These authors have also derived complicated analytical functional forms to their mechanism to explain the observed rate dependences over the temperature range 300-1000 K. More work is required to confirm the details of the mechanism of the \(C_2H_5 + O_2\) reaction.

References

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

C₂H₅ + C₂H₅ → n-C₄H₁₀ (1)
→ C₂H₆ + C₂H₄ (2)

Thermodynamic Data
ΔH₂⁹⁸ (1) = −296 kJ mol⁻¹
ΔS₂⁹⁸ (1) = −160.4 J K⁻¹mol⁻¹

ΔH₂⁹⁸ (2) = −266 kJ mol⁻¹
ΔS₂⁹⁸ (2) = −55.1 J K⁻¹mol⁻¹
K_p (2) = 1.87 × 10⁻⁵ exp(3220/T)

Rate Coefficient Data (k = k₁ + k₂)

<table>
<thead>
<tr>
<th>k [cm³ molecule⁻¹ s⁻¹]</th>
<th>T[K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
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<tbody>
<tr>
<td>1.5 × 10⁻¹¹</td>
<td>296</td>
<td>Parkes and Quinn (1976)¹</td>
<td>(a)</td>
</tr>
<tr>
<td>2.4 × 10⁻¹¹</td>
<td>296</td>
<td>Adachi, Basco, and James (1979)²</td>
<td>(b)</td>
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<tr>
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<td>Corbel, Marquaire, and Côme (1981)³</td>
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<td>Demissay and Lesclaux (1982)⁴</td>
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<tr>
<td>2.2 × 10⁻¹¹</td>
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<td>Pacey and Wimalasena (1984)⁵</td>
<td>(e)</td>
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<tr>
<td>1.9 × 10⁻¹¹</td>
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<td>Munk et al. (1986)⁶</td>
<td>(f)</td>
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<td>1.63 × 10⁻¹¹</td>
<td>300-373</td>
<td>Arthur (1986)⁷</td>
<td>(g)</td>
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<tr>
<td>1.69 × 10⁻¹¹</td>
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<td>Anastasi and Arthur (1987)⁸</td>
<td>(h)</td>
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</tbody>
</table>

Reviews and Evaluations
k₁ = 2.3 × 10⁻¹⁴
k₂ = 1.8 × 10⁻¹¹
k₃ = 2.3 × 10⁻¹²

References
³ Warnatz (1984)⁹
² Tsang and Hampson (1986)¹⁰

Comments
(a) Molecular modulation spectroscopic study. C₂H₅ produced from photolysis of (C₂H₅N)₂ in presence of N₂ and monitored by UV absorption spectroscopy. k obtained from computer simulation of concentration profiles.
(b) Flash photolysis of mixtures of (C₂H₅N)₂ and n-C₄H₁₂. [C₂H₅] monitored by UV absorption spectroscopy.
(c) Pyrolysis of C₂H₅ in a continuous-flow stirred-tank reactor with end-product analyses by GC. k determined from a fit of rates of formation of C₂H₄ as a function of residence time in the reactor, based on a mechanism of 6 elementary reactions.
(d) Flash photolysis - laser resonance absorption study of NH₂ reactions in presence of C₂H₅. NH₂ produced from photolysis of NH₃ and [NH₂] monitored by absorption at 597.73 nm. C₂H₅ produced from H + C₄H₄. k(NH₂ + C₄H₄) and k(C₂H₅ + C₂H₄) derived from a fit of [NH₂] profiles.
(f) Pulse radiolysis study with [C₂H₅] monitored by UV absorption. C₂H₅ produced from H + C₂H₆. k derived from computer simulations of [C₂H₅] profiles in real time.

Preferred Values
k₁ = 1.9 × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ over range 300-1200 K
k₂ = 2.4 × 10⁻¹² cm³ molecule⁻¹ s⁻¹ over range 300-1200 K

Reliability
Δlog k₁ = ± 0.3 over range 300-1200 K
Δlog k₂ = ± 0.4 over range 300-1200 K

Comments on Preferred Values
The preferred rate coefficient is the mean of the results of Parkes and Quinn¹, Adachi et al.², Demissay and Lesclaux³, Pacey and Wimalasena⁴, Munk et al.⁵, Arthur⁷, and Anastasi and Arthur⁸ which are all in substantial agreement. The preferred branching ratio, k₂/k₁ was then calculated from the disproportionation-combination ratio, k₂/k₁ = 0.14, which is widely accepted⁹ at low temperatures and which appears to be applicable at higher temperatures as well¹⁰.

There are very few reliable studies of this reaction at temperatures above 1200 K, hence the restricted range over which the preferred rate coefficients are recommended.

References

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ C_2H_5 + C_2H_5 \rightarrow n-C_4H_{10} \]
\[ \rightarrow C_3H_6 + C_2H_4 \]

EXPERIMENTAL DATA

- Parkes and Quinn 1976
- Adachi et al. 1979
- Corbel et al. 1981
- Demisy and Lescaux 1982
- Pacey and Wimbush 1984
- Morik et al. 1986
- Arthur 1986
- Anastasi and Arthur 1987

This Recommendation (k1) 1989
This Recommendation (k2) 1989

Thermodynamic Data

\[ \Delta H_{298} = 375 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298} = 159 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ K_p = 4.15 \times 10^7 T^{-0.29} \exp(-45700/T) \text{ atm} \]

Rate Coefficient Data

<table>
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<th>[M] [molecule cm(^{-3})]</th>
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<td>Intermediate Fall-off Range</td>
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<tr>
<td>1.2\times10^{-7}</td>
<td>823</td>
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<td>Lin and Back (1966)(^1)</td>
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<td>Olson et al. (1979)(^6)</td>
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<td>5.0\times10^{17} (Ar)</td>
<td>Chiang and Skinner (1981)(^7)</td>
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<tr>
<td>Reviews and Evaluations</td>
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<td>Warnatz (1984)(^1)</td>
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<td>( k_\omega ) = 3.2\times10^{12} T^{-1.39} exp(-45834/T)</td>
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<td>Tsang and Hampson (1986)(^1)</td>
<td><em>(n)</em></td>
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<td>300-1400</td>
<td></td>
<td>Tsang (1989)(^1)</td>
<td><em>(o)</em></td>
</tr>
</tbody>
</table>

Comments

(a) Static reactor, dissociation of pure ethane with measurement of the rate of production of methane and butane. Extrapolation to the high pressure limit and comparison with earlier work.
(b) Ethane dissociation studied in static reactor. Product analysis by gas chromatography. Extrapolation to the high pressure limit. Relative efficiencies of different bath gases: $k_0(M)/k_0(C_2H_6) = 0.25 (N_2), 0.33 (O_2), 0.17 (He), 0.18 (Ne), 0.26 (Ar), 0.30 (Kr), 0.88 (H_2O)$.
(c) Pyrolysis of ethane in static reactor. Analysis of initiation of the reaction using manometric and gas chromatographic measurements.
(d) Pyrolysis of CO/O_2/ethane/azomethane/Ar mixtures in a shock tube. The reaction was followed by measuring emission from CO and CO_2. Modelling with 8 reactions.
(e) Static reactor study of dissociation in pure ethane. Gas chromatographic analysis of reaction products.
(f) Shock tube study of ethane dissociation in Ar using laser-absorption and laser-schlieren measurements. Modelling of mechanism. Data near 1300 K are markedly lower than recombination results and shock wave results from Ref. 7. Better agreement with Ref. 7 at higher temperatures. Extrapolation to the high pressure limit uncertain due to fall-off effects.
(g) Shock tube study of ethane decomposition in Ar measuring H atom concentrations from CH_3 + C_2H_6 → CH_4 + C_2H_5, C_2H_5 → 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.
(l) Complete review of earlier literature.
(m) Data evaluation and simplified fall-off construction.
(n) Data evaluation and construction of RRKM fall-off curves.
(o) See comment (n).

Preferred Values

$k_\text{a} = 1.8 \times 10^{24} T^{-1.24} \exp(-45700/T) \text{ s}^{-1} \text{ over range 300–2000 K}$

$k_0 = [\text{Ar}] \times 10^{25} T^{-0.24} \exp(-47090/T) \text{ s}^{-1} \text{ over range 300–2000 K}$

$F_c = 0.38 \exp(-T/73) + 0.62 \exp(-T/1180)$ for $M = \text{Ar}$ over range 300–2000 K

Reliability

$\Delta \log k_\text{a} = \pm 0.3 \text{ over range 300–2000 K}$

$\Delta \log k_0 = \pm 0.5 \text{ for } M = \text{Ar}$ over range 300–2000 K

$\Delta F_c = \pm 0.1 \text{ for } M = \text{Ar}$ over range 300–2000 K

$\Delta F_e = \pm 0.1 \text{ for } M = \text{C}_2\text{H}_6 \text{ over range 800–1000 K}$

Comments on Preferred Values

The preferred values for $k_\text{a}$ and $k_0$ (for $M = \text{Ar}$) have been derived from the recommended rate coefficients of the reverse reaction $2 \text{CH}_3 + M \rightarrow \text{C}_2\text{H}_4 + \text{M}$ from this evaluation and the given expression of the equilibrium constant. They are based on the combined evaluation of dissociation and recombination data given in the review of Ref. 16 which assumes a nearly temperature independent rate coefficient $k_\text{a}$ for the reverse recombination over the range 300–2000 K. The expressions for $k_0$ and $F_c$ also follow the combination of experimental and theoretical data analysed in Ref. 16. The preferred values obtained in this way are in good agreement with the available dissociation experiments. They are not influenced by the numerous mechanistic complications of the high temperature shock tube studies of this dissociation.

