

Evaluated Chemical Kinetic Data for the Reactions of Atomic Oxygen O(³P) with Saturated Organic Compounds in the Gas Phase

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Rate constants and mechanisms for the gas phase reactions of atomic oxygen O(³P) with organic compounds having only saturated C-C bonds are compiled and critically evaluated. Data are given for the alkanes, cycloalkanes, haloalkanes, oxygen and nitrogen containing organic compounds, and free radicals. In addition, data are given for some miscellaneous compounds containing boron, silicon, germane, and mercury. From a critical examination of the data, recommended values for rate constants are given over specified temperature intervals or at specified temperatures. Error limits are assigned to all recommended values.

Key words: alcohols; aldehydes; alkanes; atomic oxygen; cycloalkanes; esters; evaluation; haloalkanes; ketones; mechanism; O(³P); radicals; rate constant; review; silanes.

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1. Introduction

1.1. General

This evaluation presents data on the rate constants and mechanisms of the reactions of atomic oxygen O(³P) with organic compounds having only saturated carbon-carbon bonds. For completeness and to facilitate comparison, data are also given for some miscellaneous

compounds containing boron, silicon, germanium, and mercury, several of which do not contain carbon. It is designed to serve as both a compilation and an evaluation. It is an update of part of the earlier review of Herron and Huie¹, and is in turn part of a larger effort on the evaluation of data on oxygen atom O(³P) reactions^{2,3}.

The goal of the review is to present in tabular form all data published since the last review, including papers overlooked in that work, and where the data merit, to provide recommended values for rate constants or rate parameters, and a critical discussion of the reaction mechanism. The period covered in this evaluation is 1974 through 1987, although in a few cases earlier data are included.

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1.2. Organization

The work is organized into eight sections. The first, the introduction, contains all the information needed to use the data summary and data sheets which follow. It also provides a general discussion of the rationale for arriving at the recommended values presented here, and a brief discussion of the problems associated with the kinetics and mechanisms of several of the classes of reactions considered here. The recommended values are summarized in Sec. 2, followed by Secs. 3-8 which consist of the data sheets for each separate reaction arranged by reactant class.

Note that we have not provided separate data sheets for the reactions included in our earlier review for which no new data have been reported. Instead, we give in Sec. 2 the original recommendations with revised error factors based on our present analysis of the uncertainties in the older data as considered in more detail in the following sections.

1.3. Criteria for Evaluation

Most experimentalists are overly optimistic about the accuracy of their measurements. In many cases, the quoted error limits imply that the chemistry is well defined. This is rarely the case, and the major source of uncertainty in measuring rate constants is in defining the chemistry of the system. A well designed experiment is one in which the reaction of interest is isolated from all other possible reactions which might complicate the measurement. In practice, and for the reactions of interest here, this usually means working under conditions such that one reactant is in great excess and the other decays in a first order manner. In addition, it is desirable to keep reactant concentrations as low as possible to minimize secondary reactions of oxygen atoms. Finally, experiments should be carried out in a "wall-less" environment. These conditions can be realized using, for example, any of the various flash or laser photolysis techniques to produce oxygen atoms followed by resonance or laser induced fluorescence detection techniques. For fast reactions these are the methods now in common use. They are applicable to reactions with rate constants as low as about $10^9 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. For very slow reactions however, these methods are of more limited value, and as a consequence there are few data of high reliability for these reactions, particularly at or below 300 K. For slow reactions in general, rate measurements are derived almost entirely from discharge flow techniques working at relatively high reactant concentrations in the presence of the ubiquitous wall. The use of more sensitive detection methods (e. g. resonance fluorescence) can lead to a considerable improvement in the reliability of discharge flow experiments. However, irrespective of the experimental approach, great caution must be taken to ensure that reactive impurities are not a complicating factor. Impurities can be present in the "pure" reactant, can be produced by photolysis or ther-

molysis, or can be present in the form of background gases, as in a shock tube experiment. Thus, minimizing reactant levels to minimize secondary chemistry may only serve to maximize impurity effects. Whenever there is a question as to the possible role of secondary chemistry or impurity effects, a full modeling calculation should be carried out. This has not always been done.

In this evaluation, the primary criterion for judging the reliability of experimental data is the experimental technique. Preference is given to measurements in systems in which the chemistry is well defined in terms of eliminating the effects of potentially complicating secondary reactions.

We place very little weight on data derived from the modeling of very complex reaction systems such as encountered in flames or shock tube experiments unless the system was very well defined and the reaction of interest reasonably isolated from the other chemistry in the system. In many cases the data base used in the modeling calculation was inadequate or incorrect, and there is no way of repeating the calculation.

In addition to considering the experimental technique, we will also make use of some very simple correlation approaches that are of use in treating data for consistency and believability. One such approach is that developed by Gaffney and Levine⁴ which relates the rate constants for oxygen atom abstraction reactions to the corresponding rate constants for hydroxyl radical abstraction reactions, both at 298 K. Fig. 1 gives a plot of $\log k(\text{O})$ vs $\log k(\text{OH})$ at 298 K. Since the hydroxyl radical reactions are all faster than the corresponding oxygen atom reactions, and have been measured using more reliable techniques, they can be assumed for our purposes to be "correct". The hydroxyl radical rate constants were taken from Atkinson⁵, except for data on acetone, 2-butanone and 3-pentanone which are from Wallington and Kurylo⁶. The solid line is a fit to the "best" oxygen atom rate constants (in general those obtained using the more recent fluorescence and chemiluminescence techniques). The other points refer to data for different classes of reactions obtained using discharge flow techniques (see the figure caption for an explanation of data types and sources). Although not universally true, there is a general bias in the discharge flow data towards higher values, particularly in the case of the alkane data, and a general scatter of the data within an error band of a factor of about 3.

1.4. General Comments on Kinetics and Reaction Mechanism

Detailed information for an individual reaction is given in the relevant data sheet. Most of the reactions considered here are hydrogen atom abstraction reactions:



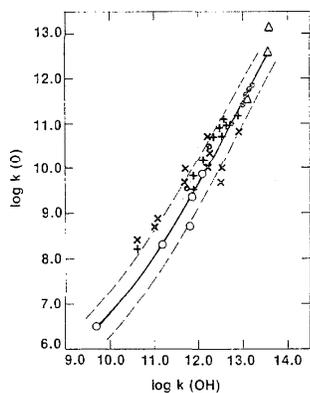


FIG. 1. $\log k(\text{OH})$ vs $\log k(\text{O})$ for selected OH and O abstraction reactions at 298 K. Data on OH from refs. 5 and 6. The symbols refer to the source of the O atom rate data: O, recommended values for alkanes from Sec. 3; \odot , recommended values for C-H-O compounds from Sec. 5; +, discharge-flow data for alkanes from Sec. 3; X, discharge-flow data for C-H-O compounds from Sec. 5; Δ , data for amines from Sec. 6.

This is the case for the alkanes, cycloalkanes, haloalkanes, and probably all of the oxygen containing compounds considered here⁷⁻¹¹. On the basis of transition state theory, we expect that the rate expression should have the form of the modified Arrhenius equation $k = AT^n \exp(-B/T)$. There are now many examples of the application of transition state theory, including the related BEBO approach, to abstraction of hydrogen atoms by oxygen atoms¹²⁻¹⁴. These all predict a significant degree of curvature in the Arrhenius plots, with values of n ranging from 0.5 to 6. However, when reliable data are available, the observed degree of curvature is almost always much less than predicted. In fact, over the 300-1000 K range, no curvature is seen, or $n=0$, with the exception of methane for which curvature is clearly seen¹⁵ ($n=1.56$). We believe that when good experimental data exist, they should be the basis for the recommended values, at least over the temperature range of the measurements, and that the quality of the data should not be compromised to fit the theory. The theoretical formulation is more useful in providing expressions for extrapolating data beyond the range of measurements and for fitting data of lower reliability. The most detailed and extensive of the theoretical calculations are those of Cohen and Westberg¹⁴, which provide a basis for fitting and extrapolating data to high temperatures. We have used their recommendations wherever possible. In other cases, we provide expressions useful for extrapolating data into the higher temperature ranges, based on transition state calculations or an equivalent BEBO calculation, adjusted to agree with the recommended values at the lower temperatures. We recognize the inconsistency of this approach, but see no other way to allow for possible upward curvature at the higher temperatures and to preserve the integrity of the reliable experimental data. It seems certain that the cor-

rect rate constant in every case will lie between the values calculated using the rate expressions for the two and three parameter Arrhenius fits of the data. In other cases, where the quality of the data or the temperature range of the measurements are limited, we discourage extrapolation beyond the range specified in the relevant data sheet and prefer in these cases to use a simple Arrhenius expression.

In conclusion, it seems apparent that transition state theory invariably errs by overestimating the degree of curvature in Arrhenius plots for the abstraction reactions treated here. This will be noted for each reaction in the appropriate data sheet. A caveat is in order; we base our conclusion that curvature is small for these reactions on the extensive data from a single laboratory, and we discount the strongly divergent viewpoint put forward by Fontijn and coworkers¹⁶ (see the data sheet on ethane).

We now wish to consider some specific problems with respect to each class of reaction treated here.

1.4.1. Alkanes and Cycloalkanes

The earlier work on the alkanes has been summarized and a conceptual basis provided for treating these reactions in terms of abstraction at different possible C-H bond sites¹⁷. From this it was possible to deduce simple Arrhenius expressions for abstraction at primary, secondary, and tertiary C-H bonds, applicable to any hydrocarbon. The range of validity of the expressions was limited (300-1000 K) since the data themselves were of limited precision. Extensive new measurements have been made for reactions of oxygen atoms with methane¹⁵, ethane^{13,16}, propane¹³, isobutane¹³, and neopentane¹⁷ by Klemm, Michael and coworkers, and new measurements have been reported by Atkinson and coworkers for the *n*-butane reaction¹⁸. Cohen¹⁹ has reviewed the older data and in combination with the newer data Cohen and Westberg¹⁴ have used transition state theory to derive expressions suitable for extrapolating the data to much higher temperatures. For many of the alkanes and cycloalkanes we have used their recommended values directly. However, there are some problems with these derived rate expressions. They predict curvature in Arrhenius plots where none exists in the experimental data (see data sheets for ethane and neopentane), they require a knowledge of the rate constant at some temperature (normally 298 K), they are uncertain as to the nature of the tunneling correction, and in too many cases they are based on older and probably less reliable rate measurements.

As noted in Sec. 1.3 there appears to be a general bias in the older data leading to rate constants at 298 K that are higher than predicted by the more recent measurements. The deviation is about a factor of 2, except for neopentane, where there is a more serious disagreement. Thus, at 500 K, near the lowest temperature used in the new measurements, the disagreement is a factor of two, but near room temperature, the extrapolated value from the new measurements differs by a factor of about six.

This problem is discussed further in the relevant data sheet, but no explanation can be given other than the probability of unrecognized sources of systematic error.

1.4.2. Haloalkanes

There have been additional measurements reported since the last review, but almost all are based on discharge flow techniques. Recommended values are given for most systems studied, but until these reactions are studied using the more reliable techniques now available, they are assigned a relatively high uncertainty factor. The same considerations apply to the earlier reported work. Thus, where Herron and Huie¹ assigned an uncertainty factor of 1.2 to the best data then available, here the error factor for the same data is taken to be 3.

In spite of the large number of haloalkanes studied, there are remarkably few generalizations that can be drawn on the role of substitution on rate constants. In the case of methane, replacement of hydrogen atoms by chlorine atoms leads to an increase in rate constant (at 298 K) for each hydrogen atom replaced, while replacement with fluorine atoms leads to a decrease. Replacement of chlorine atoms by fluorine atoms in CHCl_3 also leads to a decrease in rate constant for each atom replaced. However, it is not possible with the present data base to extend these kinds of empirical observations to more complex halocarbons.

1.4.3. Alcohols, Aldehydes, Ketones, Ethers, Esters, and Epoxides

There have been a large number of new measurements on reactions of oxygen atoms with oxygen containing organic compounds, although only a limited number have been made using the more reliable measurement techniques. There are reliable data available for methanol, ethanol, and several of the aldehydes. Some of the same problems encountered in representing the alkane data are found for these reactions. Thus, over a broad temperature range the data on methanol and formaldehyde are best represented by a conventional two parameter Arrhenius equation, and attempts to fit the data using a transition state formalism greatly exaggerate the temperature dependence. In the case of ethanol, the Arrhenius plot is distinctly curved and the modified Arrhenius form is appropriate. However, since there are three possible sites for abstraction, it is not clear as to the meaning of the curvature.

Systematic studies have been made on the reactions of the alcohols, ketones, acids, and esters, but in many cases the experimental techniques were not very reliable and/or the temperature range was too narrow to yield reliable rate parameters.

1.4.4. Amines, Nitroalkanes, Nitrites, and Nitrates

There are three sets of data bearing on the mechanism of reaction of oxygen atoms with the amines: (1) crossed

beam experiments in which the product HO internal energy distribution was measured, (2) crossed jet experiments in which products were identified by mass spectrometry, and (3) final products analysis of static experiments in which oxygen atoms were produced by the Hg photosensitized decomposition of N_2O at total pressures in the range of 10–70 kPa.

The most extensive set of data comes from the crossed jet experiments of Slagle and coworkers^{20,21}. These workers studied a series of methyl and ethyl amines, and on the basis of the products identified at room temperature, proposed a general mechanism involving formation of an energy rich amine N-oxide adduct which could be collisionally stabilized, or decompose, either directly or following isomerization. The mechanism is not completely general, depending to some extent on the nature and number of alkyl radical substituents. The major reaction channels corresponded to stabilization of the adduct, elimination of an alkyl radical directly from the adduct or following isomerization to the hydroxylamine, elimination of HO and H_2O from the hydroxylamine, and a Cope elimination of an alkene from the adduct.

In the crossed molecular beam-laser induced fluorescence studies, Kleinermanns and Luntz²² found that the HO rotational state distribution was similar to that previously found for abstraction from saturated and unsaturated hydrocarbons which was taken to indicate a direct collinear abstraction mechanism. If, as postulated by Slagle and coworkers²¹, HO is a major product of the decomposition of an initially formed adduct which has isomerized to the hydroxylamine, then in the crossed molecular beam-laser induced fluorescence studies one would have expected to see a different HO rotational distribution than that seen (more nearly statistical) and an energy threshold closer to the observed (thermal) activation energy. Yet in every case studied, the threshold energy was found to be significantly higher than the observed activation energies of the overall reaction. This suggests that HO is a direct but minor abstraction product that could become more important at higher temperatures. It was also argued in Ref. 22 that abstraction involved the hydrogen atom attached to the carbon rather than the nitrogen atom, contrary to the general conclusions drawn from the crossed jet experiments²¹.

The higher pressure static photolysis experiments of DeStefano and Heicklen²³ were limited to the diethylamine reaction. The only products found were $\text{CH}_3\text{CH}=\text{NC}_2\text{H}_5$, corresponding to loss of H_2O from the adduct, and $(\text{C}_2\text{H}_5)_2\text{NOH}$, the stabilized adduct. There was no evidence that HO, alkyl radicals, or alkenes were important products. The yield of the imine was about 10 times that of the stabilized adduct over a range of total pressures of about 10 to 70 kPa.

The conclusions one can draw from an examination of these three kinds of experimental data are: (1) the crossed jet experiments are useful in establishing the general mechanism of the reactions, but are of limited value in quantitatively establishing branching ratios, since there is no way of calibrating mass spectral peak intensi-

ties, (2) the crossed beam experiments suggest that direct HO abstraction can take place, but may not be an important channel except at higher temperature, and (3) the major product channels correspond to H₂O loss and adduct stabilization.

The situation is clearly more complex. Thus the fact that there was no effect of pressure on the quantum yields of the products in the Hg photosensitization experiments is difficult to understand if the reaction involves a common potential energy surface. Further detailed final product data would be invaluable in resolving at least some of these mechanistic problems.

With respect to the nitroalkanes, nitrites, and nitrates, all of the rate data were obtained using the same experimental approach. However, the direct experimental data of Salter and Thrush²⁴ on the methyl nitrate reaction appear to be contradicted by the data of Gaffney and coworkers²⁵. The later workers measured the rate constant for the reaction of hydroxyl radicals with CH₃ONO₂, and using the correlation scheme described in Sec. 1.3., derived a value for the corresponding oxygen atom reaction which differed considerably from the experimental value. However, in a second study²⁶, a value has been reported for the hydroxyl radical rate constant which strongly disagrees with that of Gaffney and coworkers. We feel that there is so much uncertainty in these rate constants that there is no basis for making recommendations for any of these compounds.

1.4.5. Boranes, Germane, Silanes, and Dimethylmercury

The reactions of the boron compounds are all complicated by surface effects. The rate constants are very sensitive to the conditions of the surface and there is thus a high degree of uncertainty in the data. In addition there are no definitive data on the reaction products. Thus the proposed mechanisms should be taken as highly speculative.

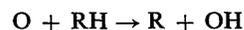
The reaction of oxygen atoms with silane and germane are probably simple hydrogen atom abstraction reactions, although products identified in matrix isolation studies in which oxygen atoms and silane were mixed and condensed onto a substrate at 17 K were interpreted to indicate that both abstraction and insertion reactions were important. This is improbable, and we suggest that abstraction is the major channel. There is compelling evidence that this is also the case for the O + (CH₃)₃SiH reaction (see data sheet). However, for reactants not having a hydrogen atom directly attached to the metal atom the kinetic data and product analysis data indicate that attack at the metal atom is the dominant mechanism. This is the case for (CH₃)₃SiSi(CH₃)₃ and (CH₃)₂Hg.

1.4.6. Free Radicals

The reactions of the alkyl free radicals have been studied directly using nozzle beam techniques²⁷. The products detected indicate that the reactions involve adduct formation followed by decomposition:



However, there is conflicting evidence. Alkenes have been found as early products of the reactions of oxygen atoms with alkanes²⁸⁻³⁰, and this has been interpreted in terms of an abstraction mechanism:



An example of the contradictory data obtained in such work is the study of Washida²⁶ on the reaction of the CH₃CH(OH) radical produced in the reaction of oxygen atoms with CH₃CH₂OH. He reported that the major product was CH₃CHO, and on the basis of isotopic substitution experiments proposed that the reaction was a hydrogen atom abstraction involving the hydrogen atom on the OH group. Experiments using labelled oxygen atoms appear to rule out any reaction other than abstraction from the OH group. Acetaldehyde accounts for about 80% of the products; no other reaction channel was identified.

Thus, although the nozzle beam experiments appear at first site to be the more direct of the studies, these other observations are in some cases very convincing, and we have at this point no way of predicting the products of these reactions. Table 1 lists the reactions for which product data have been obtained, and the conclusions as to the importance of addition vs abstraction mechanisms. Details can be found in the individual data sheets.

The problem here is analogous to that discussed in Sec. 1.4.4. on the reactions of the amines. Here again the results of nozzle beam or crossed jet experiments differ from those obtained using other techniques. The reason for the difference also applies here; the mass spectral identification of products while of great value in outlining a general mechanism, has no quantitative basis, and hence can give a distorted picture of the relative importance of different reaction channels.

1.5. Guide to Index and Summary of Recommended Rate Constants

This provides a summary of the recommended values of the kinetic parameters and the page number for the detailed data sheet. The information is given in 7 columns. Column 1 ("Reactant") contains the reactant formula and chemical name. If column 2 ("T/K") contains a single temperature, e.g., 298, the value in Column 3 ("k,A") is *k* at that temperature; if it contains a temperature range, e.g., 200-500, the value in Column 3 is the Arrhenius *A* parameter. The units of *k* and *A* are cm³ mol⁻¹ s⁻¹ and their values are given in exponential form, e.g., 1.00±0.10E11 signifies (1.00±0.10) × 10¹¹.

Column 4 ("n") and column 5 ("B"), contain, when applicable, the *n* and *B* parameters of the extended Arrhenius equation, $k = AT^n \exp(-B/T)$.

Column 6 ("k err. factor") gives the overall uncertainty factor assigned to the rate constant at the specified temperature or over the specified temperature range.

Column 7 gives the page number for the data sheet.

Note that in some cases there is no recommendation, although the reported data can be found in the indexed data sheet.

TABLE 1. The relative importance of adduct formation and hydrogen atom abstraction in the reactions of atomic oxygen with free radicals^a.

Radical	Adduct Formation	Abstraction	Experiment
CH ₃	Major		Flow
C ₂ H ₃	Major		Nozzle
	Major	Major	Flow
<i>n</i> -C ₃ H ₇	Major		Nozzle
<i>i</i> -C ₃ H ₇	Major		Nozzle
		Major	Flow
<i>i</i> -C ₄ H ₉	Major		Nozzle
<i>t</i> -C ₄ H ₉	Major		Nozzle
	Minor	Major	Flow
<i>n</i> -C ₅ H ₁₁	Major		Nozzle
neo-C ₅ H ₁₁	Major		Nozzle
		Major	Flow
cy-C ₆ H ₁₁	Minor	Major	Flow
(CH ₃) ₂ CCl	Major	Major	Flow
CH ₃ CHOH		Major	Flow
(CH ₃) ₂ C(OH)		Major	Flow

^aSee Sec. 1.4.6. for a description of the experiments.

1.6. Guide to Data Sheets

The formats of the data sheets, Secs. 3–8, are identical. Each sheet is headed with the reaction indicating the known or postulated products. The reactant name is also given here. The data sheet proper is arranged in seven columns. Column 1 (Reference code, notes) contains: Reference code and notes relevant to the experimental procedure or the nature of the reference reaction in the case of a relative rate measurement. The reference code consists of the last two digits of the year of publication, followed by the first three letters of the names of the first and second authors (if more than one) separated by a slash. An integer index is attached at the end when it is necessary to differentiate between otherwise identical codes. For example a 1978 paper of Atkinson and Pitts is cited as 78 ATK/PIT. A second paper by the same authors published in the same year would be 78 ATK/PIT2. Column 2 ("Data Type") contains the two-character data type codes listed in Sec. 1.5. If column 3 ("T/K") contains a single temperature, e.g., 298, the value in Column 4 ("k, k/k(ref), A, A/A(ref)") is *k* or *k/k(ref)* at that temperature; if it contains a temperature range, e.g., 200–500, the value in Column 4 is the Arrhenius *A* parameter (or *A/A(ref)*). The units of *k* and *A* are cm³ mol⁻¹ s⁻¹ and their values are given in exponential form, e.g., 1.00±0.10E11 signifies (1.00±0.10) × 10¹¹. Column 5 ("n") and Column 6("B, B–B(ref)"), respectively, contain, when applicable, the *n* and *B* (or *B–B(ref)*) parameters in the extended Arrhenius equa-

tion, $k = AT^n \exp(-B/T)$. *k*(ref), *A*(ref), and *B*(ref) are the kinetic parameters of reference reactions in relative rate determinations. Column 7 ("k err. factor") gives the overall uncertainty factors assigned to *k*. This normally is given only in other data evaluations which are being referenced here. The final entry is the recommendation of the present evaluation.

Following the listing of data there is a section "Comments and Recommendations", in which the basis for the recommended value is discussed, and the reaction mechanism is treated.

Finally, we list the references cited in the data sheet.

1.7. Symbols and Units

Data Type Codes:

EX - experimentally measured absolute value.

RL - experimentally measured relative value.

RN - experimentally measured relative value normalized to an absolute value.

TH - theoretical value.

SE - a recommended value from the literature.

Units for *k* and *A*: cm³ mol⁻¹ s⁻¹.

k/k(ref), *A/A*(ref), and *n* (the exponent of *T*) are dimensionless.

Temperature (*T*): in kelvins (K).

Units for *B*, *B–B*(ref): kelvins. (Activation energy $E = R \times B$).

