A Critical Review of the Gas-Phase Reaction Kinetics of the Hydroxyl Radical

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A Critical Review of the Gas-Phase Reaction Kinetics of the Hydroxyl Radical

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The literature pertinent to reactions of the hydroxyl radical has been reviewed. An extensive discussion is given for reactions of the hydroxyl radical with itself and with CO, H2, and CH4. These four reactions are: (1) OH + OH → H2O + O; (2) CO + OH → CO2 + H; (3) H2 + OH → H2O + H; (4) CH4 + OH → CH3 + H2O.

Values are recommended for k1 and k2 and for the ratio k3/k2 and k4/k2. These rate ratios are used with the previously established value of k2 to obtain recommended values for k3 and k4.

The recommended values in cm^3 mol^{-1} s^{-1}, the temperature range, and the uncertainty are:

- k1 = 1.55 × 10^{12}, 300 K, log k ± 1
- k2 = 3.1 × 10^{11} exp(-300/7), 300–2000 K, log k ± 0.3
- k3/k2 = 73 exp(2200/T), 300–2000 K, log k ± 0.3
- k4/k3 = 92 exp(2200/T), 300–2000 K, log k ± 0.3
- k4/k2 = 73 exp(-2500/T), 300–2000 K, log k ± 0.7

Rate expressions are also recommended for a number of other hydroxyl reactions whose rates are less well established.

Key words: Activation energy; chemical kinetics; combustion; rate constant; review.

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Introduction

The quantitative data produced by chemical kinetics is now being used in applied science. Numerous computer programs are in operation which require tens to hundreds of elementary rate constants. The users of rate data need a consistent source of rate constants. They also need to have a reasonable idea of the validity and uncertainty of such numbers and to know why certain measurements are preferred over others. It is hoped that this report will serve those needs for the rate constants considered. It also is hoped that this analysis will serve as a guide for additional research in OH kinetics.

This review is divided into four sections. Section A contains a general discussion of the experimental techniques, with emphasis on the methods of producing OH, and their limitations. A knowledge of this material is assumed in Section B. The four reactions which have been most frequently studied are discussed in Section B, the main body of the review. A number of other reactions involving the hydroxyl radical are reviewed less critically in Section C. In Section D some current problems in hydroxyl radical research are discussed.

The discussions of each reaction in Section B is, insofar as possible, self contained. There is, for each reaction, a general discussion, a table of the rate data, Arrhenius plots of the experimental values, and an annotated reference list. The notes in the reference list not only summarize the work in a particular paper but also comment upon it and form part of the argument leading to the choice of the recommended value. When a paper reports rates for more than one of the reactions evaluated in Section B, it is present in the various reference lists. It is the author's hope that presentation of the individual reactions in this arrangement will simplify future experimentation and evaluation.

Reaction rate constants are numbered in one sequence throughout the review. They are tabulated in Appendix A. In addition, in order to clarify the presentation, an effort has been made to identify each rate constant at least once in each paragraph in which it occurs. Thus, the rate constant for Reaction (3), \( \text{H}_2 + \text{OH} \rightarrow \text{H}_3\text{O} + \text{H} \), is identified as \( k_3(\text{H}_2 + \text{OH}) \). This rule is relaxed in Section B where an action being discussed is identified by its number only.

References are identified by a single number when they are items in the annotated list for that section, i.e., within Section A, B1–B4, and C1–C10. When a cross-reference is made to a paper in another section, it is prefixed by the section number. Thus reference B3–17 is reference 17 in Section B3, the discussion of Reaction (3).

Studies of the reverse reactions, indicated by \( k_{-3} \), are discussed with the forward reactions. Use is made of \( k_3 = K_{eq}k_{-3} \) to obtain the values shown on the Arrhenius plot. Expressions are given for \( K_{eq} \), the equilibrium constants, over a temperature range. These expressions may be used with the recommended values of the forward rate constants to obtain the rate constants of the reverse reactions.

An explanation of all symbols and abbreviations is given in Appendix B. There is, at the time this review is written, no general agreement among authors as to the proper choice of units for rate constants. The second is the universal choice as the time unit; however, both liter and cm\(^3\) are used for volume; moles, molecules and particles for concentration; and calories and kilocalories for energy. Molecules is used even when the reacting species include hydrogen atoms, hydroxyl radicals, or electrons. The following approach has been adopted in this review. In the discussion, rate constants or rate expressions which are direct quotes from the original authors are in the units used in the original article. In the tables, rates are given in both mole and particle units. The temperature dependent factor in the rate expression is given in terms of the activation energy divided by the gas constant and has units of degrees Kelvin. In the discussion, the author has used his personal preference for rate constant units, centimeters\(^3\) mole\(^{-1}\) second\(^{-1}\) (cm\(^3\) mol\(^{-1}\) s\(^{-1}\)). To facilitate conversion from one unit to another, a table of conversion factors is given in Appendix C.

The recommended rate constant values for the four principal reactions discussed in Section B are collected in the abstract. Those for the remaining reactions are summarized at the end of Section C. The suggested error limits are the author's personal assessment and perhaps should be considered the minimum error rather than the maximum. In a few cases a rate constant might be considered more reliable in one temperature regime than another. It was not felt worthwhile, however, to express the possible error as a function of temperature.
A. The Production of Kinetic Data

A1. Introduction

The hydroxyl radical has been a problem species in chemical kinetics. The accepted value for the room temperature rate constant of Reaction (2),

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

(2)

has varied by a factor of 10^6 over the last 10 years. As discussed in Section A.2, recommended activation energies have varied by a factor of 30. The major problems in hydroxyl radical kinetics are related to the difficulty of obtaining hydroxyl radicals in the absence of other reactive species which cause competing reactions. In addition to reacting with other species, hydroxyl radicals undergo a rapid disproportionation reaction as well as a recombination reaction. For these second-order reactions, absolute hydroxyl radical concentrations are required, a measurement for which there is still no completely satisfactory technique. Nevertheless, the hydroxyl radical is an important species and information is needed about its reaction kinetics in combustion processes, in recombination in nozzles, in air pollution, and in the upper atmosphere.

A1.1. Combustion Processes

A1.1a. Initial Reaction of Fuel. The reactive species important in most combustion processes are H, O, and OH. The reaction rate of hydrogen or hydrocarbon fuels with OH is much faster than with O or H. The rates of reaction of OH with fuel molecules are therefore important in predictions involving the combustion process.

A1.1b. Conversion of CO to CO2. The reaction with OH is the major pathway for converting CO to CO2 in flames. An accurate knowledge of the rate constant is needed to predict the amount of CO remaining under various conditions of reaction times and cooling rates.

A1.2. Recombination in Nozzles

The concentration of radicals in the combustion zone of flames frequently exceeds the equilibrium concentration at that temperature. In rich flames the concentrations may be orders of magnitude greater than equilibrium predictions. Although the recombination rates are not well known, it would appear that the recombination reaction

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

(21)

may dominate. This rate, and other recombination rates, are needed for calculation of the specific impulse of propulsion devices based on H2–O2 combustion. These rates are especially important for high altitude rockets and supersonic combustion ramjets because the recombination reactions produce a substantial proportion of the available thrust.

A1.3. Air Pollution

A1.3a. Photochemical Smog. The role of OH in photochemical smog was reviewed by Leighton [1] in 1961. A number of reactions which might produce OH were postulated. These included photodissociation of H2O2, HNO3, or HNO2, decomposition of peroxyalkyl and peroxyformyl radicals, the reaction of alkoxy radicals with oxygen, the reaction of hydrogen atoms with O2 and NO2, the reaction of electronically excited oxygen atoms (from the photodissociation of ozone) with water [O(\DU) + H2O \rightarrow 20H], HO2 + NO \rightarrow OH + NO2, and HNO + O2 \rightarrow OH + NO2.

Stephens [2] pointed out that the reactive species in photochemical smog must have a much higher reactivity with olefins than alkanes. From a comparison of available reaction rates he concluded that only oxygen atoms and ozone satisfied the criteria. However, his data for OH reactions were taken from the early work of Avramenko et al. [B2–15] which is now considered to be unreliable. The OH rates from this report, along with recent O atom rates, were used to obtain the rate ratios shown below. The reaction of OH with ethylene is much greater than with ethane or acetylene, in agreement with the much greater reactivity of ethylene in photochemical smog.

<table>
<thead>
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<th>Relative rate</th>
<th>( \text{C}_2\text{H}_4 )</th>
<th>( \text{C}_2\text{H}_6 )</th>
<th>( \text{C}_4\text{H}_6 )</th>
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<tr>
<td>( \text{OH} )</td>
<td>1 200</td>
<td>450 3000</td>
<td>50 200</td>
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It has recently been suggested [3, 4] that the hydroxyl radical may play an important role in the generation of ozone in photochemical smog. The reaction sequence is given below.

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

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

\[ \text{HO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{OH} \]

\[ \text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2 \]

The cycle will continue until the CO is all converted to CO2 or until the OH is removed by reaction with another species. Since the CO concentration may be 50 times that of NO, the rate of reaction of OH with other species may be a very important factor in kinetic calculations of air pollution. The importance of this sequence has been confirmed by experimental studies which demonstrate that (1) ozone is generated when CO and NO are irradiated in clean, humid air, and (2) the addition of CO to irradiated hydrocarbon + NO + clean air mixtures results in a more rapid formation of NO2 and increased ozone production [5].

A1.3b. Fate of Carbon Monoxide. Carbon monoxide does not appear to accumulate in the atmosphere even though large amounts are introduced into the air through incomplete combustion. The only known chemical reaction which converts CO to CO2 at a significant rate is Reaction (2) with OH. It is of interest therefore to know the sinks and sources of OH in the atmosphere and to determine if there are sinks for CO other than Reaction (2).
A1.4. Upper Atmosphere Chemistry

The most intense night-time radiation from the stratosphere is due to emission from vibrationally excited hydroxyl radicals [6, 7]. This nightglow, which extends from 500 to 5,000 nm, is named Meinel bands after the discoverer [8]. The excited hydroxyl radicals are thought to be generated [9] by

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

Reaction rates involving hydroxyl radicals are required for predictions of the vertical distribution of ozone [10] and for the calculation of other upper atmosphere properties [11]. The hydroxyl radical participates in a number of reactions thought to be important in the atmosphere [12] including the formation of nitric acid by \( \text{OH} + \text{NO}_2 \rightarrow \text{HNO}_3 \) [13].

A2. Production of Hydroxyl Radicals

In spite of the importance of the hydroxyl radical it is only in recent years that it has become possible to have any confidence in the kinetic measurements of OH reactions. The major reason for this lies in the difficulty of preparing OH in the absence of reactive species other than itself. There are many studies of OH reactions which must be discarded because it is now known that the variation in the parameter measured was not due to the reaction which the experiment was designed to study. There are measurements of OH rates, made in inappropriate chemical systems, which differ from presently accepted values by factors as large as \( 10^3 \).

A2.1. Electric Discharges in Water Vapor

One of the classical techniques for producing hydroxyl radicals has been the use of various types of electric discharges in water vapor. A recent English language review by Avrachenko and Kolesnikova [B2-14a] gives a good description of the extensive studies by Avrachenko and co-workers using this technique. They generated OH by a high-voltage discharge in water vapor. The OH concentration, integrated over the full length of a molybdenum flow tube, part of which could be heated, was determined by absorption spectroscopy.

Rate constants were determined by comparing the OH concentrations before and after addition of a reacting gas. The data reduction required use of rate constants for loss of OH by a three-body recombination, \( k_1(\text{OH} + \text{OH} + M) = 5.2 \times 10^{-12} \ T \ \text{cm}^3 \text{molecule}^{-2} \text{s}^{-1} \) and wall loss, \( k(\text{wall}) = 1.5 \times 10^9 \ \exp(-5,000/RT) \ \text{cm}^{-3} \). The value for \( k_1 \) of 9.6 \times 10^{-30} at 300 K may be compared with 18 \times 10^{-30} based on the work of Caldwell and Back [14]. The use of an integrated value of [OH] and a complicated data analyses would lower the precision of the results. In addition, \( k(\text{wall}) \) was not measured directly; the wall loss of O atoms was determined and it was assumed that the wall loss of OH would be the same.

The most serious problem, however, lies in the actual source of hydroxyl radicals and the presence of other reactive species in the reaction mixture. It is now fairly well established that although OH is formed in discharges in water vapor, other species such as H, O, and HO_2 are also formed. The reactions of HO_2 downstream from the discharge provide a continuous source of OH.

There are several ESR\(^2\) studies in which measurements of radicals were made which bear on the problem of OH in water vapor discharges. Howgate [15] measured the absolute concentrations of O, H, and OH in an ESR cavity downstream of a rf discharge through water vapor with added O_2. OH was observed only when the water vapor pressure was above 135 microns and O only when the water vapor pressure was below 95 microns. OH and O coexisted only in the narrow range of 95 to 135 microns pressure of water vapor. The OH concentration could be increased, up to 5 times, by the addition of O_2. H atoms were always present and small amounts of O_2 were produced by the discharge in pure water vapor. Unfortunately, no study was made of the variation of radical concentrations with reaction time. Although this supports the Russian literature claim that an electric discharge through water vapor can be used as a source of either O atoms or OH radicals [B2-14], it also indicates that other species, especially H and O_2 which will give HO_2, are present.

Another pertinent study has been reported by McDonald and Goll [16]. H atoms were generated by a microwave discharge in H_2 upstream from an ESR cavity. When water vapor or O_2 was added at the ESR cavity, the spectrum of OH was observed. OH was also formed when water vapor was added to a stream of discharged O_2. In this case, the O spectrum disappeared.