References

\[ \text{C}_{2}\text{H}_{6} + \text{M} \rightarrow \text{CH}_{3} + \text{CH}_{3} + \text{M} \]

**EXPERIMENTAL DATA**

- Lu and Bock 1966
- Trenwith 1966
- Robinson and Holbrook 1972
- Clarke and Quinn 1975
- Trenwith 1979
- Trenwith 1988

**Log(k/s)** vs. **Log(P/Torr)**

---

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[
\begin{align*}
\text{CHCO} + \text{O}_2 & \rightarrow \text{CO}_2 + \text{CHO} \quad (1) \\
& \rightarrow 2\text{CO} + \text{OH} \quad (2) \\
& \rightarrow \text{C}_2\text{O} + \text{HO}_2 \quad (3) \\
\text{CHCO} + \text{O}_2 (+ \text{M}) & \rightarrow \text{CHO}_2\text{CO} (+ \text{M}) \quad (4)
\end{align*}
\]

**Thermodynamic Data**

\[
\begin{align*}
\Delta H_{298}^\circ (1) &= -527.6 \text{kJ mol}^{-1} \\
\Delta S_{298}^\circ (1) &= -20.9 \text{J K}^{-1}\text{mol}^{-1} \\
K_p(1) &= 0.847 \exp(+63459/T) \\
\Delta H_{298}^\circ (2) &= -359.7 \text{kJ mol}^{-1} \\
\Delta S_{298}^\circ (2) &= 119.5 \text{J K}^{-1}\text{mol}^{-1} \\
K_p(2) &= 7.17 \times 10^8 \exp(+42842/T) \text{atm}
\end{align*}
\]

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

<table>
<thead>
<tr>
<th>[k [\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]]</th>
<th>Temperature [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.7 \times 10^{-14} \quad (M = \text{N}_2, 2 \text{ Torr})</td>
<td>296</td>
<td>Jones and Bayes (1973)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>2.7 \times 10^{-12} \exp(-430/T) \quad (M = \text{He}, 2 \text{ Torr})</td>
<td>–</td>
<td>Peeters, Schaekers, and Vinckier (1986)(^2)</td>
<td>(b)</td>
</tr>
</tbody>
</table>

**Comments**

(a) Discharge flow study; O atoms generated by N + NO. CHCO produced as intermediate from C\(_2\)H\(_2\) with [CHCO] and [O] measured by photoionisation mass spectrometry. [CHCO] measured in presence and absence of O\(_2\), and \(k(\text{CHCO} + \text{O}_2)/k(\text{CHCO} + \text{O}) = 0.018 \pm 0.003\) at 296 K obtained from a Stern-Volmer plot. Used \(k(\text{CHCO} + \text{O}) = 2.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\), obtained by Jones and Bayes\(^3\) in a related study. Data obtained at total pressures of 2 Torr (mostly N\(_2\)).

(b) Reported by Peeters, Schaekers, and Vinckier\(^2\). No experimental details given. Radical concentrations measured by molecular beam mass spectroscopy. [CHCO]-time profile measured in presence and absence of molecular O\(_2\). No temperature range quoted, but Peeters \textit{et al.}\(^4\) use the expression in the range 300–550 K.

**Preferred Values**

\[
k = 2.7 \times 10^{-12} \exp(-430/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range 300–550 K (M = He, 2 Torr) }
\]

**Reliability**

\(\Delta \log k = \pm 0.7\) over range 300–550 K

**Comments on Preferred Values**

Kinetic data on this reaction are very limited, and no products have been suggested. \(k\) may be pressure-dependent, although no dependency was reported. Both studies involved total pressures of about 2 Torr, but different inert gases. The \(k\) values differ by a factor of about 20 at 296 K, but use of \(k(\text{CHCO} + \text{O}) = 1.16 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) at 296 K obtained by Vinckier \textit{et al.}\(^4\) with Jones and Bayes\(^1\) ratio gives \(k = 2.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) which is only a factor of 3 greater than \(k = 6.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) obtained from the expression given by Peeters \textit{et al.}\(^2\). This factor is probably within the combined experimental error involved in the two determinations, particularly as experimental conditions are uncertain.

**References**


\(^3\) T. N. Jones and K. D. Bayes, 14th Symp. (Int.) Combust., 277 (1973).

\[
\text{CH}_2\text{CHO} + \text{O}_2 \rightarrow \text{CH}_2\text{CO} + \text{HO}_2 \quad (1) \\
\rightarrow \text{HCHO} + \text{CO} + \text{OH} \quad (2)
\]

**Thermodynamic Data**

\[
\Delta G_{\text{liq}} (1) = -66.5 \text{ kJ mol}^{-1} \\
\Delta G_{\text{liq}} (1) = -29.7 \text{ kJ mol}^{-1} \\
K_p(1) = 0.344 T^{0.592} \exp\left(\frac{7960}{T}\right) \\
\Delta G_{\text{liq}} (2) = -212.6 \text{ kJ mol}^{-1} \\
\Delta G_{\text{liq}} (2) = -126.7 \text{ kJ mol}^{-1} \\
K_p(2) = 5.5 \times 10^{8} T^{-0.62} \exp\left(\frac{25160}{T}\right) \text{ atm}
\]

**Rate Coefficient Data**

\[
k = k_1 + k_2
\]

<table>
<thead>
<tr>
<th>(k [\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}])</th>
<th>(T [\text{K}])</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2.7 \times 10^{-14} \exp(+668/T)) (100 Torr He)</td>
<td>300-500</td>
<td>Lorenz et al. (1984)</td>
<td>(a)</td>
</tr>
<tr>
<td>(2.46 \times 10^{-13}) (100 Torr N(_2))</td>
<td>295</td>
<td>Gutman and Nelson (1983)</td>
<td>(b)</td>
</tr>
<tr>
<td>(2.5 \times 10^{-13}) (90 Torr SF(_6))</td>
<td>295</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Comments**

(a) Laser photolysis of CH\(_3\)OCH = CH\(_2\) at 193 nm; laser induced fluorescence detection of CH\(_2\)CHO at 337 nm. Reaction is pressure dependent between 10 and 280 mbar (M = He). Fall-off curve analysis using \(F_s = 0.6\) gave \(k_s = (2.6 \pm 0.5) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) and \(k_0 = 2 \pm 2 \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-2} \text{ s}^{-1}\). Yield of OH product = 20% as determined by LIF, at 25 mbar He and 298 K.

(b) Laser photolysis of CI\(_3\)OCl = CI\(_2\) at 193 nm; laser induced fluorescence detection of CH\(_2\)CHO at 337 nm. Reaction is pressure dependent between 1.5 and 100 Torr. Data given are for highest pressures of N\(_2\) and SF\(_6\) used. Data for lower pressure presented in figure.

**Preferred Values**

\(k_s = 2.6 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) over range 250-500 K

\(k_2 = 3.0 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) at 300 K

**Reliability**

\(\Delta \log k_s = \pm 0.5\) at 1000 K reducing to \(\pm 0.2\) at 300 K

\(\Delta \log k_2 = \pm 0.3\) at 300 K

**Comments on Preferred Values**

The results of the two studies of this reaction using the laser photolysis-LIF technique are in excellent agreement where measurements are under comparable conditions. Both studies show that there is a pressure effect consistent with an addition reaction as one of the channels. The observation of OH product at low pressure indicates a possible bimolecular channel as well. The preferred value for \(k_s\) is based on the values of \(k\) at pressures \(\geq 100\) Torr He, N\(_2\) or SF\(_6\) from both studies at 292-300 K. The recommended value of \(k_2\) may apply to low pressures only since the pressure dependence of the OH yield is not established.

The temperature dependence of the rate coefficient at higher temperatures is difficult to define because of fall-off effects. The data indicate little variation of \(k_s\) with temperature up to 500 K. Lack of data at low pressures and the possibility of a bimolecular channel precludes the recommendation of a value for \(k_0\).

**References**

CH₂CHO + O₂ → CH₂CO + HO₂
→ HCHO + CO + OH
→ O₂CH₂CHO

T/K

\[ 10^3 T^{-1} / K^{-1} \]

Gutman and Nelson (SF₆) 1983
Gutman and Nelson (N₂) 1983
Lorenz et al. (He) 1984
This Recommendation k(inf) 1989
BAULCH ET AL.