$R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$ or $1.987 \text{ cal mol}^{-1} \text{ K}^{-1}$

1.8. Acknowledgements

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2. Index and Summary of Recommended Rate Constants

Reactant	T/K	k, A	n	B	k err. factor	Page
CH ₄ , Methane	400-2500	6.9E8	1.56	4270	1.3	975
C ₂ H ₆ , Ethane	400-1100	1.1E14		3950	1.3	976
	1100-2000	2.7E6	2.4	2940	2.5	
C ₃ H ₈ , Propane	400-1100	1.0E14		3170	1.3	977
	1100-2000	4.8E2	3.5	1280	2.5	
C ₄ H ₁₀ , n-Butane	300-2000	4.7E1	3.9	780	2.5	978
C ₄ H ₁₀ , 2-Methylpropane	400-1000	5.7E13		2650	1.3	978
	1000-2000	8.7	3.9	80	2.5	
C ₅ H ₁₂ , n-Pentane	300-2000	3.8E4	3.0	1010	3	979
C ₅ H ₁₂ , 2-Methylbutane ^a	307	8E10			3	
C ₅ H ₁₂ , 2,2-Dimethylpropane	400-1000	9.2E13		3600	1.3	980
	1000-2000	1.4E6	2.5	2720	2.5	
C ₆ H ₁₄ , n-Hexane	300-2000	1E5	2.9	1000	3	980
C ₆ H ₁₄ , 2,3-Dimethylbutane	300-2000	2.3E2	3.6	140	3	981
C ₇ H ₁₆ , n-Heptane	300-2000	9.3E4	2.9	880	3	981
C ₇ H ₁₆ , 2,2-Dimethylpentane ^a	307	6.5E10			3	
C ₇ H ₁₆ , 2,4-Dimethylpentane ^a	307	1.0E11			3	
C ₈ H ₁₈ , n-Octane	300-2000	1.9E5	2.8	840	3	982
C ₈ H ₁₈ , 2,2,4-Trimethylpentane ^a	307	5.5E10			3	
C ₈ H ₁₈ , 2,3,4-Trimethylpentane ^a	307	3E10			3	
C ₈ H ₁₈ , 2,2,3,3-Tetramethylbutane	300-2000	3.2E6	2.5	2570	3	982
C ₃ H ₆ , Cyclopropane ^a	298	5E8			3	
C ₄ H ₈ , Cyclobutane ^a	298	7E9			3	
C ₅ H ₈ , Spiropentane ^a	298-650	4.0E13		2890	3	
C ₅ H ₁₀ , Cyclopentane	300-2000	2.9E6	2.6	1390	3	982
C ₆ H ₁₂ , Cyclohexane	300-2000	2.6E6	2.6	1290	3	983
C ₇ H ₁₄ , Cycloheptane	300-2000	2.1E6	2.6	1090	3	983
CH ₃ F, Fluoromethane						984
CH ₂ Cl, Chloromethane	400-1500	2E13		3900	3	984
CH ₂ Br, Bromomethane	400-1500	2E13		3900	3	985
CH ₂ F ₂ , Difluoromethane						985
CH ₂ FCl, Fluorochloromethane	300-10000	5E12		3100	3	985
CH ₂ Cl ₂ , Dichloromethane	300-1000	6E12		2900	3	986
CHF ₃ , Trifluoromethane	300-1000	5E12		5400	3	986
CHF ₂ Cl, Difluorochloromethane	300-1000	7E12		4200	3	986
CHFCl ₂ , Fluorodichloromethane	300-1000	1E13		3700	3	987
CHCl ₃ , Trichloromethane	300-1000	3E12		2500	3	987
CF ₂ BrCl, Difluorobromochloromethane						988
CF ₂ Br, Trifluorobromomethane	500-1500	9E12		6800	3	988
CF ₃ I, Trifluoroiodomethane	300-1500	7E12			3	988
CCl ₄ , Tetrachloromethane	300-1000	3E11		2200	3	989
C ₂ H ₅ Cl, Chloroethane ^a	340-650	4.8E13		3330	3	
C ₂ H ₅ Br, Bromomethane ^a	340-650	3.1E13		3260	3	
CH ₃ CHCl ₂ , 1,1-Dichloroethane	300-700	3E12		2440	3	989
CH ₂ ClCH ₂ Cl, 1,2-Dichloroethane	300-700	5E12		2500	3	990
CH ₃ CF ₂ Cl, 1,1-Difluoro,1-chloroethane	298	4E7			3	990
CF ₃ CH ₂ Cl, 1,1-Chloro,2,2-trifluoroethane	300-700	2E12		2600	3	990

Index and Summary of Recommended Rate Constants — Continued

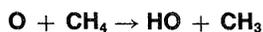
Reactant	T/K	k, A	n	B	k err. factor	Page
$C_2F_4Br_2$, Dibromotetrafluoromethane						991
C_2H_5Cl , 2-Chloropropane	300-700	2.4E13		2560	3	991
C_3H_7Br , 2-Bromopropane ^a	340-650	2.3E13		2700	3	
C_4H_9Cl , 2-Chlorobutane ^a	340-650	3.6E13		2530	3	
C_4H_9Cl , 1-Chloro,2-methylpropane ^a	340-650	3.6E13		2520	3	
C_4H_9Cl , 2-Chloro,2-methylpropane ^a	340-650	2.6E13		3010	3	
C_4H_9Br , 1-Bromobutane ^a	340-650	4.4E13		2680	3	
C_4H_9Br , 1-Bromo,2-methylpropane ^a	340-600	3.4E13		2510	3	
$C_5H_{11}Cl$, 1-Chloro,2,2-dimethylpropane ^a	340-650	3.2E13		2670	3	
$C_7H_{13}Cl$, 1-Chloroheptane ^a	298	8E10			3	
CH_3OH , Methanol	300-1000	2E13		2520	1.5	992
	1000-2000	2.4E5	2.5	1550	2.5	
C_2H_5OH , Ethanol	300-1000	6E5	2.46	930	1.5	993
C_3H_7OH , 1-Propanol	298	3E10			5	994
C_3H_7OH , 2-Propanol	298	4E10			5	994
C_4H_9OH , 1-Butanol	300-600	3E13		1800	3	995
C_4H_9OH , 2-Butanol	300-600	4.5E12		1200	3	995
C_4H_9OH , 2-Methyl,1-propanol	300-600	3.7E12		1100	3	995
C_4H_9OH , 2-Methyl,2-propanol	300-600	5E12		2200	3	996
$HCHO$, Formaldehyde	250-800	1.8E13		1543	1.5	996
	800-2000	3.3E7	1.94	522	2.5	
Cl_2CO , Dichloroformaldehyde ^a	292	6E9			3	
CH_3CHO , Acetaldehyde	300-500	7.2E12		990	1.5	997
C_2H_5CHO , Propionaldehyde	300-500	7.8E12		870	1.5	997
$CH_3(CH_2)_2CHO$, Butyraldehyde	300-500	1E13		860	1.5	998
$(CH_3)_2CHCHO$, Isobutyraldehyde	300-500	7.9E12		730	1.5	998
$(CH_3)_2CO$, Acetone	300-700	1E13		3000	3	998
$C_2H_5COCH_3$, 2-Butanone	300-600	5E11		1300	3	999
$(C_2H_5)_2CO$, 3-Pentanone	300-600	3E11		1000	3	999
$cy-C_4H_8O$, Tetrahydrofuran	300-600	8E13		1900	3	1000
$cy-C_5H_8O$, Cyclopentanone	300-600	2.4E13		2300	3	1000
$cy-C_5H_{10}O$, Tetrahydropyran	300-600	6E13		1800	3	1000
$cy-C_6H_{10}O$, Cyclohexanone	300-600	3E13		2300	3	1001
$(CH_3)_2O$, Dimethylether	300-500	5E13		2300	3	1001
$(C_2H_5)_2O$, Diethylether	300-500	6E13		2000	3	1001
$HCOOCH_3$, Methyl formate	300-500	9E12		2700	3	1002
$HCOOC_2H_5$, Ethyl formate	300-500	1E13		2600	3	1002
CH_3COOCH_3 , Methyl acetate	300-500	1E13		2900	3	1003
$CH_3COOC_2H_5$, Ethyl acetate	300-500	1.4E13		2500	3	1003
$CH_3COOC_3H_7$, n-Propyl acetate	300-500	1.6E13		2400	3	1003
C_2H_4O , Ethylene oxide	298	4E7			5	1004
CH_3NH_2 , Methylamine	300-600	5.4E12		830	1.5	1004
$(CH_3)_2NH$, Dimethylamine	300-600	9.1E12		280	1.5	1005
$(CH_3)_3N$, Trimethylamine	300-600	6.5E12		-210	1.5	1006
$C_2H_5NH_2$, Ethylamine	300-600	6.8E12		640	1.5	1006
$(C_2H_5)_3N$, Triethylamine						1007
$(C_2H_5)_2NOH$, Diethylhydroxylamine						1008
CH_3NO_2 , Nitromethane						1008
$C_2H_5NO_2$, Nitroethane						1008
CH_3ONO , Methyl nitrite						1008
C_2H_5ONO , Ethyl nitrite						1009
CH_3ONO_2 , Methyl nitrate						1009
$C_2H_5ONO_2$, Ethyl nitrate						1009
B_2H_6 , Diborane	300-1000	1E13		2500	5	1010
H_3BCO , Borane carbonyl	298	4E11			5	1010
$(CH_3)_3NBH_3$, Borane trimethylamine	300-2000	3E13			5	1011
$(C_2H_5)_3NBH_3$, Borane triethylamine	300-2000	3E13			5	1011
SiH_4 , Silane	300-1000	4E12		800	2	1011
$(CH_3)_3SiH$, Trimethylsilane	298	1.6E12			3	1012
$((CH_3)_3Si)_2$, Hexamethyldisilane	298	7.8E10			3	1012
GeH_4 , Germane	298	2E12			3	1012
$(CH_3)_2Hg$, Dimethylmercury	298	1.5E13			3	1013
CH_2 , Methylidene	300-2000	6E13			3	1013
CH_2 , Methylene	300-2000	8E13			2	1014
CH_3 , Methyl	300-2000	8.413			1.5	1015

Index and Summary of Recommended Rate Constants — Continued

Reactant	T/K	k, A	n	B	k err. factor	Page
C ₂ H ₅ , Ethyl	300-2000	1.3E14			1.5	1016
n-C ₃ H ₇ , n-Propyl	300-2000	2E14			3	1016
i-C ₃ H ₇ , Isopropyl	300-2000	3E14			3	1017
i-C ₄ H ₉ , Isobutyl	300-2000	2E14			3	1018
t-C ₄ H ₉ , tert-Butyl	300-2000	5E14			2	1018
C ₅ H ₁₁ , Neopentyl	300-2000	2E14			3	1019
cy-C ₆ H ₁₁ , Cyclohexyl	300-2000	2E14			2	1019
CCl, Chloromethylidene	300-2000	6E13			4	1020
CHF, Fluoromethylene	300-2000	9E13			3	1020
CF ₂ , Difluoromethylene	298	1E13			2	1020
CFCl, Chlorofluoromethylene	298	1E13			4	1021
CF ₃ , Trifluoromethyl	298	2E13			2	1021
CCl ₃ , Trichloromethyl	298	2.5E13			2	1021
(CH ₃) ₂ CCl, 2-Chloropropyl	300-2000	1E14			5	1022
HCO, Formyl	300-2000	6E13			3	1022
FCO, Fluoroformyl	300-2000	6E13			3	1023
CH ₃ O, Methoxy	300-2000	2E13			3	1023
CH ₂ OH, Hydroxymethyl	300-2000	5E13			5	1023
CH ₃ O ₂ , Methylperoxy	300-2000	5E13			3	1024
CH ₃ CO, Acetyl	300-2000	6E13			3	1024
CH ₃ CH(OH), Hydroxyethyl	300-2000	1E14			3	1025
(CH ₃) ₂ C(OH), 2-Hydroxypropyl	300-2000	5E13			3	1026

*No separate data sheet is given. See Sec. 1.2.

3. Alkanes and Cycloalkanes



Methane

Reference code, notes	Type	T/K	k, k/k(ref) A, A/A(ref)	n	B, B-B(ref)	k err. factor
73 HER/HUI	SE	350-1000	2.1E13		4550	1.3
74 BAR/COM	EX	298-500	3.5E13		4530	
Discharge flow-mass spectrometry.						
78 SHA	SE	300-2000	5.1E6	2	3240	
79 ROT/JUS	EX	1500-2200	4.1E14		7030	
Shock tube-atomic resonance absorption spectroscopy. See also 77 ROT/JUS.						
80 WAL/DUN	TH				5130	
81 FON	EX	420-1670	1.58 ± 0.33E6	2.36	3720 ± 40	
Flash photolysis-resonance fluorescence (High temperature photochemistry).						
81 KLE/TAN	EX	474-1136	1.21 ± 0.20E14		5435 ± 112	
Flash photolysis-resonance fluorescence and discharge flow-resonance fluorescence.						
81 KLE/TAN	SE	474-2250	3.16 ± 0.20E12	0.5	5179 ± 54	
84 WAR	SE	300-2200	1.2E7	2.1	3840	1.4
86 COH/WES	TH	300-2000	4.9E6	2.2	3820	
86 SUT/MIC	EX	763-1775	5.5E5	2.4	2838	
Flash photolysis-shock tube, atomic resonance absorption spectroscopy.						
86 SUT/MIC	SE	400-2250	6.90E8	1.56	4270	
86 TSA/HAM	SF	300-2500	1.0E9	1.5	4330	1.3
Recommended		400-2500	6.9E8	1.56	4270	1.3

Comments and Recommendations

This is one of the most accurately known gas phase rate constants. The several recent evaluations all predict rate constants in excellent agreement with the most reliable recent measurements (79 ROT/JUS, 81 FON, 81 KLE/TAN, and 86 SUT/MIC). We have chosen to use the expression given in 86 SUT/MIC since it represents

the data over the whole range with great accuracy, and is consistent with the recommendation from 86 COH/WES based on a transition state calculation. A serious problem is the lack of reliable data at $T \leq 400$ K. The rate is very low under these conditions, the role of reactive impurities exaggerated, and there is the possibility of a significant contribution from tunneling. See Sec. 1.4.

References

- 73 HER/HUI J. T. Herron and R. E. Huie, *J. Phys. Chem. Ref. Data*, **2**, 467 (1973).
- 74 BAR/COM J. Barassin and J. Combourieu, *Bull. Chem. Soc. France*, **1** (1974).
- 78 SHA R. Shaw, *J. Phys. Chem. Ref. Data*, **7**, 1179 (1978).
- 79 ROT/JUS P. Roth and T. H. Just, *Proceedings of the 10th Materials Research Symposium on Characterization of High Temperature Vapors and Gases*, J. W. Hastie, ed., NBS Special Publication 561, p1339 (1979).
- 80 WAL/DUN S. P. Walch and T. H. Dunning, Jr., *J. Chem. Phys.*, **72**, 3221 (1980).
- 81 FON A. Fontijn, Eighteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, p797 (1981).
- 81 KLE/TAN R. B. Klemm, T. Tanzawa, E. G. Skolnik, and J. V. Michael, Eighteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh PA, p785 (1981).
- 84 WAR J. Warnatz, in "Combustion Chemistry", W. C. Gardiner, Jr., ed., Springer-Verlag, New York, p197 (1984).
- 86 COH/WES N. Cohen and K. R. Westberg, *Int. J. Chem. Kinet.*, **18**, 99 (1986).
- 86 SUT/MIC J. W. Sutherland, J. V. Michael, and R. B. Klemm, *J. Phys. Chem.*, **90**, 5941 (1986).
- 86 TSA/HAM W. Tsang and R. F. Hampson, *J. Phys. Chem. Ref. Data*, **15**, 1087 (1986).



Ethane

Reference code, notes	Type	T/K	$k, k/k(\text{ref})$ $A, A/A(\text{ref})$	n	$B,$ $B-B(\text{ref})$	k err. factor
73 HER/HUI	SE	298-650	2.5E13		3200	1.3
82 CAY/PEE Discharge flow-mass spectrometry.	EX	600-1030	1.9±0.8E14		4810±160	
83 MIC/KEI Flash photolysis-resonance fluorescence and discharge flow-resonance fluorescence.	EX	416-1048	1.12±0.07E14		3950±70	
83 MIX/WAG Discharge flow-mass spectrometry.	EX	308-410	4±1.2E13		3410±680	
84 WAR	SE	300-1500	3.0E7	2.0	2580	2.5
86 COH/WES	TH	300-2000	3.5E6	2.4	2940	
86 TSA/HAM	SE	300-2500	1.2E12	0.6	3680	2
88 MAH/MAR	EX	297-1267	1.1E-7	6.5	138	1.3
	TH	300-1300	1.9E-2	4.85	1021	
Recommended		400-1100 1100-2000	1.1E14 2.7E6	 2.4	3950 2940	1.3 2.5

Comments and Recommendations

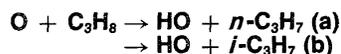
There are two sets of data which appear to be of high precision and accuracy: 83 MIC/KEI and 88 MAH/MAR. They are at best in reasonable agreement. The basic problem is that the 83 MIC/KEI data are linear in Arrhenius format while the data of 88 MAH/MAR are very clearly curved. The latter carried out a transition state calculation using an Eckart tunneling correction, which lead to a rate expression in good agreement with their measurements. However, the choice of a tunneling correction term is controversial, and the experimental observations need to be confirmed. We note that at low temperature, rate measurements for slow reactions are extremely difficult to make, and a full modeling study should be carried out to assess the role of secondary reactions including potential impurity reactions. Also, the very steep Arrhenius curve reported in 88 MAH/MAR is a cause for concern. The line is almost vertical at the highest experimental temperature. Until the problem is

resolved, we suggest using the rate expression reported in 83 MIC/KEI for the 400–1100 K temperature range. Between 1100 and 2000 K we suggest using $k = 2.7 \times 10^6 T^{2.4} \exp(-2940/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, which is based on the expression given in 86 COH/WES, adjusted to agree at 1000 K with the rate constant calculated from the recommended expression for the 400–1100 K range. We estimate the uncertainty to be a factor of 2. However, the curvature in the Arrhenius plots predicted by transition state theory is probably too great, and the high temperature rate constants calculated from this expression will probably be high. See Sec. 1.4.

References

- 73 HER/HUI J. T. Herron and R. E. Huie, *J. Phys. Chem. Ref. Data*, **2**, 467 (1973).
- 82 CAY/PEE M. Caymax and J. Peeters, Nineteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh PA, p51 (1982).

- 83 MIC/KEI J. V. Michael, D. G. Keil, and R. B. Klemm, *Int. J. Chem. Kinet.*, **15**, 705 (1983).
- 83 MIX/WAG K. H. Mix and H. Gg. Wagner, *Oxidation Communications*, **5**, 321 (1983).
- 84 WAR J. Warnatz, in "Combustion Chemistry", W. C. Gardiner, Jr., ed., Springer-Verlag, New York, 1984, p197.
- 86 COH/WES N. Cohen and K. R. Westberg, *Int. J. Chem. Kinet.*, **18**, 99 (1986).
- 86 TSA/HAM W. Tsang and R. F. Hampson, *J. Phys. Chem. Ref. Data*, **15**, 1087 (1986).
- 88 MAH/MAR K. Mahmud, P. Marshall, and A. Fontijn, *J. Chem. Phys.*, **88**, 2393 (1988).



Propane

Reference code, notes	Type	T/K	k, k/k(ref) A, A/A(ref)	n	B, B-B(ref)	k err. factor
73 HER/HUI	SE	298	9E9			2
75 HAR/BUR Modulation spectroscopy.	EX	329	3.9±0.7E10			
82 JEW/HOL Discharge flow-O+NO chemiluminescence.	EX	306	4.7±0.8E9			
83 MIC/KEI Flash photolysis-resonance fluorescence and discharge flow-resonance fluorescence.	EX	411-1018	9.96±0.96E13		3165±60	
84 WAR	SE	300-1000	5.2E13		2420	3.2
86 COH/WES	(a) TH	300-2000	3.7E6	2.4	2770	
	(b) TH	300-2000	5.5E5	2.5	1580	
	TH	300-2000	7.6E2	3.5	1280	
88 TSA	(a) SE	300-2500	1.9E5	2.68	1870	2
	(b) SE	300-2500	4.7E4	2.71	1060	2
87 WAS Discharge flow-mass spectrometry. Reactant (CD ₃) ₂ CH ₂ .	EX	381-627	1.2±0.6E14		3060±200	
Recommended		400-1100 1100-2000	1.0E14 4.8E2		3170 1280	1.3 2.5

Comments and Recommendations

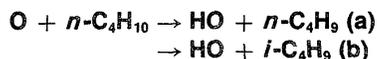
The recommendation of 84 WAR is based on rate expressions given in 75 HUI/HER and in 75 HAR/BUR, that of 86 TSA/HAM is the result of fitting data given in 73 HER/HUI using a BEBO calculation. The three entries from 86 COH/WES are rate expressions for the two abstraction channels and their sum. These are transition state theory fits to the experimental data including the new measurements reported in 83 MIC/KEI. The data given in the latter are the most reliable although the experimental details were not given. The experimental data are fit almost as well by the 86 COH/WES or the 86 TSA/HAM expressions, although they differ in their assignments of branching ratios. Over the range 400–1100 K the most reliable rate expression is that from 83 MIC/KEI with an uncertainty factor of 1.3. Between 1100 and 2000 K we suggest using $k = 4.8 \times 10^2 T^{3.5} \exp(-1280/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, which is based on the expression given in 86 COH/WES for the total rate constant, adjusted to agree at 1000 K with the rate constant calculated from the recommended expression for the 400–1100 K range. We estimate the uncertainty to be a factor of 2. However, the curvature in the Arrhenius

plots predicted by transition state theory is probably too great, and the high temperature rate constants calculated from this expression will probably be high. See Sec. 1.4.

The branching ratio can be estimated from the expressions given in 86 COH/WES, with an uncertainty of at least a factor of 2.

References

- 73 HER/HUI J. T. Herron and R. E. Huie, *J. Phys. Chem. Ref. Data*, **2**, 467 (1973).
- 75 HAR/BUR A. B. Harker and C. S. Burton, *Int. J. Chem. Kinet.*, **7**, 907 (1975).
- 75 HUI/HER R. E. Huie and J. T. Herron, *Progr. Reaction Kinetics*, **8**, Part 1, 1 (1975).
- 82 JEW/HOL S. P. Jewell, K. A. Holbrook, and G. A. Oldershaw, *Int. J. Chem. Kinet.*, **14**, 585 (1982).
- 83 MIC/KEI J. V. Michael, D. G. Keil, and R. B. Klemm, *Int. J. Chem. Kinet.*, **15**, 705 (1983).
- 84 WAR J. Warnatz, in "Combustion Chemistry", W. C. Gardiner, Jr., ed., Springer-Verlag, New York, 1984, p197.
- 86 COH/WES N. Cohen and K. R. Westberg, *Int. J. Chem. Kinet.*, **18**, 99 (1986).
- 88 TSA W. Tsang, *J. Phys. Chem. Ref. Data*, **17**, 887 (1988).
- 87 WAS N. Washida, *Bull. Chem. Soc. Japan*, **60**, 3739 (1987).

***n*-Butane**

Reference code, notes	Type	<i>T</i> /K	<i>k</i> , <i>k</i> / <i>k</i> (ref) <i>A</i> , <i>A</i> / <i>A</i> (ref)	<i>n</i>	<i>B</i> , <i>B</i> - <i>B</i> (ref)	<i>k</i> err. factor
73 HER/HUI	(a) SE	298-650	3.0E13		2920	1.3
	(b) SE	298-650	4.6E13		2410	1.3
74 ATK/PIT	EX	298	1.88±0.20E10			
Phase shift-O+NO chemiluminescence.						
77 ATK/PER	EX	299-440	1.5E13		2100±150	
Flash photolysis-O+NO chemiluminescence.						
84 WAR	SE	300-1000	6.2E13		2580	2.5
86 COH/WES	(a) TH	300-2000	4.9E6	2.4	2770	
	(b) TH	300-2000	4.3E5	2.6	1300	
	TH	300-2000	4.7E1	3.9	780	
Recommended		300-2000	4.7E1	3.9	780	2.5

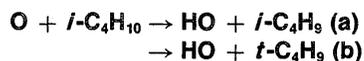
Comments and Recommendations

The 84 WAR recommendation is based on rate expressions given in 75 HUI/HER. The three entries from 86 COH/WES are rate expressions for the two abstraction channels and their sum. These are transition state theory fits to the experimental data including the measurements reported in 77 ATK/PER. We accept the 86 COH/WES evaluation. However, the curvature in the Arrhenius plots predicted by transition state theory is probably too great, and the high temperature rate constants calculated from this expression will probably be high. See Sec. 1.4.

The branching ratio can be estimated from the expressions given in 86 COH/WES, with an uncertainty of at least a factor of 2.

References

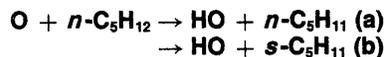
- 73 HER/HUI J. T. Herron and R. E. Huie, *J. Phys. Chem. Ref. Data*, **2**, 467 (1973).
- 74 ATK/PIT R. Atkinson and J. N. Pitts, Jr., *J. Phys. Chem.*, **78**, 1780 (1974).
- 75 HUI/HER R. E. Huie and J. T. Herron, *Progr. Reaction Kinetics*, **8**, Part 1, 1 (1975).
- 77 ATK/PER R. Atkinson, R. A. Perry, and J. N. Pitts, Jr., *Chem. Phys. Letters*, **47**, 197 (1977).
- 84 WAR J. Warnatz, in "Combustion Chemistry", W. C. Gardiner, Jr., ed., Springer-Verlag, New York, 1984, p197.
- 86 COH/WES N. Cohen and K. R. Westberg, *Int. J. Chem. Kinet.*, **18**, 99 (1986).

**2-Methylpropane**

Reference code, notes	Type	<i>T</i> /K	<i>k</i> , <i>k</i> / <i>k</i> (ref) <i>A</i> , <i>A</i> / <i>A</i> (ref)	<i>n</i>	<i>B</i> , <i>B</i> - <i>B</i> (ref)	<i>k</i> err. factor
80 WAS/BAY	EX	297	6.0±1.2E10			
Discharge flow-mass spectrometry.						
82 JEW/HOL	EX	307	7.9±1.4E10			
Discharge flow-final products.						
83 MIC/KEI	EX	397-922	5.70±0.80E13		2653±71	
Flash photolysis-resonance fluorescence and discharge flow-resonance fluorescence.						
84 WAR	SE	300-1000	4.7E13		1960	
86 COH/WES	(a) TH	300-2000	5.8E6	2.4	2780	
	(b) TH	300-2000	2.1E5	2.5	465	
	TH	300-2000	2.0E1	3.9	80	
Recommended		400-1000	5.7E13		2650	1.3
		1000-2000	8.7	3.9	80	2.5

Comments and Recommendations

The 84 WAR recommendation is based on rate expressions given in 75 HUI/HER. The three entries from 86 COH/WES are rate expressions for the two abstraction channels and their sum. These are transition state theory fits to the experimental data reported in 73 HER/HUI (no recommendation was made), 80 WAS/BAY, and 82 JEW/HOL. The data of 83 MIC/KEI (for which no experimental details were given) were not used in either evaluation. Over the range 400–1100 K the most reliable rate expression is that from 83 MIC/KEI with an uncertainty factor of 1.3. Between 1000 and 2000 K we suggest using $k = 8.7 T^{3.9} \exp(-80/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, which is based on the expression given in 86 COH/WES for the total rate constant, adjusted to agree at 1000 K with the rate constant calculated from the recommended expression for the 400–1000 K range. We estimate the uncertainty to be a factor of 2. However, the curvature in the Arrhenius plots predicted by transition state theory is probably too great, and the high temperature rate constants calculated from this expression will probably be high. See Sec. 1.4.



n-Pentane

Reference code, notes	Type	<i>T</i> /K	<i>k</i> , <i>k</i> / <i>k</i> (ref) <i>A</i> , <i>A</i> / <i>A</i> (ref)	<i>n</i>	<i>B</i> , <i>B</i> - <i>B</i> (ref)	<i>k</i> err. factor
73 HER/HUI	(a) SE	298-650	2.90E13		2920	1.3
	(b) SE	298-650	8.0E13		2320	1.3
86 COH/WES	(a) TH	300-2000	5.8E6	2.4	2780	
	(b) TH	300-2000	2.1E5	2.5	465	
	TH	300-2000	3.8E4	3.0	1010	
Recommended		300-2000	3.8E4	3.0	1010	3

Comments and Recommendations

The evaluations use the same data sets. The three entries from 86 COH/WES are rate expressions for the two abstraction channels and their sum. These are transition state theory fits to the experimental data. That evaluation is accepted here. However, the curvature in the Arrhenius plots predicted by transition state theory is probably too great, and the high temperature rate constants calculated from this expression will probably be high. See Sec. 1.4.