These two experiments indicate that OH could be generated in the flowing gas downstream of the discharge. Reference [15] indicates that H, O, and OH are produced by electric discharges in water vapor. Reference [16] indicates that OH can be produced by the reaction of H with O_2, H with water vapor, or discharged O_2 with water vapor, all components which are present in discharged water vapor. These observations suggest that OH may not be produced exclusively in the discharge but may be continually formed in the gas flowing downstream from the discharge.

The measurements in the Russian literature [B2-14], along with less extensive ones by Oldenberg [17] using similar techniques, were for many years the only rate measurements of OH available at room temperatures. These rate constants were used with measurements in flames to determine activation energies. Since the OH rate constants measured in water vapor discharges are lower than presently accepted values by factors of up to \( 10^3 \), the resulting Arrhenius plots gave activation energies which were much too large.

A2.2. The Chemical Reaction, \( \text{H} + \text{NO}_2 \rightarrow \text{NO} + \text{OH} \)

A new era in OH kinetic studies began with the publication of a note by Kaufman and Del Greco [B3-3a] in 1961, and a full description of their work [B3-3b] in 1962. The very fast reaction

\[ \text{H} + \text{NO}_2 \rightarrow \text{NO} + \text{OH} \]  

was used to generate OH in a system containing only OH, H, and NO plus an inert carrier. They also showed rather conclusively that discharges in water vapor...
vapor, although producing OH, are not suitable sources of OH for kinetic studies. The OH is produced by secondary reactions, probably H + O₂ + M → HO₂ + M and HO₂ + H → 2OH. This is shown clearly by the two OH decay curves in figure A1 taken from reference [B3–3b]. The large amount of OH produced by Reaction (5) decays rapidly giving a typical second-order decay curve. In contrast, the discharge in water vapor does not produce as high a concentration of OH, the OH concentration actually increases for a short time after the discharge, and the very slow decay does not appear to be second-order. The evidence presented in figure A1 coupled with the discussion in the previous section of the chemistry involved, would seem to be adequate for rejecting all kinetic studies in which OH was generated by an electric discharge in water vapor.

The chemical method of preparing OH by Reaction (5) has been studied extensively. The rate and stoichiometry have been determined by several workers [18, 19] and its reliability as a source of OH for kinetic studies is amply established [B3–3, B1–1, B1–3]. Normal procedure is to produce H atoms in a microwave discharge through a few percent of H₂ in an inert carrier gas. It is possible to obtain 100 percent dissociation of the H₂ if traces of water vapor or O₂ are present. A small amount of NO₂ is added and the following sequence of reactions take place:

$$\text{H} + \text{NO}_₂ \rightarrow \text{OH} + \text{NO} \quad (5)$$
$$\text{OH} + \text{OH} \rightarrow \text{H}_₂\text{O} + \text{O} \quad (1)$$
$$\text{O} + \text{OH} \rightarrow \text{O}_₂ + \text{H} \quad (6)$$

Since NO₂ will react with both H and O which are generated in the reaction, the stoichiometry of the overall reaction depends on the H/NO₂ ratio. Most flow tube studies in which [OH] is measured as a function of distance (or reaction time) use excess H. In this case the reactants added should be ones that are relatively inert to H.

2 Traces of NO₂ however, are thought to lead to the production of NH₃ and subsequent deposition of NH₄NO₃ on the tube surface. This causes rapid and unproductive surface recombination of OH.

**Figure A1. Experimental decay profiles of hydroxyl radicals.**

A. Generated by H + NO₂ → NO + OH.
B. Generated by discharge through water vapor.

Flows in mmol/s, pressure in torr:
A. 0.33 Hz, 3.30 torr, 1.94 torr.
B. 0.28 Hz, 3.70 Hz, 2.18 torr.
Reference [B3-3b].

In a series of papers Greiner [20, 21] has shown that photolysis of H₂O₂ occurs primarily by reaction

$$\text{H}_₂\text{O}_₂ = 2\text{OH}(^1\text{Π})$$

but that this reaction is followed by the rapid reaction

$$\text{OH} + \text{H}_₂\text{O}_₂ \rightarrow \text{H}_₂\text{O} + \text{HO}_₂ \quad (17)$$

with $k_{17} = 5.67 \times 10^{11} \text{ cm}^2 \text{ mol}^{-1} \text{ s}^{-1}$ at 303 K. Therefore, any system in which OH is produced by dissociation of H₂O₂ (or for that matter in which H₂O₂ is formed by recombination of OH) will contain substantial quantities of HO₂.

The reactions of HO₂ therefore become of considerable importance in such systems. Greiner has investigated the reactions of H₂, CH₄, and CO in photolyzed H₂O₂. When 1.0 torr H₂O₂ + 100 torr Ar was flash photolyzed, the OH disappeared by a mechanism first order in [OH] at a rate of ~4 × 10⁵ s⁻¹. When 200 torr H₂ or 50 or 100 torr CH₄ was added, the rate for OH disappearance did not change appreciably from ~4 × 10⁵ s⁻¹ although OH must have been reacting with H₂ or CH₄ with a rate much greater than ~4 × 10⁵ s⁻¹. Evidently some additional reaction was regenerating OH nearly as fast as it reacted. Greiner suggested the following sequence for regeneration of OH:

$$\text{OH} + \text{HR} \rightarrow \text{H}_₂\text{O} + \text{R},$$
$$\text{R} + \text{H}_₂\text{O}_₂ \rightarrow \text{ROH} + \text{OH}.$$

For the addition of CO, Greiner reports, “When 10 torr of CO was added in the H₂O₂ photolysis, [OH], after about 50 × 10⁻⁶ s, appeared to be larger than when H₂O₂ was photolyzed alone. This would require that even some of the OH that reacts with H₂O₂ be regenerated. The reaction

$$\text{HO}_₂ + \text{CO} \rightarrow \text{CO}_₂ + \text{OH},$$

is an attractive possibility for OH regeneration” [B2–2a].

This reaction appears to be a likely candidate for regenerating OH in the system with added CO. However, the H generated by reaction of CO or H₂ with OH could also regenerate OH directly.
by \( H + H_2O_2 \rightarrow OH + H_2O \) or by the sequence
\[
H + H_2O_2 \rightarrow H_2 + HO_2 \\
H + HO_2 \rightarrow 2OH.
\]
The reaction of alkyl radicals with \( HO_2 \), \( R + HO_2 \rightarrow RO + OH \) provides another possibility for regenerating \( OH \).

These studies provide an adequate experimental justification for regarding as unreliable any rate data determined in systems containing \( H_2O_2 \).

**A2.4. Photolysis of Water Vapor**

The photolysis of water vapor has been used as a source of hydroxyl radicals by several workers [22, 23]. The primary photolytic step [24] (136.5 "\( \lambda \"5 186.0 \text{ nm} \) has been shown to yield \( H \) atoms and \( OH \) radicals in their ground states with the excess energy going into kinetic rather than rotational energy.

\[
H_2O \overset{hv}{\rightarrow} OH (^3 \Pi) + H (^2 \Sigma).
\]

This technique has been used at higher pressures where the recombination of hydroxyl to form hydrogen peroxide may occur. Since hydrogen atoms are present, the hydrogen peroxide may be a problem as is shown in the following sequence of reactions:

\[
\begin{align*}
OH + OH + M &\rightarrow H_2O_2 + M \\
H + H_2O_2 &\rightarrow H_2 + OH \\
H + H_2O_2 &\rightarrow HO_2 + H_2 \\
H + HO_2 &\rightarrow 2OH \\
OH + HO_2 &\rightarrow H_2O_3 + O_2.
\end{align*}
\]

The \( HO_2 \) might also react with species which had been added to the system in order to study their reaction with \( OH \).

Photolysis of water vapor probably offers a satisfactory source of \( OH \) for kinetic studies if conditions are such that the three-body recombination of \( OH \) does not contribute appreciably, i.e., low total pressure, short reaction time, low \( OH \) concentration, or high temperature.

**A2.5. Thermal Methods**

Hydroxyl radicals may also be produced in a variety of high temperature systems. A great many studies have been made in premixed, flat flames [25, 26]. Studies of slow combustion and explosion limits, and at higher temperatures in shock tubes, have all contributed information. In all of these systems \( OH \) coexists with other radicals: \( H, O \), and \( HO_2 \); and numerous assumptions and substantial processing of data are required to obtain rate constants.

**A2.6. Conclusion: Methods of Production of \( OH \)**

There is no way to produce \( OH \) in the absence of other radicals or atoms. The most satisfactory methods for producing \( OH \) are chemically by reaction of \( H \) with \( NO_2 \) or by photolysis of water vapor. Either technique yields appreciable quantities of \( H \) atoms. Thermal methods yield a large variety of reactive species in addition to \( OH \) but since equilibrium, or at least partial equilibrium, conditions will exist some estimate can be made of the concentrations of other species. \( HO_2 \) is produced by electric discharges in water vapor and by the thermal or photolytic dissociation of \( H_2O_2 \). Since little is known of the reactions of \( HO_2 \) and the concentration of \( HO_2 \) cannot be predicted, these systems are not satisfactory for producing \( OH \) for kinetic studies.

### A3. Measurement of Hydroxyl Radicals

The measurement of hydroxyl radical concentration has been a serious problem. In most studies of \( H \) and \( O \), the reaction may be treated as pseudo-first order and relative concentration measurements are satisfactory. In \( OH \) studies, however, there are second-order losses from the \( OH + OH \) disproportionation and it is normally necessary to make absolute concentration measurements. The simple and inexpensive methods of determining radicals such as Wrede gages, catalytic probes, and light generating reactions which have been used for \( O \) and \( H \) are not applicable to \( OH \).

The recombination of \( OH \) does not produce a large pressure change, there are no simple light producing reactions involving \( OH \), and the heat of recombination on a catalyst is uncertain because of the complicated mechanism and the presence of other reactive species.

**A3.1. Initial Concentration by Chemical Analysis**

Measurements of the initial concentration of \( OH \) produced by Reaction (5): \( H + NO_2 \rightarrow NO + OH \), may be made by chemical means. A measurement of either the \( NO_2 \) used or the \( O \), or \( H_2O_2 \) formed by Reactions (1) and (6) may be used to give \([OH]_o\). This has been used to calculate the \("f"\) number [B3-30] and \( k_5(\text{OH} + H_2) \) determinations by Kaufman [B3-3] and the determination of rate ratios involving \( k_6(\text{CO} + OH) \) by others [B1-5, B1-6, B1-7]. It is not completely satisfactory however because the predicted \([OH]_o\) is never completely attained. The relative rates are such that decay of \( OH \) by Reaction (1) begins before formation of \( OH \) by Reaction (5) is complete. (See fig. B2, Sec. B1.)

**A3.2. Ultraviolet Absorption Spectroscopy**

The most widely used technique for measuring \( OH \) concentration is absorption spectroscopy. The technique is well developed although calibration remains a problem. In spectroscopic notation this reduces to an \("f"\) number or effectively a calibration factor. Relative \("f"\) numbers have been determined by a variety of techniques. However, except for the study by Golden, Del Greco and Kaufman [B3-30], all measurements of absolute \("f"\) numbers depend on an equilibrium calculation of \( OH \) concentration. A gas mixture must be maintained at a uniform temperature sufficiently high to produce measurable quantities of \( OH \). Containing the gas and maintaining a uniform temperature of 1800 K or greater is a difficult experimental problem. Changes in the dissociation energy of \( OH \) in recent years have led to changes in the calculated equilibrium \( OH \) concentrations and the corresponding \("f"\) numbers. The most recent studies give \("f"\) numbers of \(7.1 \times 10^{-4} \) [B3-30] and \(14.8 \times 10^{-4} \) [B3-31] and contain reviews of earlier work. Some reasons for preferring the higher value are given.

in Section B.1. There are also problems involved in the proper use of line shape and line width parameters [B3–29].

A3.3. Mass Spectroscopy

The hydroxyl radical is difficult to observe by mass spectroscopy because water, which is usually present in any system containing OH, gives a fragment at mass 17. However, by reducing the energy of the ionizing electrons to 18 eV, it is possible to ionize OH but not dissociate H2O and thus obtain satisfactory relative measurements of OH. Provided OH reacts according to Reactions (1) and (6), an absolute calibration may be obtained by comparing the decrease in OH to the increase in O2 or H2O2, stable species for which calibration is possible.

A3.4. Equilibrium Calculations

Most of the high temperature OH rate information comes from flame studies [25, 26]. The concentration of OH in flames may be estimated by assuming equilibrium values at the hot gas boundary or by measuring OH by UV absorption spectroscopy, neither method being completely satisfactory. The equilibrium assumption has been used by Westenberg and Fristrom [B2–6], and by Wilson et al. [B2–9]. It is a fairly good approximation in lean flames. In rich flames however the radical concentration may be hundreds of times greater than equilibrium. It is likely that the radical concentration in lean flames is also slightly higher than equilibrium predictions (see Sec. B2).

A3.5. Quantitative Electron Spin Resonance

A recently developed method for the absolute determination of hydroxyl radical concentration is the quantitative electron spin resonance technique developed by Westenberg et al. [27, B1–1, B1–3]. Hydroxyl radicals, in the presence of a magnetic field of the proper strength, will absorb microwave energy due to electric-dipole transitions between opposite members of the A doublet in the \( J = 3/2, \pi \nu \) state. The sensitivity, with standard instrumentation, is approximately 1011 molecules/cm². The problems of calibration are overcome by using a stable free radical, NO, which has similar transitions, to calibrate the instrument variables. The theoretical relationships between the intensities of OH and NO are derived in reference [27].