\( \text{CH}_3\text{CO} + \text{O}_2 (+ \text{M}) \rightarrow \text{CH}_3\text{CO}_3 (+ \text{M}) \)

### Rate Coefficient Data

<table>
<thead>
<tr>
<th>( k [\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}] )</th>
<th>( T [\text{K}] )</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate Coefficient Measurements</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 2 \times 10^{-12} )</td>
<td>298</td>
<td>McDade et al. (1982)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>Reviews and Evaluations</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 3 \times 10^{-12} )</td>
<td>298</td>
<td>Tsang and Hampson (1986)(^2)</td>
<td>(b)</td>
</tr>
<tr>
<td>( 2 \times 10^{-12} ) (1-4 Torr)</td>
<td>298</td>
<td>IUPAC (1989)(^3)</td>
<td>(c)</td>
</tr>
<tr>
<td>( 5 \times 10^{-12} )</td>
<td>200-300</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### Comments

(a) Flash photolysis of \( \text{CH}_3\text{COCH}_3 \) or \( \text{CH}_3\text{COCH}_2\text{COCH}_3 \)-photoionisation mass spectrometric detection of \( \text{CH}_3\text{CO} \) in excess \( \text{O}_2 \). Independent of pressure 1-4 Torr.

(b) Based on results of McDade et al.\(^1\).

(c) Based on results for analogous reaction of \( \text{C}_2\text{H}_5 \) with \( \text{O}_2 \).

**Preferred Values**

\[ k = 2 \times 10^{-12} \ \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \] at 298 K

**Reliability**

\[ \Delta \log k = \pm 0.3 \] at 298 K

### Comments on Preferred Values

There is only one direct study of this reaction which was conducted at room temperature. The rate coefficient obtained is comparable to that found for the reaction of \( \text{C}_2\text{H}_5 \) under similar conditions. The latter reaction has a substantial negative temperature coefficient, a pressure dependence, and an additional channel forming \( \text{HO}_2 \). The same complex kinetic behaviour probably applies to \( \text{CH}_3\text{CO} + \text{O}_2 \), but in the absence of data, we can only recommend a value for \( k \) at 298 K.

#### References

\(^3\) R. Atkinson et al., IUPAC Task Group on Data Evaluation (1989).

### Thermodynamic Data

\( \Delta H_{298} = 361 \ \text{kJ mol}^{-1} \)

\( \Delta S_{298} = 117 \ \text{J K}^{-1} \text{mol}^{-1} \)

\( K_c = 5.92 \times 10^9 \exp(-43100/T) \) atm

### Rate Coefficient Data

<table>
<thead>
<tr>
<th>( k [\text{s}^{-1}] )</th>
<th>( T [\text{K}] )</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate Coefficient Measurements</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 2.0 \times 10^{13} \exp(-39800/T) )</td>
<td>753-813</td>
<td>Liu and Laidler (1968)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>( 7.1 \times 10^{15} \exp(-41100/T) )</td>
<td>1000-1200</td>
<td>Colket et al. (1975)(^3)</td>
<td>(b)</td>
</tr>
<tr>
<td>Reviews and Evaluations</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 2.0 \times 10^{15} \exp(-39800/T) )</td>
<td>500-2000</td>
<td>Warnatz (1984)(^3)</td>
<td>(c)</td>
</tr>
</tbody>
</table>

#### Comments

(a) Static reactor. Pyrolysis of \( \text{CH}_3\text{CHO} \); \( k \) determined from time dependence of product \( \text{C}_2\text{H}_6 \) and \( \text{C}_2\text{H}_4 \).

(b) Turbulent flow reactor at 1 atm pressure. \( M = \text{N}_2 \); \( k \) determined as in (a).

(c) Based on expression of Liu and Laidler\(^1\).

#### Preferred Values

\[ k = 7.1 \times 10^{15} \exp(-41100/T) \] s\(^{-1}\) over range 750-1200 K at 1 atm pressure

**Reliability**

\[ \Delta \log k = \pm 0.4 \] over range 750-1200 K

**Comments on Preferred Values**

Preferred value is based on the data of Colket et al.² which are in good agreement with the earlier work. The reaction is in the fall-off region in the specified temperature region and the expression applies to 1 atm pressure only.

**Thermodynamic Data**

\[ \Delta H_{298} = 70.0 \text{ kJ mol}^{-1} \]

**Comments**

There are no reliable experimental data for the thermal decomposition of \( \text{C}_2\text{H}_5\text{O} \). Leggett and Thynne¹ studied pyrolysis of \( \text{C}_2\text{H}_5\text{O}_2 \) and extracted a rate coefficient for decomposition of \( \text{C}_2\text{H}_5\text{O} \) over the range 422–449 K of \( 1.4 \times 10^{12} \exp(-11120/1') \text{ s}^{-1} \), independent of pressure. Since the reaction is almost certainly in the fall-off region under their conditions, this result is doubtful. In a recent review, Batt² has suggested the following expression for the high pressure limit: \( k_a = 8.0 \times 10^{13} \exp(-10830/T) \text{ s}^{-1} \).

**References**


---

<table>
<thead>
<tr>
<th>Rate Coefficient Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k ) [cm³ molecule⁻¹ s⁻¹]</td>
</tr>
<tr>
<td>--------------------------</td>
</tr>
<tr>
<td><strong>Rate Coefficient Measurements</strong></td>
</tr>
<tr>
<td>( 8.0 \times 10^{-12} )</td>
</tr>
<tr>
<td>( 9.8 \times 10^{-15} )</td>
</tr>
<tr>
<td>( 1.2 \times 10^{-13} \exp(-924/T) )</td>
</tr>
<tr>
<td><strong>Reviews and Evaluations</strong></td>
</tr>
<tr>
<td>( 8.0 \times 10^{-15} )</td>
</tr>
</tbody>
</table>

**Comments**

(a) Laser photolysis of \( \text{C}_2\text{H}_5\text{ONO} \) at 266 nm; \( \text{C}_2\text{H}_5\text{O} \) monitored by LIF. Pseudo first order conditions with excess \( \text{O}_2 \).
(b) Steady state photolysis of \( \text{C}_2\text{H}_5\text{ONO} \) at 366 nm in the presence of \( \text{O}_2 \) and \( \text{NO} \). \( k \) measured relative to \( \text{C}_2\text{H}_5\text{O} + \text{NO} \rightarrow \) products; i.e. \( k/k(\text{C}_2\text{H}_5\text{O} + \text{NO}) = 6.8 \times 10^{-3} \exp(-924/T) \). Pressure > 155 Torr, \( M = \text{N}_2 \).
(c) Based on data of Gutman et al.¹.

**Preferred Values**

\[ k = 1.0 \times 10^{-12} \exp(-830/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range 300–1000 K} \]

**Reliability**

\[ \Delta \log k = \pm 0.3 \text{ at 300 K rising to } \pm 0.5 \text{ at 1000 K} \]
C₂H₂OOH (+ M) → C₂H₂O + OH (+ M)

Comment
There are no experimental data for the thermal decomposition of C₂H₂OOH. The high pressure limit rate constant \( k_\infty = 4.0 \times 10^{15} \exp(-21600/T) \) s\(^{-1}\) is recommended by analogy with the decomposition of CH₂OOH.

\[ \text{C}_6\text{H}_5(\pm \text{M}) \rightarrow \text{C}_2\text{H}_2 + \text{C}_4\text{H}_3(\pm \text{M}) \quad (1) \]
\[ \rightarrow \text{C}_2\text{H}_2 + \text{C}_4\text{H}_3(\pm \text{M}) \quad (2) \]
\[ \rightarrow \text{linear-C}_6\text{H}_5(\pm \text{M}) \quad (3) \]

Thermodynamic Data

\( \Delta H_{298}^\circ (1) = 325.0 \text{ kJ mol}^{-1} \)
\( \Delta S_{298}^\circ (1) = 185.6 \text{ J K}^{-1}\text{mol}^{-1} \)
\( K_p(1) = 9.7 \times 10^{18} \exp(-39600/T) \text{ atm} \)

\( \Delta H_{298}^\circ (2) = 425.2 \text{ kJ mol}^{-1} \)
\( \Delta S_{298}^\circ (2) = 193.3 \text{ J K}^{-1}\text{mol}^{-1} \)
\( K_p(2) = 9.2 \times 10^{10} \exp(-51680/T) \text{ atm} \)

\( \Delta H_{298}^\circ (3) = 97.2 \text{ kJ mol}^{-1} \)
\( \Delta S_{298}^\circ (3) = 261.9 \text{ J K}^{-1}\text{mol}^{-1} \)
\( K_p(3) = 7.9 \times 10^{12} \exp(-41176/T) \text{ atm} \)

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

<table>
<thead>
<tr>
<th>Rate Coefficient Measurements</th>
<th>( T ) [K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 + k_2 = 1.2 \times 10^{13} \exp(-41265/T) )</td>
<td>1570-1790</td>
<td>Rao and Skinner (1984)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>( k_1 = 1.6 \times 10^{13} \exp(-41265/T) )</td>
<td>1900-2400</td>
<td>Kiefer et al. (1985)(^2)</td>
<td>(b)</td>
</tr>
<tr>
<td>( k_2 = 3.5 \times 10^{13} \exp(-32700/T) )</td>
<td>1500-2400</td>
<td>Colket (1987)(^3)</td>
<td>(c)</td>
</tr>
<tr>
<td>( 5.0 \times 10^{13} \exp(-36736/T) )</td>
<td>1500-1900</td>
<td>Rao and Skinner (1988)(^4)</td>
<td>(d)</td>
</tr>
<tr>
<td>( k_3 = 3.0 \times 10^{13} \exp(-36736/T) )</td>
<td>1500-1900</td>
<td>(e)</td>
<td></td>
</tr>
<tr>
<td>( k_3 = 4.5 \times 10^{13} \exp(-35500/T) )</td>
<td>1450-1730</td>
<td>Braun-Unkukoff et al. (1989)(^5)</td>
<td>(f)</td>
</tr>
</tbody>
</table>

Comments

(a) Dissociation of chlorobenzene behind reflected shock waves at total pressures of about 2.7 bar. Hydrogen atom production was monitored by ARAS during pyrolysis of 10 ppm chlorobenzene in argon. From the measured profiles it was deduced that the hydrogen atoms are formed in a secondary reaction step. Therefore it was not possible to discriminate between reaction pathway (1) or (2). An Arrhenius expression is evaluated for the overall process C₆H₅ → C₂H₂ + C₄H₃ + H₂.O.