The branching ratio can be estimated from the expressions given in 86 COH/WES, with an uncertainty of at least a factor of 2.

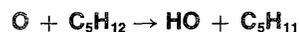
The expressions given in 86 COH/WES for the branching ratio probably leads to a high value for *k*(b)/*k*(a).

References

- 73 HER/HUI J. T. Herron and R. E. Huie, *J. Phys. Chem. Ref. Data*, **2**, 467 (1973).
 75 HUI/HER R. E. Huie and J. T. Herron, *Progr. Reaction Kinetics*, **8**, Part 1, 1 (1975).
 80 WAS/BAY N. Washida and K. D. Bayes, *J. Phys. Chem.*, **84**, 1309 (1980).
 82 JEW/HOL S. P. Jewell, K. A. Holbrook, and G. A. Oldershaw, *Int. J. Chem. Kinet.*, **14**, 585 (1982).
 82 MIC/KEI J. V. Michael, D. G. Keil, and R. B. Klemm, *Nineteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh PA*, p39 (1982).
 84 WAR J. Warnatz, in "Combustion Chemistry", W. C. Gardiner, Jr., ed., Springer-Verlag, New York, 1984, p197.
 86 COH/WES N. Cohen and K. R. Westberg, *Int. J. Chem. Kinet.*, **18**, 99 (1986).

References

- 73 HER/HUI J. T. Herron and R. E. Huie, *J. Phys. Chem. Ref. Data*, **2**, 467 (1973).
 86 COH/WES N. Cohen and K. R. Westberg, *Int. J. Chem. Kinet.*, **18**, 99 (1986).



2,2-Dimethylpropane

Reference code, notes	Type	T/K	$k, k/k(\text{ref})$ $A, A/A(\text{ref})$	n	$B,$ $B-B(\text{ref})$	k err. factor
73 HER/HUI	SE	298-650	5.9E13		2920	1.4
82 MIC/KEI	EX	415-922	9.16±1.69E13		3595±100	
Flash photolysis-resonance fluorescence and discharge flow-resonance fluorescence.						
86 COH/WES	TH	300-2000	2.5E6	2.5	2720	
Recommended		400-1000	9.2E13		3600	1.3
		1000-2000	1.4E6	2.5	2720	2.5

Comments and Recommendations

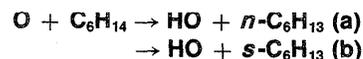
The experimental data used in 73 HER/HUI as a basis for a recommended value are in serious disagreement with the more recent data given in 82 MIC/KEI. The ratio of rate constants $k(73 \text{ HER/HUI})/k(82 \text{ MIC/KEI}) = 6.3, 2.9,$ and 1.3 at 298, 400, and 1000 K respectively. The recommendation given in 86 COH/WES is based on a fit to the data reported in 82 MIC/KEI using transition state theory. We believe the data reported in 82 MIC/KEI to be the most accurate data set, and they provide the basis for the recommendation between 400 and 1000 K. Between 1000 and 2000 K we suggest using $k = 1.4 \times 10^6 T^{2.5} \exp(-2720/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, which is based on the expression given in 86 COH/WES, adjusted to agree at 1000 K with the rate constant calculated from the recommended expression for the 400–1000 K range. We estimate the uncertainty to be a factor of 2. However, the curvature in the Arrhenius

plots predicted by transition state theory is probably too great, and the high temperature rate constants calculated from this expression will probably be high. See Sec. 1.4.

It is also of interest that neopentane is the only alkane for which the correlation between hydroxyl and oxygen atom rate constants does not appear to hold. From the correlation we would predict that $k(298 \text{ K}) = 2 \times 10^9 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, whereas the recommended value is $4.2 \times 10^8 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, which differs by a factor of about 5.

References

- 73 HER/HUI J. T. Herron and R. E. Huie, *J. Phys. Chem. Ref. Data*, **2**, 467 (1973).
 82 MIC/KEI J. V. Michael, D. G. Keil, and R. B. Klemm, *Nineteenth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh PA, p39 (1982).
 86 COH/WES N. Cohen and K. R. Westberg, *Int. J. Chem. Kinet.*, **18**, 99 (1986).

*n*-Hexane

Reference code, notes	Type	T/K	$k, k/k(\text{ref})$ $A, A/A(\text{ref})$	n	$B,$ $B-B(\text{ref})$	k err. factor
73 HER/HUI	(a) SE	298-650	2.9E13		2920	1.3
	(b) SE	298-650	1.1E14		2250	1.3
86 COH/WES	(a) TH	300-2000	4.7E6	2.4	2770	
	(b) TH	300-2000	6.9E5	2.6	1060	
	TH	300-2000	1.0E5	2.9	1000	
Recommended		300-2000	1E5	2.9	1000	3

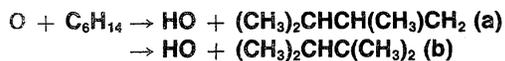
Comments and Recommendations

The evaluations use the same data sets. The three entries from 86 COH/WES are rate expressions for the two abstraction channels and their sum. These are transition state theory fits to the experimental data reported in 73 HER/HUI. That evaluation is accepted here. However, the curvature in the Arrhenius plots predicted by transition state theory is probably too great, and the high temperature rate constants calculated from this expression will probably be high. See Sec. 1.4.

The branching ratio can be estimated from the expressions given in 86 COH/WES, with an uncertainty of at least a factor of 2.

References

- 73 HER/HUI J. T. Herron and R. E. Huie, *J. Phys. Chem. Ref. Data*, **2**, 467 (1973).
 86 COH/WES N. Cohen and K. R. Westberg, *Int. J. Chem. Kinet.*, **18**, 99 (1986).

**2,3-Dimethylbutane**

Reference code, notes	Type	T/K	$k, k/k(\text{ref})$ $A, A/A(\text{ref})$	n	$B,$ $B-B(\text{ref})$	k err. factor
73 HER/HUI	(a) SE	298-650	5.9E13		2920	1.3
	(b) SE	298-650	3.1E13		1650	1.3
86 COH/WES	(a) TH	300-2000	6.0E6	2.4	2780	
	(b) TH	300-2000	3.6E5	2.5	445	
	TH	300-2000	2.3E2	3.6	140	
Recommended		300-2000	2.3E2	3.6	140	3

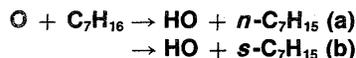
Comments and Recommendations

The evaluations use the same data sets. The three entries from 86 COH/WES are rate expressions for the two abstraction channels and their sum. These are transition state theory fits to the experimental data reported in 73 HER/HUI. That evaluation is accepted here. However, the curvature in the Arrhenius plots predicted by transition state theory is probably too great, and the high temperature rate constants calculated from this expression will probably be high. See Sec. 1.4.

The expressions given in 86 COH/WES for the branching ratio probably leads to a high value for $k(\text{b})/k(\text{a})$.

References

- 73 HER/HUI J. T. Herron and R. E. Huie, *J. Phys. Chem. Ref. Data*, **2**, 467 (1973).
 86 COH/WES N. Cohen and K. R. Westberg, *Int. J. Chem. Kinet.*, **18**, 99 (1986).

***n*-Heptane**

Reference code, notes	Type	T/K	$k, k/k(\text{ref})$ $A, A/A(\text{ref})$	n	$B,$ $B-B(\text{ref})$	k err. factor
73 HER/HUI	(a) SE	298-650	2.9E13		2920	1.3
	(b) SE	298-650	1.2E14		2190	1.3
86 COH/WES	(a) TH	300-2000	2.9E6	2.4	2770	
	(b) TH	300-2000	6.9E5	2.6	960	
	TH	300-2000	9.3E4	2.9	880	
Recommended		300-2000	9.3E4	2.9	880	3

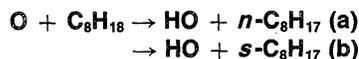
Comments and Recommendations

The evaluations use the same data sets. The three entries from 86 COH/WES are rate expressions for the two abstraction channels and their sum. These are transition state theory fits to the experimental data reported in 73 HER/HUI. That evaluation is accepted here. However, the curvature in the Arrhenius plots predicted by transition state theory is probably too great, and the high temperature rate constants calculated from this expression will probably be high. See Sec. 1.4.

The branching ratio can be estimated from the expressions given in 86 COH/WES, with an uncertainty of at least a factor of 2.

References

- 73 HER/HUI J. T. Herron and R. E. Huie, *J. Phys. Chem. Ref. Data*, **2**, 467 (1973).
 86 COH/WES N. Cohen and K. R. Westberg, *Int. J. Chem. Kinet.*, **18**, 99 (1986).

***n*-Octane**

Reference code, notes	Type	<i>T</i> /K	<i>k</i> , <i>k</i> / <i>k</i> (ref) <i>A</i> , <i>A</i> / <i>A</i> (ref)	<i>n</i>	<i>B</i> , <i>B</i> - <i>B</i> (ref)	<i>k</i> err. factor
73 HER/HUI	(a) SE	298-650	2.9E13		2920	1.3
	(b) SE	298-650	9.3E13		2030	1.3
86 COH/WES	(a) TH	300-2000	2.5E6	2.4	2770	
	(b) TH	300-2000	6.9E5	2.6	890	
	TH	300-2000	1.9E5	2.8	840	
Recommended		300-2000	1.9E5	2.8	840	3

Comments and Recommendations

The evaluations use the same data sets. The three entries from 86 COH/WES are rate expressions for the two abstraction channels and their sum. These are transition state theory fits to the experimental data reported in 73 HER/HUI. That evaluation is accepted here. However, the curvature in the Arrhenius plots predicted by transition state theory is probably too great, and the high temperature rate constants calculated from this expression will probably be high. See Sec. 1.4.

The branching ratio can be estimated from the expressions given in 86 COH/WES, with an uncertainty of at least a factor of 2.

References

- 73 HER/HUI J. T. Herron and R. E. Huie, *J. Phys. Chem. Ref. Data*, **2**, 467 (1973).
 86 COH/WES N. Cohen and K. R. Westberg, *Int. J. Chem. Kinet.*, **18**, 99 (1986).



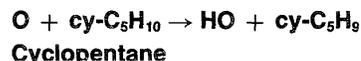
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73 HER/HUI	SE	307	8E9			1.5
86 COH/WES	TH	300-2000	3.2E6	2.5	2570	
Recommended		300-2000	3.2E6	2.5	2570	3

Comments and Recommendations

The evaluations use the same data. The values given in 86 COH/WES are transition state theory fits to the experimental data. That evaluation is accepted here. However, the curvature in the Arrhenius plots predicted by transition state theory is probably too great, and the high temperature rate constants calculated from this expression will probably be high. See Sec. 1.4.

References

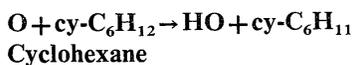
- 73 HER/HUI J. T. Herron and R. E. Huie, *J. Phys. Chem. Ref. Data*, **2**, 467 (1973).
 86 COH/WES N. Cohen and K. R. Westberg, *Int. J. Chem. Kinet.*, **18**, 99 (1986).



Reference code, notes	Type	<i>T</i> /K	<i>k</i> , <i>k</i> / <i>k</i> (ref) <i>A</i> , <i>A</i> / <i>A</i> (ref)	<i>n</i>	<i>B</i> , <i>B</i> - <i>B</i> (ref)	<i>k</i> err. factor
73 HER/HUI	SE	298-650	1.3E14		2210	1.3
86 COH/WES	TH	300-2000	2.9E6	2.6	1390	
Recommended		300-2000	2.9E6	2.6	1390	3

Comments and Recommendations

The evaluations use the same data sets. The evaluation of 86 COH/WES which uses transition state theory to provide a basis for extrapolating the data to high temperature, is accepted. However, the curvature in the Arrhenius plots predicted by transition state theory is probably too great, and the high temperature rate constants calculated from this expression will probably be high. See Sec. 1.4.



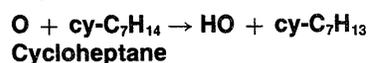
Reference code, notes	Type	T/K	k, k/k(ref) A, A/A(ref)	n	B, B-B(ref)	k err. factor
73 HER/HUI	SE	298-650	2.2E14		2350	1.3
75 KIM/TIM	EX	344-513	3.2±0.6E14		2210±200	
Discharge flow-mass spectrometry.						
82 WAS/TAK	EX	298	5.8±0.4E10			
Discharge flow-mass spectrometry.						
86 COH/WES	TH	300-2000	2.6E6	2.6	1290	
Recommended		300-2000	2.6E6	2.6	1290	3

References

- 73 HER/HUI J. T. Herron and R. E. Huie, *J. Phys. Chem. Ref. Data*, **2**, 467 (1973).
 86 COH/WES N. Cohen and K. R. Westberg, *Int. J. Chem. Kinet.*, **18**, 99 (1986).

Comments and Recommendations

The evaluation of 86 COH/WES which uses transition state theory to provide a basis for extrapolating the data to high temperature, uses data reported in 73 HER/HUI, and more recent data reported in 75 KIM/TIM and 82 WAS/TAK. That recommendation is accepted. However, the curvature in the Arrhenius plots predicted by transition state theory is probably too great, and the high temperature rate constants calculated from this expression will probably be high. See Sec. 1.4.



Reference code, notes	Type	T/K	k, k/k(ref) A, A/A(ref)	n	B, B-B(ref)	k err. factor
73 HER/HUI	SE	298-650	2.9E14		2230	1.3
86 COH/WES	TH	300-2000	2.1E6	2.6	1090	
Recommended		300-2000	2.1E6	2.6	1090	3

References

- 73 HER/HUI J. T. Herron and R. E. Huie, *J. Phys. Chem. Ref. Data*, **2**, 467 (1973).
 75 KIM/TIM P. Kim and R. B. Timmons, *Int. J. Chem. Kinet.*, **7**, 143 (1975).
 82 WAS/TAK N. Washida and H. Takagi, *J. Am. Chem. Soc.*, **104**, 168 (1982).
 86 COH/WES N. Cohen and K. R. Westberg, *Int. J. Chem. Kinet.*, **18**, 99 (1986).

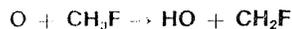
Comments and Recommendations

The evaluations use the same data sets. The evaluation of 86 COH/WES which uses transition state theory to provide a basis for extrapolating the data to high temperature, is accepted. However, the curvature in the Arrhenius plots predicted by transition state theory is probably too great, and the high temperature rate constants calculated from this expression will probably be high. See Sec. 1.4.

References

- 73 HER/HUI J. T. Herron and R. E. Huie, *J. Phys. Chem. Ref. Data*, **2**, 467 (1973).
 86 COH/WES N. Cohen and K. R. Westberg, *Int. J. Chem. Kinet.*, **18**, 99 (1986).

4. Haloalkanes



Fluoromethane

Reference code, notes	Type	T/K	$k, k/k(\text{ref})$ $A, A/A(\text{ref})$	n	$B,$ $B-B(\text{ref})$	k err. factor
67 PAR/AZA	EX	858-948	7.8E12		4880±400	
77 KNE/WOL	EX	298	<7.9E8			

Discharge flow-laser induced fluorescence. Reactant CH₃F(2ν₃,ν₁,ν₄).

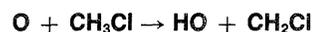
Comments and Recommendations

The data given in 67 PAR/AZA can be used to calculate a rate constant at 298 K which is lower than the limiting value given in 77 KNE/WOL. However, the data are too limited to provide a basis for a recommended value.

The reaction mechanism is not known, although hydrogen atom abstraction is almost certainly the major path up to very high temperatures.

References

- 7 KNE/WOL M. Kneba and J. Wolfrum, Ber. Bunsenges. Physik. Chem., **81**, 1275 (1977).
67 PAR/AZA N. I. Parsamyan, V. V. Azatyan, and A. B. Nalbandyan, Arm. Khim. Zh., **20**, 950 (1967).



Chloromethane

Reference code, notes	Type	T/K	$k, k/k(\text{ref})$ $A, A/A(\text{ref})$	n	$B,$ $B-B(\text{ref})$	k err. factor
73 HER/HUI	SE	350-1000	1.7E13		3690	1.3
73 HER/HUI	SE	298	7.2E7			1.5
74 BAR/COM	EX	298-500	1.3E13		3470	
Discharge flow-mass spectrometry.						
75 WES/DEH	RN	511-1000	4E13		4300	
Discharge flow-mass spectrometry. Reference reaction: O + CF ₃ Br.						
Recommended		400-1500	2E13		3900	3

Comments and Recommendations

The relative rate measurements reported in 75 WES/DEH establish that the rate constants for reaction with CH₃Cl and CH₃Br are identical over the range of the measurements. This rate ratio is probably more reliable than any of the absolute rate measurements. Therefore, we have chosen to treat all of the data on the two systems as a single data set. The recommended value is based on data reported in 73 HER/HUI for CH₃Cl and CH₃Br and the newer measurements reported in 74 BAR/COM for CH₃Cl and in 75 WES/DEH for CH₃Br (see the data sheet for CH₃Br). The uncertainty in the recommended value increases below 400 K.

The reaction mechanism is not known, although hydrogen atom abstraction is almost certainly the major path up to very high temperatures.

References

- 73 HER/HUI J. T. Herron and R. E. Huie, J. Phys. Chem. Ref. Data, **2**, 467 (1973).
74 BAR/COM J. Barassin and J. Combourieu, Bull. Chem. Soc. France, **1** (1974).
75 WES/DEH A.A. Westenberg and N. deHaas, J. Chem. Phys., **62**, 4477 (1975).

O + CH₃Br → HO + CH₂Br
Bromomethane

Reference code, notes	Type	T/K	k, k/k(ref) A, A/A(ref)	n	B, B-B(ref)	k err. factor
73 HER/HUI	SE	350-1000	3.0E13		3800	2
75 WES/DEH Discharge flow-mass spectrometry.	EX	517-1000	3.5E13		4560	
Recommended		400-1500	2E13		3900	3

Comments and Recommendations

The recommended value is the same as that for CH₃Cl. See the data sheet for that reaction.

The reaction mechanism is not known, although hydrogen atom abstraction is almost certainly the major path up to very high temperatures.

References

- 73 HER/HUI J. T. Herron and R. E. Huie, *J. Phys. Chem. Ref. Data*, **2**, 467 (1973).
 75 WES/DEH A. A. Westenburg and N. deHaas, *J. Chem. Phys.*, **62**, 4477 (1975).

O + CH₂F₂ → HO + CHF₂
Difluoromethane

Reference code, notes	Type	T/K	k, k/k(ref) A, A/A(ref)	n	B, B-B(ref)	k err. factor
68 PAR/NAL Ignition limits.	EX	873-953	2.65E12		4430	

Comments and Recommendations

The data are too limited to provide a basis for a recommendation.

The reaction mechanism is not known, although hydrogen atom abstraction is almost certainly the major path up to very high temperatures.

References

- 68 PAR/NAL N. I. Parasamyam and A. B. Nalbandyan, *Arm. Khim. Zh.*, **21**, 1003 (1968).

O + CH₂FCI → HO + CHFCI
Fluorochloromethane

Reference code, notes	Type	T/K	k, k/k(ref) A, A/A(ref)	n	B, B-B(ref)	k err. factor
78 JOU/LEB Discharge flow-mass spectrometry. Temperature range uncertain. Details given in 77 JOU/POU and 77 JOU/POU2.	EX	390-620	4.7E12		3100	
Recommended		300-1000	5E12		3100	3

Comments and Recommendations

The only data are those reported in 78 JOU/LEB, which are the basis for the recommended value.

The reaction mechanism is not known, although hydrogen atom abstraction is almost certainly the major path up to very high temperatures.

References

- 77 JOU/POU J. L. Jourdain, G. Poulet, J. Barassin, G. LeBras, and J. Combourieu, *IV Congress International on Pure Air*, p484 (1977).
 77 JOU/POU2 J. L. Jourdain, G. Poulet, J. Barassin, G. LeBras, and J. Combourieu, *Atmospheric Pollution*, **75**, 256 (1977).
 78 JOU/LEB J. L. Jourdain, G. LeBras, and J. Combourieu, *J. Chim. Phys.*, **75**, 318 (1978).

$O + CH_2Cl_2 \rightarrow HO + CHCl_2$
Dichloromethane

Reference code, notes	Type	T/K	$k, k/k(\text{ref})$ $A, A/A(\text{ref})$	n	$B,$ $B-B(\text{ref})$	k err. factor
73 BAR/COM Discharge flow-mass spectrometry.	EX	298-500	5.94E12		2870	
Recommended		300-1000	6E12		2900	3

Comments and Recommendations

The only data are those reported in 73 BAR/COM, which are the basis for the recommended value.

The reaction mechanism is not known, although hydrogen atom abstraction is almost certainly the major path up to very high temperatures.

References

73 BAR/COM J. Barassin and J. Combourieu, Bull. Chem. Soc. France, 2173 (1973).

$O + CHF_3 \rightarrow HO + CF_3$
Trifluoromethane

Reference code, notes	Type	T/K	$k, k/k(\text{ref})$ $A, A/A(\text{ref})$	n	$B,$ $B-B(\text{ref})$	k err. factor
68 WIL/ODO Discharge flow-mass spectrometry. Reference reaction: $O + CH_4$.	RN	1000	<5E9			
78 JOU/LEB Discharge flow-mass spectrometry. Temperature range uncertain. Details given in 77 JOU/POU and 77 JOU/POU2.	EX	390-620	4.9E12		5400	
Recommended		300-1000	5E12		5400	3

Comments and Recommendations

The limiting relative rate constant at 1000 K given in 68 WIL/ODO was put on an absolute basis using the recommended value for $O + CH_4$ from this evaluation. The data reported in 78 JOU/LEB lead to a rate constant (extrapolated to 1000 K) of $2.2 \times 10^{10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, which is about a factor of 4 higher than the limiting value. The recommended value is based on the data in 78 JOU/LEB.

The reaction mechanism is not known, although hydrogen atom abstraction is almost certainly the major path up to very high temperatures.

References

68 WIL/ODO Wm. E. Wilson and J. T. O'Donovan, J. Chem. Phys., 48, 2829 (1968).
77 JOU/POU J. L. Jourdain, G. Poulet, J. Barassin, G. LeBras, and J. Combourieu, IV Congress International on Pure Air, p484 (1977).
77 JOU/POU2 J. L. Jourdain, G. Poulet, J. Barassin, G. LeBras, and J. Combourieu, Atmospheric Pollution, 75, 256 (1977).
78 JOU/LEB J. L. Jourdain, G. LeBras, and J. Combourieu, J. Chim. Phys., 75, 318 (1978).

$O + CHF_2Cl \rightarrow HO + CF_2Cl$
Difluorochloromethane

Reference code, notes	Type	T/K	$k, k/k(\text{ref})$ $A, A/A(\text{ref})$	n	$B,$ $B-B(\text{ref})$	k err. factor
78 JOU/LEB Discharge flow-mass spectrometry. Temperature range uncertain. Details given in 77 JOU/POU and 77 JOU/POU2.	EX	390-620	6.67E12		4200	
79 EGO/TEM Discharge flow-electron spin resonance spectroscopy.	EX	298	1.2E8			
Recommended		300-1000	7E12		4200	3

Comments and Recommendations

Extrapolation of the data from 78 JOU/LEB leads to a rate constant at 298 K of $5 \times 10^6 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, which is in accord with the limiting value given in 79 EGO/TEM. The recommendation is based on the data of 78 JOU/LEB.

The reaction mechanism is not known, although hydrogen atom abstraction is almost certainly the major path up to very high temperatures.

References

- 77 JOU/POU J. L. Jourdain, G. Poulet, J. Barassin, G. LeBras, and J. Combourieu, IV Congress International on Pure Air, p484 (1977).
 77 JOU/POU2 J. L. Jourdain, G. Poulet, J. Barassin, G. LeBras, and J. Combourieu, Atmospheric Pollution, **75**, 256 (1977).
 78 JOU/LEB J. L. Jourdain, G. LeBras, and J. Combourieu, J. Chim. Phys., **75**, 318 (1978).
 79 EGO/TEM V. I. Egorov, S. M. Temchin, N. I. Gorban, and V. P. Balakhnin, Kinetics and Catalysis, **20**, 850 (1979). Translated from Kin. I.Kat., **20**, 1039 (1979).

O + CHFCI₂ → HO + CFCI₂
Fluorodichloromethane

Reference code, notes	Type	T/K	k, k/k(ref) A, A/A(ref)	n	B, B-B(ref)	k err. factor
78 JOU/LEB Discharge flow-mass spectrometry. Temperature range uncertain. Details given in 77 JOU/POU and 77 JOU/POU2.	EX	390-620	9.6E12		3700	
Recommended		300-1000	1E13		3700	3

Comments and Recommendations

The only data are those reported in 78 JOU/LEB, which are the basis for the recommended value.