Quantitative determinations of OH require the knowledge of a number of experimental parameters. These are the effective g value, the partition function, and the dipole moment of both the radical species and the stable gas used for calibration. The technique is limited to pressure of a few torr or lower because line broadening decreases the sensitivity. This technique has been used at room temperature only although efforts are being made to extend it to higher temperatures.

The accuracy of the method has been demonstrated with measurements of O and N atoms. For these species absolute concentrations may be obtained by titration reactions: 

\[
\text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O}
\]

for both N and O and 

\[
\text{O} + \text{NO}_2 \rightarrow \text{NO} + \text{O}_2
\]

for O.

The study indicated that ESR measurements of O and N, using \( \text{O}_2 \) as the stable calibration gas, were accurate to ±10 percent. Similar accuracy may be expected for the OH measurements.

A3.6. Flame Photometry

A number of flame photometric techniques have been developed, largely by Sugden and co-workers [29–39], for studies of radical recombination rates in the post-reaction zones of rich, laminar, \( \text{H}_2 - \text{O}_2 \) flames. The techniques have been extended to lean flames by McEwan and Phillips [40]. The most frequently used technique, the \( \text{Li}/\text{LiOH} \) method [31, 37–42], measures the absolute H atom concentration. However, the OH concentration may be inferred through the equilibrium constant of reactions such as

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

which are balanced in the flame gases. The \( \text{Li}/\text{LiOH} \) method is based on the balanced reaction

\[
\text{Li} + \text{H}_2\text{O} \rightarrow \text{LiOH} + \text{H}
\]

Flame photometric techniques (either emission [31, 39] or absorption [40, 41, 42]) are used to measure the concentration of free Li atoms. The \( \text{LiOH} \) concentration may then be inferred from a knowledge of the concentration of lithium salt added to the flame. Water is a bulk constituent of the post-reaction gases and its concentration may be calculated from the flow rates and stoichiometry. The H concentration then may be calculated using the equilibrium constant.

Relative OH concentration [32] may be obtained directly from the intensity of the continuum near 400 nm due to

\[
\text{Na} + \text{OH} \rightarrow \text{NaOH} + \text{hv}
\]

For lean flames a correction must be made for the proportion of Na that combines as \( \text{Na}_2\text{O} \) [40].

Other flame photometric techniques for relative concentration measurements include: [H] from emission of \( \text{CaH} \) (rich flames only) [35, 40]; [O] from the emission of \( \text{IO} \) or \( \text{BrO} \) (rich or lean) [36, 40]; and \( \text{[O]} \times [\text{H}] \) from the emission of \( \text{Pb} \) [34, 40]. These relative measurement techniques may be calibrated by absolute measurements of H atom concentrations using the \( \text{Li}/\text{LiOH} \) method in either lean or rich flames or in rich flames by a method [31, 40] based on the balanced reaction

\[
\text{Na} + \text{HCl} \rightarrow \text{NaCl} + \text{H}
\]

The absolute techniques depend on a knowledge of the equilibrium constant which is fairly well known for the \( \text{Li}/\text{LiOH} \) reaction [40, 43, 44].

A3.7. Conclusion: Measurement of OH

All of the techniques mentioned above, except chemical analysis for initial concentration, are satisfactory within the limits imposed by the techniques themselves. Of these, ESR is the most accurate and specific and ultraviolet absorption the most versatile. The mass spectroscopic technique is also useful because of the possibility of measuring stable species as well as radicals.
A4. Determination of Kinetic Data

Ideally, the rate of the reaction \( A + B \rightarrow C + D \) would be determined in the following manner. A chemical system would be chosen in which there were no competing or interfering reactions. An experimental apparatus would be chosen in which it would be possible to (1) in a constant concentration of \( A \), measure \(-d[B]/dt\), \(-d[C]/dt\), and \( d[D]/dt\), and (2) in a constant concentration of \( B \), measure \(-d[A]/dt\), \(-d[C]/dt\), and \( d[D]/dt\). Such measurements would be made over a range of concentration, pressure, and temperature. If all the various measurements gave good agreement one could have confidence that a reliable rate constant had been determined.

In practice, unfortunately, there are usually side reactions which must be accounted for; the experimental technique may be limited to certain temperature and pressure regions; and it is seldom possible to measure the rate of decay (or formation) of more than one species. Recourse must be had to a comparison of results from different techniques.

In studies using discharge-flow tubes or the flash photolysis-kinetic spectroscopy technique, the rate of decay of \( \text{OH} \) is measured in a large excess (and therefore relatively constant concentration) of reactant. In flames and shock tubes, the \( \text{OH} \) concentration is maintained relatively constant by partial equilibrium and the rate of decay of the reactant or the rate of formation of a product is monitored. These techniques, and others such as slow combustion and explosion limit studies, may be used to obtain relative rates by measuring the relative reaction or formation of two species. Each technique has its own advantages and disadvantages.

A4.1. Discharge-Flow Technique

The simple discharge-flow system is being used by many workers to measure reactions of ions, atoms, and radicals. Schematics of several systems used to study \( \text{OH} \) reactions are shown in figure A2. This technique requires a source of radicals, a reactant of \( \text{OH} \) or more, a mixing zone, a long, cylindrical flow tube, a radical detector, and a means of varying the time between radical source and detector.

In studies of hydroxyl radicals, the \( \text{OH} \) is generated by introducing \( \text{NO}_2 \) into a flowing gas stream containing \( \text{H}_2 \). These are generated by a microwave discharge (~100 W at 2450 Mc/s) through \( \text{Ar} \) or \( \text{He} \) containing a few percent of \( \text{H}_2 \). A trace of \( \text{H}_2\text{O} \) or \( \text{O}_2 \) is frequently added to insure complete dissociation of the \( \text{H}_2 \). This avoids problems that might be caused by vibrationally excited \( \text{H}_2 \) [45].

The pressure in the system is normally a few torr and mixing is rapid. The flow tube, usually quartz, is several centimeters in diameter and perhaps a meter long. Reaction time may be varied by moving the \( \text{NO}_2 \) inlet or the detector. Electron spin resonance and ultraviolet absorption have been used to measure \( \text{OH} \). It would be desirable to have a stable species detector in addition to the radical detector. However, no such combination has been utilized although stable species have been measured by mass spectroscopy far downstream of the reaction zone.

The major limitations of the flow tube technique are imposed by fluid dynamics and wall effects. An exact mathematical description of the flow becomes extremely complicated, even for a simple, parabolic radial velocity distribution, when volume and surface recombination, radial and axial diffusion, and the viscous pressure drop are taken into account. Calculations have been made to determine limiting conditions, and if the conditions are carefully observed, the various effects can be neglected or corrections can be calculated [46]. The techniques for handling surface recombination remain an art rather than a science. Methods have been developed for eliminating the effect of wall recombination for situations involving first-order reactions only [B3-28]. Unfortunately, they are not applicable to \( \text{OH} \) reactions since the second-order recombination or disproportionation reactions cannot be avoided. One attempts then to work with surfaces of low but reproducible reactivity. Some workers find that HF washed quartz is satisfactory [B3-2, B3-3]. Others find it necessary to coat the tubes with acid materials such as \( \text{H}_3\text{BO}_3 \) [B1-10] or \( \text{H}_3\text{PO}_4 \) [B3-9c]. In the author's experience both the source of the quartz and the skill of the glassblower are important. When a cracked quartz flow tube was repaired by an inexperienced glassblower, the wall recombination became so rapid that \( \text{H} \) atoms could no longer be detected. Flow-tube systems of identical design but prepared from quartz from different sources may have quite different surface reactivities.

In most studies of atoms, wall recombination will not affect the homogeneous processes because...
the reaction at the wall will yield the same diatomic molecule which is already present in the gas phase. With OH, however, two wall reactions are possible: 2OH → H₂O + O or 2OH → H₂O₃. If O is produced, it will react with OH radicals in the gas phase. If H₂O₃ is produced, it can react with the H atoms present in the gas phase to regenerate OH.

A4.2. Flash Photolysis-Kinetic Spectroscopy

This technique has been used extensively by Greiner to measure reaction rates of OH with a variety of other species [B2-2, B3-4, B4-4, C4-1, C6.1-1, 20, 21]. Flash photolysis of water vapor is used to generate OH and the concentration of OH is followed by ultraviolet absorption spectroscopy. Figure A3 shows the basic elements of the experimental arrangement. The photolysis cell was an integrated lamp-cell formed from two concentric tubes of quartz. The material to be photolyzed was placed in the inner tube, and the 1000 J photolytic flash was induced in the outer tube between the ring electrodes, E, in 35 torr of Xe. A reflector of Al foil was wrapped around the outside of the cell. The design was an attempt to provide uniform illumination of the material under study. Absorption spectra were recorded with a high-resolution plane grating spectrophotograph, with the 250 J spectroscopic flash lamp providing the continuum.

H₂O is admitted to the cell to a pressure of 1.00 torr. After the line has been pumped out, the reactant gas is dosed into the cell through the capillary A and Ar is added to give a total pressure of 100 torr. The gases are allowed to mix for 7 min with the aid of the magnetically driven, all-glass pump. The mixture is then flash photolyzed, and the absorption spectrum of the OH 306.4 nm band is recorded at the selected delay time. To obtain adequate exposure it was necessary to repeat the flash sequence eight times. Strong absorption lines were corrected for deviations from Beer's law and line broadening caused by the slit function of the spectrometer.

There are a number of significant advantages to this method. Due to the high sensitivity it is possible to work with very low concentrations of OH and high concentrations of reactants. Therefore, second-order reactions of OH with OH are avoided and the first-order rates can be determined in a straightforward manner from a plot of log [OH] versus time. During the short reaction time (≈200 × 10⁻⁶ s), there is insignificant diffusion of OH to the surface, thus eliminating wall effects. There are no concentration or pressure gradients. The large ratio of reactant to OH minimizes secondary reactions. However, this method is limited to reactants which do not absorb the photolysis radiation and whose reactions with H atoms are much slower than with OH.

All factors considered, this technique appears to be the most straightforward and reliable technique available for the study of hydroxyl radical reactions. The rates obtained by this technique at room temperature agree well with those determined in flow tubes. However, activation energies, determined from flash photolysis-kinetic spectroscopy experiments over the 300 to 500 K temperature range do not agree with the activation energies obtained from a consideration of the available high temperature data. Consequently, the data obtained with this technique has not been given great weight in determining the suggested values. The discrepancy between this technique and all others represents a major problem in OH kinetics and is further discussed in references [B2-2, B3-4, B4-4, C4-1, C6.1-1, and Sec. D].

A4.3. Microstructure of Premixed-Laminar Flames

To the kineticist the flame offers a wall-less, high temperature reactor. Since the flame is a steady-state system time is transformed into distance and there are no limitations on the time available to make a measurement. Very slow burning flames or low-pressure flames are normally used in order to expand the flame zone and permit measurements over a greater distance. Accurate measurements of the stable species may be made by extracting samples through a fine quartz or metal probe which quenches the flame reactions and analyzing the sample in a mass spectrometer. Temperature can be measured by thermocouples or by spectroscopic techniques. An example of a low-pressure flame and microprobe is shown in figure A4.

There are two major problem areas in the use of flames to obtain kinetic data: obtaining accurate
profiles of atomic and radical species and making corrections for diffusion processes. Hydroxyl radicals may be measured by ultraviolet absorption. Various chemical techniques have been developed for determining H and O which depend on the knowledge of a rate constant. Radial measurements are therefore limited to an accuracy of a factor of two by the OH "f" number and the rate constants needed for O and H determinations.

For a flat, one-dimensional flame the equations used in calculating $K_i$, the net reaction rate of species $i$, are,

$$K_i = \frac{\phi_{0i} \text{d}G_i}{M_i \text{d}z}$$

where $\phi_0$ is density, $v_0$ is velocity, subscript 0 refers to the cold boundary, $M_i$ is molecular weight of species $i$, and $G_i$ is the fraction of the total mass flux per unit area which is due to species $i$, and $z$ is the flame coordinate (usually the distance from the burner surface).

$$G_i = \frac{N_i m_i (\nu + V_i)}{\rho v}$$

where $N_i$ is the number of moles of species $i$, $m_i$ the molecular weight of species $i$, $\nu$ the gas velocity, and $V_i$ the diffusion velocity. $V_i$ is proportional to $dn_i/dz$. Because of the very steep gradients in flames, $V_i$ will frequently be the same order of magnitude as $\nu$. In some cases $V_i$ for atomic or radical species may be negative and larger than $\nu$. The lack of experimental measurements of diffusion coefficients at high temperature and the computational difficulties of treating multi-component diffusion processes lead to some uncertainties in the final results of flame studies. The data reduction requires obtaining the second derivative of the composition profile. Therefore, accurate profiles and careful data reduction techniques are required.

Many reactions occur in the flame zone and it is sometimes difficult to obtain information on one specific reaction rate without using other rate data in the analysis. Nevertheless, much useful kinetic information has been obtained from flames. The mathematical and experimental techniques for obtaining kinetic data from flames are described in "Flame Structure" by Fristrom and Westenberg [26].

**A4.4. Other Experimental Techniques**

**Shock Tubes.** The shock tube is the only technique that is capable of kinetic studies above 2000 K. It has the advantage that, because of the very short reaction times, reactions on the wall can be neglected. However, as with flames, many reactive species are present and it is often difficult to determine one reaction rate independently from the many other reactions occurring [B3-8]. The correct application of the shock tube to chemical kinetic studies also requires a knowledge of both the ideal and nonideal behavior of the gas flow. This experimental technique, and its application to kinetics, has been reviewed recently [48].