(b) Mixtures of 1 and 2 mol% benzene in krypton have been studied in a shock tube at \( 0.2 < p < 1 \) atm using the laser schlieren technique. The measured density gradient profiles and some time-of-flight mass spectra were modelled by a 26 step reaction mechanism. RRKM calculations are also presented. A high pressure limiting rate coefficient for reaction pathway (1) was derived at total pressures around 1 bar. For total pressures of 0.47 and 0.2 bar second-order rate coefficient expressions are deduced, indicating significant fall-off behaviour for the lower pressure regime.

(c) Single-pulse shock tube experiments on acetylene and vinylacetylene pyrolysis for the temperature range 1100-2400 K at total pressures of about 8 bar. Initial concentrations of the hydrocarbon in argon ranged from 100 ppm to 4%. Gas samples were collected and analyzed using gas chromatography. The rate coefficients for the ring formation process \( n-\text{C}_4\text{H}_5(\pm \text{C}_2\text{H}_2) \rightarrow \text{linear-C}_4\text{H}_5 \rightarrow \text{C}_6\text{H}_5 \) were deduced by applying a comprehensive reaction mechanism. The rate coefficient for reaction (3) was calculated using a heat of formation for the linear-C₆H₅ radical of 582 kJ/mol. No sensitivity calculations of reaction (3) are given.

(d) Highly dilute mixtures of C₆D₆, C₆H₅Cl, C₆H₅Br, and C₆H₃ were pyrolyzed behind incident shock waves at \( p = 0.4 \) atm. The formation of H and D atoms was monitored by the ARAS technique. RRKM calculations were carried out to evaluate unimolecular fall-off rate expressions. Rate coefficient expressions for the dissociation of phenyl radicals were deduced from the pyrolysis of chloro- and bromobenzene. From these experiments it was found that about 18% of the phenyl radicals dissociate in some way without formation of H atoms, while the remainder produces...
hydrogen atoms, presumably via a linear-C$_6$H$_5$ radical.

(e) Experimental conditions of (d). From the iodobenzene results it was found necessary to introduce additional reactions into the model, especially the dissociation of iodobenzene into phenyl and iodine atoms, which has been measured by Robaugh and Tsang$^6$. RRKM calculations indicate that the phenyl dissociation should proceed with a rate constant approaching the limiting high pressure value.

(f) Dissociation of phenyl radicals behind reflected shock waves has been investigated by monitoring H atoms with ARAS. The density range was $(1.0-1.7)\times10^{-3}$ mol cm$^{-3}$. Nitrosobenzene C$_6$H$_5$NO served as thermal source for the phenyl radicals. The test gas mixtures consisted of argon with relative concentrations of 1 to 100 ppm nitrosobenzene. For a first order formation rate in the early stage of the phenyl decomposition a value for the activation energy of $306 \pm 8$ kJ/mol was found. From thermodynamic data together with the experimental value for the activation energy it is impossible to attribute the high temperature H-atom formation to a direct decomposition pathway of phenyl. Therefore a two step reaction mechanism, starting with isomerisation from the aromatic phenyl to a linear structure, which dissociates immediately to products which include H atoms, has been assumed. The experimental rate expression for the isomerisation reaction is in good accord with the findings of Ref. 4.

**Preferred Values**

$$k_3 = 4.0 \times 10^{13} \exp(-36700/T) \text{ s}^{-1} \text{ over range 1450-1900 K}$$

Presumably not far from $k_\infty$

**Reliability**

$$\Delta \log k = \pm 0.4 \text{ over whole range}$$

**Comments on Preferred Values**

The heats of reaction for different decomposition pathways of phenyl give values on the order of 335 to 502 kJ/mol. These findings are incompatible with a high activation energy of about 306 kJ/mol. For the linear aliphatic structure C$_6$H$_5$ a value of about 586 $\pm$ 12.6 kJ/mol for the heat of formation was estimated by applying Benson's method$^7$. Together with 329–340 kJ/mol$^8$ for the heat of formation for the phenyl radical, values of 255–268 kJ/mol are found for the heat of reaction for pathway (3), which are compatible with the experimentally derived apparent activation energy of about 306 kJ/mol (Refs. 4 and 5). Consequently a rate coefficient for only the isomerisation reaction (3) is recommended. RRKM calculations$^9$ indicate that at temperatures around 1500 K and at total pressures of about 1 bar the rate of reaction (3) is not far from the high pressure limiting value ($k/k_\infty = 0.5-0.7$).

**References**

\[ \text{C}_6\text{H}_5 \rightarrow \text{C}_2\text{H}_2 + \text{C}_4\text{H}_3 \]
\[ \rightarrow \text{C}_2\text{H}_2 + \text{C}_4\text{H}_2 \]
\[ \rightarrow \text{linear-C}_6\text{H}_5 \]

**Experimental Data**
- Rao and Skinner (k1+k2) 1984
- Kiefer et al (k1) 1985
- Rao and Skinner 1985
- Rao and Skinner (k1) 1985
- Braun-Unkhoff et al (k3) 1989
- Calkin (k3) 1987
- This Recommendation (k3) 1989
EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

C₆H₆(+ M) → H + C₆H₅(+ M)  \hspace{1cm} (1)

→ C₆H₄ + C₂H₆(+M)  \hspace{1cm} (2)

**Thermodynamic Data**

- \( \Delta H_{\text{fus}} (1) = 463.5 \text{ kJ mol}^{-1} \)
- \( \Delta S_{\text{fus}} (1) = 133.7 \text{ J K}^{-1} \text{mol}^{-1} \)
- \( K_p (1) = 9.7 \times 10^{17} \text{ T}^{-1/2} \exp(-55840/T) \text{ atm} \)

- \( \Delta H_{\text{fus}} (2) = 451.9 \text{ kJ mol}^{-1} \)
- \( \Delta S_{\text{fus}} (2) = 210.4 \text{ J K}^{-1} \text{mol}^{-1} \)
- \( K_p (2) = 1.1 \times 10^{15} \text{ T}^{-1/2} \exp(-54940/T) \text{ atm} \)

**Rate Coefficient Data** \( k = k_1 + k_2 \)

<table>
<thead>
<tr>
<th>( k \text{[s}^{-1}] )</th>
<th>( T \text{[K]} )</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2 \times 10^{18} \exp(-53432/T)</td>
<td>1300-1700</td>
<td>Fujii and Asaba (1972)⁴</td>
<td>(a)</td>
</tr>
<tr>
<td>1.6 \times 10^{18} \exp(-51329/T)</td>
<td>1200-1900</td>
<td>Fujii and Asaba (1977)⁵</td>
<td>(b)</td>
</tr>
<tr>
<td>3.9 \times 10^{10} \exp(-18935/T)</td>
<td>1400-2200</td>
<td>Singh and Kern (1983)⁶</td>
<td>(c)</td>
</tr>
<tr>
<td>7.0 \times 10^{13} \exp(-47801/T)</td>
<td>1630-1940</td>
<td>Rao and Skinner (1984)⁷</td>
<td>(d)</td>
</tr>
<tr>
<td>4.6 \times 10^{12} \exp(-44787/T)</td>
<td>1515-2500</td>
<td>Kern et al. (1984)⁸</td>
<td>(e)</td>
</tr>
<tr>
<td>1.3 \times 10^{13} \exp(-44284/T)</td>
<td>1515-2500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.0 \times 10^{12} \exp(-54300/T)</td>
<td>1600-2300</td>
<td>Hsu, Lin, and Lin (1984)⁹</td>
<td>(f)</td>
</tr>
<tr>
<td>2.0 \times 10^{12} \exp(-59381/T)</td>
<td>1900-2400</td>
<td>Kieter et al. (1975)¹⁰</td>
<td>(g)</td>
</tr>
<tr>
<td>9.3 \times 10^{12} \exp(-53432/T)</td>
<td>1500-1900</td>
<td>Rao and Skinner (1988)⁵</td>
<td>(h)</td>
</tr>
</tbody>
</table>

**Comments**

(a) Rich mixtures of benzene and oxygen were pyrolyzed in a single pulse shock tube. The reaction progress was followed by light absorption (formation of biphenyl in the wavelength range of 315 to 600 µm) and IR emission (formation of CO in the wavelength range of 3000 to 5000 µm) behind incident shock waves. The products were also analyzed by GC. The experimental data could be modelled by a simple reaction scheme in the initial stage.