The reaction mechanism is not known, although hydrogen atom abstraction is almost certainly the major path up to very high temperatures.

References

- 77 JOU/POU J. L. Jourdain, G. Poulet, J. Barassin, G. LeBras, and J. Combourieu, IV Congress International on Pure Air, p484 (1977).
 77 JOU/POU2 J. L. Jourdain, G. Poulet, J. Barassin, G. LeBras, and J. Combourieu, Atmospheric Pollution, **75**, 256 (1977).
 78 JOU/LEB J. L. Jourdain, G. LeBras, and J. Combourieu, J. Chim. Phys., **75**, 318 (1978).

O + CHCl₃ → HO + CCl₃
Trichloromethane

Reference code, notes	Type	T/K	k, k/k(ref) A, A/A(ref)	n	B, B-B(ref)	k err. factor
68 FRO Discharge flow-electron spin resonance spectroscopy.	EX	300	1.5E9			
74 BAR/COM Discharge flow-mass spectrometry.	EX	298-500	2.9E12		2520	
Recommended		300-1000	3E12		2500	3

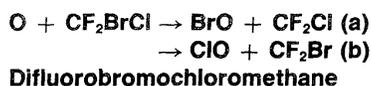
Comments and Recommendations

The rate constant reported in 68 FRO is about twice as large as that reported in 74 BAR/COM. The recommended value is based on data from the latter source.

The reaction mechanism is not known, although hydrogen atom abstraction is almost certainly the major path up to very high temperatures.

References

- 68 FRO F. W. Froben, Ber. Bunsenges. Phys. Chem., **72**, 996 (1968).
 74 BAR/COM J. Barassin and J. Combourieu, Bull. Chem. Soc. France, **1** (1974).



Reference code, notes	Type	T/K	<i>k</i> , <i>k</i> / <i>k</i> (ref) <i>A</i> , <i>A</i> / <i>A</i> (ref)	<i>n</i>	<i>B</i> , <i>B</i> - <i>B</i> (ref)	<i>k</i> err. factor
82 MKR/SAR Discharge flow-electron spin resonance spectroscopy.	EX	529-893	4 ± 1.2E13		4840 ± 250	

Comments and Recommendations

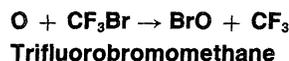
The only data are those reported in 82 MKR/SAR. Data from the same laboratory using the same experimental approach for the CF₃Br reaction were rejected (see data sheet), so these data are also suspect. No recommendation is given.

There are two possible paths, involving bromine and chlorine atom abstraction. There are no data on the rela-

tive importance of the two channels, but on thermochemical grounds one would expect (a) to be the major path.

References

- 81 MKR/SAR T. G. Mkryan, E. N. Sarkisyan, S. A. Arutyunyan, and S. G. Gabrielyan, *Kinetics and Catalysis*, **22**, 1052 (1981). Translated from *Kin. I. Kat.*, **22**, 1336 (1981).



Reference code, notes	Type	T/K	<i>k</i> , <i>k</i> / <i>k</i> (ref) <i>A</i> , <i>A</i> / <i>A</i> (ref)	<i>n</i>	<i>B</i> , <i>B</i> - <i>B</i> (ref)	<i>k</i> err. factor
74 FRA/WIL Discharge flow-mass spectrometry.	EX	800-1200	9.0E12		6790 ± 500	
78 MKR/CHO Discharge flow-electron spin resonance spectroscopy.	EX	588-1081	7.92 ± 3.0E12		4600	
Recommended		500-1500	9E12		6800	3

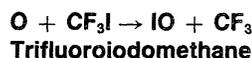
Comments and Recommendations

The two sets of experimental data are in serious disagreement, differing by a factor of 10 at 900 K. We prefer the data given in 74 FRA/WIL since no stoichiometry correction was required.

The reaction mechanism is not known, although bromine atom abstraction is almost certainly the major path up to very high temperatures.

References

- 74 FRA/WIL T. C. Frankiewicz, F. W. Williams and R. G. Gann, *J. Chem. Phys.*, **61**, 402 (1974).
78 MKR/CHO T. G. Mkryan, S. A. Chobanyan, E. N. Sarkisyan, and A. N. Baratov, *Arm. Khim. Zh.*, **31**, 72 (1978).



Reference code, notes	Type	T/K	<i>k</i> , <i>k</i> / <i>k</i> (ref) <i>A</i> , <i>A</i> / <i>A</i> (ref)	<i>n</i>	<i>B</i> , <i>B</i> - <i>B</i> (ref)	<i>k</i> err. factor
79 ADD/DON Flash photolysis-resonance absorption.	EX	300	6.6E12			
Recommended		300-1500	7E12			3

Comments and Recommendations

Unlike the other alkyl halides, the alkyl iodides react very rapidly with atomic oxygen. The only data are those reported in 79 ADD/DON, which are the basis for the recommended value. The rate constant probably has little or no temperature dependence.

The mechanism was discussed in our earlier review (75 HUI/HER). In molecular beam studies of the reaction IO is the only product detected (79 GOR/NOW and 83 BUS/SIB). However, there is a fundamental disagreement between the molecular beam studies on the distribution of energy in the product IO. This is dis-

cussed in detail in 83 BUS/SIB, where it is also argued that the reaction involves formation of a CF_3IO intermediate having a lifetime of about one rotational period.

References

- 75 HUI/HER R. E. Huie and J. T. Herron, *Progr. Reaction Kinetics*, **8**, Part 1, 1 (1975).
 79 ADD/DON M. C. Addison, R. J. Donovan, and J. Garraway, *Disc. Faraday Soc.*, **67**, 286 (1979).
 79 GOR/NOW P. A. Gorry, C. V. Nowikow, and R. Grice, *Mol. Phys.*, **38**, 1485 (1979).
 83 BUS/SIB R. J. Buss, S. J. Sibener, and Y. T. Lee, *J. Phys. Chem.*, **87**, 4840 (1983).

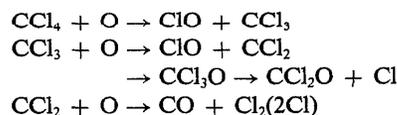
O + CCl₄ → ClO + CCl₃ Tetrachloromethane

Reference code, notes	Type	T/K	k, k/k(ref) A, A/A(ref)	n	B, B-B(ref)	k err. factor
73 HER/HUI	SE	270-380	2.0E10		2260	1.5
74 BAR/COM Discharge flow-mass spectrometry.	EX	298-500	1.6E11		2160	
Recommended		300-1000	3E11		2200	3

Comments and Recommendations

The recommendation given in 73 HER/HUI was based on discordant data sets. The data given in 74 BAR/COM are more extensive and reliable, and the basis for the recommendation given here.

The reaction products are CO, Cl₂, and COCl₂ (62 UNG/SCH). Since the reaction enthalpy is about 30 kJ mol⁻¹ and the activation energy is unlikely to exceed about 20 kJ mol⁻¹, it can be argued that this is not an abstraction reaction. However, the thermochemical and kinetic data are not reliable enough to draw that conclusion on the basis of a 10 kJ mol⁻¹ difference. It seems preferable to treat it as an abstraction reaction followed by successive abstraction and decomposition channels:



References

- 62 UNG/SCH A. Y.-M. Ung and H. I. Schiff, *Can. J. Chem.*, **40**, 486 (1962).
 73 HER/HUI J. T. Herron and R. E. Huie, *J. Phys. Chem. Ref. Data*, **2**, 467 (1973).
 74 BAR/COM J. Barassin and J. Combourieu, *Bull. Chem. Soc. France*, **1** (1974).

O + CH₃CHCl₂ → HO + CH₃CCl₂ (a) → HO + CH₂CHCl₂ (b)

1,1-Dichloroethane

Reference code, notes	Type	T/K	k, k/k(ref) A, A/A(ref)	n	B, B-B(ref)	k err. factor
77 BAR/RIC Discharge flow-mass spectrometry.	EX	290-650	2.85E12		2440	
Recommended		300-700	3E12		2440	3

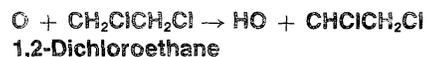
Comments and Recommendations

The only data are those reported in 77 BAR/RIC, which are the basis for the recommended value.

The reaction mechanism is not known, although hydrogen atom abstraction from two possible sites is almost certainly the major path up to very high temperatures.

References

- 77 BAR/RIC J. Barassin, M. Richoux, and J. Combourieu, *Bull. Soc. Chim. France*, **69** (1977).



Reference code, notes	Type	T/K	$k, k/k(\text{ref})$ $A, A/A(\text{ref})$	n	$B,$ $B-B(\text{ref})$	k err. factor
77 BAR/RIC Discharge flow-mass spectrometry.	EX	290-650	4.91E12		2530	
Recommended		300-700	5E12		2500	3

Comments and Recommendations

The only data are those reported in 77 BAR/RIC, which are the basis for the recommended value.

The reaction mechanism is not known, although hydrogen atom abstraction is almost certainly the major path up to very high temperatures.

References

77 BAR/RIC J. Barassin, M. Richoux, and J. Combourieu, Bull. Soc. Chim. France, 69 (1977).



Reference code, notes	Type	T/K	$k, k/k(\text{ref})$ $A, A/A(\text{ref})$	n	$B,$ $B-B(\text{ref})$	k err. factor
78 JOU/LEB Discharge flow-mass spectrometry. Details given in 77 JOU/POU and 77 JOU/POU2.	EX	298	3.6±1.2E7			
Recommended		298	4E7			3

Comments and Recommendations

The only datum is that reported in 78 JOU/LEB, which is the basis for the recommended value.

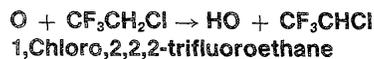
The reaction mechanism is not known, although hydrogen atom abstraction is almost certainly the major path up to very high temperatures.

References

77 JOU/POU J. L. Jourdain, G. Poulet, J. Barassin, G. LeBras, and J. Combourieu, IV Congress International on Pure Air, p484 (1977).

77 JOU/POU2 J. L. Jourdain, G. Poulet, J. Barassin, G. LeBras, and J. Combourieu, Atmospheric Pollution, 75, 256 (1977).

78 JOU/LEB J. L. Jourdain, G. LeBras, and J. Combourieu, J. Chim. Phys., 75, 318 (1978).



Reference code, notes	Type	T/K	$k, k/k(\text{ref})$ $A, A/A(\text{ref})$	n	$B,$ $B-B(\text{ref})$	k err. factor
78 JOU/LEB Discharge flow-mass spectrometry.	EX	391-621	1.6E12		2600±250	
Recommended		300-700	2E12		2600	3

Comments and Recommendations

The only data are those reported in 78 JOU/LEB, which are the basis for the recommended value.

The reaction mechanism is not known, although hydrogen atom abstraction is almost certainly the major path up to very high temperatures.

References

78 JOU/LEB J. L. Jourdain, G. LeBras, and J. Combourieu, J. Chim. Phys., 75, 318 (1978).

O + C₂F₄Br₂ → BrO + C₂F₄Br
Dibromotetrafluoroethane

Reference code, notes	Type	T/K	<i>k</i> , <i>k</i> / <i>k</i> (ref) <i>A</i> , <i>A</i> / <i>A</i> (ref)	<i>n</i>	<i>B</i> , <i>B</i> - <i>B</i> (ref)	<i>k</i> err. factor
78 MKR/HAR Discharge flow-electron spin resonance spectroscopy.	EX	408-735	4.8±2.0E12		2950±250	

Comments and Recommendations

The data are suspect. See the data sheet on CF₃Br. No recommendation is made.

The reaction is probably a bromine atom abstraction.

References

78 MKR/HAR T. G. Mkrian, S. A. Harutyunian, and E. N. Sarkissian, *Arm. Khim. Zh.*, **31**, 377 (1978).

O + (CH₃)₂CHCl → HO + (CH₃)₂CCl
2-Chloropropane

Reference code, notes	Type	T/K	<i>k</i> , <i>k</i> / <i>k</i> (ref) <i>A</i> , <i>A</i> / <i>A</i> (ref)	<i>n</i>	<i>B</i> , <i>B</i> - <i>B</i> (ref)	<i>k</i> err. factor
73 HER/HUI	SE	340-650	2.6E13		2620	1.3
87 WAS/HAT Discharge flow-mass spectrometry. Reactant (CD ₃) ₂ CHCl.	EX	399-628	2.1±0.7E13		2500±140	
Recommended		300-700	2.4E13		2560	3

Comments and Recommendations

The new measurements reported in 87 WAS/HAT are in excellent agreement with the earlier recommendation given in 73 HER/HUI. The new recommendation is based on both sets of data.

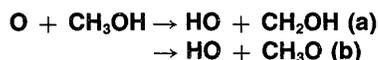
The primary product when the reactant is (CD₃)₂CHCl is the (CD₃)₂CCl radical, there being no evidence for attack at a primary C-D bond site (87WAS/HAT).

References

73 HER/HUI J. T. Herron and R. E. Huie, *J. Phys. Chem. Ref. Data*, **2**, 467 (1973).

87 WAS/HAT N. Washida and S. Hatakeyama, *Bull. Chem. Soc. Japan*, **60**, 3751 (1987).

5. Alcohols, Aldehydes, Ketones, Ethers, Esters, and Epoxides



Methanol

Reference code, notes	Type	<i>T</i> /K	<i>k</i> , <i>k</i> / <i>k</i> (ref) <i>A</i> , <i>A</i> / <i>A</i> (ref)	<i>n</i>	<i>B</i> , <i>B</i> - <i>B</i> (ref)	<i>k</i> err. factor
75 BAS/KOG Discharge flow-electron spin resonance spectroscopy.	EX	350-800	4.3±0.1E12		1020±65	
76 OWE/ROS Re-analysis of data of 72 LEF/MEA. <i>A</i> unchanged at 1.70±0.66E12.	DE				1370±280	
76 OWE/ROS Discharge flow-O+NO chemiluminescence.	EX	301-451	1.45±0.50E12		1540±140	
80 LAL/VER Pulsed photolysis-resonance fluorescence.	EX	298	3.6±0.6E7			
81 GRO/JUS Discharge flow-mass spectrometry.	EX	300-1006	3.4±1.1E13		2750±150	
81 KEI/TAN Flash photolysis-resonance fluorescence and discharge flow-resonance fluorescence.	EX	298-998	1.62±0.30E13		2532±80	
82 FAI/SIN Phase shift-O+NO chemiluminescence.	EX	297-544	9.79±2.71E12		2267±111	
84 WAR	SE	300-1000	1.0E13		2360	2.5
87 TSA	SE	300-1100	3.9E5	2.5	1550	2
Recommended		300-1000 1000-2000	2E13 2.4E5		2520 1550	1.5 2.5

Comments and Recommendations

The recommended value given in 84 WAR is based on data published through 1981 while that given in 87 TSA covers the literature through 1982. For the latter, the recommendation is based on a BEBO calculation using the data given in 81 GRO/JUS, 81 KEI/TAN, and 82 FAI/SIN. No new data have been published since that evaluation. Since there is no evidence for curvature in the Arrhenius plots of the data from 81 GRO/JUS, 81 KEI/TAN, or 82 FAI/SIN, we have used these data to derive a recommended value over the 300 to 1000 K temperature range. For the 1000-2000 K range, we suggest using the expression, $k = 2.4 \times 10^5 T^{2.5} \exp(-1550/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, which is the BEBO expression derived in 87 TSA, adjusted to agree at 1000 K with the value calculated from the recommendation for the 300-1000 K range. We estimate the uncertainty to be a factor of 2. However, the curvature in the Arrhenius plots predicted by transition state theory is probably too great, and the high temperature rate constants calculated from this expression will probably be high.

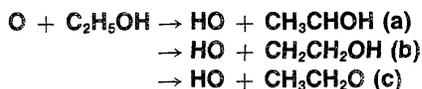
There are some significant disagreements between the recommended value and data listed in the data sheet. Thus, the values of *A* and *B* reported in 75 BAS/KOG are considerably lower than those recommended (a factor of 10 at the lowest temperature range of the measurements). The data of 76 OWE/ROS while in reasonable agreement over the range of the measurements, lead to low values of *A* and *B*. This is of importance in considering data on other alcohols reported from the same laboratory. Both of these sets of studies involved experimental techniques in which secondary reactions

are of potential importance and this may be the reason for the discrepancy. The room temperature rate constant reported in 80 LAL/VER differs by about a factor of 100 from the recommended value and clearly reflects a serious unrecognized experimental problem in that work.

The major product of the reaction studied using the Hg photosensitized decomposition of N₂O as the atom source was (CH₂OH)₂ as would be expected from the dimerization of the primary product of channel (a) (68 KAT/CVE). This has been confirmed in studies of the effects of isotopic substitution on the rate constants (81 GRO/JUS). Channel (b) can only be important at much higher temperatures.

References

- 68 KAT/CVE A. Kato and R. J. Cvetanovic, *Can. J. Chem.*, **46**, 235 (1968).
 75 BAS/KOG V. Ya. Basevich, S. M. Kogarko, and G. A. Furman, *Bull. Acad. Sci. USSR*, **24**, 948 (1975).
 76 OWE/ROS C. M. Owens and J. M. Roscoe, *Can. J. Chem.*, **54**, 984 (1976).
 80 LAL/VER C. Lalo and C. Vermeil, *J. Chim. Phys.*, **77**, 131 (1980).
 81 GRO/JUS H. H. Grotheer and Th. Just, *Chem. Phys. Letters*, **78**, 71 (1981).
 81 KEI/TAN D. G. Keil, T. Tanzawa, E. G. Skolnik, R. B. Klemm, and J. V. Michael, *J. Chem. Phys.*, **75**, 2693 (1981).
 82 FAI/SIN R. L. Failes, D. L. Singleton, G. Paraskopoulos, and R. S. Irwin, *Int. J. Chem. Kinet.*, **14**, 371 (1982).
 84 WAR J. Warnatz, in "Combustion Chemistry", W. C. Gardiner, Jr., ed., Springer-Verlag, New York, p197 (1984).
 87 TSA W. Tsang, *J. Phys. Chem. Ref. Data*, **16**, 471 (1987).



Ethanol

Reference code, notes	Type	T/K	$k, k/k(\text{ref})$ $A, A/A(\text{ref})$	n	$B,$ $B-B(\text{ref})$	k err. factor
73 HER/HUI	SE	298	8.7E10			1.5
76 OWE/ROS Discharge flow-O+NO chemiluminescence.	EX	301-439	4.17±0.51E11		760±200	
79 AYU/ROS Re-interpretation of data of 76 OWE/ROS.	EX	301-439	6.70±0.78E11		760±200	
81 WAS Discharge flow-mass spectrometry.	EX	298	1.0±0.2E11			
81 WAS Discharge flow-mass spectrometry. Reactant C ₂ D ₅ OH.	EX	298	6.6±2.4E10			
86 GRO/NES Flash photolysis-resonance fluorescence and discharge flow-resonance fluorescence.	EX	298-886	5.95E5	2.46	932	
Recommended		300-1000	6E5	2.46	930	1.5

Comments and Recommendations

The recommended value given in 73 HER/HUI was based on the relative rate measurements reported in 67 KAT/CVE. The recommended rate constant given here is based solely on the extensive data given in 86 GRO/NES. The Arrhenius plot is curved in contrast to data from the same laboratory on the CH₃OH reaction, which is linear (81 KEI/TAN). The curvature probably reflects different sites for oxygen atom attack, and extrapolation of the data very far outside the range of the measurements should be undertaken with caution. Fitting of these data to a double exponential (86 GRO/NES) yields expressions which were tentatively identified with $k(a+b)$ and $k(c)$: $k(a+b) = 1.9 \times 10^{13} \exp(-990/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, and $k(c) = 4.8 \times 10^{13} \exp(-1740/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Under beam conditions involving translational temperatures of about 3500 K, there is evidence that channel (c) becomes important, with $k(c)/k(a+b) \approx 0.5$ (85 DUT/FLE). An almost identical ratio can be calculated from the expressions given above for these rate constants from 86 GRO/NES.

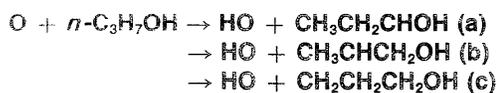
Data reported by other workers, and the earlier recommended value of 73 HER/HUI are a factor of 2 or 3 higher than the recommended value at room temperature. The data given in 79 AYU/ROS while in reasonable agreement over the range of the measurements, lead to low values for A and B . Thus the reported A factor is about a factor of 30 lower than that derived over the same temperature range from the data of 86 GRO/NES. This is important in considering data on other alcohols reported from the same laboratory. 86 GRO/NES have considered some possible secondary reactions which

could lead to errors in the rate constants reported in 67 KAT/CVE (relative rate measurements with respect to the reaction of oxygen atoms with 1-butene). They concluded that the system could be more complex than originally appreciated, and the derived rate measurements subject to considerable uncertainty. If this analysis is correct then other rate measurements using this approach also could be in error.

The major product of the reaction at 298 K as studied using the Hg photosensitized decomposition of N₂O as the atom source was 2,3-butanediol, the dimer of the primary product of channel (a) (67 KAT/CVE). In studies of the products formed under discharge flow conditions at 298 K, it was concluded that channel (a) accounted for at least 99% of the reaction (81 WAS). There are no independent data on the relative importance of (b).

References

- 67 KAT/CVE A. Kato and R. J. Cvetanovic, *Can. J. Chem.*, **45**, 1845 (1967).
 73 HER/HUI J. T. Herron and R. E. Huie, *J. Phys. Chem. Ref. Data*, **2**, 467 (1973).
 76 OWE/ROS C. M. Owens and J. M. Roscoe, *Can. J. Chem.*, **54**, 984 (1976).
 79 AYU/ROS A. L. Ayub and J. M. Roscoe, *Can. J. Chem.*, **57**, 1269 (1979).
 81 KEI/TAN D. G. Keil, T. Tanzawa, E. G. Skolnik, R. B. Klemm, and J. V. Michael, *J. Chem. Phys.*, **75**, 2693 (1981).
 81 WAS N. Washida, *J. Chem. Phys.*, **75**, 2715 (1981).
 85 DUT/FLE N. J. Dutton, I. W. Fletcher, and J. C. Whitehead, *J. Phys. Chem.*, **89**, 569 (1985).
 86 GRO/NES H. Grotheer, F. L. Nesbitt, and R. B. Klemm, *J. Phys. Chem.*, **90**, 2512 (1986).

**1-Propanol**

Reference code, notes	Type	T/K	$k, k/k(\text{ref})$ $A, A/A(\text{ref})$	n	$B,$ $B-B(\text{ref})$	k err. factor
79 AYU/ROS Discharge flow-O+NO chemiluminescence.	EX	308-463	7.92±0.75E11		1500±165	
Recommended		298	3E10			5

Comments and Recommendations

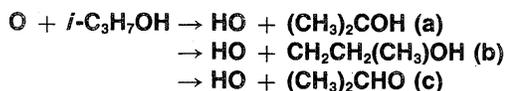
The only data are from 79 AYU/ROS. The A and B parameters are probably not reliable. Using the correlation shown in Fig. 1 (see Sec. 1.3 and 1.4) we estimate $k(298 \text{ K}) = 3 \times 10^{10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. From the expression given in 79 AYU/ROS, one derives $k(298 \text{ K}) = 5 \times 10^9 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, a factor of 6 lower. While in general lower rate constants are likely to be more correct than higher ones, it would imply in this case that 1-propanol is less reactive than ethanol, which is highly unlikely. We

prefer the estimated value with a large uncertainty factor.

There is no information on the mechanism, but by analogy with the other alcohols, we expect abstraction of a non-hydroxy hydrogen atom to be the major channel at other than very high temperatures.

References

- 79 AYU/ROS A. L. Ayub and J. M. Roscoe, *Can. J. Chem.*, **57**, 1269 (1979).

**2-Propanol**

Reference code, notes	Type	T/K	$k, k/k(\text{ref})$ $A, A/A(\text{ref})$	n	$B,$ $B-B(\text{ref})$	k err. factor
73 HER/HUI	SE	298	1.3E11			1.5
79 AYU/ROS Discharge flow-O+NO chemiluminescence.	EX	308-463	3.19±0.23E11		1100±140	
87 WAS Discharge flow-mass spectrometry. Reactant (CD ₃) ₂ CHOH.	EX	298	2.6±0.3E11			
87 WAS Discharge flow-mass spectrometry. Reactant (CH ₃) ₂ CDOH.	EX	298	1.6±0.2E11			
Recommended		298	4E10			5

Comments and Recommendations

The recommended value in 73 HER/HUI is based on relative rate measurements of Kato and Cvetanovic (68 KAT/CVE). The data of 79 AYU/ROS lead to a rate constant at 298 K of $8 \times 10^9 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ which is about a factor of 16 lower than the value given in 68 KAT/CVE. The value given in 87 WAS is a factor of 2 higher again than that of 68 KAT/CVE. From Fig. 1 (see Sec. 1.3 and 1.4), we estimate a rate constant at 298 K of $4 \times 10^{10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The agreement is not very good. We prefer the estimated value with a large uncertainty factor.

From a study of the products of the Hg photosensitized decomposition of N₂O (68 KAT/CVE), (a) was identified as the major channel. The other channels may become more important at higher temperatures.

References

- 68 KAT/CVE A. Kato and R. J. Cvetanovic, *Can. J. Chem.*, **46**, 235 (1968).
 73 HER/HUI J. T. Herron and R. E. Huie, *J. Phys. Chem. Ref. Data*, **2**, 467 (1973).
 79 AYU/ROS A. L. Ayub and J. M. Roscoe, *Can. J. Chem.*, **57**, 1269 (1979).
 87 WAS N. Washida, *Bull. Chem. Soc. Japan*, **60**, 3757 (1987).