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**Explosion Limits.** This technique can determine only ratios of reaction rates. In this case also a limited amount of data must be fitted to an elaborate kinetic mechanism [B3-12].

**A5. References—Section A**


[34] Rosenfeld, J. L. J., and Sugden, T. M., Burning velocity and free radical recombination rates in low temperature hydrogen flames—II. Rate constants for recombination reactions, Comb. and Flame 8, 44 (1964).  

B. Evaluation of Rate Constants

B1. $k_1$, Rate Constant for the Reaction, \( \text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O} \)

B1.1. General Discussion

B1.1a. Experimental Measurements

The measured rate constants for \( k_1 \), the rate of disproportionation of hydroxyl radicals at room temperature, are given in table I. There are three direct measurements which differ by a factor of three and several indirect measurements, some of which tend to confirm the higher rate. Since this reaction is second order in OH, the OH concentra-

tion appears in the rate expression. An accurate measurement of the absolute concentration of OH is required, therefore. This is in contrast to other OH reactions in which relative OH concentrations are sufficient, or in which the calibration factors cancel out in the data analysis.

The difficulty with the room temperature rate lies in the discrepancies among the Kaufman and Del Greco measurement [2] and the Dixon-Lewis, Wilson, Westenberg measurement [1], and the Breen and Glass measurement [10]. The chemistry

<table>
<thead>
<tr>
<th>( \text{cm}^3 \text{ mol}^{-1} \cdot \text{s}^{-1} )</th>
<th>( \text{cm}^3 \text{ particles}^{-1} \cdot \text{s}^{-1} )</th>
<th>( T(\text{K}) )</th>
<th>Ref.</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.55 \pm 0.15 \times 10^{12}$</td>
<td>$2.57 \pm 0.25 \times 10^{12}$</td>
<td>300</td>
<td>1</td>
<td>ESR.</td>
</tr>
<tr>
<td>$0.75 \pm 0.20 \times 10^{12}$</td>
<td>$1.40 \pm 0.30 \times 10^{12}$</td>
<td>300</td>
<td>2</td>
<td>Abs. spec.</td>
</tr>
<tr>
<td>$0.50 \pm 0.16 \times 10^{12}$</td>
<td>$0.84 \pm 0.26 \times 10^{12}$</td>
<td>300</td>
<td>10</td>
<td>ESR.</td>
</tr>
<tr>
<td>$0.43 \times 10^{12}$</td>
<td>$0.72 \times 10^{12}$</td>
<td>300</td>
<td>20</td>
<td>Calculation.</td>
</tr>
<tr>
<td>$\geq 0.1 \times 10^{12}$</td>
<td>$\geq 0.17 \times 10^{12}$</td>
<td>300</td>
<td>4</td>
<td>Surface recombination of H atoms.</td>
</tr>
<tr>
<td>$10 \times 10^{12}$</td>
<td>$1.7 \times 10^{-11}$</td>
<td>1600</td>
<td>9</td>
<td>Shock tube reverse.</td>
</tr>
<tr>
<td>$100 \times 10^{12}$</td>
<td>$32 \times 10^{-11}$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For reverse $\Delta E/R \sim 8$

Several mass-spectrometric studies support the higher value of $k_1$. If $k_1$, \( \text{(CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}) = 10 \pm 2 \times 10^{10} \text{ cm}^3 \text{ mol}^{-1} \cdot \text{s}^{-1} \) is accepted.

Recommended value at 300 K

<table>
<thead>
<tr>
<th>( \text{cm}^3 \text{ mol}^{-1} \cdot \text{s}^{-1} )</th>
<th>( \text{cm}^3 \text{ particles}^{-1} \cdot \text{s}^{-1} )</th>
<th>Error limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.55 \times 10^{12}$</td>
<td>$2.57 \times 10^{-12}$</td>
<td>log $k_1 + 0.1$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\pm 0.5$</td>
</tr>
</tbody>
</table>
is the same in both cases, the reactions involved being

\[ H + NO_2 \rightarrow NO + OH \]  \hspace{1cm} (5)

\[ OH + OH \rightarrow H_2O + O \]  \hspace{1cm} (1)

\[ O + OH \rightarrow O_2 + H. \]  \hspace{1cm} (6)

When \( H \) is in excess the \( O \) generated by Reaction (1) will react with \( OH \) according to Reaction (6). A steady-state system will rapidly be set up and

\[ (-d[OH]/dt)_{1+6} = 3k_1[OH]^2. \]

The subscript refers to the reactions included in the \( OH \) decay. In this report \( k_1 \) is defined as

\[ (-d[OH]/dt)_{1} = 2k_1[OH]^2. \]

Some authors define \( k_1 \) as

\[ (-d[OH]/dt)_{1+6} = 2k_1[OH]^2. \]

then

\[ (-d[OH]/dt)_{1+6} = 3/2k_1[OH]^2. \]

In references [1 and 2] the measurements were made in low pressure flow tubes and the \( OH \) decay was second order over two orders of magnitude. However, the absolute values obtained for \( k_1 \) differ by a factor of two although a measurement of \( k_6(H_2O+OH) \) by both groups is in agreement. An examination of the relevant equations shows that the only explanation for this agreement on \( k_6 \) but disagreement on \( k_1 \) is a difference in the calibration of the absolute \( OH \) concentration. Errors due to differences in surface recombination, for example, would also effect \( k_5 \).

The Dixon-Lewis, Wilson, Westenberg [1] study used quantitative electron spin resonance to follow the decay and measure the absolute \( OH \) concentration. The ESR spectrometer was calibrated for \( OH \) by comparison with the ESR signal from a measured quantity of \( NO \). The absolute \( OH \) concentration depends only on the dipole moments and partition functions of \( NO \) and \( OH \) which are known with fair accuracy. Measurements of \( O \) and \( N \) by ESR agree to \( \pm 10 \) percent with the values determined by chemical titration. The absolute \( OH \) measurements should also be good to \( \pm 10 \) percent.

In the Kaufman and Del Greco [2] studies ultraviolet absorption spectroscopy was used to follow the \( OH \) decay. The absolute concentration was determined by assuming the initial absorption measurement was of a concentration of \( OH \) given by the \( NO_2 \) flow rate, i.e., there was a region where Reaction (5) had gone to completion but where Reaction (1) had not yet begun. The optical system sampled a section of tube 1 cm long which correspond to 1/3 ms. However, visual observations of light generating reactions indicated that complete mixing required a length of 3 cm or 1 ms.

In order to determine if reaction or incomplete mixing might have caused the actual \( OH \) to be lower then that assumed by Kaufman, computer calculations were made to determine the \( OH \) profile in the first ms. Figure B1 shows the calculated \( OH \) concentration as a function of time. For case A, \( k_6 = 2.9 \times 10^{13} \text{ cm}^{-2} \text{ mol}^{-1} \text{ s}^{-1} \), for B, \( k_6 = 1 \times 10^{12} \). The latter value of \( 10^{12} \) gives complete reaction in about 1 ms. This simulates what might happen if mixing was not complete for 1 ms. For both cases \([NO_2]_0 = 3 \times 10^{-10} \text{ mol cm}^{-3} \), \( k_1 = 1.5 \times 10^{12} \), \( k_6 = 1 \times 10^{13} \), and \([O + NO_2 \rightarrow NO + O_2] = 1.5 \times 10^{12} \text{ cm}^{-3} \text{ mol}^{-1} \text{ s}^{-1} \). The latter reaction was too slow to be significant. The Kaufman and Del Greco assumption [2] requires that the \( OH \) concentration be \( 3 \times 10^{-10} \) for 1/3 ms or from the start of the reaction to the vertical bar shown on the graph. As can be seen from the graph, the value of \([OH]\), never reaches \( 3 \times 10^{-10} \). Assuming that mixing is instantaneous complete, a peak value of \( 2.9 \times 10^{-10} \) is reached, but if the \( OH \) concentration is integrated over the first cm or 1/3 ms, as the optical absorption would, the observed concentration is only about 85 percent of that anticipated. This effect would be more pronounced for higher \( OH \) concentrations since the decay is proportional to \([OH]^3\). Lowering the rate of \( H + NO_2 \rightarrow NO + OH \) to give complete reaction at the time of complete mixing is a crude way to approximate the effect of a finite mixing time but it probably gives a reasonable approximation to the variation in \( OH \) concentration. In this case the integrated \( OH \) concentration is only one-half that anticipated. If Kaufman and Del Greco [2] had overestimated the value of \([OH]\) by a factor of two their results would agree almost exactly with the ESR study. The above argument indicates that such an error might have been possible.

The discrepancy between these two studies and the Breen and Glass [10] study appears to lie in surface reactions. Breen and Glass, also using a flow tube and ESR, observed appreciable loss of \( H \) atoms on the surface and also first-order surface recombination of \( OH \) on the wall. In order to overcome the loss of \( H \) atoms and to obtain a constant surface recombination of \( OH \), they coated their surfaces with boric acid. In the Dixon-Lewis, Westenberg, Wilson study, the surfaces were uncoated, HF washed, quartz. No surface recombination of \( H \) atoms could be detected and no first-order decay of \( OH \) was observed although a wall recombination of the magnitude observed by Breen and

![Figure B1. Calculated decay profiles in hydroxyl radicals.](image)

Curve A: Instantaneous mixing assumed.
Curve B: Finite mixing time of 0.3 ms approximated by lowering value of \( k_{OH + NO_2} \).

Glass should have been evident. However, the Breen and Glass study extended to lower OH concentrations where first-order reaction would become more important.

Breen and Glass used a fixed detector and a moveable source whereas the other two studies used a moveable detector and a fixed source. The pressure correction (due to viscous flow losses) is more complicated in the former system. However, pressure effects can hardly account for the differences in the rate constants obtained and a major part of the discrepancy must be attributed to surface effects. Possibly there is a second-order recombination on HF washed quartz, which could not be separated from the second-order homogeneous combination reaction. Alternately, the boric acid coated surface might promote formation [22] of a substance such as H 2 O or HO 2 which would react to form OH along the flow tube and decrease the observed rate. Since more OH was reacted by heterogeneous recombination on the walls than by disproportionation in the gas phase, the compound formed on the wall, and its subsequent reactions needs to be known. It is hoped that mass spectroscopic studies, in which formation of H 2 O and O 2 by Reaction (6) and (1) as well as the decay of OH can be measured, will resolve this problem.

There are some other independent measurements which support the higher ESR value of \( k_1 \). Two measurements of the ratio of \( k_0/\text{(CO + OH)}/k_2 \) indicate that if a value of \( k_0 = (10 \pm 2) \times 10^{10} \) is accepted (and this value seems fairly reliable) the value of \( k_1 \) must be near \( 1.55 \times 10^{12} \) in agreement with the ESR measurement [6, 7].

There is very little experimental information on this reaction in high temperature systems. However, there is some experimental information from shock tube studies which should be mentioned [21]. In the shock-initiated combustion of lean hydrogen-oxygen-argon mixtures at low pressure (-200 torr) and temperatures of \(-1400 \) K, the concentration profiles of OH radicals are found to exhibit pronounced spikes prior to attainment of partial equilibrium. These spikes cannot be accounted for within the accepted mechanism of the H 2 -O 2 reaction. In particular, if \( k_1 \) is as fast as the room temperature measurements indicate there must be another means of producing OH at high temperatures.

**B1.1b. Other Evaluations**

Best estimates for OH + OH → H 2 O + O have been made a number of times. They are listed in table Ia. The first three are current and use Reference 1 as their base point. The others were made before that work became available.

Directly or indirectly all the earlier estimates use the room temperature measurement of Kaufman and Del Greco [2] (or are derived from their evaluation and the activation energies described below). Slight variations in the rate parameters in these earlier estimates become unimportant in view of the uncertainties assigned in reference [2]. None of these older estimates is recommended.

The temperature coefficients are based on two items. \( E_b = 18 \) kcal/mol is cited, in passing, by Voevodsky and Kouidiativ [8] from preliminary work by Azatyan. Kaufman and Del Greco [2] suggested \( E_b = 1 \) kcal/mol. Neither is certain, but both are probably reasonable.

**B1.2 References and Comments**

**B1.2a. Experimental Measurements**


The OH was generated by H + NO 2 → NO + OH. Quantitative electron spin resonance was used to determine the initial concentration and to follow the second order OH decay in a fast flow system at \( \approx 1 \) torr.


The OH was generated by H + NO 2 → NO + OH and the second order decay measured by absorption spectroscopy near 300 nm. The initial OH concentration \([\text{OH}]_0\) was determined by

**Table Ia. Evaluations of the rate of disproportionation of OH**

<table>
<thead>
<tr>
<th>( \text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O} )</th>
<th>( k_1 )</th>
<th>( \text{H}_2\text{O} + \text{O} \rightarrow \text{OH} + \text{OH} )</th>
<th>( k_{-1} )</th>
<th>Temp. range, K</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( -11.59 \pm 0.07 ) (log ( k ))</td>
<td>( -11.02 \pm 0.45^a )</td>
<td>( -10.86 )</td>
<td>( -10.90 \pm 0.3 )</td>
<td>( -11.28 \pm 0.21 )</td>
<td>( -10.96 )</td>
</tr>
<tr>
<td>( -23.15 ) (log ( k ))</td>
<td>( -10.02 \pm 0.45^a )</td>
<td>( -9.85 )</td>
<td>( -9.86 \pm 0.8 )</td>
<td>( -10.16 \pm 0.19 )</td>
<td>( -10.16 \pm 0.19 )</td>
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</tbody>
</table>

\( k = 10^4 T^n \exp \left[ -C/(1000/T) \right] \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}, \quad -d[\text{OH}]/dt = 2k_1[\text{OH}]^2 \)

\( ^a \)Overall uncertainty in log \( k \): ±0.1 at 300 K, ±0.2 at 2000 K.
HYDROXYL RADICAL REACTION KINETICS

B1.2a. Rate Constant Measurements

B2. 