(b) The high temperature pyrolysis of benzene was studied in a single pulse shock tube. Gas samples were heated by reflected shock waves; the products were analyzed by GC. The reaction progress was also followed by light absorption at 200–600 nm (benzene, biphenyl). The experimental data are explained by a chain mechanism consisting of 7 elementary reactions (channel (1)).

(c) The pyrolysis of mixtures of 2.1–5% benzene diluted with neon was studied behind reflected shock waves. Products were analyzed by recording time-of-flight mass spectra. The data could be reproduced from a five step reaction mechanism. The first order rate expression as presented in the table has been calculated for a density of 2.6 \times 10^{-5} \text{ mol cm}^{-3} from the second order rate coefficient evaluated by the authors.

(d) Dilute mixtures of 3–20 ppm C₆D₆ were pyrolyzed behind reflected shock waves at \( p < 3 \text{ atm} \). The formation of D atoms was monitored by time resolved ARAS. A six step reaction mechanism was used to model the experimental data. The rate coefficient for H atom production was determined by using approximate isotope effect calculations.

(e) The rate coefficients for both product channels were derived in a collaborative study on C₆H₆ and C₆D₆ pyrolysis using three independent shock tube methods: time-of-flight mass spectrometry, time resolved ARAS, and laser schlieren density gradient profiles.

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

(g) Mixtures of 1 and 2 mol% benzene in krypton have been heated in a shock tube at 0.2 < \( p < 1 \text{ atm} \) using the laser schlieren technique. The measured density gradient profiles and some time-of-flight mass spectra were modelled by a 26 step reaction mechanism. RRKM calculations are also presented. A high pressure limiting rate coefficient for reaction pathway (1) was derived.

(h) The rate coefficient for the production of H atoms in channel (1) was derived from approximate isotope effect calculations. Highly dilute mixtures of C₆D₆, C₆H₅Cl, C₆H₅Br, and C₆H₅I were pyrolyzed behind incident shock waves at \( p = 0.4 \text{ atm} \). The formation of H and D atoms was monitored by the ARAS technique. RRKM calculations were carried out to account for unimolecular fall-off and to distinguish the rate constant for dissociation of C₆H₆ to that for the dissociation of C₆D₆.

**Preferred Values**

\[ k = 9.0 \times 10^{12} \exp(-54060/T) \text{ s}^{-1} \text{ over range 1200–2500 K} \]

**Reliability**

\[ \log k = ± 0.4 \text{ at 1200 K reducing to ±0.3 at 2000 K} \]

**Comments on Preferred Values**

From the present data a first order rate expression for benzene decomposition is evaluated. Although most of the experimental work is interpreted by the authors as indicating that the H-atom producing reaction channel (1)
is the dominant one, it should be mentioned that the diagnostic methods of many of the experiments do not permit a distinction between product channels. Consequently a rate coefficient for the overall reaction is recommended.

References

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ C_6H_6 + M \rightarrow C_6H_5 + H + M \]
\[ \rightarrow C_4H_4 + C_2H_2 + M \]

T/K

0.4 0.5 0.6
0.7 0.8

Log(k/s⁻¹)

10³T⁻¹/K⁻¹

EXPERIMENTAL DATA
- Fuji and Asaba (k1) 1972
- Fuji and Asaba (k1) 1977
- Singh and Kern (k1) 1983
- Rao and Skinner (k1) 1984
- Kern et al (k1) 1984
- Hsu et al (k1) 1984
- Kister et al (k1) 1985
- Roo and Skinner (k1) 1989

This Recommendation 1989
**Thermodynamic Data**

\[ \Delta H_{298}^o = 94.5 \text{ kJ mol}^{-1} \]

\[ \Delta S_{298}^o = 184.2 \text{ J K}^{-1} \text{mol}^{-1} \]

\[ K_p = 1.1 \times 10^{11} \exp(-11561/T) \text{ atm} \]

**Rate Coefficient Data**

<table>
<thead>
<tr>
<th>( k \text{[s}^{-1}] )</th>
<th>( T \text{[K]} )</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 ± 5</td>
<td>1000</td>
<td>Colussi et al. (1977)(^1)</td>
<td>(a)</td>
</tr>
<tr>
<td>(1.0 \times 10^2 \exp(-24000/T))</td>
<td>1010-1430</td>
<td>Lin and Lin (1985)(^2)</td>
<td>(b)</td>
</tr>
<tr>
<td>(2.5 \times 10^4 \exp(-22100/T))</td>
<td>1000-1580</td>
<td>Lin and Lin (1986)(^3)</td>
<td>(c)</td>
</tr>
</tbody>
</table>

**Comments**

(a) Pyrolysis of phenyl allyl ether in a VLPP reactor. Above 983 K the ether is mostly decomposed so that the phenoxy radical decays are isolated. Mass spectrometric detection of radical fragments (at m/e = 41 and 94). No experimental data reported. Based on thermochemical grounds, a decomposition mechanism via a bicyclic radical intermediate is proposed.

(b) Pyrolysis of phenyl methyl ether (anisole) in high dilution (0.1% and 0.5% in Ar) in a shock tube between 1010 and 1430 K and 0.5–0.9 atm. \(k_1\) is deduced from CO profiles (probed by resonance absorption, cw CO laser) by assuming that anisole decomposition and phenoxy decomposition are the only important reactions.

(c) Extension of the above study\(^2\). Same method. The kinetic mechanism is extended and the deduction of \(k\) is based on computer simulation.

**Preferred Values**

\[ k = 2.5 \times 10^{11} \exp(-22100/T) \text{ s}^{-1} \text{ over range 1000–1580 K} \]

**Reliability**

\[ \Delta \log k = \pm 0.2 \]

**Comments on Preferred Values**

The preferred expression is that one of Lin and Lin\(^3\).

**References**


\[ C_6H_5CH_2(\pm M) \rightarrow C_3H_3 + 2 C_2H_2 (\pm M) \quad (1) \]
\[ \rightarrow C_7H_4 + C_3H_3 (\pm M) \quad (2) \]
\[ \rightarrow C_5H_5 + C_2H_2 (\pm M) \quad (3) \]
\[ \rightarrow C_7H_7 (\pm M) \quad (4) \]

**Thermodynamic Data**

\[ \Delta H_{\text{int}} (2) = 428.1 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{int}} (2) = 213.2 \text{ K}^{-1} \text{mol}^{-1} \]
\[ k_p(2) = 2.3 \times 10^{-19} \text{ T}^{1.26} \exp(-50752/T) \text{ atm} \]
\[ \Delta H_{\text{int}} (3) = 463.6 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{int}} (3) = 179.1 \text{ K}^{-1} \text{mol}^{-1} \]
\[ k_p(3) = 1.7 \times 10^{-10} T^{-0.13} \exp(-56155/T) \text{ atm} \]

**Rate Coefficient Data**

<table>
<thead>
<tr>
<th>( k [\text{s}^{-1}] )</th>
<th>( T [\text{K}] )</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 2.0 \times 10^{-14} \exp(-51357/T) )</td>
<td>1500-1800</td>
<td>Astholz et al. (1981)</td>
<td>(a)</td>
</tr>
<tr>
<td>( k_2 + k_3 = 1.6 \times 10^{14} \exp(-42698/T) )</td>
<td>1550-2020</td>
<td>Astholz and Troe (1982)</td>
<td>(b)</td>
</tr>
<tr>
<td>( k_2 + k_5 = 2.5 \times 10^{13} \exp(-53402/T) )</td>
<td>1550-2020</td>
<td>(c)</td>
<td></td>
</tr>
<tr>
<td>( k_1 = 1.3 \times 10^{14} \exp(-42674/T) )</td>
<td>1300-1800</td>
<td>Mizerka and Kiefer (1986)</td>
<td>(d)</td>
</tr>
<tr>
<td>( 2.0 \times 10^{-10} \exp(-42048/T) ) + ( 1.0 \times 10^{10} \exp(-21409/T) )</td>
<td>1400-1900</td>
<td>Mueller-Markgraf and Troe (1987)</td>
<td>(e)</td>
</tr>
<tr>
<td>( k_1 = 1.8 \times 10^{14} \exp(-42674/T) )</td>
<td>1600-2100</td>
<td>Pamidimukkala et al. (1987)</td>
<td>(f)</td>
</tr>
<tr>
<td>( 5.3 \times 10^{16} \exp(-21327/T) )</td>
<td>1430-1740</td>
<td>Rao and Skinner (1987)</td>
<td>(g)</td>
</tr>
<tr>
<td>( 1.6 \times 10^{19} \exp(-22491/T) ) + ( 2.0 \times 10^{10} \exp(-42048/T) )</td>
<td>1250-1900</td>
<td>Mueller-Markgraf and Troe (1988)</td>
<td>(h)</td>
</tr>
<tr>
<td>( k_4 = 1.3 \times 10^{13} \exp(-34600/T) )</td>
<td>1350-1800</td>
<td>Braun-Unkhoff et al. (1989)</td>
<td>(i)</td>
</tr>
</tbody>
</table>

**Comments**

(a) The temporal absorption of toluene and benzyl were monitored during the thermal dissociation of toluene behind reflected shock waves. Rate expressions for the benzyl decay were determined for the density range \((5-1) \times 10^{-5} \text{ mol cm}^{-3}\). The presented rate expression corresponds to \(1 \times 10^{-5} \text{ mol cm}^{-3}\). The determination of the overlapping absorption profiles was performed on the assumption of high thermal stability of the benzyl radical.