**1-Butanol**

Reference code, notes	Type	T/K	k, k/k(ref) A,A/A(ref)	n	B, B-B(ref)	k err. factor
83 ROS Discharge flow-O+NO chemiluminescence.	EX	300-600	2.99±0.48E13		1780±190	
Recommended		300-600	3E13		1800	3

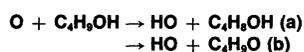
Comments and Recommendations

The only data are from 83 ROS. The *A* and *D* parameters are probably not reliable, and the data should not be extrapolated much beyond the range of the experimental measurements.

There is no information on the mechanism, but by analogy with the other alcohols, we expect abstraction of a non-hydroxy hydrogen atom (a) to be the major channel at other than very high temperatures.

References

83 ROS J. M. Roscoe, Can. J. Chem., 61, 2716 (1983).

**2-Butanol**

Reference code, notes	Type	T/K A,A/A(ref)	k, k/k(ref)	n B-B(ref)	B, factor	k err. factor
83 ROS Discharge flow-O+NO chemiluminescence.	EX	300-600	4.47±0.71E12		1190±190	
Recommended		300-600	4.5E12		1200	3

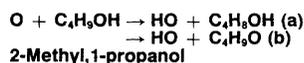
Comments and Recommendations

The only data are from 83 ROS. The *A* and *B* parameters are probably not reliable, and the data should not be extrapolated much beyond the range of the experimental measurements.

There is no information on the mechanism, but by analogy with the other alcohols, we expect abstraction of a non-hydroxy hydrogen atom (a) to be the major channel at other than very high temperatures.

References

83 ROS J. M. Roscoe, Can. J. Chem., 61, 2716 (1983).

**2-Methyl,1-propanol**

Reference code, notes	Type	T/K	k, k/k(ref) A,A/A(ref)	n	B, B-B(ref)	k err. factor
83 ROS Discharge flow-O+NO chemiluminescence.	EX	300-600	3.66±0.48E12		1100±150	
Recommended		300-600	3.7E12		1100	3

Comments and Recommendations

The only data are from 83 ROS. The *A* and *B* parameters are probably not reliable, and the data should not be extrapolated much beyond the range of the experimental measurements.

There is no information on the mechanism, but by analogy with the other alcohols, we expect abstraction

of a non-hydroxy hydrogen atom (a) to be the major channel at other than very high temperatures.

References

83 ROS J. M. Roscoe, Can. J. Chem., 61, 2716 (1983).

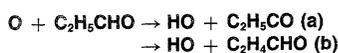
the data should not be extrapolated much beyond the range of the experimental measurements.

In crossed molecular beam-laser induced fluorescence studies (82 KLE/LUN) it was found that the HO rotational state distribution was similar to that previously found for abstraction from saturated hydrocarbons which was taken to indicate a direct collinear abstraction mechanism. The energy threshold was found to be 10±1 kJ mol⁻¹, which may be compared to the measured activation energy of 8 kJ mol⁻¹.

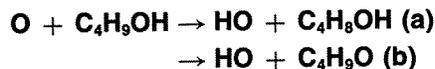
77 SIN/IRW D. L. Singleton, R. S. Irwin, and R. J. Cvetanovic Can. J. Chem., 55, 3321 (1977).

81 MOR S. Mori, Bull. Inst. Chem. Res., Kyoto Univ., 59, 116 (1981).

82 KLE/LUN K. Kleinermanns and A. C. Luntz, J. Chem. Phys., 77, 3774 (1982).

**Propionaldehyde**

Reference code, notes	Type	T/K	k, k/k(ref) A,A/A(ref)	n	B, B-B(ref)	k err. factor
77 SIN/IRW	EX	298-472	7.78±0.75E12		869±33	

**2-Methyl,2-propanol**

Reference code, notes	Type	T/K	$k, k/k(\text{ref})$ $A, A/A(\text{ref})$	n	$B,$ $B-B(\text{ref})$	k err. factor
83 ROS	EX	300-600	$4.99 \pm 1.00\text{E}12$		2190 ± 270	
Discharge flow-O+NO chemiluminescence.						
Recommended		300-600	5E12		2200	3

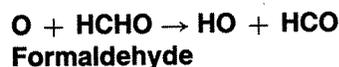
Comments and Recommendations

From Fig. 1 (see Sec. 1.3), we estimate a rate constant at 298 K of $2.5 \times 10^9 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, in good agreement with the value calculated from the expression given in 83 ROS. However, the A and B parameters are probably not reliable, and the data should not be extrapolated much beyond the range of the experimental measurements.

There is no information on the mechanism, but by analogy with the other alcohols, we expect abstraction of a non-hydroxy hydrogen atom (a) to be the major channel at other than very high temperatures.

References

- 83 ROS J. M. Roscoe, *Can. J. Chem.*, **61**, 2716 (1983).

**Formaldehyde**

Reference code, notes	Type	T/K	$k, k/k(\text{ref})$ $A, A/A(\text{ref})$	n	$B,$ $B-B(\text{ref})$	k err. factor
73 HER/HUI	SE	300	9.0E10			1.3
73 HER/HUI	SE	300	4.9E10			1.3
Reactant CHDO.						
74 CAD/WIC	EX	298	3.7E12		1200	
Discharge flow.						
79 CHA/BAR	EX	296-437	$2.3 \pm 0.5\text{E}13$		1583	
79 KLE	EX	250-498	$1.67 \pm 0.19\text{E}13$		1525 ± 40	
Flash photolysis-resonance fluorescence.						
80 KLE/SKO	EX	298-748	$1.83 \pm 0.48\text{E}13$		1554 ± 126	
Discharge flow-resonance fluorescence.						
80 KLE/SKO	TH	300-750	4.8E12		1670	
80 KLE/SKO	SE	250-748	$1.77 \pm 0.16\text{E}13$		1543 ± 34	
84 WAR	SE	300-2500	3.5E13		1770	1.5
86 TSA/HAM	SE	298-750	1.8E13		1550	1.2
Recommended		250-800 800-2000	1.8E13 3.3E7	1.94	1543 522	1.5 2.5

Comments and Recommendations

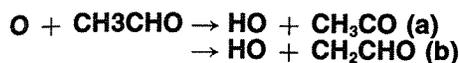
The recommendation given in 84 WAR is based on the the very reliable low temperature data ($T \leq 1000 \text{ K}$) and the much less reliable high temperature data derived from shock tube experiments. That of 86 TSA/HAM is the NASA recommendation (85 NAS). We believe that the best data is that recommended in 80 KLE/SKO, and use that as the basis for the recommendation. The theoretical data reported in 80 KLE/SKO is the result of a BEBO calculation which yields rate constants a factor of about 5 lower than the experimental results. Over the temperature range 800-2000 K we suggest using the expression, $k = 3.3 \times 10^7 T^{1.94} \exp(-522/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, which is based on a BEBO calculation adjusted to yield the same rate constant at 700 K as calculated from the recommended value for the 250-800 K temperature range. However, the curvature in the Arrhenius plots predicted by transition state theory is probably too great,

and the high temperature rate constants calculated from this expression will probably be high. See sec. 1.4.

The reaction is almost certainly a hydrogen atom abstraction, although it had been suggested that it might proceed in part through intermediate formation of an H_2COO adduct (79 CHA/BAR). This has not been confirmed experimentally, and no allowance is made for that reaction channel.

References

- 73 HER/HUI J. T. Herron and R. E. Huie, *J. Phys. Chem. Ref. Data*, **2**, 467 (1973).
 74 CAD/WIC R. D. Cadle, H. H. Wickmann, C. B. Hall, and K. M. Eberle, *Chemosphere*, **3**, 115 (1974).
 79 CHA/BAR J. S. Chang and J. R. Barker, *J. Phys. Chem.*, **84**, 3059 (1979).
 79 KLE R. B. Klemm, *J. Chem. Phys.*, **71**, 1987 (1979).
 80 KLE/SKO R. B. Klemm, E. G. Skolnik, and J. V. Michael, *J. Chem. Phys.*, **72**, 1256 (1980).

**Acetaldehyde**

Reference code, notes	Type	T/K	$k, k/k(\text{ref})$ $A, A/A(\text{ref})$	n	$B,$ $B-B(\text{ref})$	k err. factor
73 HER/HUI	SE	298-500	1.4E13		1140	2
73 HER/HUI	SE	298	3.1E11			2
74 MAC/THR	EX	300	2.88±0.3E11			
Discharge flow-O+NO chemiluminescence, electron spin resonance spectroscopy.						
77 MIC/LEE	EX	298	2.9±0.3E11			
Discharge flow-resonance fluorescence.						
77 SIN/IRW	EX	298-472	7.21±1.49E12		986±77	
Phase shift-O+NO chemiluminescence.						
81 MOR	EX	298	2.9±0.4E11			
Discharge flow-mass spectrometry.						
84 WAR	SE	300-2000	5E12		900	2
Recommended		300-500	7.2E12		990	1.5

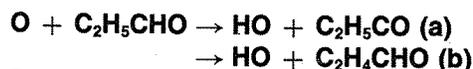
Comments and Recommendations

The recommendation is based on data given in 77 SIN/IRW. The other room temperature measurements are in good agreement. 77 SIN/IRW also give a derived expression for channel (a) of $k(a) = 7 \times 10^{12} \exp(-980/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Since there are multiple abstraction sites, the data should not be extrapolated much beyond the range of the experimental measurements.

In crossed molecular beam-laser induced fluorescence studies (82 KLE/LUN) it was found that the HO rotational state distribution was similar to that previously found for abstraction from saturated hydrocarbons which was taken to indicate a direct collinear abstraction mechanism. The energy threshold was found to be $10 \pm 1 \text{ kJ mol}^{-1}$, which may be compared to the measured activation energy of 8 kJ mol^{-1} .

References

- 73 HER/HUI J. T. Herron and R. E. Huie, *J. Phys. Chem. Ref. Data*, **2**, 467 (1973).
- 74 MAC/THR G. P. R. Mack and B. A. Thrush, *J. Chem. Soc. Faraday Trans. 1*, **70**, 178 (1974).
- 77 MIC/LEE J. V. Michael and J. H. Lee, *Chem. Phys. Letters*, **51**, 303 (1977).
- 77 SIN/IRW D. L. Singleton, R. S. Irwin, and R. J. Cvetanovic *Can. J. Chem.*, **55**, 3321 (1977).
- 81 MOR S. Mori, *Bull. Inst. Chem. Res., Kyoto Univ.*, **59**, 116 (1981).
- 82 KLE/LUN K. Kleinermanns and A. C. Luntz, *J. Chem. Phys.*, **77**, 3774 (1982).

**Propionaldehyde**

Reference code, notes	Type	T/K	$k, k/k(\text{ref})$ $A, A/A(\text{ref})$	n	$B,$ $B-B(\text{ref})$	k err. factor
77 SIN/IRW	EX	298-472	7.78±0.75E12		869±33	
Phase shift-O+NO chemiluminescence.						
Recommended		300-500	7.8E12		870	1.5

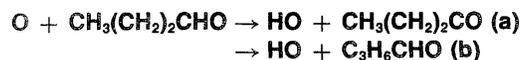
Comments and Recommendations

The only data are those reported in 77 SIN/IRW which are the basis for the recommendation.

The major channel is (a), abstraction of the aldehydic hydrogen atom. 77 SIN/IRW give a derived expression for channel (a) of $k(a) = 5.7 \times 10^{12} \exp(-780/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Since there are multiple abstraction sites, the data should not be extrapolated much beyond the range of the experimental measurements.

References

- 77 SIN/IRW D. L. Singleton, R. S. Irwin, and R. J. Cvetanovic *Can. J. Chem.*, **55**, 3321 (1977).

**Butyraldehyde**

Reference code, notes	Type	T/K	<i>k</i> , <i>k</i> / <i>k</i> (ref) <i>A</i> , <i>A</i> / <i>A</i> (ref)	<i>n</i>	<i>B</i> , <i>B</i> - <i>B</i> (ref)	<i>k</i> err. factor
77 SIN/IRW Phase shift-O+NO chemiluminescence.	EX	298-472	9.99±0.56E12		857±20	
Recommended		300-500	1E13		860	1.5

Comments and Recommendations

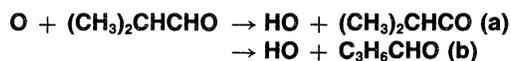
The only data are those reported in 77 SIN/IRW which are the basis for the recommendation.

The major channel is (a), abstraction of the aldehydic hydrogen atom. 77 SIN/IRW give a derived expression for channel (a) of $k(a) = 6.2 \times 10^{12} \exp(-720/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Since there are multiple abstraction sites, the

data should not be extrapolated much beyond the range of the experimental measurements.

References

- 77 SIN/IRW D. L. Singleton, R. S. Irwin, and R. J. Cvetanovic
Can. J. Chem., 55, 3321 (1977).

**Isobutyraldehyde**

Reference code, notes	Type	T/K	<i>k</i> , <i>k</i> / <i>k</i> (ref) <i>A</i> , <i>A</i> / <i>A</i> (ref)	<i>n</i>	<i>B</i> , <i>B</i> - <i>B</i> (ref)	<i>k</i> err. factor
77 SIN/IRW Phase shift-O+NO chemiluminescence.	EX	298-472	7.92±1.02E12		727±46	
Recommended		300-500	7.9E12		730	1.5

Comments and Recommendations

The only data are those reported in 77 SIN/IRW which are the basis for the recommendation.

The major channel is (a), abstraction of the aldehydic hydrogen atom. 77 SIN/IRW give a derived expression for channel (a) of $k(a) = 7.2 \times 10^{12} \exp(-700/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Since there are multiple abstraction sites, the

data should not be extrapolated much beyond the range of the experimental measurements.

References

- 77 SIN/IRW D. L. Singleton, R. S. Irwin, and R. J. Cvetanovic
Can. J. Chem., 55, 3321 (1977).

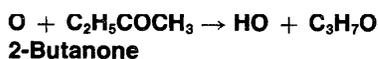
**Acetone**

Reference code, notes	Type	T/K	<i>k</i> , <i>k</i> / <i>k</i> (ref) <i>A</i> , <i>A</i> / <i>A</i> (ref)	<i>n</i>	<i>B</i> , <i>B</i> - <i>B</i> (ref)	<i>k</i> err. factor
76 AMB/BRA Discharge flow-electron spin resonance spectroscopy.	EX	298-621	4.3±1.0E12		2860±85	
77 LEE/TIM Discharge flow-mass spectrometry.	EX	298-478	1.9±0.4E12		2540±90	
82 FAU/HOY Discharge flow-mass spectrometry.	EX	298	6.8±2.9E8			
83 MIX/WAG Discharge flow-mass spectrometry.	EX	300-400	3.5±1.1E13		3310±660	
86 ROS Discharge flow-O+NO chemiluminescence.	EX	301-565	6.4±4E11		2100±200	
Recommended		300-700	1E13		3000	3

Comments and Recommendations

The recommendation is based on data given in 76 AMB/BRA, 77 LEE/TIM, and 83 MIX/WAG. These data agree to within a factor of 2 over the range of the measurements. From Fig. 1 (see Sec. 1.3) we estimate a rate constant at 298 K which is about a factor of 2 lower than that calculated from the recommended rate expression. The data of 86 ROS while in reasonable agreement over the range of the measurements, lead to low values of A and B . A similar observation was made in the case of measurements from the same laboratory on the alcohols (see data sheet on methanol). This is important in considering data on other ketones reported from the same laboratory.

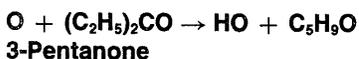
The data reported in 83 MIX/WAG are part of a much larger set of data on the reactions of oxygen atoms with oxygen containing organic compounds. As pointed out in the data sheet for $O + C_2H_6$, the ethane rate constant reported in 83 MIX/WAG is a factor of 3.1 and 1.6 higher than the recommended values at 300 and 400 K respectively. There is thus reason to suspect that the A



Reference code, notes	Type	T/K	$k, k/k(\text{ref})$ $A, A/A(\text{ref})$	n	$B,$ $B-B(\text{ref})$	k err. factor
86 ROS Discharge flow-O+NO chemiluminescence.	EX	301-565	$5.0 \pm 0.9E11$		1300 ± 300	
Recommended		300-600	$5E11$		1300	3

Comments and Recommendations

The only data are from 86 ROS which are the basis for the recommendation. However, the A and B parameters are probably not reliable, and the data should not be extrapolated much outside the range of the measurements. From Fig. 1 (see Sec. 1.3), we estimate $k = 3 \times 10^9$



Reference code, notes	Type	T/K	$k, k/k(\text{ref})$ $A, A/A(\text{ref})$	n	$B,$ $B-B(\text{ref})$	k err. factor
86 ROS Discharge flow-O+NO chemiluminescence.	EX	301-565	$2.9 \pm 0.9E11$		1000 ± 500	
Recommended		300-600	$3E11$		1000	3

Comments and Recommendations

The only data are from 86 ROS which are the basis for the recommendation. However, the A and B parameters are probably not reliable (see the data sheet on 2-butanone), and the data should not be extrapolated much outside the range of the measurements.

and B factors reported by these workers are low. This is probably also the case for the A and B factors reported in 76 AMB/BRA and 77 LEE/TIM, as well as for the recommended values given here, and the data should not be extrapolated much outside the range of the experimental measurements. See also Sec. 1.4.3.

The reaction is almost certainly a hydrogen atom abstraction. A primary kinetic isotope effect of between 3 and 4 was measured over the temperature range 517-614 K, which is indicative of an abstraction mechanism (77 LEE/TIM).

References

- 76 AMB/BRA P. F. Ambidge, J. N. Bradley, and D. N. Whytcock, J. Chem. Soc. Faraday Trans. 1, **72**, 1870 (1976).
 77 LEE/TIM J. H. Lee and R. B. Timmons, Int. J. Chem. Kinetics, **9**, 133 (1977).
 82 FAU/HOY C. Faubel, K. Hoyerman, and H. Gg. Wagner, Z. Phys. Chem., N. F., **130**, 1 (1982).
 83 MIX/WAG K. H. Mix and H. Gg. Wagner, Oxidation Communications, **5**, 321 (1983).
 86 ROS J. M. Roscoe, Can. J. Chem., **64**, 1458 (1986).

$\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$, which is about a factor of 2 lower than that calculated from the recommendation.

There is no information on the mechanism, but it is almost certainly a hydrogen atom abstraction.

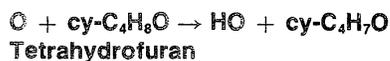
References

- 86 ROS J. M. Roscoe, Can. J. Chem., **64**, 1458 (1986).

There is no information on the mechanism, but it is almost certainly a hydrogen atom abstraction.

References

- 86 ROS J. M. Roscoe, Can. J. Chem., **64**, 1458 (1986).



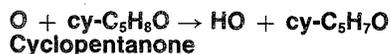
Reference code, notes	Type	T/K	$k, k/k(\text{ref})$ $A, A/A(\text{ref})$	n	$B,$ $B-B(\text{ref})$	k err. factor
86 SCH/MIX Discharge flow-mass spectrometry.	EX	298-498	$7.8 \pm 2.9\text{E}13$		1900 ± 660	
Recommended		300-600	8E13		1900	3

Comments and Recommendations

The only data are from 86 SCH/MIX which are the basis for the recommendation. However, as noted in the data sheet for the $\text{O} + \text{C}_2\text{H}_6$ reaction, the A and B factors may be low. See also Sec. 1.4.3. The data should not be extrapolated much beyond the range of the experimental measurements.

References

- 86 SCH/MIX V. Schliephake, K. H. Mix, and H. Gg. Wagner, Z. Phys. Chem. N. F., 150, 1 (1986).



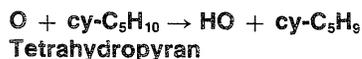
Reference code, notes	Type	T/K	$k, k/k(\text{ref})$ $A, A/A(\text{ref})$	n	$B,$ $B-B(\text{ref})$	k err. factor
86 SCH/MIX Discharge flow-mass spectrometry.	EX	300-492	$2.4 \pm 0.8\text{E}13$		2270 ± 680	
Recommended		300-600	2.4E13		2300	3

Comments and Recommendations

The only data are from 86 SCH/MIX which are the basis for the recommendation. However, as noted in the data sheet for the $\text{O} + \text{C}_2\text{H}_6$ reaction, the A and B factors may be low. See also Sec. 1.4.3. The data should not be extrapolated much beyond the range of the experimental measurements.

References

- 86 SCH/MIX V. Schliephake, K. H. Mix, and H. Gg. Wagner, Z. Phys. Chem. N. F., 150, 1 (1986).



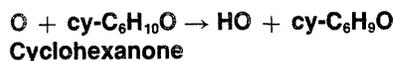
Reference code, notes	Type	T/K	$k, k/k(\text{ref})$ $A, A/A(\text{ref})$	n	$B,$ $B-B(\text{ref})$	k err. factor
86 SCH/MIX Discharge flow-mass spectrometry.	EX	298-503	$6.0 \pm 2.9\text{E}13$		1800 ± 630	
Recommended		300-600	6E13		1800	3

Comments and Recommendations

The only data are from 86 SCH/MIX which are the basis for the recommendation. However, as noted in the data sheet for the $\text{O} + \text{C}_2\text{H}_6$ reaction, the A and B factors may be low. See also Sec. 1.4.3. The data should not be extrapolated much beyond the range of the experimental measurements.

References

- 86 SCH/MIX V. Schliephake, K. H. Mix, and H. Gg. Wagner, Z. Phys. Chem. N. F., 150, 1 (1986).



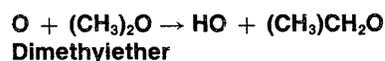
Reference code, notes	Type	T/K	k, k/k(ref) A, A/A(ref)	n	B, B-B(ref)	k err. factor
86 SCH/MIX Discharge flow-mass spectrometry.	EX	300-488	3.2±1.0E13		2270±680	
Recommended		300-600	3E13		2300	3

Comments and Recommendations

The only data are from 86 SCH/MIX which are the basis for the recommendation. However, as noted in the data sheet for the O + C₂H₆ reaction, the A and B factors may be low. See also Sec. 1.4.3. The data should not be extrapolated much beyond the range of the experimental measurements.

References

- 86 SCH/MIX V. Schliephake, K. H. Mix, and H. Gg. Wagner, Z. Phys. Chem. N. F., 150, 1 (1986).



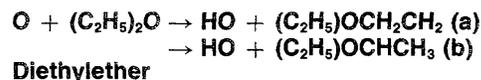
Reference code, notes	Type	T/K	k, k/k(ref) A, A/A(ref)	n	B, B-B(ref)	k err. factor
73 HER/HUI	SE	200-500	5.9E12		1520	1.3
82 FAU/HOY Discharge flow-mass spectrometry.	EX	298	2.3±0.7E10			
83 MIX/WAG Discharge flow-mass spectrometry.	EX	293-408	4.8±1.4E13		2280±460	
Recommended		300-500	5E13		2300	3

Comments and Recommendations

The data from 82 FAU/HOY and 86 SCH/MIX (the same laboratory) are the basis for the recommendation. They are in good agreement with the older recommendation over the range of the measurements, but predict higher A and B factors. However, as noted in the data sheet for the O + C₂H₆ reaction, the A and B factors are still probably too low. See also Sec. 1.4.3. The data should not be extrapolated much beyond the range of the experimental measurements.

References

- 73 HER/HUI J. T. Herron and R. E. Huie, J. Phys. Chem. Ref. Data, 2, 467 (1973).
 82 FAU/HOY C. Faubel, K. Hoyerman, and H. Gg. Wagner, Z. Phys. Chem., N. F., 130, 1 (1982).
 83 MIX/WAG K. H. Mix and H. Gg. Wagner, Oxidation Communications, 5, 321 (1983).



Reference code, notes	Type	T/K	k, k/k(ref) A, A/A(ref)	n	B, B-B(ref)	k err. factor
82 FAU/HOY Discharge flow-mass spectrometry.	EX	298	6.7±3.5E10			
83 MIX/WAG Discharge flow-mass spectrometry.	EX	293-408	6±1.8E13		1960±390	
Recommended		300-500	6E13		2000	3

Comments and Recommendations

The only data are from 82 FAU/HOY and 86 SCH/MIX (the same laboratory) which are the basis for the recommendation. However, as noted in the data sheet for the $O + C_2H_6$ reaction, the A and B factors may be low. See also Sec. 1.4.3. The data should not be extrapolated much beyond the range of the experimental measurements.

From a study of the yields of reaction products over the temperature range 298-345 K using the Hg photosensitized decomposition of N_2O as the oxygen atom source, Neumann (73 NEU) deduced that $B(a)/B(b)=4.4$, and

 $O + HCOOCH_3 \rightarrow HO + HCOOCH_2$
Methyl formate

Reference code, notes	Type	T/K	$k, k/k(\text{ref})$ $A, A/A(\text{ref})$	n	$B, B-B(\text{ref})$	k err. factor
81 MOR Discharge flow-mass spectrometry.	EX	298	$5.6 \pm 1.1E11$			
82 FAU/HOY Discharge flow-mass spectrometry.	EX	298	$6.4 \pm 2.5E8$			
86 MIX/SCH Discharge flow-mass spectrometry.	EX	295-417	$9.0 \pm 2.2E12$		2680 ± 150	
Recommended		300-500	9E12		2700	3

Comments and Recommendations

The data from 82 FAU/HOY and 86 SCH/MIX (the same laboratory) are the basis for the recommendation. However, as noted in the data sheet for the $O + C_2H_6$ reaction, the A and B factors may be low. See also Sec. 1.4.3. The data should not be extrapolated much beyond the range of the experimental measurements.