B2.1. General Discussion

B2.1a. Rate Constant Measurements

The reaction of CO with OH has an important one

for several reasons. This is the primary means of

converting CO to CO₂ in flames and may be

a significant sink for atmospheric CO. Much of

the information about OH kinetics is in the form of

ratios of the rate of CO + OH to other reactions.

In particular the rates of H₂ + OH and CH₂ + OH

are best determined from measurements of rate

ingredients of CO + OH and a value for the rate of

CO + OH. (See fig. B3.)

This argument could, of course, be inverted and

some other reaction chosen as the base for

interpretation of rate ratio data. The only other choice

at present is H₂ + OH → H₂O + H. There are three

reasons for preferring CO + OH: (1) The available

data on H₂ + OH suitable for setting an absolute value

for the rate constant, including its temperature

dependence, are less extensive and probably

less reliable as those for CO + OH. (2) The

activation energy of the CO + OH reaction is lower.
Errors in its determination will therefore have little effect on the rates of the other reactions. (3) There are more rate ratio measurements involving CO + OH than any other OH reaction.

The pertinent experimental data are presented in figure B2 and table II. Rate ratio information which requires the use of another hydroxyl rate constant to obtain $k_T$ is not used here but is considered in later sections in which rate ratio information involving $k_a$($H + OH$) and $k_d$($CH + OH$) is discussed. The recommended value was obtained by assuming the room temperature point of reference [1] to be correct and subjectively weighing the various high temperature points. The line was then adjusted to give only one significant figure in the activation energy. The quality of the data is not sufficient to justify more sophisticated fitting techniques.

It is also possible to fit the experimental points by plotting $\log kT^{1/2}$ versus $1/T$. In this case a good fit to all but the two highest flame points is obtained by $\log k_T = 9.8 \pm 0.2 T^{1/2} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ with zero activation energy.

The large variation in the points obtained from flames requires some discussion. In the determination of $k_T$ in the forward direction by flame structure techniques the concentration of CO, [CO], the concentration of OH, [OH], and the rate of formation of $CO_2$, $R_{CO_2}$, must be known. Then $k_T$ is obtained from $R_{CO_2} = k_T[CO][OH]$. Three important assumptions are involved in this technique: (1) The OH concentration can be determined, (2) CO$_2$ is not formed or destroyed by any other reaction, (3) The concentration profiles can be corrected for diffusion so that the flux of CO$_2$ due to chemical reaction can be separated from that due to diffusion. Because of the large concentration gradient the diffusive flux of CO$_2$ toward the flame holder may be of the same order of magnitude as the flux due to Reaction (2). Most flame structure studies have used binary diffusion coefficients and have obtained activation energies which appear to be high. Brown et al. [12] found that the use of multicomponent diffusion coefficients led to much lower activation energies for the reaction of CO with OH. It has generally been accepted that CO + OH is the only source of CO$_2$ in high temperature systems. Recent work, however, has suggested that the reaction of HO$_2$ may be of some significance [B3-12a]. If part of the conversion of CO to CO$_2$ in flames is due to reaction with HO$_2$, the measured values of $k_T$ would be too high. It is usually possible to make adequate corrections for $k_T$, $H + CO_2 \rightarrow CO + OH$.

The flame structure studies which yielded the higher values for $k_T$ (shown with filled symbols) all calculated [OH] by assuming that the OH concentration at the hot boundary was given by the equilibrium concentration calculated at the flame temperature. Radical concentrations in rich flames are known to be as much as several orders of magnitude higher than the calculated equilibrium values. While such high excess concentrations are not likely in the lean flames normally used for OH studies, the OH concentration could easily be higher than equilibrium. Failure of the assumption would cause the measured rate to be high. Measurements of the forward reaction in flames, in which the [OH] was determined by absorption spectroscopy, and flame measurements of the rate of the reverse reaction all give lower values for $k_T$. The values of $k_T$ obtained from flame structure studies using the equilibrium approximation for [OH] should, therefore, probably be considered as upper limits.

The measurement of the rate of the reverse reaction in flames requires a measurement of the hydrogen atom concentration, i.e., $k_{-2} = -\frac{R_{CO_2}}{[H][CO_3]}$. Most frequently [H] is obtained by adding D$_2$O, measuring the rate of formation of HD, $R_{HD}$, and [D$_2$O], and using a value of $k_{-3p}$ (H + D$_2$O) to obtain [H]. This [H] is then used with the rate of formation of CO$_2$, $R_{CO_2}$, and [CO$_2$] to obtain $k_{-4}$(H + CO$_2$). The forward rate constant may then be obtained via the equilibrium constant, $k_T = k_{eq}k_{-4}$. In several rate evaluations, a determination of $k_{-3p}/k_{-2}$ by Fenimore and Jones [5] has been used with various values of $k_{-4}$(H + D$_2$O) to obtain $k_T$. Since this is really a rate ratio measurement, it has been used in determining the value of $k_T$ [B3-14] but not for determining $k_T$.

Dixon-Lewis [4] et al. have also reported values of $k_{-3p}/k_{-2}$ and have used them to obtain a value of $k_T$. However, their value of $k_T$ was not based on an assumed value of $k_T$ since the parameters from which $k_{-3p}$ could be calculated were all measured in the same flame system. Their value of $k_T$ depends ultimately on $k_T$(H + D$_2$) which was used in determining the hydrogen atom concentration. Although their measurement is still a rate ratio, it is independent of other hydroxyl radical rate constants.
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Table II. CO + OH → CO₂ + H

<table>
<thead>
<tr>
<th>A</th>
<th>C</th>
<th>Ref.</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mol units</td>
<td>Particle units</td>
<td>T range K</td>
<td></td>
</tr>
<tr>
<td>1.3 × 10¹⁰</td>
<td>2.16 × 10⁻¹⁸</td>
<td>115</td>
<td>300-500</td>
</tr>
<tr>
<td>3.55 × 10¹⁰</td>
<td>5.9 × 10⁻¹⁸</td>
<td>350</td>
<td>600-1000</td>
</tr>
<tr>
<td>3.7 × 10¹⁰</td>
<td>6.15 × 10⁻¹⁸</td>
<td>1000-3000</td>
<td>12</td>
</tr>
<tr>
<td>6.2 × 10¹⁰</td>
<td>1.0 × 10⁻¹²</td>
<td>500</td>
<td>1500-2200</td>
</tr>
<tr>
<td>3.5 × 10¹⁰</td>
<td>5.8 × 10⁻¹²</td>
<td>600</td>
<td>300-600</td>
</tr>
</tbody>
</table>

Rate constant

<table>
<thead>
<tr>
<th>k₂ in 10⁻¹⁰ cm⁻³ mol⁻¹ s⁻¹</th>
<th>k₂ in 10⁻¹³ cm² particles⁻¹ s⁻¹</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1.15 ± 0.05</td>
<td>1.91 ± 0.08</td>
<td>300</td>
</tr>
<tr>
<td>0.89 ± 0.09</td>
<td>1.48 ± 0.35</td>
<td>300</td>
</tr>
<tr>
<td>2.21</td>
<td>3.67</td>
<td>1400</td>
</tr>
<tr>
<td>2.3</td>
<td>3.8</td>
<td>1072</td>
</tr>
<tr>
<td>1.0</td>
<td>1.66</td>
<td>1200</td>
</tr>
<tr>
<td>1.26</td>
<td>2.09</td>
<td>1350</td>
</tr>
<tr>
<td>1.5 ± 0.2</td>
<td>2.5 ± 0.3</td>
<td>1000-1200</td>
</tr>
<tr>
<td>9</td>
<td>15</td>
<td>1950</td>
</tr>
<tr>
<td>2.6</td>
<td>7.2</td>
<td>1720</td>
</tr>
<tr>
<td>7.5 ± 7.5</td>
<td>11.5 ± 1.5</td>
<td>2000</td>
</tr>
<tr>
<td>5.1 ± 1.0</td>
<td>8.3 ± 2</td>
<td>2150</td>
</tr>
<tr>
<td>9.0 ± 1.0</td>
<td>15.2 ± 2</td>
<td>2000</td>
</tr>
<tr>
<td>7.75 ± 0.25</td>
<td>12.5 ± 0.5</td>
<td>2150</td>
</tr>
<tr>
<td>0.51 ± 0.2</td>
<td>0.85 ± 0.3</td>
<td>300</td>
</tr>
<tr>
<td>1.04 ± 0.01</td>
<td>1.73 ± 0.02</td>
<td>300</td>
</tr>
<tr>
<td>5.6</td>
<td>9.3</td>
<td>310</td>
</tr>
<tr>
<td>10.1</td>
<td>16.8</td>
<td>440</td>
</tr>
<tr>
<td>15.6</td>
<td>21.7</td>
<td>610</td>
</tr>
</tbody>
</table>

Recommended values 300–2000 K

<table>
<thead>
<tr>
<th>Units</th>
<th>Rate expression</th>
<th>k₂ at 1000 K</th>
<th>Error limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>cm⁻³ mol⁻¹ s⁻¹</td>
<td>k₂ = 5.1 × 10¹¹ exp (−300/T)</td>
<td>2.3 × 10¹¹</td>
<td>0.3</td>
</tr>
<tr>
<td>cm⁻² particles⁻¹ s⁻¹</td>
<td>k₂ = 5.1 × 10⁻¹³ exp (−300/T)</td>
<td>3.8 × 10⁻¹³</td>
<td></td>
</tr>
</tbody>
</table>

The room temperature measurements of k₂ appear to be reliable. The ESR [1] and the flash photolysis-kinetic spectroscopy (FP-KS) [2a] measurements are in reasonable agreement. The ESR measurements are preferred to the FP-KS ones because of the large scatter in the latter. However, the two sets of measurements provide an important confirmation of each other. The errors that might occur in the two experimental systems are quite different. In particular, catalytic wall reactions which might occur in a flow tube would not be a problem in the short times involved in the FP-KS experiment. Additional support for the room temperature value comes from three measurements of k₂/k₁ which confirm a value of this order of magnitude from measurements of the initial OH and the amount of CO₂ formed [10, 11, 14]. While a single kinetic measurement is not sufficient to give a reliable rate, the agreement among a variety of techniques susceptible to different kinds of errors lends confidence to the value of k₂ at room temperature. Greiner [2b] has recently measured k₂ over the temperature range from 300 to 500 K using the FP-KS technique. Unfortunately his points do not yield an activation energy in agreement with other work. The implications of this lack of agreement are discussed later [B3-4, B4-4, Sec. D].

It is frequently difficult to determine the various rate data and assumptions that are used in obtaining a given rate constant. The complexity of the analysis can be seen from the data chain shown in table IIa. This was constructed to determine the source of a value of k₂ which was quoted in the literature. As can be seen from the data chain this value of k₂ was really based on a measurement of k₋₂(H + CO₂)/k₋₃D(H + D₂O). A rather complicated sequence was used to establish the relation between k₋₃D(H + D₂O) and k₋₃(H + H₂O). This value of k₂ depends ultimately on the value of k₋₁(H + D₂). The value used was 4.2 × 10¹¹ cm² mol⁻¹ s⁻¹ at 900 K. The most recent experimental
value is $2.6 \times 10^{13}$ at that temperature. In a sequence of relationships such as these there exists the possibility of an accumulation of errors.

**B2.1b. Relation to Other Evaluations**

Schofield [23] and Baulch, Drysdale and Lloyd [24a] have recently reported evaluations of $k_5$. Schofield [23] gives $6.6 \times 10^{11}$ exp ($-1050/RT$) cm$^3$ mol$^{-1}$ s$^{-1}$ (1.1 $\times 10^{12}$ in particle units) and Baulch et al. give $5.6 \pm 0.8 \times 10^{11}$ exp ($-1080 \pm 500/RT$) cm$^3$ mol$^{-1}$ s$^{-1}$ (9.3 $\pm 1.3 \times 10^{12}$ in particle units). These evaluations differ from the present one mainly in the treatment of rate ratio data. In addition to references [2, 3, 6a, 7, 12, and 14], Baulch et al. [24a], also include data from references [B3–11, B3–12, B3–13, and B3–14] which are actually rate ratio measurement of $k_5/k_3$, $k_2/k_3$, or $k_3/k_2$. A value must be assumed for $k_3$, $k_2$, or $k_3/k_2$ and used to calculate $k_5$ from the ratio. In some cases this was done by the author of the original paper and the direct experimental observation, the rate ratio, may not be obvious. In other cases, Baulch et al. [24a] have chosen a $k_3$ value to use with the ratio. For the ratios given in their references [20, 21, and 22] (which correspond to this report's references [B3–12a, B3–14c, and B3–11]) Baulch et al. [24a] have chosen Kaufman's [B3–3c] suggested value of $k_3 = 10^{10.2} \times 10^{10.7}$ exp ($-5.900 \pm 1000/RT$) but have not indicated the uncertainty suggested by Kaufman. This rate expression is based on Kaufman's room temperature rate for $k_5$ [B3–3c] and a value for 1500 K calculated from a rate expression due to

\[ k = \text{rate constant} \]

\[ K = \text{Equilibrium constant} \]

\[ \Delta E = \text{Activation energy} \]

*Indicates an experimental rate measurement, the reference is given in parentheses.