(b) Toluene pyrolysis behind shock waves. Experimental setup as in comment (a). From the product analysis of Smith it was assumed that two dissociation channels (2) and (3) compete during thermal decay of benzyl. The density range covered was \(1.4 \times 10^{-5} \text{ to } 1.5 \times 10^{-4} \text{ mol cm}^{-3}\). The presented rate expression corresponds to the lowest density value.

(c) Same as in comment (b). The rate expression corresponds to a density of \(1.5 \times 10^{-4} \text{ mol cm}^{-3}\).

(d) Investigation of high temperature pyrolysis of ethylbenzene in shock waves with the laser schlieren technique. Benzyl and methyl radicals are found as the dominant products of the dissociation process. For modelling the schlieren profiles it is assumed that benzyl dissociation ultimately generates acetylene and the propargyl radical (1). High stability of the benzyl radical leads to a rate expression just slightly below that of Refs. 1 and 2.

(e) High temperature UV absorption spectra of benzyl radicals were monitored over the wavelength range 190-330 nm following shock wave induced thermal decomposition of different precursor molecules (benzyl iodide, benzyl chloride, and methyl benzyl ketene). It was found that benzyl radicals exhibit an unexpected low thermal stability. The marked curvature of the Arrhenius plot, together with the lack of any systematic dependence of the rate coefficient on the concentration, is considered as indicating the contribution of two benzyl fragmentation pathways with very different activation energies.

(f) The thermal decomposition of toluene has been investigated by time-of-flight mass spectrometry and by laser schlieren densitometry behind shock waves at total pressures of 0.2-0.5 bar. It is found that the dissociation of toluene proceeds mainly by C-C scission to phenyl and methyl. This result involves the assumption that benzyl radicals have a high stability which makes the concurrent reaction pathway leading to benzyl and hydrogen atoms reversible.

(g) Dilute mixtures of deuterated ethylbenzene in argon were pyrolyzed behind incident shock waves at total pressures around 0.55 bar. H and D atom concentrations were monitored by ARAS. A first order rate constant was found for the dissociation of benzyl into smaller fragments.

(h) Benzyl radicals were generated by the thermal decomposition of benzyl iodide into benzyl and iodide atoms. Benzyl concentration was monitored by UV absorption. From the results, which are in good agreement with previous findings (Ref. 4) it is concluded that the evaluated Arrhenius expressions cannot be definitely attributed to the product channels (2) and (3).
(i) Investigation of benzyl decomposition behind reflected shock waves in highly diluted mixtures of benzylidide with argon. Hydrogen atoms were monitored by ARAS. The temperatures ranged between 1300 and 1800 K at total pressured around 2 bar. In each experiment the initial concentrations of benzylidide were determined by monitoring the iodine atom concentration with ARAS during benzylidide decay. This procedure of applying very low initial concentrations of the benzyl precursor ([Xl = 0.5–5 ppm) allowed to evaluate a reaction scheme for the initiation reaction(s) and for some fast subsequent reaction steps. Thermodynamic considerations favour a fast intramolecular rearrangement of the benzyl radical to structures like the bicycloheptadienyl radical, the tropylium radical or an open chain structure, from which fast hydrogen abstraction occurs. Therefore the deduced Arrhenius expression is considered to describe the rate limiting isomerization reaction step.

Preferred Values

\[ k = 5.1 \times 10^{13} \exp(-36370/T) \text{ s}^{-1} \] over range 1350–1900 K

Reliability

\[ \Delta \log k = \pm 0.3 \text{ at 1350 K increasing to } \pm 0.5 \text{ at 1900 K} \]

Comments on Preferred Values

The recommended rate coefficient has been evaluated from the only direct measurements of benzyl radical absorption4,7 and of H-atom production during benzyl decay8 at elevated temperatures. The product distribution measurements of Smith9 give evidence for benzyl decomposing predominantly via reaction pathways (2) and (3), but no direct specific measurements of intermediates other than H atoms during the decomposition process are available. The ARAS measurements of Braun-Unkhoff et al.8 indicate that the decay of benzyl leads to the formation of H atoms in considerable amounts. Therefore it was necessary to reinterpret the benzyl decay rates reported by Mueller-Markgraf and Troe4,7. The reevaluation was done by Hippler et al.10 by taking the recombination reaction \( C_7H_7 + H \rightarrow C_7H_8 \) \( (k_2 = 2 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}) \) into account. Their resulting Arrhenius plot for the thermal decay of benzyl is now in good accord with the one derived in Ref. 8 on the basis of the production of H atoms during the benzyl decomposition. Therefore the recommended rate expression is considered to apply to the overall dissociation process of benzyl radicals.

References

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ C_6H_5CH_2 \rightarrow C_3H_3 + C_2H_2 + C_2H_2 \]

\[ \rightarrow C_4H_4 + C_2H_2 \]

\[ \rightarrow C_5H_5 + C_2H_2 \]

\[ \rightarrow C_7H_7 \]

\[ T/K \]

The graph shows the Arrhenius plot with the logarithm of the rate constant (k) in cm^3 mol^-1 s^-1 on the y-axis and the inverse temperature (1000/T in K^-1) on the x-axis. The experimental data points are indicated by various lines, and the recommendation is shown by a solid line.

EXPERIMENTAL DATA
- Astholz et al. 1981
- Astholz and Troe (k2 + k3) 1982
- Astholz and Troe (k2 + k3) 1982
- Müller-Markgraf and Troe (k2) 1987
- Müller-Markgraf and Troe (k3) 1987
- Müller-Markgraf and Troe (k1) 1986
- Pembinakaka et al. (k1) 1987
- Reo and Skinner 1987
- Müller-Markgraf and Troe (k3) 1986
- Müller-Markgraf and Troe (k2) 1986
- Braun-Unkhoff et al. (k4) 1988
- Braun-Unkhoff et al. (k4) 1988

This Recommendation (k) 1989

Thermodynamic Data

\[ \Delta H_{\text{fus}} (1) = 367.9 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{fus}} (1) = 110.9 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ K_p(1) = 5.6 \times 10^9 T^{1.46} \exp(-44030/T) \text{ atm} \]

\[ \Delta H_{\text{fus}} (2) = 424.1 \text{ kJ mol}^{-1} \]
\[ \Delta S_{\text{fus}} (2) = 162.5 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ K_p(2) = 2.1 \times 10^{10} T^{-0.86} \exp(-51450/T) \text{ atm} \]

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

<table>
<thead>
<tr>
<th>(k [\text{s}^{-1}])</th>
<th>(T [\text{K}])</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_1)</td>
<td>2.0 \times 10^{13} \exp(-38900/T)</td>
<td>1011-1138</td>
<td>Szwarc (1948)(^1)</td>
</tr>
<tr>
<td>(k_2)</td>
<td>2.5 \times 10^{12} \exp(-37090/T)</td>
<td>1011-1122</td>
<td>Takahashi (1960)(^2)</td>
</tr>
<tr>
<td>(k_3)</td>
<td>1.3 \times 10^{14} \exp(-52340/T)</td>
<td>1185-1206</td>
<td></td>
</tr>
<tr>
<td>(k_4)</td>
<td>6.3 \times 10^{14} \exp(-42770/T)</td>
<td>913-1142</td>
<td>Price (1962)(^3)</td>
</tr>
<tr>
<td>(k_5)</td>
<td>3.4 \times 10^{15} \exp(-40262/T)</td>
<td>1073-1373</td>
<td>Errede and DeMaria (1964)(^4)</td>
</tr>
<tr>
<td>(k_6)</td>
<td>9.2 \times 10^{15} \exp(-44737/T)</td>
<td>920-970</td>
<td>Brooks et al. (1971)(^5)</td>
</tr>
<tr>
<td>(k_7)</td>
<td>1.7 \times 10^{14} \exp(-41268/T)</td>
<td>1410-1730</td>
<td>Rao and Skinner (1984)(^6)</td>
</tr>
<tr>
<td>(k_8)</td>
<td>2.0 \times 10^{15} \exp(-44933/T)</td>
<td>1500-1900</td>
<td>Mueller-Markgraf and Troe (1986)(^7)</td>
</tr>
<tr>
<td>(k_9)</td>
<td>8.1 \times 10^{12} \exp(-36534/T)</td>
<td>1300-1800</td>
<td>Mizerka and Kiefer (1986)(^8)</td>
</tr>
<tr>
<td>(k_{10})</td>
<td>4.9 \times 10^{13} \exp(-45291/T)</td>
<td>1300-1800</td>
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<tr>
<td>(k_{11})</td>
<td>8.9 \times 10^{12} \exp(-36534/T)</td>
<td>1600-2100</td>
<td>Pamidimukkala et al. (1987)(^9)</td>
</tr>
<tr>
<td>(k_{12})</td>
<td>2.8 \times 10^{13} \exp(-44700/T)</td>
<td>1450-1900</td>
<td>Brouwer et al. (1988)(^10)</td>
</tr>
<tr>
<td>(k_{13})</td>
<td>3.6 \times 10^{13} \exp(-45000/T)</td>
<td>1380-1700</td>
<td>Braun-Unkhoff et al. (1989)(^11)</td>
</tr>
</tbody>
</table>