The data from 81 MOR are high by a factor of 6 for no apparent reason. The same workers report data for

$E(a)-E(b)=6.7 \text{ kJ mol}^{-1}$. While the numbers are reasonable, there is so much scatter in the data that these observations are only of qualitative value. They do indicate that (b) is the major channel at room temperature, with $k(b)/k(a) \approx 3$. The rate constants would be equal at about 500 K.

References

- 73 NEU M. G. Neumann, Z. Phys. Chem. N. F., 85, 221 (1973).
82 FAU/HOY C. Faubel, K. Hoyerman, and H. Gg. Wagner, Z. Phys. Chem., N. F., 130, 1 (1982).
83 MIX/WAG K. H. Mix and H. Gg. Wagner, Oxidation Communications, 5, 321 (1983).

acetaldehyde that is in good agreement with the recommendation.

References

- 81 MOR S. Mori, Bull. Inst. Chem. Res., Kyoto Univ., 59, 116 (1981).
82 FAU/HOY C. Faubel, K. Hoyerman, and H. Gg. Wagner, Z. Phys. Chem., N. F., 130, 1 (1982).
86 MIX/SCH K. H. Mix, V. Schliephake, and H. Gg. Wagner, Z. Phys. Chem. N. F., 150, 17 (1986).

 $O + HCOOC_2H_5 \rightarrow HO + HCOOC_2H_4$
Ethyl formate

Reference code, notes	Type	T/K	$k, k/k(\text{ref})$ $A, A/A(\text{ref})$	n	$B, B-B(\text{ref})$	k err. factor
82 FAU/HOY Discharge flow-mass spectrometry.	EX	298	$1 \pm 0.4E9$			
86 MIX/SCH Discharge flow-mass spectrometry.	EX	298-428	$1.1 \pm 0.4E13$		2600 ± 210	
Recommended		300-500	1E13		2600	3

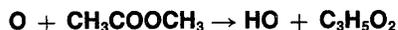
Comments and Recommendations

The only data are from 82 FAU/HOY and 86 SCH/MIX (the same laboratory) which are the basis for the recommendation. However, as noted in the data sheet for the $O + C_2H_6$ reaction, the A and B factors may be low. See also Sec. 1.4.3. The data should not be extrapolated much beyond the range of the experimental measurements.

lated much beyond the range of the experimental measurements.

References

- 82 FAU/HOY C. Faubel, K. Hoyerman, and H. Gg. Wagner, Z. Phys. Chem., N. F., 130, 1 (1982).
86 MIX/SCH K. H. Mix, V. Schliephake, and H. Gg. Wagner, Z. Phys. Chem. N. F., 150, 17 (1986).

**Methyl acetate**

Reference code, notes	Type	T/K	k, k/k(ref) A, A/A(ref)	n	B, B-B(ref)	k err. factor
82 FAU/HOY Discharge flow-mass spectrometry.	EX	298	4.9±2E8			
86 MIX/SCH Discharge flow-mass spectrometry.	EX	295-423	1.2±0.3E13		2860±360	
Recommended		300-500	1E13		2900	3

Comments and Recommendations

The only data are from 82 FAU/HOY and 86 SCH/MIX (the same laboratory) which are the basis for the recommendation. However, as noted in the data sheet for the O + C₂H₆ reaction, the A and B factors may be low. From Fig. 1 (see Sec. 1.3), we estimate $k(298\text{ K}) = 1.3 \times 10^8 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ which is considerably lower than the value of $8 \times 10^8 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ calculated from

the experimental data. See also Sec. 1.4.3. The data should not be extrapolated much beyond the range of the experimental measurements.

References

- 82 FAU/HOY C. Faubel, K. Hoyerman, and H. Gg. Wagner, Z. Phys. Chem., N. F., 130, 1 (1982).
86 MIX/SCH K. H. Mix, V. Schliephake, and H. Gg. Wagner, Z. Phys. Chem. N. F., 150, 17 (1986).

**Ethyl acetate**

Reference code, notes	Type	T/K	k, k/k(ref) A, A/A(ref)	n	B, B-B(ref)	k err. factor
86 MIX/SCH Discharge flow-mass spectrometry.	EX	300-413	1.4±0.5E13		2490±170	
Recommended		300-500	1.4E13		2500	3

Comments and Recommendations

The only data are from 86 SCH/MIX which are the basis for the recommendation. However, as noted in the data sheet for the O + C₂H₆ reaction, the A and B factors may be low. See also Sec. 1.4.3. The data should not

be extrapolated much beyond the range of the experimental measurements.

References

- 86 MIX/SCH K. H. Mix, V. Schliephake, and H. Gg. Wagner, Z. Phys. Chem. N. F., 150, 17 (1986).

**n-Propyl acetate**

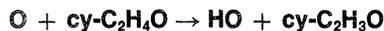
Reference code, notes	Type	T/K	k, k/k(ref) A, A/A(ref)	n	B, B-B(ref)	k err. factor
86 MIX/SCH Discharge flow-mass spectrometry.	EX	295-403	1.6±0.6E13		2430±300	
Recommended		300-500	1.6E13		2400	3

Comments and Recommendations

The only data are from 86 SCH/MIX which are the basis for the recommendation. However, as noted in the data sheet for the O + C₂H₆ reaction, the A and B factors may be low. See also Sec. 1.4.3. The data should not be extrapolated much beyond the range of the experimental measurements.

References

- 86 MIX/SCH K. H. Mix, V. Schliephake, and H. Gg. Wagner, Z. Phys. Chem. N. F., 150, 17 (1986).



Ethylene oxide

Reference code, notes	Type	T/K	$k, k/k(\text{ref})$ $A, A/A(\text{ref})$	n	$B,$ $B-B(\text{ref})$	k err. factor
73 HER/HUI	SE	298	7E8			1.5
78 BOG/HAN Discharge flow-mass spectrometry.	EX	298-691	$1.91 \pm 0.31\text{E}12$		2640 ± 75	
Recommended		298	4E7			5

Comments and Recommendations

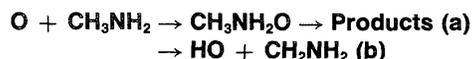
The only extensive set of data is that given in 78 BOG/HAN. From Fig. 1 (see Sec. 1.3), we estimate $k(298 \text{ K}) = 4 \times 10^7 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ which is about a factor of 10 lower than that calculated from the expression given in 78 BOG/HAN. The experimental data are suspect, and we recommend using the estimated value at 298 K.

The reaction is almost certainly a hydrogen atom abstraction, and measurements of kinetic isotope effects support that conclusion (78 BOG/HAN).

References

- 73 HER/HUI J. T. Herron and R. E. Huie, *J. Phys. Chem. Ref. Data*, **2**, 467 (1973).
78 BOG/HAN D. J. Bogan and C. W. Hand, *J. Phys. Chem.*, **82**, 2067 (1978).

6. Amines, Nitroalkanes, Nitrites, and Nitrates



Methylamine

Reference code, notes	Type	T/K	$k, k/k(\text{ref})$ $A, A/A(\text{ref})$	n	$B,$ $B-B(\text{ref})$	k err. factor
74 KIR/MER Discharge flow-mass spectrometry.	EX	300-450	$2.7 \pm 0.3\text{E}12$		770 ± 35	
78 ATK/PIT Flash photolysis-O+NO chemiluminescence.	EX	298-440	5.4E12		830 ± 100	
Recommended		300-600	5.4E12		830	1.5

Comments and Recommendations

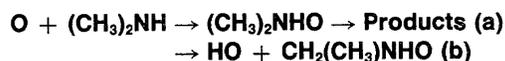
The two sets of data are in fairly good agreement. The recommended value is based on the data given in 78 ATK/PIT. Because of the complexity of the reaction mechanism, the data should not be extrapolated too far beyond the range of the experimental data.

The reaction mechanism is complex, but there is little question that the major path at room temperature involves formation of an energy rich adduct which can be collisionally stabilized, or decompose, either directly or following isomerization. Products identified using a crossed jet reactor (79 SLA/DUD) corresponded in mass to the adduct and to the adduct less HO. It was proposed that the HO was formed from the rearrangement of an energy rich amine N-oxide to the hydroxylamine which then eliminated HO.

In crossed molecular beam-laser induced fluorescence studies (82 KLE/LUN) it was found that the HO rotational state distribution was similar to that previously found for abstraction from saturated and unsaturated hydrocarbons which was taken to indicate a direct collinear abstraction mechanism. If, as postulated in 79 SLA/DUD, HO is a major product of the decomposition of an initially formed adduct which has isomerized to the hydroxylamine, then in the crossed molecular beam-laser induced fluorescence studies one would have expected to see a different HO rotational distribution than that seen (more nearly statistical) and an energy threshold closer to the observed (thermal) activation energy. The threshold energy was found to be 10 kJ mol^{-1} which is significantly higher than the observed activation energy of the overall reaction of 6.9 kJ mol^{-1} , and suggests that an abstraction channel might become im-

portant at higher temperatures. It was also argued in 82 KLE/LUN that abstraction involved the hydrogen atom attached to the carbon rather than the nitrogen atom, contrary to the general conclusions given in 79 SLA/DUD.

See Sec. 1.4.4.



Dimethylamine

Reference code, notes	Type	T/K	k, k/k(ref) A, A/A(ref)	n	B, B-B(ref)	k err. factor
74 KIR/MER Discharge flow-mass spectrometry.	EX	300	3.2E12			
78 ATK/PIT Flash photolysis-O+NO chemiluminescence.	EX	298-440	9.12E12		275±100	
Recommended		300-600	9.1E12		280	1.5

Comments and Recommendations

The two sets of data are in fairly good agreement. The recommended value is based on the data given in 78 ATK/PIT. Because of the complexity of the reaction mechanism, the data should not be extrapolated too far beyond the range of the experimental data.

The reaction mechanism is complex, but there is little question that the major path at room temperature involves formation of an energy rich adduct which can be collisionally stabilized, or decompose, either directly or following isomerization. Products identified using a crossed jet reactor (79 SLA/DUD, 79 SLA/DUD2) corresponded in mass to the adduct, to the adduct less HO and H₂O, and to CH₃. It was proposed that these products were formed from the quenching, decomposition, and rearrangement of an energy rich amine N-oxide. The methyl could arise by direct decomposition of the initially formed adduct, or could be formed following isomerization of the adduct to the hydroxylamine. HO and HO₂ were proposed to arise from decomposition of the hydroxylamine. On the basis of deuterium substitution experiments it was further established that the HO loss channel involved exclusively the hydrogen atom originally attached to the nitrogen atom.

In crossed molecular beam-laser induced fluorescence studies (82 KLE/LUN) it was found that the HO rotational state distribution was similar to that previously found for abstraction from saturated and unsaturated hydrocarbons which was taken to indicate a direct

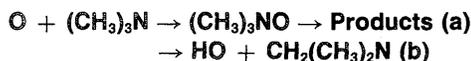
- #### References
- 74 KIR/MER K. Kirchner, N. Merget, and C. Schmidt, Chem. Ing. Tech., **46**, 661 (1974).
 78 ATK/PIT R. Atkinson and J. N. Pitts, Jr., J. Chem. Phys., **68**, 911 (1978).
 79 SLA/DUD I. R. Slagle, J. F. Dudich, and D. Gutman, J. Phys. Chem., **83**, 3065 (1979).
 82 KLE/LUN K. Kleinermanns and A. C. Luntz, J. Chem. Phys., **77**, 3537 (1982).

collinear abstraction mechanism. If, as postulated in 79 SLA/DUD and 79 SLA/DUD2, HO is a major product of the decomposition of an initially formed adduct which has isomerized to the hydroxylamine, then in the crossed molecular beam-laser induced fluorescence studies one would have expected to see a different HO rotational distribution than that seen (more nearly statistical) and an energy threshold closer to the observed (thermal) activation energy. The threshold energy was found to be 8.4 kJ mol⁻¹ which is significantly higher than the observed activation energy of the overall reaction of 2.3 kJ mol⁻¹, and suggests that an abstraction channel might become important at higher temperatures. It was also argued in 82 KLE/LUN that abstraction involved the H atom attached to the carbon rather than the nitrogen atom, contrary to the general conclusions given in 79 SLA/DUD and 79 SLA/DUD2.

See Sec. 1.4.4.

References

- 74 KIR/MER K. Kirchner, N. Merget, and C. Schmidt, Chem. Ing. Tech., **46**, 661 (1974).
 78 ATK/PIT R. Atkinson and J. N. Pitts, Jr., J. Chem. Phys., **68**, 911 (1978).
 79 SLA/DUD I. R. Slagle, J. F. Dudich, and D. Gutman, Chem. Phys. Letters, **61**, 620 (1979).
 79 SLA/DUD2 I. R. Slagle, J. F. Dudich, and D. Gutman, J. Phys. Chem., **83**, 3065 (1979).
 82 KLE/LUN K. Kleinermanns and A. C. Luntz, J. Chem. Phys., **77**, 3537 (1982).

**Trimethylamine**

Reference code, notes	Type	T/K	<i>k</i> , <i>k</i> / <i>k</i> (ref) <i>A</i> , <i>A</i> / <i>A</i> (ref)	<i>n</i>	<i>B</i> , <i>B</i> - <i>B</i> (ref)	<i>k</i> err. factor
74 KIR/MER Discharge flow-mass spectrometry.	EX	300	9.4E12			
78 ATK/PIT Flash photolysis-O + NO chemiluminescence.	EX	298-440	6.48E12		-210±100	
81 JEF/BAU Discharge flow-mass spectrometry.	EX	298	4.5±1E12			
Recommended		300-600	6.5E12		-210	1.5

Comments and Recommendations

The rate constants reported in 74 KIR/MER and 78 ATK/PIT are in fairly good agreement, while that of 81 JEF/BAU is about a factor of 3 lower. The recommended value is based on the data given in 78 ATK/PIT. Because of the complexity of the reaction mechanism, the data should not be extrapolated too far beyond the range of the experimental data.

The reaction mechanism is complex, but there is little question that the major path at room temperature involves formation of an energy rich adduct which can be collisionally stabilized, or decompose, either directly or following isomerization. Products identified using a crossed jet reactor (79 SLA/DUD) corresponded in mass to the adduct less HO and to CH₃. Methyl could arise by direct decomposition of the initially formed adduct, or could be formed following isomerization of the adduct to the hydroxylamine. HO was proposed to arise from decomposition of the hydroxylamine.

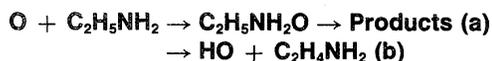
In crossed molecular beam-laser induced fluorescence studies (82 KLE/LUN) it was found that the HO rotational state distribution was similar to that previously found for abstraction from saturated and unsaturated hydrocarbons which was taken to indicate a direct collinear abstraction mechanism. If, as postulated in 79 SLA/DUD, HO is a major product of the decomposition of an initially formed adduct which has isomerized to a hydroxylamine, then in the crossed molecular beam-

laser induced fluorescence studies one would have expected to see a different HO rotational distribution than that seen (more nearly statistical) and an energy threshold closer to the observed (thermal) activation energy. The threshold energy was found to be 6.3 kJ mol⁻¹ which is significantly higher than the observed activation energy of the overall reaction of -1.7 kJ mol⁻¹ (the negative activation energy has been interpreted in terms of adduct formation (78 ATK/PIT)), and suggests that an abstraction channel might become important at higher temperatures. It was also argued in 82 KLE/LUN that abstraction involved the hydrogen atom attached to the carbon rather than the nitrogen atom, contrary to the general conclusions given in 79 SLA/DUD.

See Sec. 1.4.4.

References

- 74 KIR/MER K. Kirchner, N. Merget, and C. Schmidt, *Chem. Ing. Tech.*, **46**, 661 (1974).
 78 ATK/PIT R. Atkinson and J. N. Pitts, Jr., *J. Chem. Phys.*, **68**, 911 (1978).
 78 FIL/GUS W. G. Filby and H. Gusten, *Atmos. Environment*, **12**, 1563 (1978).
 79 SLA/DUD I. R. Slagle, J. F. Dudich, and D. Gutman, *J. Phys. Chem.*, **83**, 3065 (1979).
 81 JEF/BAU P. M. Jeffers and S. H. Bauer, *Chem. Phys. Letters*, **80**, 29 (1981).
 82 KLE/LUN K. Kleinermanns and A. C. Luntz, *J. Chem. Phys.*, **77**, 3537 (1982).

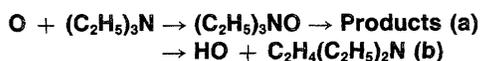
**Ethylamine**

Reference code, notes	Type	T/K	<i>k</i> , <i>k</i> / <i>k</i> (ref) <i>A</i> , <i>A</i> / <i>A</i> (ref)	<i>n</i>	<i>B</i> , <i>B</i> - <i>B</i> (ref)	<i>k</i> err. factor
74 KIR/MER Discharge flow-mass spectrometry.	EX	300-450	3.9±0.3E12		530±250	
78 ATK/PIT Flash photolysis-O + NO chemiluminescence.	EX	298-440	6.78E12		640±100	
78 FIL/GUS Discharge flow-electron spin resonance spectroscopy.	EX	298	2.3E12			
Recommended		300-600	6.8E12		640	1.5

Comments and Recommendations

The rate constants reported in 74 KIR/MER and 78 ATK/PIT are in fairly good agreement, but that of 78 FIL/GUS is about a factor of 3 higher. The recommended value is based on the data given in 78 ATK/PIT. Because of the complexity of the reaction mechanism, the data should not be extrapolated too far beyond the range of the experimental data.

The reaction mechanism is complex, but there is little question that the major path at room temperature involves formation of an energy rich adduct which can be collisionally stabilized, or decompose, either directly or following isomerization. Products identified using a crossed jet reactor (79 SLA/DUD) corresponded in mass to the adduct less HO and less H₂O. It was proposed that these products were formed from the rearrangement of an energy rich amine N-oxide to the hydroxylamine followed by decomposition.



Triethylamine

Reference code, notes	Type	T/K	k, k/k(ref) A, A/A(ref)	n	B, B-B(ref)	k err. factor
78 FIL/GUS Discharge flow-electron spin resonance.	EX	298	6.5E12			

Comments and Recommendations

There is only one measurement. The rate constant for the ethylamine reaction from the same source was about a factor of 3 higher than the recommended value so one might expect that for the triethylamine reaction the correct value would be lower than that reported in 78 FIL/GUS. However, from the trends observed in rate constants for the three methylamines, one would expect the rate constant for triethylamine to be even higher than the reported value, e.g., 10¹³ cm³ mol⁻¹ s⁻¹. Since other factors may be important in determining reactivity, no recommendation is made.

The reaction mechanism is complex, but there is little question that the major path at room temperature involves formation of an energy rich adduct which can be collisionally stabilized, or decompose, either directly or following isomerization. Products have been identified using a crossed jet reactor (79 SLA/DUD) corresponded in mass to the adduct less HO, H₂O and C₂H₄, and to C₂H₅. C₂H₅ could be formed through decomposi-

tion of the initially formed adduct or isomerization of the adduct to the hydroxylamine followed by decomposition. HO and H₂O were thought to arise from decomposition of the hydroxylamine, and C₂H₄ from a Cope elimination from the initially formed adduct.

See Sec. 1.4.4.

References

- 74 KIR/MER K. Kirchner, N. Merget, and C. Schmidt, Chem. Ing. Tech., **46**, 661 (1974).
 78 ATK/PIT R. Atkinson and J. N. Pitts, Jr., J. Chem. Phys., **68**, 911 (1978).
 78 FIL/GUS W. G. Filby and H. Gusten, Atmos. Environment, **12**, 1563 (1978).
 79 SLA/DUD I. R. Slagle, J. F. Dudich, and D. Gutman, J. Phys. Chem., **83**, 3065 (1979).
 82 KLE/LUN K. Kleinermanns and A. C. Luntz, J. Chem. Phys., **77**, 3537 (1982).

tion of the initially formed adduct or isomerization of the adduct to the hydroxylamine followed by decomposition. HO and H₂O were thought to arise from decomposition of the hydroxylamine, and C₂H₄ from a Cope elimination from the initially formed adduct.

However, in crossed molecular beam-laser induced fluorescence studies (82 KLE/LUN) of the HO internal state distribution in the methylamines, it was found that the HO rotational state distribution was similar to that previously found for abstraction from saturated and unsaturated hydrocarbons which was taken to indicate a direct collinear abstraction mechanism.

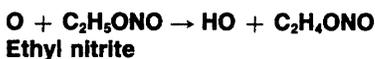
See Sec. 1.4.4.

References

- 78 FIL/GUS W. G. Filby and H. Gusten, Atmos. Environment, **12**, 1563 (1978).
 79 SLA/DUD I. R. Slagle, J. F. Dudich, and D. Gutman, J. Phys. Chem., **83**, 3065 (1979).
 82 KLE/LUN K. Kleinermanns and A. C. Luntz, J. Chem. Phys., **77**, 3537 (1982).

Comments and Recommendations

The data are suspect. See the data sheet on O + CH₃ONO₂ and Sec. 1.4.4. No recommendation is given. The reaction is probably a hydrogen atom abstraction.



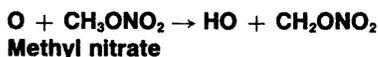
Reference code, notes	Type	T/K	k, k/k(ref) A, A/A(ref)	n	B, B-B(ref)	k err. factor
75 DAV/THR Discharge flow-O+NO chemiluminescence.	EX	300-410	2.6E13		2440±250	

References

75 DAV/THR J. A. Davidson and B. A. Thrush, J. Chem. Soc. Faraday Trans. 1, 71, 2413 (1975).

Comments and Recommendations

The data are suspect. See the data sheet on O + CH₃ONO₂ and Sec. 1.4.4. No recommendation is given. The reaction is probably a hydrogen atom abstraction.



Reference code, notes	Type	T/K	k, k/k(ref) A, A/A(ref)	n	B, B-B(ref)	k err. factor
77 SAL/THR Discharge flow-O+NO chemiluminescence.	EX	294-473	1.5E13		2650±120	
86 GAF/FAJ	DE	298	5.4E7			

References

75 DAV/THR J. A. Davidson and B. A. Thrush, J. Chem. Soc. Faraday Trans. 1, 71, 2413 (1975).

Comments and Recommendations

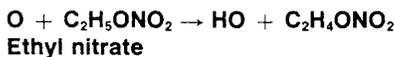
The direct experimental data given in 77 SAL/THR are strongly contradicted by the data reported in 86 GAF/FAJ. In the later, the rate constant for reaction of HO radicals with CH₃ONO₂ was measured to be $2.0 \times 10^{10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and used to derive a value for the corresponding oxygen atom reaction of $5.4 \times 10^7 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ using the correlation discussed in Section 1.3 (79 GAF/LEV). We have repeated the calculation using Fig. 1, and derived $k(\text{CH}_3\text{ONO}_2 + \text{O}) = 1.5 \times 10^7 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. In both cases the derived values differ sharply from the experimental one. There is thus reason to question the validity of the experimental measurement. However, a second direct measurement of the HO + CH₃ONO₂ rate constant (86 KER/STO) yielded $k = 2.2 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, which differs by a factor of 10 from the rate constant given in 86 GAF/FAJ. This

value of the rate constant, in conjunction with Fig. 1, leads to a value for the corresponding oxygen atom rate constant of $4 \times 10^8 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, which is only a factor of 5 lower than the experimental value. Until the serious uncertainty in the hydroxyl radical rate constant is resolved, we hesitate to provide recommended values for this or any other compound in this general series.

The reaction is probably a hydrogen atom abstraction.

References

77 SAL/THR L. F. Salter and B. A. Thrush, J. Chem. Soc. Faraday Trans. 1, 73, 1098 (1977).
79 GAF/LEV J. S. Gaffney and S. Z. Levine, Int. J. Chem. Kinet., 11, 1197 (1979).
86 GAF/FAJ J. S. Gaffney, R. Fajer, G. I. Senum, and J. H. Lee, Int. J. Chem. Kinet., 18, 399 (1986).
86 KER/STO J. A. Kerr and D. W. Stocker, J. Atmos. Chem., 4, 253 (1986).



Reference code, notes	Type	T/K	k, k/k(ref) A, A/A(ref)	n	B, B-B(ref)	k err. factor
77 SAL/THR Discharge flow-O+NO chemiluminescence.	EX	294-473	2.6E13		2600±310	

Comments and Recommendations

The experimental data are suspect. See the data sheet on $O + CH_3ONO_2$ and Sec. 1.4.4. No recommendation is given.

The reaction is probably a hydrogen atom abstraction.

References

- 77 SAL/THR L. F. Salter and B. A. Thrush, *J. Chem. Soc. Faraday Trans. 1*, **73**, 1098 (1977).

7. Boranes, Germane, Silanes, and Dimethylmercury

 $O + B_2H_6 \rightarrow$ Products
Diborane

Reference code, notes	Type	T/K	$k, k/k(\text{ref})$ $A, A/A(\text{ref})$	n	$B,$ $B-B(\text{ref})$	k err. factor
74 HAN/DER Discharge flow-mass spectrometry.	EX	300-506	1.3E13		2510	
77 AND/BAU Discharge flow-mass spectrometry.	EX	298	2.7E9			
Recommended		300-1000	1E13		2500	5

Comments and Recommendations

Hand and Derr (74 HAN/DER) presented their data in the form of an Arrhenius plot. We have calculated the parameters A and B from that plot. Although these data are in good agreement with the data of Anderson and Bauer (77 AND/BAU), the reaction is very sensitive to the conditions of the surface. There is thus a high degree of uncertainty in the data.

There are no definitive product analysis data, and the mechanism is basically unknown, although it is probable that the reaction involves attack at the boron atom.

References

- 74 HAN/DER C. W. Hand and L. K. Derr, *Inorg. Chem.*, **13**, 339 (1974).
77 AND/BAU G. K. Anderson and S. H. Bauer, *J. Phys. Chem.*, **81**, 1146 (1977).