Arrows indicate transfer of numerical values

- CO + OH + CO$_2$ + H

- HD + OD + D$_2$O + H

- k$_5$(H + D$_2$) at 1000 K used with

\[ \Delta E(H + D_2)_{1072} \] to give k$_5$(H + D$_2$) at 1072 K.

- k$_3$ is given in parentheses.

- Baulch et al. [24b] have recently reported evaluations of $k_5$. In a later review they recommend a value for $k_5$ of $2.19 \times 10^{10}$ exp ($-5150/RT$) cm$^3$ mol$^{-1}$ s$^{-1}$ [cf. Kaufman's [B3–3c] $6.3 \times 10^{10}$ exp ($-5900/RT$)]. If their recommended value of $k_5$ were to be used to calculate the rate ratio data, the points would be lowered by a factor of 2.86 ($-750/RT$). Baulch et al. [24a], also chose Greiner's room temperature value [2a] for the room temperature point rather than the higher point due to Dixon-Lewis, Wilson, and Westenberg [1]. This choice also contributes to their higher activation energy.

Schofield's evaluation [23] and this report share the low temperature point [1, 2a] and the flame results of reference [6a]. Schofield [23] also shows points derived from rate ratios. The original author's calculation is used from reference [3–13]. For references [3–11, 3–12, and 3–14], Schofield [23] uses his recommended value for $k_5$ or $k_3$. His evaluation of $k_5$ is based on Kaufman's room temperature point [B3–3] and the shock tube results of Ripley and Gardner [B3–8a]. The latter are no longer considered reliable [B3–8b]. Schofield's [B2–3] higher activation energy for $k_5$ is due largely to his use of a high value of $k_5$ in the calculation of $k_2$ points from $k_5/k_2$ rate ratios.

Bahn [17], Cherry et al. [18], Tunder et al. [19], and Jensen and Kurzius [20] all selected the rate expression of Dixon-Lewis, Wilson, and Westenberg [1] which is that recommended here. Fristrom and Westenberg [21] and also Kaskan and Browne [22] included the low temperature results of Avremenko [14] in these early evaluations. The inclusion of these results, which are now known to be incorrect, accounts for the higher activation energies in the two evaluations.

**B2.2 References and Comments, C$_3$H$_7$OH$\rightarrow$H$+\text{CO}_2$, Reaction 2**

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**B2.2a. Experimental Measurements**


The OH was generated by H$+\text{NO}_2\rightarrow$HO$+\text{OH}$. Quantitative electron spin resonance was used to determine the initial concentration and to follow the hydroxyl radical decay in a fast flow system at $\sim 1$ torr.


The OH was generated by flash photolysis of H$_2$O and the decay followed by kinetic spectroscopy (absorption, static system, pressure 20 to 200 torr). Because of the short time of reaction ($<200 \times 10^{-4}$ s) and the large ratio of reactant to OH the reaction could be treated as pseudo first order in OH and wall and three-body reactions should not be significant.


The FP/KS apparatus was adapted so that the temperature could be varied from 300 to 500 K. The data reported for $k_5$ in cm$^3$ mol$^{-1}$ s$^{-1}$ are: average of 4 measurements at 300 K, $8.56 \pm 0.43 \times 10^{10}$; $334$ K, $8.92 \pm 0.53 \times 10^{10}$; $375$ K, $8.84 \pm 0.27 \times 10^{10}$; $421$ K, $8.43 \pm 0.24 \times 10^{10}$; average of 4 measurements at 495 K, $9.93 \pm 0.33 \times 10^{10}$. The author reports that a least
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squares fits gives \( A = (3.9 \text{ cm}^3 \text{ molecule}^{-1} \text{ torr}^{-1}) \times 1.1 \times 10^2 \text{ at } E = 230 \pm 140 \text{ cal/mole}. \) These points were not considered in determining the suggested rate equation because of the large scatter and the general problems associated with the technique used. (See ref. [3c-4, 5] and [25].) These points do fall well within the uncertainty limits of \( \pm 2 \times 0.3 \) given with the suggested rate equation.


Addition of both \( \text{D}_2 \text{O} \) and \( \text{CO}_2 \) to a flat \( \text{H}_2 \text{O} \) flame with a final temperature of 1072 K at atmospheric pressure made possible the measurement of the ratio, \( k_{30}(\text{H}+\text{D}_2 \text{O})/k_{30}(\text{H}+\text{H}_2 \text{O}) \approx 4.3 \pm 0.5 \). The value of \( k_{30} \) given, \( 2.3 \times 10^6 \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1} \), was calculated from the equilibrium constant and \( k_{30} \approx 9.4 \times 10^6 \text{ in} \) reference [25]. However, in the flame study, the rate of formation of \( \text{HD} \) from \( \text{H}_2 \text{O} \) and \( \text{D}_2 \text{O} \), the concentration of \( \text{D}_2 \text{O} \) was measured experimentally. The derived \( k_3 \) therefore, does not require the use of \( k_{30} \) and is given as \( k_3 \approx 3.0 \times 10^8 \text{ s}^{-1} \). (The Combustion Institute, 1965), p. 473.


Reference [5a] reports work in which \( k_{30}(\text{H}+\text{CO}_2) \text{ or } k_{30}(\text{H}+\text{D}_2 \text{O}) \) was measured. In reference [5b] the ratio is given as \( 0.35 \times 10^3 \text{ (torr)}^{-1} \). This is a not a direct measurement of \( k_3 \). The references state that they have frequently been used with a value for \( k_{30}(\text{H}+\text{D}_2 \text{O}) \) or \( k_{30}(\text{H}+\text{H}_2 \text{O}) \) to obtain a value of \( k_3 \). From which \( k_{30} \) is calculated and shown on Arthur’s plots. In addition to the uncertainty due to use of a value for \( k_{30}(\text{H}+\text{D}_2 \text{O}) \) the derived \( k_3 \) may be low because no diffusion corrections were made in the original treatment of the experimental data. This experimental data is used in determining \( k_2/k_3 \) [B3-14].


[6c] \( k_3 \) was determined in low pressure (1/10 atm) flames \([6a]: \text{CH}_2 \text{O} \text{ (dual) } \text{CH}_3 \text{H}_2 \text{O } \text{(dual) } \text{CH}_3 \text{H}_2 \text{O} \text{ + O}_2 \text{ (measured by } \text{CO} \text{),} \text{O} \text{ atom formation } [\text{OH}] \text{ at } \text{OH} \text{ formation} \) is given by chemical equilibrium conditions. Since [OH] may well exceed equilibrium values these rates may be too high.


The burnt gas from a hydrocarbon flame at atmospheric pressure was passed into a flow tube maintained at high temperature, and further CO was then added. It was assumed, first, that the gas had reached their own equilibrium before the point of CO addition, so that equilibrium OH could be assumed, and, second, that mixing of the CO was complete in about 20 cm of the flow tube. Investigation of the reaction of the added CO with OH gave \( k_3 \approx 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) at 1250 1550 K. As the authors stress, the apparent activation energy is a small difference between large numbers involved \( 2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) and \( 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \). Other unpublished results from their laboratory would indicate a smaller \( k_{30} \). At the end points of their temperature range, \( k_{30} \approx 1.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) at 1250 1550 K. The authors have also measured the rate of conversion of \( \text{CO} \text{ and } \text{CO}_2 \text{ by gas chromatography.} \text{OH} \text{ was measured by absorption spectroscopy of the Q, 6 line in the 00 band of } \text{H}_2 \text{O} \text{ at } f = 10^{-10} \text{ mol} \text{ s}^{-1} \text{ (Arkelseth and Perry-Thorne [B3-3]) found } f \approx 1.2 \times 10^{-10} \text{ for } f_{\text{OH}} \). (N. B.) Bonne, Ulrich, Inst. Phys. Chem., Univ. Göttingen, private communication.

The flame structure of a \( \text{CO}+\text{O} \text{ flame} \) with a tracer of \( \text{H}_2 \) at 20 torr. CO and \( \text{CO}_2 \) were measured by gas chromatography. OH was measured by absorption spectroscopy of the Q, 6 line in the 00 band of \( \text{H}_2 \text{O} \text{ at } f = 10^{-10} \text{ mol} \text{ s}^{-1} \text{ (Arkelseth and Perry-Thorne [B3-3]).} \text{ OH was measured by ultraviolet absorption of } \text{OH} \text{ at emission of} \text{ J. Phys. Chem. Ref. Data, Vol. 1, No. 2, 1972} \)
CO\textsubscript{2} and the visible continuum chemiluminescence of CO + O. The data were reduced by comparing the experimental profiles with computer-generated profiles resulting from numerical integration of a complete mechanism. The authors report that \( k_3 \) is about twice the value calculated from the rate equation suggested in reference [1].


An electric discharge in water vapor was used as the OH source. This is now known to be an unsatisfactory source of OH for kinetic studies. See Section A2.1a. The high activation energy, 10 kcal/mol, reported in this paper is the source of the many erroneous values of \( \Delta E = 10 \) kcal/mol found in the early literature. The experimental technique is discussed in reference [14a], a review in English.


A mass-spectrometer stirred reactor study was used to obtain \( k = 5.6 \times 10^7 \) at 320 K, \( 1.3 \times 10^9 \) at 440 K, and \( 1.3 \times 10^{10} \) at 610 K in cm\(^3\) mol\(^{-1}\) s\(^{-1}\), a least-squares fit gave \( k = (3.5 \pm 1.1) \times 10^9 \) at 1000 K, \( 1.6 \times 10^8 \) at 1120 K, and \( 6.1 \times 10^7 \) at 1200 K. In the analysis \([\text{OH}]_0\) is assumed equal to \([\text{NO}]_0\) and \( k_2 \) is calculated from the reaction time (obtained from flow rates and reactor volume) and the conc. of water formed by the reaction (obtained from mass-spectrometric analysis). As discussed in Sections A3.1 and B1.1a, this will give \([\text{OH}]_0\) which is too high. In the data analysis used in this study this will cause \( k_2 \) to be low (as it indeed appears to be when compared to the other room temperature measurements).

B2.2b. Rate Calculations

[16] Mayer, S. W., Computed activation energies for bimolecular reactions of \( \text{O}_3, \text{N}_2, \text{NO}, \text{NO}_2, \text{CO}_2, \text{CO} \), and \( \text{CO}_3 \), J. Phys. Chem. 71, 4159 (1967).

The Johnston-Parr bond-energy method was modified to handle multivalent atoms and to account for spin repulsion. The calculated activation energy for Reaction 2 in kcal/mol was zero for ground state spin and one when the spin conservation postulates were applied.

B2.2c. Rate Evaluations


B2.2d. General References


[26] Westenberg, A. A., and De Haas, N., Atom-molecule kinetics using ESR detection, II. results for D + \( \text{H}_2 \rightarrow \text{H} + \text{H} \) and \( \text{H} + \text{D}_2 \rightarrow \text{HD} + \text{D} \), J. Chem. Phys. 47, 4 (1967).

[27] A value of \( k(\text{H} + \text{D}_2) = 4.9 \times 10^{13} \) exp \( -(9300/\text{RT}) \) cm\(^3\) mol\(^{-1}\) s\(^{-1}\) was obtained which gives \( k(\text{H} + \text{D}_2) = 2.6 \times 10^{11} \) at 900 K. This may be compared with the value of \( k = 4.2 \times 10^{11} \) used by Dixon-Lewis and Williams \([\text{B5-6a}]\) in calculating \( \text{H} \) and ultimately \( k_2 \) and \( k_5 \). Had they used the most recent value, their \( k_2 \) and \( k_5 \) would have been lower, although not by the full 4.2\%/26 ratio. To obtain \( k = 4.2 \times 10^{11} \) at 900 K, Dixon-Lewis and Williams \([\text{B6}a]\) used a value at 1000 K, due to Boato et al. \([\text{27}]\), and an activation energy from Van Meersche \([\text{28}]\).

[27] Boato, G., Careri, G., Cemino, A., Molenari, E., and Volpi, G. G., Homogeneous exchange reaction between hydrogen and deuterium, J. Chem. Phys. 24, 785 (1956). \( k(\text{H} + \text{D}_2) \) at 1000 K is given as \( 0.1 \times 10^{11} \) cm\(^3\) mol\(^{-1}\) s\(^{-1}\).


B3. \( k_2 \), Rate Constant for the Reaction, \( \text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H} \)

B3.1. General Discussion

This reaction has received much attention since it is important in the interpretation of the hydrogen-oxygen combustion system. The room temperature value of the rate constant is well established. Four measurements, in different laboratories by different techniques, all give very good agreement at higher temperatures the ratios of \( k_2 \) to other rate constants have been measured in studies of flame structure, explosion limits, shock waves, and other competitive rate experiments. There are, however, few direct measurements of \( k_3 \) at flame temperature.

As with most OH reactions there is better information on rate ratios than on direct determinations of individual rates. In this study, \( k_2 \) the rate constant for \( \text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H} \) has been established first. This value is then used with rate ratio data to establish other OH rate constants. Alternatively the rate for \( \text{H}_2 + \text{OH} \) could have been established first and used as a base. Reasons for preferring Reaction (2) are given in Section A.
The rate ratio data are shown in figure B3. The ratios at 300 K are not from competitive studies but were calculated from direct measurements of the two reactions. The room temperature data of Dixon-Lewis, Wilson, and Westenberg [2] rather than that of Greiner [4a] is used as the tie point on the graph because of the large scatter in Greiner’s room temperature measurements of $k_3$ and because of the low activation energy given by his OH measurements. In the higher temperature region, the points of Baldwin et al., and Dixon-Lewis et al. are considered most reliable. The suggested ratio line falls within the error limits of these measurements and splits the difference between the high point of Fenimore and Jones and the lower values of Ung and Back. Figure B4 shows the recommended rate constant as a function of temperature and a number of other measurements of $k_3$. The additional data do not seem adequate to change the value of $k_3$ originally recommended in reference [2].