Reviews and Evaluations

| \(k_1\) | 3.2 \times 10^{12} \exp(-44439/T) | 920-1140 | Benson and O'Neal (1970)\(^11\) |
| \(k_2\) | 2.7 \times 10^{12} \exp(-41722/T) | 1050-1600 | Rao and Skinner (1984)\(^6\) |

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 (Ref. 11): the obtained preexponential factor and the activation energy seem unlikely for this reaction.
(e) Pyrolysis of toluene/nitrogen mixtures in a static system at total pressures below 300 mbar (\(p_{\text{toluene}} \leq 30\) mbar). Stable compounds analysis by gas chromatography.
(f) Shock tube study with initial mixtures of toluene-\(d_8/Ar\) and neopentane/toluene-\(d_8/Ar\) mixtures. D and H atoms are monitored as function of time by ARAS. Investigation covered a temperature range from 1200-1460 K for neopentane/toluene, and from 1410-1730 K for toluene experiments at total 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 \(k_H\) is about \(\log k = \pm 0.2\).
(g) In an earlier shock tube study on toluene decomposition using light absorption of toluene and benzyl in the 200-350 nm range (Ref. 12) rate constants were derived with the assumption that the benzyl radical exhibits sufficient thermal stability. The measurements were reinterpreted and superseded by experimental results on benzyl decomposition (Ref. 7). These experiments indicate an unexpectedly low thermal stability of the benzyl radical. With these results, from a reinterpretation of the experiments of Ref. 12 rate coefficients for channel (1) were derived for the density range (1-3) \(10^{-3}\) mol cm\(^{-3}\). The given Arrhenius expression in the present table corresponds to 1.05 \(10^{-5}\) mol cm\(^{-3}\).
(h) Shock tube study on high temperature pyrolysis of ethylbenzene with the laser schlieren technique. Rate expressions for channels (1) and (2) have been included into the reaction system by the authors and originate from their unpublished LS measurements of toluene pyrolysis.
(i) Two independent shock tube techniques (time-of-flight mass spectrometry and laser schlieren densitometry) were used to investigate the high temperature pyrolysis of toluene in mixtures with Kr and Ne, respectively. A rate coefficient for the formation of methyl and phenyl (channel (2)) was deduced at total pressures around 0.5 bar. A high pressure limiting
EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

rate coefficient of $1.2 \times 10^{16} \exp(-47505/T)$ s$^{-1}$ has also been calculated for reaction pathway (2).

(j) The thermal decomposition of toluene has been reinvestigated in shock waves detecting toluene, benzyl, and benzyl fragment concentrations by UV absorption spectrometry. The results give evidence for dominant toluene dissociation to benzyl radicals and H atoms (channel (1)). The derived thermally averaged rate coefficient for channel (1) is consistent with specific rate constants $k(E,1)$ from laser excitation experiments.

(k) Reevaluation of earlier flow system results in the pressure range 2-22 Torr. The preferred parameters for reaction pathway (1) are obtained by accepting the rate constant of Ref. 6 and scaling the parameters to fit the thermodynamic enthalpy.

(l) See comment (f). The limiting high pressure rate constant for toluene decomposition (channel (1)) is derived from RRKM calculations and $k_1 = 1.5 \cdot k_D$.

(m) Decomposition of toluene and nitrosobenzene highly diluted in argon behind reflected shock waves. The hydrogen atom formation was followed by ARAS. Nitrosobenzene served as thermal source of phenyl radicals in the separative study of the phenyl decomposition mechanism. The results for phenyl dissociation indicated that the main product channel is the H atom abstraction channel (1) and that the rate coefficient for channel (2) should not exceed $0.2 \cdot k_1$. The rate expression for channel (1) is in excellent agreement with the results of Brouwer et al. 10.

Preferred Values

$k_1 = 3.1 \times 10^{19} \exp(-44890/T)$ s$^{-1}$ over range 920-2200 K

Reliability

$\Delta \log k_1 = \pm 0.5$ at 2200 K reducing to $\pm 0.3$ at 900 K

Comments on Preferred Values

There exists a large variety of studies on toluene pyrolysis in the lower temperature range up to approximately 1000 K. But most of these studies were conducted under experimental conditions under which bimolecular reactions of toluene leading to bibenzyl and other compounds dominate. The investigation of 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 covers a density range of about $(1-3) \times 10^{-5}$ mol cm$^{-3}$, very close to the high pressure limit. The experimental data for the second decomposition channel leading to phenyl and methyl radicals (channel (2)) are insufficient to permit a recommendation of a rate expression. Thermochemical arguments together with the findings of some of the authors give evidence that the rate for this channel should not exceed 10 to 20% of the rate for channel (1) for $T \leq 2000$ K.

References

\[ \text{C}_6\text{H}_5\text{CH}_3 + \text{M} \rightarrow \text{H} + \text{C}_6\text{H}_5\text{CH}_2 + \text{M} \]

\[ \rightarrow \text{CH}_3 + \text{C}_6\text{H}_5 + \text{M} \]
EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ p \cdot C_6H_4(CH_3)_2(+M) \rightarrow p \cdot C_6H_4CH_2CH_3 + H(+M) \]

Rate Coefficient Data

<table>
<thead>
<tr>
<th>Rate Coefficient Measurements</th>
<th>T[K]</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5.0 \times 10^{13} \exp(-38300/T)$</td>
<td>1018–1133</td>
<td>Szwarc (1948)$^1$</td>
<td>(a)</td>
</tr>
<tr>
<td>$9.3 \times 10^{13} \exp(-38200/T)$</td>
<td>1213–1383</td>
<td>Errede and DeMaria (1962)$^2$</td>
<td>(b)</td>
</tr>
<tr>
<td>$4.0 \times 10^{14} \exp(-40100/T)$</td>
<td>1400–1800</td>
<td>Brouwer et al. (1984)$^3$</td>
<td>(c)</td>
</tr>
<tr>
<td>$3.2 \times 10^{15} \exp(-42600/T)$</td>
<td>1400–1800</td>
<td></td>
<td>(d)</td>
</tr>
<tr>
<td>$4.0 \times 10^{15} \exp(-42600/T)$</td>
<td>1400–1800</td>
<td></td>
<td>(e)</td>
</tr>
</tbody>
</table>

Comments

(a) Flow reactor at pressure of 2.7–20 mbar.
(b) Fast flow pyrolysis.
(c) Shock tube study. Reactants highly diluted in Ar. UV absorption at 266.5 nm of para methyl benzyl. [Ar] $= 1.3 \times 10^{18}$ cm$^{-3}$.
(d) Same method as in (c). [Ar] $= 3.7 \times 10^{19}$ cm$^{-3}$.
(e) Same method as in (c). [Ar] $= 1.1 \times 10^{20}$ cm$^{-3}$.

Preferred Values

$k_\infty = 4.0 \times 10^{15} \exp(-42600/T)$ s$^{-1}$ over range 1400–1800 K

Reliability

$\Delta \log k = \pm 0.5$

Comments on Preferred Values

It has been assumed that in the temperature range 1400–1800 K the rate coefficient given by Brouwer et al.$^3$ for the highest pressure is close to the high pressure limit $k_\infty$. The data given for the lower densities are in the fall-off region.

References

$p$-C$_6$H$_4$(CH$_3$)$_2 \rightarrow p$-C$_6$H$_4$CH$_2$CH$_3$ + H

BAULCH ET AL.