 $O + H_3BCO \rightarrow$ Products
Borane carbonyl

Reference code, notes	Type	T/K	$k, k/k(\text{ref})$ $A, A/A(\text{ref})$	n	$B,$ $B-B(\text{ref})$	k err. factor
77 AND/BAU Discharge flow-mass spectrometry.	EX	298	3.9E11			
Recommended		298	4E11			5

Comments and Recommendations

There is only a single measurement. The reaction is very sensitive to the conditions of the surface. There is thus a high degree of uncertainty in the data.

There are no definitive product analysis data, and the mechanism is basically unknown, although it is probable

that the reaction involves attack at the boron atom, and possibly hydrogen atom abstraction.

References

- 77 AND/BAU G. K. Anderson and S. H. Bauer, *J. Phys. Chem.*, **81**, 1146 (1977).

O + (CH₃)₃NBH₃ → Products
Borane trimethylamine

Reference code, notes	Type	T/K	k, k/k(ref) A, A/A(ref)	n	B, B-B(ref)	k err. factor
81 JEF/BAU Discharge flow-mass spectrometry.	EX	298	>1.4E13			
Recommended		300-2000	3E13			5

Comments and Recommendations

The reaction is too fast to measure accurately using discharge flow methods. The recommended rate constant is therefore quite uncertain.

The mechanism may involve initial displacement of the (CH₃)₃N group.

References

81 JEF/BAU P. M. Jeffers and S. H. Bauer, Chem. Phys. Letters, 80, 29 (1981).

O + (C₂H₅)₃NBH₃ → Products
Borane triethylamine

Reference code, notes	Type	T/K	k, k/k(ref) A, A/A(ref)	n	B, B-B(ref)	k err. factor
81 JEF/BAU Discharge flow-mass spectrometry.	EX	298	>1.4E13			
Recommended		300-2000	3E13			5

Comments and Recommendations

The reaction is too fast to measure accurately using discharge flow methods. The recommended rate constant is therefore quite uncertain.

The mechanism may involve initial displacement of the (C₂H₅)₃N group.

References

81 JEF/BAU P. M. Jeffers and S. H. Bauer, Chem. Phys. Letters, 80, 29 (1981).

O + SiH₄ → HO + SiH₃
Silane

Reference code, notes	Type	T/K	k, k/k(ref) A, A/A(ref)	n	B, B-B(ref)	k err. factor
78 ATK/PIT Flash photolysis-O+NO chemiluminescence.	EX	297-438	4.10E12		800±150	
84 KHA/MKR Discharge flow-electron spin resonance spectroscopy.	EX	288-549	1.6±0.3E13		1360±120	
Recommended		300-1000	4E12		800	2

Comments and Recommendations

The two sets of experimental data are in fairly good agreement over the entire common temperature range (within a factor of 1.5). We believe the data given in 78 ATK/PIT are the more reliable, and these are the basis for the recommended value.

The rate data have been interpreted in terms of an abstraction reaction (78 ATK/PIT). Products identified in matrix isolation studies in which oxygen atoms and

silane were mixed and condensed onto a substrate at 17 K included H₃SiSiH₃ and SiH₃OH (85 WIT/AND). The former product confirms the abstraction mechanism, while the latter was interpreted to mean that a parallel insertion channel was active. This seems improbable, and we suggest that SiH₃OH is formed by abstraction followed by combination of HO and SiH₃. There is compelling evidence that abstraction is the major mechanism in the O + (CH₃)₃SiH reaction (see data sheet).

References

- 78 ATK/PIT R. Atkinson and J. N. Pitts, Jr., *Int. J. Chem. Kinet.*, **10**, 1151 (1978).
- 84 KHA/MKR S. A. Kharutunyan, T. G. Mkryan, and E. N. Sarkisyan, *Oxidation Communications*, **7**, 49 (1984).
- 85 WIT/AND R. Withnall and L. Andrews, *J. Phys. Chem.*, **89**, 3261 (1985).

O + (CH₃)₃SiH → HO + (CH₃)₃Si
Trimethylsilane

Reference code, notes	Type	T/K	k, k/k(ref) A, A/A(ref)	n	B, B-B(ref)	k err. factor
85 HOF/HOR Discharge flow-mass spectrometry.	EX	298	1.6±0.2E12			
Recommended		298	1.6E12			3

Comments and Recommendations

The recommended value is based on the data given in 85 HOF/HOR. This rate constant may be compared to that for the corresponding SiH₄ reaction at 298 K (see data sheet), which on a per Si-H bond basis is $7 \times 10^{10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. As pointed out in 85 HOF/HOR, assuming that abstraction involves only hydrogen atoms attached to the silicon atom, one might have expected the rate constants per Si-H bond to be about the same, since the Si-H bond energies are about equal (82 MCM/GOL).

The major products of the reaction as studied using Hg photosensitization of N₂O, were N₂,

(CH₃)₃SiSi(CH₃)₃, (CH₃)₂SiOSi(CH₃)₃, and (CH₃)₃SiOH. These are explicable on the basis of a primary hydrogen atom abstraction reaction followed by secondary reactions of (CH₃)₃Si and (CH₃)₂SiO radicals (the latter arising from the reaction of (CH₃)₃Si with N₂O). Isotopic labelling experiments establish that the site of attack of the oxygen atom is the Si-H bond.

References

- 82 MCM/GOL D. F. McMillen and D. M. Golden, *Ann. Rev. Phys. Chem.*, **33**, 493 (1982).
- 85 HOF/HOR H. Hoffmeyer, O. Horie, P. Potzinger, and B. Reimann, *J. Phys. Chem.*, **89**, 2901 (1985).

O + ((CH₃)₂Si)₂ → (CH₃)₂SiOSi(CH₃)₂ → Products
Hexamethyldisilane

Reference code, notes	Type	T/K	k, k/k(ref) A, A/A(ref)	n	B, B-B(ref)	k err. factor
85 HOF/POT Discharge flow-mass spectrometry.	EX	298	7.8±1.8E10			
Recommended		298	7.8E10			3

Comments and Recommendations

The recommended value is based on the data given in 85 HOF/HOR.

The rate constant is higher by about a factor of 100 than that for a hydrocarbon having the same number of primary C-H bonds, which suggests that the reaction may not involve hydrogen atom abstraction. The reac-

tion products determined in studies using the Hg photosensitized photolysis of N₂O as the atom source, are explicable on the basis of an insertion mechanism (85 HOF/POT).

References

- 85 HOF/POT H. Hoffmeyer, P. Potzinger, and B. Reimann, *J. Phys. Chem.*, **89**, 4829 (1985).

O + GeH₄ → HO + GeH₃
Germane

Reference code, notes	Type	T/K	k, k/k(ref) A, A/A(ref)	n	B, B-B(ref)	k err. factor
81 AGR/MAN Discharge flow-chemiluminescence. Ref. reac. O + HI.	RE	300	2.1E12			
Recommended		298	2E12			3

Comments and Recommendations

The relative rate measurements reported in 81 AGR/MAN were put on an absolute basis using $k(\text{O} + \text{HI}) = 9.5 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ from 78 SIN/CVE.

The reaction is probably a hydrogen atom abstraction, and chemiluminescence from HO has been observed (81 AGR/MAN).

References

- 78 SIN/CVE D. L. Singleton and R. J. Cvetanovic, *Can. J. Chem.*, **56**, 2934 (1978).
81 AGR/MAN B. S. Agrawalla, A. S. Manocha, and D. W. Setser, *J. Phys. Chem.*, **85**, 2873 (1981).

O + (CH₃)₂Hg → (CH₃)₂HgO → Products
Dimethylmercury

Reference code, notes	Type	T/K	k, k/k(ref) A, A/A(ref)	n	B, B-B(ref)	k err. factor
86 THO/EGS Discharge flow-electron spin resonance spectroscopy and mass spectrometry.	EX	298	1.5 ± 0.1E13			
Recommended		298	1.5E13			3

Comments and Recommendations

The recommended value is based on the data given in 86 THO/EGS.

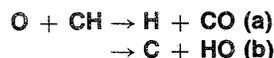
The rate constant is about a factor of 10⁵ higher than that for a hydrocarbon having the same number of primary C-H bonds, which suggests that the reaction is not a hydrogen atom abstraction. The mechanism probably proceeds via addition at the mercury atom followed by

decomposition of the adduct involving sequential loss of methyl radicals. HCHO was detected as a product, which can be taken as evidence that CH₃ radicals are produced (86 THO/EGS).

References

- 86 THO/EGS E. L. Thomsen and H. Egsgaard, *Chem. Phys. Letters*, **125**, 378 (1986).

8. Free Radicals

**Methylidene**

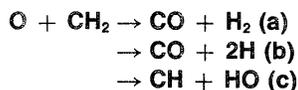
Reference code, notes	Type	T/K	k, k/k(ref) A, A/A(ref)	n	B, B-B(ref)	k err. factor
81 MES/FIL Multi-photon infrared photolysis. See also 80 MES/CAR.	EX	298	5.7 ± 0.8E13			
84 WAR	SE	300-2000	4.0E13			3
86 MUR/ROD	(a) TH (b) TH	1600-6000 10-6000	6.1E13 1.5E13		940 2400	
Recommended		300-2000	6E13			3

Comments and Recommendations

The recommended value of Warnatz (84 WAR) is based on data given in 81 MES/FIL and estimates given in 81 HOM/SCH. We recommend using the experimental value at all temperatures. The theoretical calculations (86 MUR/ROD) indicate that (b) can only be important at very high temperatures; typical calculated rate ratios are: $k_a/k_b = 3 \times 10^3$, 20, and 8 at 298, 1000, and 2000 K respectively. Until these calculated ratios are experimentally verified, it is suggested that only reaction (a) be treated as active.

References

- 80 MES/CAR I. Messing, T. Carrington, S. V. Filseth, and C. M. Sadowski, *Chem. Phys. Letters*, **74**, 56 (1980).
81 HOM/SCH K. H. Homann and H. Schweinfurth, *Ber. Bunsenges. Phys. Chem.*, **85**, 569 (1981).
81 MES/FIL I. Messing, S. V. Filseth, C. M. Sadowski, and T. Carrington, *J. Chem. Phys.*, **74**, 3874 (1981).
84 WAR J. Warnatz, in "Combustion Chemistry", W. C. Gardiner, Jr., ed., Springer-Verlag, New York, p197 (1984).
86 MUR/ROD J. N. Murrell and J. A. Rodriguez, *J. Molec. Struc.(Theochem)*, **139**, 267 (1986).

**Methylene**

Reference code, notes	Type	T/K	$k, k/k(\text{ref})$ $A, A/A(\text{ref})$	n	$B,$ $B-B(\text{ref})$	k err. factor
78 VIN/DEB Discharge flow-mass spectrometry.	EX	295	$7.8 \pm 1.8\text{E}13$			
79 VIN/DEB Discharge flow-mass spectrometry. Reference reaction: $\text{O} + \text{C}_2\text{H}_2$.	RN	290-600			-630	
81 LAU	SE	298	1.1E13			
84 BOH/TEM Discharge flow-laser magnetic resonance spectroscopy.	EX	296	$8.1 \pm 3.0\text{E}13$			
84 FRA/JUS	(a) DE	2000	6E13			
	(b) DE	2000	1.6E13			
	(c) DE	2000	3E14		6000	
Shock tube-resonance absorption spectroscopy.						
84 WAR	SE	300-2000	5.0E13			2
86 TSA/HAM	SE	298	1.1E13			2
Recommended		300-2000	8E13			2

Comments and Recommendations

The recommendation of Warnatz (84 WAR) is based on data reported in 79 VIN/DEB and estimates given in 81 HOM/SCH, while that of Tsang and Hampson (86 TSA/HAM) is based on the review of Laufer (81 LAU). We recommend using a rate constant of $8 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ based on the experimental data reported in 78 VIN/DEB, 84 BOH/TEM, and 84 FRA/JUS. The data of 79 VIN/DEB were put on an absolute basis using the recommended value for $B(\text{O} + \text{C}_2\text{H}_2) = 1030 \text{ K}$ from 87 CVE. The derived negative activation energy is too small to be significant and the rate constant should be taken as temperature independent. According to 81 SHA/HSU, channels (a) and (b) are of comparable importance. However, recent modeling studies discussed in 84 BOH/TEM suggest that the molecular channel (a) may be the major one. Frank and Just (84 FRA/JUS) on the basis of a modeling study of the decomposition of ketene in the presence of oxygen atoms derived values for the rate constants for all three channels. Since these are based on modeling calculations, they are subject to considerable uncertainty. On the basis of these data, the rate constants for (b) and (c) would be equal at 2000 K.

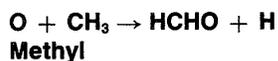
The reaction presumably takes place through formation of an energy rich CH_2O adduct which then decomposes. However, channel (c) could be a direct hydrogen atom abstraction.

Although Tsang and Hampson (86 TSA/HAM) distinguish between the triplet and singlet states of

methylene, recommending for the latter a rate constant of $3 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, we suggest that the rate constant will be about the same as for the triplet state reaction.

References

- 78 VIN/DEB C. Vinckier and W. Debruyne, Seventeenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh PA, p623 (1978).
- 79 VIN/DEB C. Vinckier and W. Debruyne, *J. Phys. Chem.*, **83**, 2057 (1979).
- 81 HOM/SCH K. H. Homann and H. Schweinfurth, *Ber. Bunsenges. Phys. Chem.*, **85**, 569 (1981).
- 81 LAU A. H. Laufer, *Rev. Chem. Int.*, **4**, 225 (1981).
- 81 SHA/HSU W. M. Shaub, D. S. Y. Hsu, T. L. Burks, and M. C. Lin, Eighteenth Symposium (International) on Combustion, the Combustion Institute, Pittsburgh PA, p811, (1981).
- 84 BOH/TEM T. Bohland, F. Temps, and H. Gg. Wagner, *Ber. Bunsenges. Phys. Chem.*, **88**, 1222 (1984).
- 84 FRA/JUS P. Frank and Th. Just, "Shock Tubes and Waves", Proceedings of the 14th International Symposium on Shock Tubes and Shock Waves, Sydney Shock Tube Symposium Publishers, p705, (1984).
- 84 WAR J. Warnatz, in "Combustion Chemistry", W. C. Gardiner, Jr., ed., Springer-Verlag, New York, p197 (1984).
- 86 TSA/HAM W. Tsang and R. F. Hampson, *J. Phys. Chem. Ref. Data*, **15**, 1087 (1986).
- 87 CVE R. J. Cvetanovic, *J. Phys. Chem. Ref. Data*, **16**, 261 (1987).



Reference code, notes	Type	T/K	k, k/k(ref) A, A/A(ref)	n	B, B-B(ref)	k err. factor
73 WAS/BAY Discharge flow-mass spectrometry.	EX	297	7.4±1.5E13			
74 SLA/PRU Discharge flow-mass spectrometry.	EX	300	1.10±0.17E14			
76 BIO/LAZ Flame-mass spectrometry.	DE	1550-1750	8.2E13			2
76 WAS/BAY Discharge flow-mass spectrometry.	EX	259-341	6.0E13			
80 BHA/FRA Shock tube-atomic resonance absorption spectroscopy. See also 79 ROT/JUS.	EX	1700-2300	7.8E13			
80 WAS Discharge flow-mass spectrometry.	EX	298	8.3±2.8E13			
82 PLU/R YA Discharge flow-mass spectrometry.	EX	295	6.8±1.7E13			
84 WAR	SE	300-2500	7.0E13			1.5
86 TSA/HAM	SE	300-2500	7.8E13			1.5
87 SLA/SAR Flow photolysis-mass spectrometry.	EX	294-900	8.4E13			
Recommended		300-2000	8.4E13			1.5

Comments and Recommendations

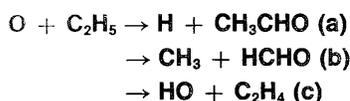
The rate data given in 87 SLA/SAR are the most extensive and reliable, and the basis for the recommendation. All other reported rate constants are in excellent agreement. There is no evidence for a temperature dependence over the entire range of experimental studies, although there is some indication of a falloff in rate at temperatures in excess of 2200 K (80 BHA/FRA). However, this could be an experimental artifact.

The reaction presumably proceeds through the formation of an energy rich CH₃O adduct which then decomposes to CH₂O + H. In nozzle beam experiments (79 HOY/SIE) it was found that CH₂O was the only detectable product. This was confirmed by 87 SLA/SAR who report that the rate of formation of CH₂O is within 10% of the rate of loss of CH₃, and no other products such as CH₂ or HCO were detected.

References

- 73 WAS/BAY N Washida and K. D. Bayes, Chem. Phys. Letters, **23**, 373 (1973).
 74 SLA/PRU I. R. Slagle, F. J. Pruss, Jr., and D. Gutman, Int. J. Chem. Kinet., **6**, 111 (1974).

- 76 BIO/LAZ J. C. Biordi, C. P. Lazzara, and J. F. Papp, Comb. Flame, **26**, 57 (1976).
 76 WAS/BAY N. Washida and K. D. Bayes, Int. J. Chem. Kinet., **8**, 777 (1976).
 79 HOY/SIE K. Hoyer mann and R. Sievert, Seventeenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh PA, p517 (1979).
 79 ROT/JUS P. Roth and T. H. Just, Proceedings of the 10th Materials Research Symposium on Characterization of High Temperature Vapors and Gases, J. W. Hastie, ed., NBS Special Publication 561, p1339 (1979).
 80 BHA/FRA K. A. Bhaskaran, P. Frank, and Th. Just, "Shock Tubes and Waves", Proceedings of the 12th International Symposium on Shock Tubes and Waves, Magnus Press, Jerusalem, p503, 1980.
 80 WAS N. Washida, J. Chem. Phys., **73**, 1665 (1980).
 82 PLU/R YA I. C. Plumb and K. R. Ryan, Int. J. Chem. Kinet., **14**, 861 (1982).
 84 WAR J. Warnatz, in "Combustion Chemistry", W. C. Gardiner, Jr., ed., Springer-Verlag, New York, p197 (1984).
 86 TSA/HAM W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data, **15**, 1087 (1986).
 87 SLA/SAR I. R. Slagle, D. Sarzynski, and D. Gutman, J. Phys. Chem., **91**, 4375 (1987).

**Ethyl**

Reference code, notes	Type	T/K	$k, k/k(\text{ref})$ $A, A/A(\text{ref})$	n	$B,$ $B-B(\text{ref})$	k err. factor
79 HOY/SIE Discharge flow-mass spectrometry.	RL	300	$k_a/k_b = 5 \pm 1$			
84 WAR	SE	300-2000	5.0E13			2
86 TSA/HAM	SE	300-2500	7.8E13			2
88 SLA/SAR	EX	295-600	$1.3 \pm 0.2\text{E}14$			
	RL	298-450	$k_a/k = 0.40 \pm 0.04$ $k_b/k = 0.32 \pm 0.07$ $k_c/k = 0.23 \pm 0.08$			
Flow photolysis-mass spectrometry.						
Recommended		300-2000	1.3E14			1.5

Comments and Recommendations

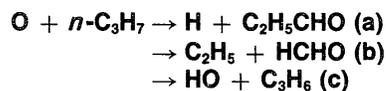
The recommended values given in 84 WAR and 86 TSA/HAM are estimates. The only measured value is that given in 88 SLA/SAR. The rate constant is independent of temperature over the range of the experiments.

There is conflicting evidence as to the relative importance of the possible reaction channels. 79 HOY/SIE report products corresponding to (a) and (b), while 88 SLA/SAR find products corresponding to all three channels. The reported branching ratios for (a) and (b) also differ greatly between the two groups of workers. Thus, where 79 HOY/SIE find $k_a/k_b = 5 \pm 1$, the data of 88 SLA/SAR lead to $k_a/k_b = 1.25$. However, in view of the serious interpretive problems associated with the nozzle beam type experiments (see Sec. 1.4.6), we prefer the analysis given in 88 SLA/SAR. The latter also argue

convincingly that (c) is a direct hydrogen atom abstraction reaction, whereas (a) and (b) involve formation of an energy rich $\text{C}_2\text{H}_5\text{O}$ adduct which then decomposes to products. The experimental study of the branching ratios was further supported by a detailed theoretical study (88 SLA/SAR).

References

- 79 HOY/SIE K. Hoyermann and R. Sievert, Seventeenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh PA, p517 (1979).
- 84 WAR J. Warnatz, in "Combustion Chemistry", W. C. Gardiner, Jr., ed., Springer-Verlag, New York, p197 (1984).
- 86 TSA/HAM W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data, 15, 1087 (1986).
- 88 SLA/SAR I. R. Slagle, D. Sarzynski, D. Gutman, J. A. Miller, and C. F. Melius, J. Chem. Soc. Faraday Trans. 2, (1988).

**n-Propyl**

Reference code, notes	Type	T/K	$k, k/k(\text{ref})$ $A, A/A(\text{ref})$	n	$B,$ $B-B(\text{ref})$	k err. factor
79 HOY/SIE Discharge flow-mass spectrometry.	RL	300	$k_a/k_b = 6 \pm 1.5$			
84 WAR	SE	300-2000	4.4E13			2
86 TSA/HAM	SE	300-2500	9.6E13			2
Recommended		300-2000	2E14			3

Comments and Recommendations

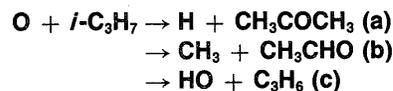
The recommended values in 84 WAR and 86 TSA/HAM are estimates. We recommend a value of 2×10^{14} $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$ by analogy with the rate constants for other alkyl radical reactions.

Hoyermann and Sievert (79 HOY/SIE) detected products corresponding to channels (a) and (b), which is what would be expected if the reaction involved formation and decomposition of an energy rich adduct. However, for other alkyl radical reactions there is strong evidence that a direct hydrogen atom abstraction chan-

nel (c) may be important. There may be serious interpretive problems associated with the nozzle beam type experiments. See Sec. 1.4.6.

References

- 79 HOY/SIE K. Hoyermann and R. Sievert, Seventeenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh PA, p517 (1979).
 84 WAR J. Warnatz, in "Combustion Chemistry", W. C. Gardiner, Jr., ed., Springer-Verlag, New York, p197 (1984).
 86 TSA/HAM W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data, **15**, 1087 (1986).



Isopropyl

Reference code, notes	Type	T/K	$k, k/k(\text{ref})$ $A, A/A(\text{ref})$	n $B-B(\text{ref})$ factor	$B,$	k err.
79 HOY/SIE Discharge flow-mass spectrometry.	RL	300	$k_a/k_b = 1 \pm 0.2$			
84 WAR	SE	300-2000	4.5E13			2
86 TSA/HAM	SE	300-2500	9.6E13			2
87 WAS Discharge flow-mass spectrometry. Reactant $(\text{CD}_3)_2\text{CH}$. Reference reaction $(\text{CD}_3)_2\text{CH} + \text{O}_2$.	RN	298	2.9E14			
Recommended		300-2000	3E14			3

Comments and Recommendations

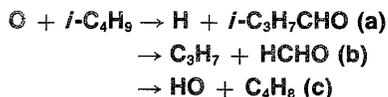
The recommended values in 84 WAR and 86 TSA/HAM are estimates. We recommend a value of 3×10^{14} $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$ based on the relative rate data reported in 87 WAS. The relative rate data were put on an absolute basis (87 WAS) using $k((\text{CH}_3)_2\text{CH} + \text{O}_2) = 8.5 \times 10^{12}$ $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$ (84 RUI/BAY), assuming no isotope effect.

Hoyermann and Sievert (79 HOY/SIE) detected products corresponding to channels (a) and (b), which is what would be expected if the reaction involved formation and decomposition of an energy rich adduct. However, there may be serious interpretive problems associated with the nozzle beam type experiments. Thus, Jewell and coworkers (81 JEW/HOL), report that propene is an important intermediate product in the reaction $\text{O} + \text{propane}$, and propose that (c) is the major channel. This could be a direct hydrogen atom abstraction channel. In his study of the reaction using isotopically labelled reactants, Washida (87 WAS) reported that (c) accounted for 61% of the reaction and the remainder involved addition followed by decomposition, with 18% going via (a) and 21% via (b).

See Sec. 1.4.6.

References

- 79 HOY/SIE K. Hoyermann and R. Sievert, Seventeenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh PA, p517 (1979).
 81 JEW/HOL S. P. Jewell, K. A. Holbrook, and G. A. Oldershaw, Int. J. Chem. Kinet., **14**, 585 (1982).
 84 RUI/BAY R. P. Ruiz and K. D. Bayes, J. Phys. Chem., **88**, 2592 (1984).
 84 WAR J. Warnatz, in "Combustion Chemistry", W. C. Gardiner, Jr., ed., Springer-Verlag, New York, p197 (1984).
 86 TSA/HAM W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data, **15**, 1087 (1986).
 87 WAS N. Washida, Bull. Chem. Soc. Japan, **60**, 3739 (1987).

**Isobutyl**

Reference code, notes	Type	T/K	$k, k/k(\text{ref})$ $A, A/A(\text{ref})$	n	$B,$ $B-B(\text{ref})$	k err. factor
79 HOY/SIE Discharge flow-mass spectrometry.	RL	300	$k_a/k_b=7\pm 2$			
84 WAR	SE	300-2000	4.0E13			2
Recommended		300-2000	2E14			3

Comments and Recommendations

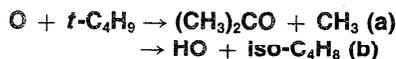
The recommended value in 84 WAR is an estimate. We recommend $2 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ by analogy with the rate constants for other alkyl radical reactions.

Hoyermann and Sievert (79 HOY/SIE) detected products corresponding to channels (a) and (b), which is what would be expected if the reaction involved formation and decomposition of an energy rich adduct. However, for other alkyl radical reactions there is strong evidence that a direct hydrogen atom abstraction chan-

nel (c) may be important. There may be serious interpretive problems associated with the nozzle beam type experiments. See Sec. 1.4.6.