Numerical data are summarized in table III and a value is recommended for $k_3$. The individual studies are discussed in the References and Comments Section.

B3.1b. Relation to Other Evaluations

The differences between this evaluation and earlier ones are due to the use of the new room temperature values, a more realistic appraisal of the rate ratio data, and the rejection of some data now known to be incorrect. A summary of some evaluations in current use is contained in table IIIA.

One of the more recent reviews of this reaction is that of Baulch, Drysdale, and Lloyd [24b]. Their recommended value of $k_3 = 2.19 \times 10^{12} \exp(-5150/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ is in close agreement with the value of $2.3 \times 10^{13} \exp(-5200/RT)$ recommended in this report. The agreement, however, is somewhat fortuitous due to differing treatments of rate ratios.

In an earlier review of $k_3$ by these authors [24a] the ratios of $k_3/k_2$ determined by Baldwin et al. [12a], Ung and Back [11], and Fenimore and Jones [7a] were used with a rate expression for $k_3$ suggested by Kaufman [3c] to obtain values for $k_3$ at several temperatures. These points were then used to establish the temperature dependence of $k_3$. In the later review of $k_1 + \cdot OH$ rate measurements Baulch, Drysdale, and Lloyd [24b] use their evaluation of $k_3$ and the $k_3/k_2$ ratios of Baldwin et al. [12] and Ung and Back [11] to provide points on the Arrhenius plot of $k_3$ which are used to establish an expression for $k_3$.

The resulting value $k_3 = 2.19 \times 10^{12} \exp(-5150/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ is inconsistent with Kaufman’s expression [3c] of $k_3 = 5.3 + 5 \times 10^{12} \exp(-5900 \pm 1000/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, which was used to calculate the points on which their value for $k_3$ is based.

B3.2. References and Comments. $H_1 + \cdot OH = H_2O + H$, Reaction 3

B3.2a. Determinations of $k_3$


The point from the work of Fenimore and Jones [7] is omitted, although their flame studies were the basis for the activation energy estimate for $k_3$.

The value of $k_3=2.0$ was first reported in Baldwin and Duran [27] and attributed to unpublished work of Baldwin and Duran. This estimate was later confirmed by Baldwin et al. [12a]. The original value was used in the evaluation of $k_3$ and a revised value, $k_3=(4.5)\times10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, in the evaluation of $k_3$.

The expression was based on Kaufman’s [3] room temperature value and a value at 1500 K calculated from an expression due to Fenimore and Jones [7].

FIGURE B4. Arrhenius plot of $k_3(H_3 + OH)$.


Greiner, reference [4a].

Greiner, reference [4b].

Dixon-Lewis, Sutton, and Williams, reference [6]. O is direct measurement with OH measured by absorption spectroscopy. $k_3$ is from reverse reaction.

$\circ$, Schott, reference [15]. $k_3$ from reference [28a] and $k_3$: $\circ$ upper bound for $k_3$.

Brown et al., reference [5].

Meyer, Schacter, and Johnson, reference [10].

$+$ Ung and Back, reference [11], $k_3$: $\times$ ratio used with upper limit of $k_3$. (this paper) poor upper bound; and Greiner’s reference [10], $k_3$: $\triangle$ lower bound.

$\bullet$, rate ratio data from Fenimore and Jones, reference [14]; Dixon-Lewis, Sutton, and Williams, reference [6c]; and Baldwin et al., reference [12], used with $k_3$ limits (this paper, see B2).

$\triangle$, Weng and Bulles, reference [9d].

Balakhin et al., reference [9e]. Recommended value.

The OH was generated by $H + NO \rightarrow NO + OH$. Qualitative electron spin resonance was used to determine the initial concentration and to follow the hydroxyl radical decay in a fast-flow system at $\sim 1$ torr. The data analysis is such that only relative measurements of OH concentrations are required, as would be expected since reaction 3 is first order in OH. References [2] [3], therefore, can be in agreement on $k_3$ but disagree on $k_3$ ($OH + H_2O \rightarrow OH + H_2O$), which requires absolute measurements of OH.


WM. E. WILSON, JR.

Table III. \( \text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H} \)

Equilibrium constant, \( K_{eq} = 0.211 \exp (7640/T), 1000-6000 \text{ K} \)

\[ \Delta H_{\text{mol}}^o/R = -7.56 \]

Rate constant, \( k = A T^B \exp (C/T) \text{ cm}^3 \text{ concentration units}^{-1} \text{ s}^{-1} \)

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>T range K</th>
<th>Ref.</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mol units</td>
<td>Particle units</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.2 ( \times 10^{11} )</td>
<td>3.65 ( \times 10^{-13} )</td>
<td>0.56</td>
<td>2,000</td>
<td>1000-4000</td>
<td>10 Calculation.</td>
</tr>
<tr>
<td>2.5 ( \times 10^{12} )</td>
<td>4.67 ( \times 10^{-13} )</td>
<td>0</td>
<td>1,960</td>
<td>300-500</td>
<td>4b Flash photolysis-kinetic spectroscopy.</td>
</tr>
<tr>
<td>2.5 ( \times 10^{12} )</td>
<td>2.5 ( \times 10^{-12} )</td>
<td>0</td>
<td>2,500</td>
<td>1000-1700</td>
<td>5 Flame.</td>
</tr>
<tr>
<td>4 ( \times 10^{12} )</td>
<td>4.2 ( \times 10^{-12} )</td>
<td>0</td>
<td>2,250</td>
<td>1285-1700</td>
<td>7 Flame.</td>
</tr>
<tr>
<td>4.2 ( \times 10^{12} )</td>
<td>7.0 ( \times 10^{-12} )</td>
<td>0.5</td>
<td>5,000</td>
<td>378-489</td>
<td>8 Shock tube, not reliable.</td>
</tr>
<tr>
<td>4.7 ( \times 10^{12} )</td>
<td>7.8 ( \times 10^{-12} )</td>
<td>0</td>
<td>2,100</td>
<td>300-500</td>
<td>9c Stirred reactor.</td>
</tr>
</tbody>
</table>

\( k \), mol units \( k \), particle units

| 3.9 \( \pm 0.2 \times 10^9 \) | 6.5 \( \pm 0.3 \times 10^{-15} \) | 300 | 2 Electron spin resonance. |
| 4.3 \( \pm 1.0 \times 10^9 \) | 7.2 \( \pm 1.0 \times 10^{-15} \) | 300 | 3 Absorption spectroscopy. |
| 4.0 \( \pm 0.2 \times 10^9 \) | 6.6 \( \pm 0.3 \times 10^{-15} \) | 301 | 4a Flash photolysis-kinetic spectroscopy. |
| 6.0 \( \pm 3.0 \times 10^9 \) | 10 \( \pm 5 \times 10^{-15} \) | 300 | 1 Electron spin resonance of H. |
| 1.1 \( \times 10^{10} \) | 1.8 \( \times 10^{-18} \) | 915 | 6 Flame, OH absorption spectroscopy. |
| 1.75 \( \times 10^{10} \) | 2.9 \( \times 10^{-12} \) | 1072 | 6 Flame, reverse. |
| 5.0 \( \pm 3.0 \times 10^9 \) | 8.3 \( \pm 5.0 \times 10^{-15} \) | 304 | 9c Stirred reactor with mass spectrometric analysis for H2O. |
| 3.6 \( \pm 0.4 \times 10^9 \) | 6.0 \( \pm 7 \times 10^{-16} \) | 403 | 9c analysis for H2O. |
| 6.5 \( \pm 3 \times 10^9 \) | 1.8 \( \pm 2 \times 10^{-12} \) | 504 | 9c |
| 9.6 \( \times 10^{10} \) | 1.6 \( \times 10^{-12} \) | 900 | 9c |
| 1.3 \( \times 10^{11} \) | 2.1 \( \times 10^{-12} \) | 943 | 9c Flame reactor-electron spin resonance analysis. |
| 1.6 \( \times 10^{11} \) | 2.6 \( \times 10^{-12} \) | 993 | 9c |
| 2.0 \( \times 10^{11} \) | 3.4 \( \times 10^{-12} \) | 1052 | 9c |

Rate ratio: \( k_3 (\text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H})/k_2(\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}) \)

<table>
<thead>
<tr>
<th>Rate ratio</th>
<th>( T ) K</th>
<th>Ref.</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.034 ( \pm 0.003 )</td>
<td>300</td>
<td>2 Direct studies.</td>
<td></td>
</tr>
<tr>
<td>0.045 ( \pm 0.006 )</td>
<td>301</td>
<td>4 Both ( k )'s.</td>
<td></td>
</tr>
<tr>
<td>0.429</td>
<td>473</td>
<td>11 H2O photolysis.</td>
<td></td>
</tr>
<tr>
<td>0.615</td>
<td>523</td>
<td>12 Explosion limits.</td>
<td></td>
</tr>
<tr>
<td>0.675</td>
<td>573</td>
<td>13 Flame, reverse.</td>
<td></td>
</tr>
<tr>
<td>1.221</td>
<td>623</td>
<td>14 Flame.</td>
<td></td>
</tr>
<tr>
<td>4.5 ( \pm 0.5 )</td>
<td>773</td>
<td>14 Flame, reverse.</td>
<td></td>
</tr>
<tr>
<td>8.4</td>
<td>1072</td>
<td>15 Flame, reverse.</td>
<td></td>
</tr>
<tr>
<td>7-9</td>
<td>1000-1200</td>
<td>14b Flame.</td>
<td></td>
</tr>
<tr>
<td>12.5</td>
<td>1200-1350</td>
<td>14a &amp; c Flame, reverse.</td>
<td></td>
</tr>
<tr>
<td>22.3</td>
<td>1200-1350</td>
<td>14a &amp; c Flame, calculation of reference 2, reverse.</td>
<td></td>
</tr>
</tbody>
</table>

Recommended Values

300-2000 K

Rate ratio, \( k_3/k_2 \)

<table>
<thead>
<tr>
<th>( k_3/k_2 = 73 \exp 2300/T )</th>
<th>( \log k_3/k_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \pm 0.3 )</td>
<td></td>
</tr>
</tbody>
</table>

\( k_3 \), rate constant for the Reaction \( \text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H}^* \)

<table>
<thead>
<tr>
<th>Units</th>
<th>Rate expression</th>
<th>( k_3 ) at 1000 K</th>
<th>Error limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1} )</td>
<td>( k_3 = 2.3 \times 10^{-10} \exp (-2600/T)^{***} )</td>
<td>( 1.7 \times 10^{-12} )</td>
<td>( \log k_3 \pm 0.3 )</td>
</tr>
<tr>
<td>( \text{cm}^3 \text{ particles}^{-1} \text{ s}^{-1} )</td>
<td>( k_3 = 3.8 \times 10^{-11} \exp (-2600/T)^{**} )</td>
<td>( 2.8 \times 10^{-12} )</td>
<td></td>
</tr>
</tbody>
</table>

*The recommended value for \( k_3 \) is determined from the value for \( k_3/k_2 \) recommended above and the value for \( k_2 \) recommended in Section B2.

**Using \( k_2 = 5.1 \times 10^{-13} \exp (-300/T) \).

***Using \( k_3 = 3.1 \times 10^{11} \exp (-300/T) \).
HYDROXYL RADICAL REACTION KINETICS

Table IIIA. Evaluations of the rate of hydrogen with hydroxyl

| A     | B   | C   | D   | E   | F   | G   | H   | I   | J   | K   | L   | M   | N   | O   | P   | Q   | R   | S   | T   | U   | V   | W   | X   | Y   | Z   | aa  |
|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| H₂ + OH → H₂O + H     | H₂O + H → H₂ + OH     | k₃ | Temp. range, K | Reference |
| A     | B   | C   | D   | E   | F   | G   | H   | I   | J   | K   | L   | M   | N   | O   | P   | Q   | R   | S   | T   | U   | V   | W   | X   | Y   | Z   | aa  |
| 10.4±0.3 | 10.4±0.14 | 10.20 | 10.4±0.5 | 10.45 | 9.98 | 12.0 | +0.5 | 2.5 | 12.32 | 0.7 | 9.1 | 300–1500 | This work. |
| 10.2±0.25 | 10.40 | 300–2000 | Schofield [19]. |
| 10.4±0.3 | 10.42 | 300–2000 | Jensen & Kurzus [21]. |
| 10.4±0.3 | 9.42 | 300–2000 | Bascombe [18]. |

\[ k = 10^4 T^p \exp \left( -\frac{C(1000\text{~T})}{10^3} \right) \text{ cm}^3 \text{ molecule}^{-1} \cdot s^{-1} \text{ units.} \]

The OH was generated by H + NO₂ → NO + OH. Absorption spectroscopy was used to determine the initial concentration and to monitor OH decay in a fast system. In the experiments H₂ + OH and OH + OH are competitive. The first three papers describe the experimental work. The value is quoted from the last. In [34] the authors fit an Arrhenius expression to their room temperature value for k₃ and a value for k₃ at 1500 K calculated from an expression due to Fennimore and Jones [7]. The reaction is treated as second order and wall and three-body reactions were not significant.