EXPERIMENTAL DATA
- Szwarz 1948
- Errede and DelMoro 1962
- Brouwer et al. 0.05 Atm. Ar 1984
- Brouwer et al. 1.4 Atm. Ar 1984
- Brouwer et al. 4 Atm. Ar 1984
- This Recommendation k(nl) 1989

EVALUATED KINETIC DATA FOR COMBUSTION MODELLING

\[ C_6H_5C_2H_6 (+M) \rightarrow C_6H_5CH_2 + CH_3 (+M) \]  
\[ C_6H_5 + C_2H_4 (+M) \]  
\[ C_6H_5 + C_2H_5 (+M) \]  
\[ C_6H_5C_2H_4 + H (+M) \]

**Thermodynamic Data**
\[ \Delta H_{298} (1) = 315.9 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298} (1) = 149.9 \text{ J K}^{-1} \text{ mol}^{-1} \]
\[ k_1 = 4.0 \times 10^4 \text{ T}^{-0.134} \exp(-38330/T) \text{ atm} \]
\[ \Delta H_{298} (2) = 105.6 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298} (2) = 128.1 \text{ J K}^{-1} \text{ mol}^{-1} \]
\[ k_2 = 4.0 \times 10^8 \text{ T}^{-0.042} \exp(-12930/T) \text{ atm} \]
\[ \Delta H_{298} (3) = 117.6 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298} (3) = 115.3 \text{ J K}^{-1} \text{ mol}^{-1} \]
\[ k_3 = 5.7 \times 10^5 \text{ T}^{-0.678} \exp(-14280/T) \text{ atm} \]
\[ \Delta H_{298} (4) = 415.9 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298} (4) = 179.7 \text{ J K}^{-1} \text{ mol}^{-1} \]
\[ k_4 = 4.8 \times 10^{13} \text{ T}^{-1.147} \exp(-50560/T) \text{ atm} \]
\[ \Delta H_{298} (5) = 341.4 \text{ kJ mol}^{-1} \]
\[ \Delta S_{298} (5) = 110.3 \text{ J K}^{-1} \text{ mol}^{-1} \]
\[ k_5 = 5.2 \times 10^7 \text{ T}^{1.125} \exp(-40900/T) \text{ atm} \]

**Rate Coefficient Data** \( k = k_1 + k_2 + k_3 + k_4 + k_5 \)

<table>
<thead>
<tr>
<th>( k [\text{s}^{-1}] )</th>
<th>( T [\text{K}] )</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 = 1.0 \times 10^4 \exp(-31800/T) )</td>
<td>888-1018</td>
<td>Szwarc (1949) ( ^1 )</td>
<td>(a)</td>
</tr>
<tr>
<td>( k_2 = 4.0 \times 10^4 \exp(-35300/T) )</td>
<td>876-1000</td>
<td>Esteban et al. (1963) ( ^2 )</td>
<td>(b)</td>
</tr>
<tr>
<td>( k_3 = 5.0 \times 10^4 \exp(-34800/T) )</td>
<td>906-1010</td>
<td>Crowne et al. (1969) ( ^3 )</td>
<td>(c)</td>
</tr>
<tr>
<td>( k_4 = 5.0 \times 10^4 \exp(-35300/T) )</td>
<td>910-1089</td>
<td>Clark and Price (1970) ( ^4 )</td>
<td>(d)</td>
</tr>
<tr>
<td>( k_5 = 1.1 \times 10^4 \exp(-26000/T) )</td>
<td>910-1089</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( k_6 = 5.0 \times 10^4 \exp(-32200/T) )</td>
<td>910-1089</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( k_7 = 2.0 \times 10^4 \exp(-36700/T) )</td>
<td>800-1100</td>
<td>Ebert et al. (1978) ( ^5 )</td>
<td>(e)</td>
</tr>
<tr>
<td>( k_8 = 1.0 \times 10^4 \exp(-41800/T) )</td>
<td>800-1100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( k_9 = 7.1 \times 10^4 \exp(-37400/T) )</td>
<td>990-1190</td>
<td>McMillen et al. (1980) ( ^6 )</td>
<td>(f)</td>
</tr>
<tr>
<td>( k_{10} = 2.0 \times 10^4 \exp(-36600/T) )</td>
<td>1053-1234</td>
<td>Robaugh and Stein (1981) ( ^7 )</td>
<td>(g)</td>
</tr>
<tr>
<td>( k_{11} = 2.5 \times 10^4 \exp(-35200/T) )</td>
<td>770-820</td>
<td>Brooks et al. (1982) ( ^8 )</td>
<td>(h)</td>
</tr>
<tr>
<td>( k_{12} = 5.0 \times 10^4 \exp(-37500/T) )</td>
<td>873-998</td>
<td>Davis (1983) ( ^9 )</td>
<td>(i)</td>
</tr>
<tr>
<td>( k_{13} = 1.3 \times 10^4 \exp(-40900/T) )</td>
<td>1250-1600</td>
<td>Brouwer et al. (1983) ( ^10 )</td>
<td>(j)</td>
</tr>
<tr>
<td>( k_{14} = 2.5 \times 10^4 \exp(-30100/T) )</td>
<td>1250-1600</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( k_{15} = 2.0 \times 10^5 \exp(-36600/T) )</td>
<td>1000-1110</td>
<td>Grela and Colussi (1985) ( ^11 )</td>
<td>(k)</td>
</tr>
<tr>
<td>( k_{16} = 3.1 \times 10^4 \exp(-30200/T) )</td>
<td>1300-1800</td>
<td>Mizerka and Kiefer (1986) ( ^12 )</td>
<td>(m)</td>
</tr>
<tr>
<td>( k_{17} = 3.5 \times 10^4 \exp(-36900/T) )</td>
<td>1200-1650</td>
<td>Mueller-Markgraf and Troe (1988) ( ^13 )</td>
<td>(n)</td>
</tr>
</tbody>
</table>

**Comments**

(a) Pyrolysis of ethylbenzene in the presence of excess of toluene in a flow reactor at pressure between 10 and 22 mbar.
(b) Pyrolysis of ethylbenzene in the presence of excess of aniline in a flow reactor at pressure between 12.5 and 17.9 mbar.
(c) Stirred flow reactor at pressure between 8 and 18 mbar. Gas analysis by GC.
(d) Toluene carrier flow system at pressure between 26 and 48 mbar. Gas analysis by GC.
(e) Flow reactor study at pressure between 0.13-1.3 mbar and at normal pressure. GC- and TOF-analysis of the reaction products.
(f) Very low pressure pyrolysis in a Knudsen cell reactor at pressure between 1.3\( \times 10^{-3} \) to 1.3\( \times 10^{-3} \) mbar. Mass spectrometric analysis of the reaction products. Rate expression for high pressure limit.
(g) Very low pressure pyrolysis at pressure lower than \( 1.3 \times 10^{-3} \) mbar in a stirred flow reactor. Rate expression for high pressure limit. Gas analysis by mass spectrometry.
(h) Static reactor at pressure between 10-65 mbar. GC analysis.
(i) Conventional flow equipment at atmospheric pressure. Analysis by rate of formation of toluene.
(j) Shock tube. High dilution by argon. UV-absorption of ethylbenzene and reaction products. \( 2.4 \times 10^{18} \) cm\(^{-2}\). \( \lambda = 1.4 \times 10^{18} \) cm\(^{-2}\). Rate expression for \( 4.8 \times 10^{18} \) cm\(^{-2}\), \( \lambda = 1.4 \times 10^{20} \) cm\(^{-2}\).
(k) Shock tube. High dilution by argon. UV-absorption of ethylbenzene and reaction products. \( 1.8 \times 10^{18} \) cm\(^{-2}\), \( \lambda = 1.5 \times 10^{20} \) cm\(^{-2}\). Rate expression for \( 4.1 \times 10^{18} \) cm\(^{-2}\), \( \lambda = 1.5 \times 10^{20} \) cm\(^{-2}\).
(m) Shock tube. Laser schlieren technique. Density range
4.3\times10^{17} - 4.2\times10^{18} \text{ cm}^{-3}.

(n) Shock tube. High dilution by argon. UV-absorption
between 190-330 nm. 1.2\times10^{19} \leq [\text{Ar}] \leq 1.4\times10^{20} \text{ cm}^{-3}.

(o) Critical evaluation of kinetic data on gas phase uni­molecular reactions.

** Preferred Values 

\[ k_1 = 7.1\times10^{11}\exp(-37800/T) \text{ s}^{-1} \] over range 770-1800 K

** Reliability 

\[ \Delta \log k_1 = \pm 0.4 \text{ at } 1800 \text{ K reducing to } \pm 0.1 \text{ at } 770 \text{ K} \]

** Comments on Preferred Values 

The preferred value is based on the data of Szwarc\(^1\), Esteban \textit{et al.}\(^2\), Crowne \textit{et al.}\(^3\), Clark and Price\(^4\), Ebert \textit{et al.}\(^6\), McMillen \textit{et al.}\(^7\), Robaugh and Stein\(^8\), Brooks \textit{et al.}\(^9\), Davis\(^10\), Brouwer \textit{et al.}\(^11\), Grela and Colussi\(^12\), Mizerka and Kiefer\(^13\), Mueller-Markgraf and Troe\(^14\), and Benson and O'Neal\(^5\). It is assumed that the given expression for \( k_1 \) represents values close to the high pressure limit.

Insufficient experimental data are available for the other channels (2)-(5) to allow recommended rate expressions.

** References 