References

- 79 HOY/SIE K. Hoyermann and R. Sievert, Seventeenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh PA, p517 (1979).
- 84 WAR J. Warnatz, in "Combustion Chemistry", W. C. Gardiner, Jr., ed., Springer-Verlag, New York, p197 (1984).

**tert-Butyl**

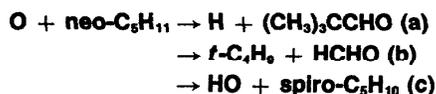
Reference code, notes	Type	T/K	$k, k/k(\text{ref})$ $A, A/A(\text{ref})$	n	$B,$ $B-B(\text{ref})$	k err. factor
80 WAS/BAY	RL	297	$k_a/k_b=0.24$			
80 WAS/BAY Discharge flow-mass spectrometry. Reference reaction: $t\text{-C}_4\text{H}_9 + \text{O}_2$.	RN	297	$5.2 \pm 0.8\text{E}14$			
82 JEW/HOL Discharge flow-final products.	EX	307	$k_a/k_b=0.3$			
84 WAR	SE	300-2000	4.0E13			2
Recommended		300-2000	5E14			2

Comments and Recommendations

The recommended value given in 84 WAR is an estimate. The data from 80 WAS/BAY were put on an absolute basis using $k(t\text{-C}_4\text{H}_9 + \text{O}_2) = 1.4 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ from 80 LEN/MCD. This is the basis for the recommended value. There should be little or no temperature effect on the rate constant or the branching ratio. Hoyermann and Sievert (79 HOY/SIE) detected products corresponding to channel (a) which is what would be expected if the reaction involved formation and decomposition of an energy rich adduct. However, 80 WAS/BAY and 82 JEW/HOL argue that the direct abstraction channel (b) is the major reaction path. There may be serious interpretive problems associated with the nozzle beam type experiments. See Sec. 1.4.6.

References

- 79 HOY/SIE K. Hoyermann and R. Sievert, Seventeenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh PA, p517 (1979).
- 80 LEN/MCD T. M. Lenhardt, C. E. McDade, and K. D. Bayes, J. Chem. Phys., **72**, 304 (1980).
- 80 WAS/BAY N. Washida and K. D. Bayes, J. Phys. Chem., **84**, 1309 (1980).
- 82 JEW/HOL S. P. Jewell, K. A. Holbrook, and G. A. Oldershaw, Int. J. Chem. Kinet., **14**, 585 (1982).
- 84 WAR J. Warnatz, in "Combustion Chemistry", W. C. Gardiner, Jr., ed., Springer-Verlag, New York, p197 (1984).

**Neopentyl**

Reference code, notes	Type	T/K	$k, k/k(\text{ref})$ $A, A/A(\text{ref})$	n	$B,$ $B-B(\text{ref})$	k err. factor
79 HOY/SIE Discharge flow-mass spectrometry. Ref. reac. O + CH ₃ .	RL	298	5E13			
Recommended		300-2000	2E14			3

Comments and Recommendations

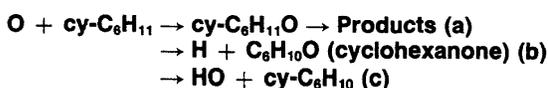
The rate constant reported in 79 HOY/SIE was put on an absolute basis using the recommended value for $k(\text{O} + \text{CH}_3)$ from this evaluation. The derived value is much lower than expected by analogy with the behaviour of other alkyl radicals. We recommend using a somewhat higher value.

Hoyermann and Sievert (79 HOY/SIE) detected products corresponding to channels (a) and (b), which is what would be expected if the reaction involved formation and decomposition of an energy rich adduct. The branching ratios were not reported. The formation of

spiropentane in the reaction of oxygen atoms with neopentane has been explained on the basis of reaction (c) (75 HUI/HER), and for other alkyl radical reactions there is strong evidence that a direct hydrogen atom abstraction channel may be important. See Sec. 1.4.6.

References

- 75 HUI/HER R. E. Huie and J. T. Herron, *Progr. Reaction Kinetics*, **8**, Part 1, 1 (1975).
79 HOY/SIE K. Hoyermann and R. Sievert, *Ber. Bunsenges. Phys. Chem.*, **83**, 732 (1979).

**Cyclohexyl**

Reference code, notes	Type	T/K	$k, k/k(\text{ref})$ $A, A/A(\text{ref})$	n	$B,$ $B-B(\text{ref})$	k err. factor
82 WAS/TAK	RL	298	$k_r/k = 0.45$ $k_s/k = 0.03$ $k_c/k = 0.52$			
82 WAS/TAK Discharge flow-mass spectrometry. Reference reaction: cy-C ₆ H ₁₁ + O ₂ .	RN	298	2E14			
Recommended		300-2000	2E14			2

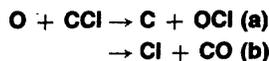
Comments and Recommendations

The relative rate measurement of 82 WAS/TAK was put on an absolute basis using $k(\text{cy-C}_6\text{H}_{11} + \text{O}_2) = 8.4 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ from 86 WU/BAY. It is the basis for the recommended value.

Washida and Takagi (82 WAS/TAK) proposed that (c), a direct hydrogen atom abstraction, was the major channel, while (a) and (b) involved formation and decomposition of an energy rich adduct. See Sec. 1.4.6.

References

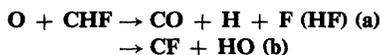
- 82 WAS/TAK N. Washida and H. Takagi, *J. Am. Chem. Soc.*, **104**, 168 (1982).
86 WU/BAY D. Wu and K. D. Bayes, *Int. J. Chem. Kinet.*, **18**, 547 (1986).

**Chloromethylidene**

Reference code, notes	Type	T/K	$k, k/k(\text{ref})$ $A, A/A(\text{ref})$	n	$B,$ $B-B(\text{ref})$	k err. factor
79 GAR/TRU	TH	300-1000	8.3E13		16000	
Recommended		300-2000	6E13			4

Comments and Recommendations

The theoretical value refers to channel (a), which is about 70 kJ mol⁻¹ endothermic. Channel (b) is strongly exothermic, and is probably the major channel, having a rate constant comparable to that for the O + CH reaction, independent of temperature.

**Fluoromethylene**

Reference code, notes	Type	T/K	$k, k/k(\text{ref})$ $A, A/A(\text{ref})$	n	$B,$ $B-B(\text{ref})$	k err. factor
84 HAN/KET Discharge flow-laser induced fluorescence.	EX	295	9.0 ± 1.2E13			
Recommended		300-2000	9E13			3

Comments and Recommendations

The reaction is very fast, and the recommended value is based on data reported in 84 HAN/KET, independent of temperature.

There are no data on which product channels are active, although CO has been observed in chemilumines-

cence. The mechanism should be similar to that for the O + CH₂ reaction, and (b) can only be important at high temperature.

References

84 HAN/KET G. Hancock, G. W. Ketley, and A. J. MacRobert, J. Phys. Chem., **88**, 2104 (1984).

**Difluoromethylene**

Reference code, notes	Type	T/K	$k, k/k(\text{ref})$ $A, A/A(\text{ref})$	n	$B,$ $B-B(\text{ref})$	k err. factor
84 RYA/PLU Discharge flow-mass spectrometry.	EX	295	1.1 ± 0.2E13			
86 HAN/HAR Multiphoton infrared photolysis-laser induced fluorescence.	EX	295	1.05 ± 0.21E13			
Recommended		298	1E13			2

Comments and Recommendations

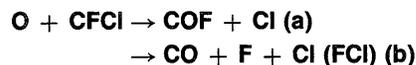
The two measured values are in excellent agreement and are the basis of the recommendation.

Ryan and Plumb (84 RYA/PLU) report that (a) is the major channel, with $k_a/k_b \geq 3$.

References

84 RYA/PLU K. R. Ryan and I. C. Plumb, Plasma Chem. Plasma Process., **4**, 271 (1984).

86 HAN/HAR G. Hancock, P. D. Harrison, and A. J. MacRobert, J. Chem. Soc., Faraday Trans. 2, **82**, 647 (1986).

**Chlorofluoromethylene**

Reference code, notes	Type	T/K	<i>k</i> , <i>k</i> / <i>k</i> (ref) <i>A</i> , <i>A</i> / <i>A</i> (ref)	<i>n</i>	<i>B</i> , <i>B</i> - <i>B</i> (ref)	<i>k</i> err. factor
80 MEU/PUR Discharge flow-laser induced fluorescence.	EX	298	1.7±1.2E12			
Recommended		298	1E13			4

Comments and Recommendations

The reported rate constant was derived from curve fitting experimental data in which the relative rate ratio $k(\text{O} + \text{CF}_2\text{CFCl})/k(\text{O} + \text{CFCl})$ was an adjustable parameter. We have adjusted the data using the rate constant for $\text{O} + \text{CF}_2\text{CFCl}$ from 87 CVE which yields a rate constant of $1.9 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. This is much lower than the rate constant for the reaction $\text{O} + \text{CF}_2$ of $1 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. We recommend using the later value for $\text{O} + \text{CFCl}$.

There is no information on the products, but the mechanism should be similar to that for the CF_2 reaction.

References

- 80 MEU/PUR H. Meunier, J. R. Purdy, and B. A. Thrush, *J. Chem. Soc. Faraday II*, **76**, 1304 (1980).
 87 CVE R. J. Cvetanovic, *J. Phys. Chem. Ref. Data*, **16**, 261 (1987).

**Trifluoromethyl**

Reference code, notes	Type	T/K	<i>k</i> , <i>k</i> / <i>k</i> (ref) <i>A</i> , <i>A</i> / <i>A</i> (ref)	<i>n</i>	<i>B</i> , <i>B</i> - <i>B</i> (ref)	<i>k</i> err. factor
82 RYA/PLU Discharge flow-mass spectrometry.	EX	295	1.9±0.5E13			
Recommended		298	2E13			2

Comments and Recommendations

The recommended value is based on the data reported in 82 RYA/PLU. It probably has little or no temperature dependence.

The reaction is written as shown by analogy with the $\text{O} + \text{CH}_3$ reaction. On the basis of ab initio calculations, it has been argued (87 FRA/LI) that the reaction in-

volves formation of an energy rich CF_3O adduct followed by fluorine atom elimination.

References

- 82 RYA/PLU K. R. Ryan and I. C. Plumb, *J. Phys. Chem.*, **86**, 4678 (1982).
 87 FRA/LI J. S. Francisco, Z. Li, and I. H. Williams, *Chem. Phys. Letters*, **140**, 531 (1987).

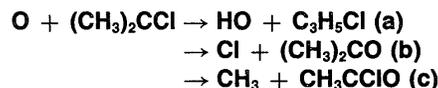
**Trichloromethyl**

Reference code, notes	Type	T/K	<i>k</i> , <i>k</i> / <i>k</i> (ref) <i>A</i> , <i>A</i> / <i>A</i> (ref)	<i>n</i>	<i>B</i> , <i>B</i> - <i>B</i> (ref)	<i>k</i> err. factor
84 RYA/PLU Discharge flow-mass spectrometry.	EX	295	2.5±0.4E13			
Recommended		298	2.5E13			2

Comments and Recommendations

The recommended value is based on the data reported in 84 RYA/PLU. It probably has little or no temperature dependence.

The reaction is written as shown by analogy with the $O + CH_3$ reaction. CCl_2CO has been identified as a product (84 RYA/PLU).



2-Chloropropyl

Reference code, notes	Type	T/K	k, k/k(ref) A, A/A(ref)	n	B, B-B(ref)	k err. factor
87 WAS/HAT Discharge flow-mass spectrometry. Reactant $(CD_3)_2CCl$. Reference reaction: $(CD_3)_2CCl + O_2$.	RL	298	127 ± 16			
Recommended		300-2000	1E14			5

Comments and Recommendations

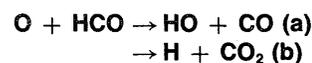
There is no basis for estimating the rate constant for the reaction $(CD_3)_2CCl + O_2$. The recommended value was estimated by analogy with the rate constants for the corresponding alkyl radical reactions, and is probably independent of temperature.

The mechanism is complex. Washida and Hatekeyama (87 WAS/HAT), from a study of the $(CD_3)_2CHCl$ reaction, report that the major products correspond to (a),

31% and (b), 24%. Channel (c) presumably accounts for the balance of the products. Channel (a) was interpreted in terms of a direct abstraction reaction, and (b) and (c) as the result of the formation of an energy rich adduct which decomposed to the observed products. See Sec. 1.4.6.

References

- 87 WAS/HAT N. Washida and S. Hatakeyama, Bull. Chem. Soc. Japan, **60**, 3751 (1987).



Formyl

Reference code, notes	Type	T/K	k, k/k(ref) A, A/A(ref)	n	B, B-B(ref)	k err. factor
75 HUI/HER	SE	298	$k_a/k_b = 1.2$			
84 WAR	SE	300-2000	$k_a/k_b = 1$			
84 WAR	SE	300-2000	6E13			2
86 TSA/HAM	SE	300-2500	3E13			2
Recommended		300-2000	6E13			3

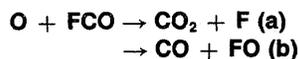
Comments and Recommendations

The recommendation given in 86 TSA/HAM is an estimate, while those given in 75 HER/HUI and 84 WAR come from various studies of the reaction of oxygen atoms with formaldehyde. There are no new data. We recommend using the value given in 84 WAR.

The reaction probably proceeds through formation and decomposition of an energy rich adduct, although (a) could be a direct hydrogen atom abstraction reaction.

References

- 75 HUI/HER R. E. Huie and J. T. Herron, Progr. Reaction Kinetics, **8**, Part 1, 1 (1975).
84 WAR J. Warnatz, in "Combustion Chemistry", W. C. Gardiner, Jr., ed., Springer-Verlag, New York, p197 (1984).
86 TSA/HAM W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data, **15**, 1087 (1986).

**Fluoroformyl**

Reference code, notes	Type	T/K	<i>k</i> , <i>k</i> / <i>k</i> (ref) <i>A</i> , <i>A</i> / <i>A</i> (ref)	<i>n</i>	<i>B</i> , <i>B</i> - <i>B</i> (ref)	<i>k</i> err. factor
84 RYA/PLU Discharge flow-mass spectrometry.	DE	295	5.6±1.3E13			
Recommended		300-2000	6E13			3

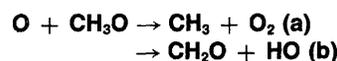
Comments and Recommendations

The measured value (84 RYA/PLU) is based on an analysis of the rate of formation of COF in the O + CF₂ reaction and its subsequent loss in the O + FCO reaction. It is therefore tied to the value for *k*(O + CF₂). Ryan and Plumb identified (a) as the major channel but

were unable to give any indication of the importance of (b) as a minor channel.

References

- 84 RYA/PLU K. R. Ryan and I. C. Plumb, *Plasma Chem. Plasma Process.*, **4**, 271 (1984).

**Methoxy**

Reference code, notes	Type	T/K	<i>k</i> , <i>k</i> / <i>k</i> (ref) <i>A</i> , <i>A</i> / <i>A</i> (ref)	<i>n</i>	<i>B</i> , <i>B</i> - <i>B</i> (ref)	<i>k</i> err. factor
87 EWI/RHA Laser photolysis-laser induced fluorescence. See also 86 RHA/ZEL.	EX	298	1.5±0.4E13			
86 TSA/HAM	SE	300-2500	6E13			5
Recommended		300-2000	2E13			3

Comments and Recommendations

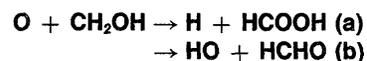
The recommendation given in 86 TSA/HAM is an estimate. We recommend using the experimental value reported in 87 EWI/RHA with no temperature dependence.

The major channel is presumably (a). Direct evidence for (b) was obtained by following the temporal profile of HO using laser induced fluorescence (87 EWI/RHA), from which it was found that *k*(b)/*k*(a)=0.12(+0.08/-0.04). Channel (b) may involve the isomerization of an initially formed CH₃O₂ adduct to the hydroperoxide CH₂OOH which in turn decomposes. However, in view of the conflicting data on the mechanisms of oxygen

atom-alkyl radical reactions (see Sec. 1.4.6), (b) could be a direct hydrogen atom abstraction reaction. The significance of these data in terms of the role of the reverse of channel (b) in combustion has been discussed in detail in 87 EWI/RHA.

References

- 86 RHA/ZEL D. Rhasa and R. Zellner, *Chem. Phys. Letters*, **132**, 474 (1986).
86 TSA/HAM W. Tsang and R. F. Hampson, *J. Phys. Chem. Ref. Data*, **15**, 1087 (1986).
87 EWI/RIIA F. Ewig, D. Rhasa, and R. Zellner, *Der. Dunsenges. Phys. Chem.*, **91**, 708 (1987).

**Hydroxymethyl**

Reference code, notes	Type	T/K	<i>k</i> , <i>k</i> / <i>k</i> (ref) <i>A</i> , <i>A</i> / <i>A</i> (ref)	<i>n</i>	<i>B</i> , <i>B</i> - <i>B</i> (ref)	<i>k</i> err. factor
81 GRO/JUS Discharge flow-mass spectrometry.	DE	300-1006	1.2E12			3
87 TSA	SE	300-2500	4E13			2
Recommended		300-2000	5E13			5

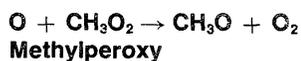
Comments and Recommendations

The recommended value given in 87 TSA is an estimate. The value reported in 81 GRO/JUS was derived from a computer modeling study of experimental data for the $O + CH_3OH$ reaction. It is a factor of 80 lower than the rate constant for $O + CH_3$, and 12 lower than that for $O + CH_3O$. In the case of C_2H_5 and $CH_3CH(OH)$, the rate constants are almost the same (see relevant data sheets). The experimentally derived number is therefore suspect. However, it was argued in 86 GRO/NES that the reaction is slow in contrast to the $O + CH_3CHOH$ reaction which was found to be fast (see the data sheet on $O + CH_3CH(OH)$). We suggest using

a rate constant somewhat smaller than that for CH_3 with no dependence on temperature. Because of the uncertainty in the data, the error factor is large. The reaction probably proceeds through formation and decomposition of an energy rich adduct. However, (b) could be a direct hydrogen atom abstraction reaction. See Sec. 1.4.6.

References

- 81 GRO/JUS H. H. Grotheer and Th. Just, Chem. Phys. Letters, **78**, 71 (1981).
 86 GRO/NES H. Grotheer, F. L. Nesbitt, and R. B. Klemm, J. Phys. Chem., **90**, 2512 (1986).
 87 TSA W. Tsang, J. Phys. Chem. Ref. Data, **16**, 471 (1987).



Reference code, notes	Type	T/K	$k, k/k(\text{ref})$ $A, A/A(\text{ref})$	n	$B,$ $B-B(\text{ref})$	k err. factor
76 WAS/BAY Discharge flow-mass spectrometry.	EX	256	$>2E13$			
86 TSA/HAM	SE	300-2500	4E13			3
Recommended		300-2000	5E13			3

Comments and Recommendations

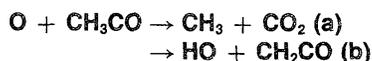
The recommended value given in 86 TSA/HAM is an estimate. The limiting value reported in 76 WAS/BAY is based on the assumption that this reaction is the sole loss process for CH_3O_2 in the $C_2H_4 + O + O_2$ system. The recommended value is an estimate.

Formaldehyde was found to be a major product (76 WAS/BAY). The reaction probably proceeds through formation of CH_3OOO followed by decomposition of the energy rich adduct to $CH_3O + O_2$, followed in turn by decomposition of the CH_3O radical to $HCHO + H$.

The alternative reaction involving direct hydrogen atom abstraction would lead to formation of a "Criegee intermediate" which would decompose to give H, H_2 , HO, CO, and CO_2 , but not to CH_2O (77 HER/HUI).

References

- 76 WAS/BAY N. Washida and K. D. Bayes, Int. J. Chem. Kinet., **8**, 777 (1976).
 77 HER/HUI J. T. Herron and R. E. Huie, J. Am. Chem. Soc., **99**, 5430 (1977).
 86 TSA/HAM W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data, **15**, 1087 (1986).



Acetyl

Reference code, notes	Type	T/K	$k, k/k(\text{ref})$ $A, A/A(\text{ref})$	n	$B,$ $B-B(\text{ref})$	k err. factor
84 WAR	SE	>300	2E13			10
86 TSA/HAM	SE	300-2500	1E13			3
Recommended		300-2000	6E13			3

Comments and Recommendations

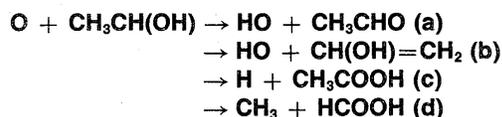
The recommended value given in 84 WAR appears to be an estimate as is that given in 86 TSA/HAM. We recommend a somewhat higher number by analogy with the rate constants for oxygen atom-alkyl radical reactions.

The reaction probably proceeds through formation and decomposition of an energy rich adduct. The main reaction channel appears to be (a). Ketene has been found as a minor product (81 MOR), so that there is some possibility that channel (b) may be a minor process.

However, (b) could be a direct hydrogen atom abstraction reaction.

References

- 81 MOR S. Mori, Bull. Inst. Chem. Res., Kyoto Univ., **59**, 116 (1981).
 84 WAR J. Warnatz, in "Combustion Chemistry", W. C. Gardiner, Jr., ed., Springer-Verlag, New York, p197 (1984).
 86 TSA/HAM W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data, **15**, 1087 (1986).



Hydroxyethyl

Reference code, notes	Type	T/K	k, k/k(ref) A, A/A(ref)	n	B, B-B(ref)	k err. factor
81 WAS Discharge flow-mass spectrometry. Reference reaction: CH ₃ CH(OH) + O ₂ .	RL	298	7±2			
86 GRO/NES Discharge flow-resonance fluorescence.	DE	298	1E14			
Recommended		300-2000	1E14			3

Comments and Recommendations

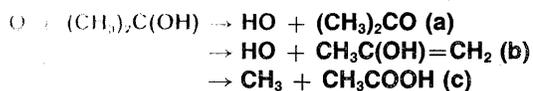
By analogy with the rate constant for the C₂H₅ + O₂ reaction (81 PLU/R YA), we estimate that $k(\text{CH}_3\text{CH}(\text{OH}) + \text{O}_2) = 2 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at a total pressure of about 0.5 Pa (corresponding to the pressure used in the experiment of 81 WAS), and hence $k(\text{CH}_3\text{CH}(\text{OH}) + \text{O}) = 1.4 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, which is the basis of the recommendation. A similar value was obtained from a modeling study of the ethanol reaction (86 GRO/NES). The rate constant is almost equal to that for the O + C₂H₅ reaction, and is probably independent of temperature.

Washida (81 WAS) found that the major product of the reaction at 298 K is CH₃CHO, and on the basis of isotopic substitution experiments proposed that the reaction is a hydrogen atom abstraction (channel (a)) involving the hydrogen atom on the OH group. Although a simple displacement reaction might seem more likely, or a reaction involving initial formation of an energy rich

CH₃CH(OH)O adduct which could decompose in reactions analogous to those reported for the O + C₂H₅ reaction, experiments using labelled oxygen atoms appear to rule out any reaction other than abstraction from the OH group (81 WAS). Acetaldehyde accounts for about 80% of the products; no other reaction channel was identified. However, in a latter publication, Washida (87 WAS) pointed out that the presence of even small amounts of molecular oxygen can have a serious effect on the ability to detect minor products such as those characteristic of channels (b), (c), and (d). See the data sheet on O + (CH₃)₂C(OH) and Sec. 1.4.6.

References

- 81 PLU/R YA I. C. Plumb and K. R. Ryan, Int. J. Chem. Kinetics, **13**, 1011 (1981).
 81 WAS N. Washida, J. Chem. Phys., **75**, 2715 (1981).
 86 GRO/NES H. Grotheer, F. L. Nesbitt, and R. B. Klemm, J. Phys. Chem., **90**, 2512 (1986).
 87 WAS N. Washida, Bull. Chem. Soc. Japan, **60**, 3757 (1987).

**2-Hydroxypropyl**

Reference code, notes	Type	T/K	$k, k/k(\text{ref})$ $A, A/A(\text{ref})$	n	$B,$ $B-B(\text{ref})$	k err. factor
87 WAS Discharge flow-mass spectrometry. Reactant $(\text{CD}_3)_2\text{C}(\text{OH})$. Reference reaction: $(\text{CD}_3)_2\text{C}(\text{OH}) + \text{O}_2$.	RL	298	6.3 ± 1.6			
Recommended		300-2000	5E13			3

Comments and Recommendations

On the assumption that $k((\text{CH}_3)_2\text{C}(\text{OH}) + \text{O}_2) = k((\text{CH}_3)_2\text{CH} + \text{O}_2) = 8.5 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (84 RUI/BAY), we estimate $k((\text{CH}_3)_2\text{C}(\text{OH}) + \text{O}) = 5 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, probably independent of temperature.

The mechanism is complex. Washida (87 WAS), from a study of the $(\text{CD}_3)_2\text{C}(\text{OH})$ reaction, found that the major product was $(\text{CD}_3)_2\text{CO}$, accounting for about 62% of the reaction products. It was concluded that most of this was the result of a direct abstraction reaction, but that a

small fraction was a consequence of the formation of an energy rich adduct which then decomposed. Products were also detected corresponding to channels (b) and (c). These are less important but no quantitative data were given. See Sec. 1.4.6.

References

- 84 RUI/BAY R. P. Ruiz and K. D. Bayes, *J. Phys. Chem.*, **88**, 2592 (1984).
87 WAS N. Washida, *Bull. Chem. Soc. Japan*, **60**, 3757 (1987).