The OH was generated by flash photolysis of H₂O and the decay followed by kinetic spectroscopy (absorption) in a static system over a pressure range of 20 to 200 torr. Because of the short time of reaction (< 200 × 10^-6 s) and the large ratio of reactant to OH the reaction could be treated as second order and wall and three-body reactions were not significant.

The flash photolysis–kinetic spectroscopy technique (FP-KS) was extended to higher temperatures. The H₂ (except for the one at 305 K) form a very good straight line when log k is plotted versus 1/T (fig. B4). The ratio k₂/k₃ was formed using the individual equations determined by a least squares fit of the k₂ and k₃ data points (fig. B3). The k₂/k₃ ratios determined by Ung and Back [11] fall very nicely on an extension of the calculated ratio. Both the Ung and Back [11] and the Cremer measurements, made in systems in which OH is generated by photolysis of H₂O vapor, give activation energies for k₂ and k₃/k₄ which are lower than those extracted from flame and shock tube studies. Since the FP-KS rates are determined by a simple pseudo first-order treatment of OH decay, and in the absence of H, the OH decay is small, it is difficult to conceive of any competing reactions which would reduce the rate of OH decay. In addition the FP-KS rates at room temperature are in very good agreement with flow tube measurements at that temperature. In the FP-KS technique a given mixture is flashed eight times to obtain sufficient OH absorption and background intensity. It is possible that some H₂O or O₃ could be formed and be photolysed or OH by reaction with H. The H₂O might interfere by the reaction H + H₂O → OH. Another possible argument is that H₂O is present in the high temperature systems and reacts with OH, leading to an erroneously high reaction rate. These measurements were not used in the following arguement. However, this anomaly between FP-KS using water vapor and other measurements must be resolved before the reliability of k₃ can be considered well established. (See Sec. D.)

The data reported for k₃ in cm⁻³ molecule⁻¹ · s⁻¹ units are: average of 8 measurements at 300 K = 4.75 ± 0.23 × 10¹⁰; 332 K = 8.57 ± 1.42 × 10¹⁰; 358 K = 1.40 ± 0.03 × 10¹¹; 373 K = 3.40 ± 0.09 × 10¹²; average of 5 measurements at 495 K = 6.89 ± 0.32 × 10³ cm⁻³ molecule⁻¹ · s⁻¹.


A set of kinetic coefficients are presented which satisfactorily characterize several low-pressure CO + O₃ flames, some with added CO and H₂. The flame equations, consisting of the species continuity equations and the multicomponent diffusion equations, were integrated over the 1000 to 1700 K range. The experimental temperature and OH profiles (measured by absorption spectroscopy, Kaskan’s technique) [29] were used in the analysis. The calculated species profiles gave adequate agreement with the experimental profiles for the major stable species. k₃ was reported to be 1.5 ± 0.10⁷ exp (−5000/RT) cm⁻³ molecule⁻¹ · s⁻¹. The experimental value of OH, used in the data analysis, increases the reliability of this measurement. However, it is always possible that other sets of rate constants could be chosen that would also reproduce the species profiles.


These papers report studies of the structure of a flat H₂ – N₂ – O₂ flame with a final temperature of 1072 K at atmospheric pressure. Measurements were obtained for k₃, k₃(3D₂O), and k₃(3H₂O).k₃. The ratio rate is discussed in reference [13]. k₃. Assuming k₄ = k₅, the authors fit an Arrhenius expression to the data and determined k₅ = 1.1 ± 10⁻¹⁰ cm⁻³ molecule⁻¹ · s⁻¹ at 915 K. The measurement of [OH] was made using absorption spectroscopy. The technique and a value of k₅ [29] were used in the broad 0.0 band at 306.4 nm in the flame of the narrow emission line from a cooled water discharge lamp. k₅ was determined to be 12.3 ± 10⁻¹⁰ based on the yield of [OH] (100 ± 10 kcal). A correction factor of 1.34 is introduced in revising M₅₆₆₃ to 9.3 kcal in agreement with the JANAF tables. This gives f₅₆₆₃ = 9.2 ± 10⁻¹⁰. Golden, Del Greco, and Kaufman [30] obtained f₅₆₆₃ = 7.1 ± 10⁻¹⁰ using a chemical method to establish the hydroxyl concentration. It is possible that they overestimated [OH] by a factor of 2 (see Sec. A2.2a). This would lead to a value of 14 ± 10⁻¹⁰ in agreement with the recent determination of Ankettell and Perry-Thorne [31] of 14.8 ± 13 ± 10⁻¹⁰. An uncertainty of log ± 0.2 is therefore introduced to account for the f₅₆₆₃ uncertainty with the lower value of 8 being considered more likely.

k₃. This rate measurement requires an absolute value of [H]. The D₂O trace technique was used to give relative values of [H] in the burned gas portion of the flame and Na chemiluminescence to give a relative value in the central portion of the flame. An absolute value of [H] was obtained in the early part of the flame by addition of D₂ and measurement of (d[H]/dτ) chem. Since the measurement regions overlap this absolute value of [H] could be used to scale the others. A measurement of (d[D₂O]/dτ) chem with the [H] gave k₃(3D₂O). D₃O. In [6b] a revised value of [H] was obtained to join k₃(3H₂O) = 3.6 ± 10⁻¹⁰ cm⁻³ molecule⁻¹ · s⁻¹ at 1072 K. Due to uncertainties in equilibration conditions, upon which [H] depends, the authors state [6b] that "this may be an upper limit." The [H] also depends on the value of k₃ = (H + Dcket - H + D₂k₃) used. Recent studies of this reaction [22-26] indicate that the k₃ used by Dixon-Lewis et al. may be high by a factor of two. This would give a low [H] concentration resulting in k₃(3H₂O) and k₃ being high by something less than a factor of two.

To obtain a value of k₃(3H₂O), it is necessary to make some
assumptions about the ratio \( k_3 \cdot (H+H_2O) \cdot k_3 \cdot (H+D_2O) \). In reference [2] a value of 1.64 was obtained by assuming \( k_3 \cdot (H_2O) \) to be larger than \( k_3 \cdot (H_2O) \) by a factor determined by the zero point energy difference between single \( OH \) and \( OD \) bonds (≈ 1.3 kcal mol\(^{-1}\)).

Using the equilibrium constant this yields \( k_a = 1.75 \times 10^{22} \) cm\(^3\) mol\(^{-1}\) s\(^{-1}\). In the graph this has been given an uncertainty range of a factor of two lower to account for errors in isotope effect and [H].


[7b] Fenimore, C. P., and Jones, G. W., Rate of Reaction, \( n \cdot H \rightarrow OH \cdot H \), in flames, J. Phys. Chem. 65, 993 (1961).

Potentially this work would provide a measurement of the rate that is independent of rates of other hydroxyl radical reactions. \( D_2O \) was added to rich \( H_2 \) and \( H_2 + CO \) flames and \( (d \cdot HD/d)_{\text{sum}} \) and \( (d \cdot H_2D/d)_{\text{sum}} \) was determined. The temperature range was 1285 K to 1500 K in \( H_2 \) flames and 1345 K to 1850 K in hydrocarbon flames. The Avramenko and Lorentso [9] value for \( k_a \) and the equilibrium constant were used to obtain \( k_a \). This value was then increased by a factor of two and used to determine [H]. (All isotope ratios were assumed to be the same.) The [H] found was said to be consistent with that of Bulewicz, James, and Sugden [25] measured by a different method at a higher temperature. The consistency was based on log [H]/(H) being linear with 1/2T for both sets of flames.

Considering the number and extent of assumptions made and that Avramenko and Lorentso’s value is low by 100 to 1000 in the temperature in which they measured it, the agreement between the [H] of Bulewicz et al., and that reported here is more accidental than meaningful.

The rate \( (d \cdot D_2O/d)_{\text{sum}} \) was also measured in rich hydrocarbon flames. A value of \( k_a \cdot (H+D_2O) \) = 10\(^{22}\) used earlier gave [H] equal to the equilibrium constant. This is better evidence for \( k_a \) but still can hardly be considered to be of better order of magnitude accuracy.

In the second paper, the rate equation \( k = 2.5 \times 10^{12} \) exp \((-10000/T) \) was stated for these experiments. This retains the Avramenko and Lorentso temperature dependence. Kaufman [3c] used his room temperature value and a value for 1500 K calculated from this equation to give \( k = 10^{10} \) exp \((-2930/5000) \). This value has been widely quoted in the literature, usually without the large uncertainty given by Kaufman.


[8b] Gardiner, W. C., Jr., University of Texas, Austin, Texas, Personal Communication.

Induction time measurements on the \( H_2O_2 \) reaction (9400 K) were interpreted in terms of hydrogen and oxygen dissociation, \( k_1 \cdot (H+O) \), \( k_2 \cdot (O+H) \), and \( k_3 \). Trial rate expressions were used to calculate induction times. These rate expressions were then adjusted to give improved agreement with the experimental measurements. However, the results suggested that the behavior of the system was not very sensitive to \( k_3 \). More recent work [8b, 15] indicates that the data are sensitive, not to \( k_3 \), but to the product \( k_3 \cdot (O+H) \). The equation given in this reference, \( k_3 \cdot 10^{-10} \times \frac{1}{(7000/T)} \times 10^{-4} \times 10^{-3} \), is therefore not considered reliable. Although this rate expression is in reasonable agreement with the suggested value, it may not be used in support of a suggested value.


An electric discharge in water vapor was used as the OH source. This is now known to be an unsatisfactory source of OH for kinetic studies. See Section A3.1 and B1.1a, this can give [OH] which is too high. In the data analysis used in this study, this would cause \( k_a \) to be low. This apparently was the case in a similar measurement of \( k_3 \cdot (CO+OH) \) [B2-15]. The measured \( k_3 \) values, however, are in good agreement with the recommended rate expression. Since a much greater quantity of \( H_2 \) is required than of \( CO \), it is possible that the disproportionation reaction would be less important in the measurement of \( k_3 \) and that \( k_3 \cdot (CO+OH) \) is determined from the amount of water formed rather than from the rate of decay of OH, any loss of OH on the walls would cause the measured \( k_3 \) to be low. This is evidence that there is no significant wall recombination of OH on the walls of the apparatus [B1-10]. (The Pyrex reactor and tubing were coated with \( H_2PO_4 \).)


Values of \( k_a \cdot 10^{-3} \), \( 5.5, \) and \( 6.0 \times 10^{-3} \) cm\(^3\) mol\(^{-1}\) s\(^{-1}\) at 913, 823, and 843 K were obtained from a study of the ignition limits of the \( H_2O_2 \) reaction. These rates are almost an order of magnitude lower than the recommended value.


Quantitative ESR was used to follow the concentration of \( H_2O \) and \( OH \) as a function of flow rate in a flame type reactor at 2.86 torr for a \( H_2O \cdot H_2 \) mixture ratio of 1:1. Water concentration was measured by freeze-out techniques. Values obtained were \( k_a \cdot 10^{-2} \), 3.3, 4.3, and \( 5.7 \times 10^{-2} \) cm\(^3\) mol\(^{-1}\) s\(^{-1}\) at 900, 943, 1063, and 1522 K. The Arrhenius expression obtained, \( k_a \cdot (b-3) \times 10^{10} \exp [(8600+1200)/RT] \), gives too high an activation energy but the experimental points are in good agreement with the recommended value.

B3.2b. Rate Calculations


Equation fits calculated rates from 1000 to 4000 K. This equation agrees well, within a factor of 2, with the suggested value of 300 to 2500 K.

B3.2c. Rate Ratio Determinations


The OH was generated by photolysis of water, \( CO \) was formed when \( CO \) was present. The rate ratio, \( k_4/k_2 \), was determined from the decrease in \( CO_2 \) when \( H_2O \) was added to a slowly reacting \( CO \) flame. Evidently the three-body recombination to form \( H_2O \) was sufficiently fast to interfere at lower temperatures.


The \( k_4/k_2 \) ratio was used, 4.5 ± 0.5, is based on a recent computer examination and is a revision of the 3.0 ratio reported in [12a]. The ratio was obtained by measuring the relative yields of \( CO \) and \( H_2O \) when \( CO \) added to a slowly reacting \( H_2O_2 \) mixture at 773 K. The \( [H_2O]/[CO] \) ratio was determined over a range of mixture ratio, pressure, and concentration of added \( CO \). An analysis of this reaction system, involving 10 reactions including those of \( H_2O \) and \( CO_2 \), led to the following conclusions:

1. Neither \( CO + O \) or \( CO + O + M \) produce appreciably \( CO \).
2. \( CO + OH \) and \( CO + H_2 \) contribute roughly equally to the production of \( CO_2 \).
3. The ratio \( k_4 \cdot (H+OH)/k_2 \cdot (CO+OH) \) = 4.5 ± 0.5.

Particularly important aspect of this work is the indication that \( CO + H_2 \) is an important source of \( CO \) during slow \( H_2 \rightarrow \) mixture at 773 K.


The addition of both \( DO \) and \( CO_2 \) to a flat \( H_2 \) - \( N_2 \) - \( O_2 \) flame with a final temperature of 1072 K at atmospheric pressure made

possible the measurement of the ratio, $k_5/(H+D_2)/k_5(H+O_2) = 4.3 \pm 0.5$. Assuming $k_{32}(H+H_2O)/k_{32}(H+O_2) = 1.84$ (as in ref. [6]), $k_{32}(H+H_2O)/k_{32}(H+O_2) = 7.9 \pm 1$ and using the equilibrium constant of the water gas reaction, $CO_2 + H_2 = CO + H_2O$, $k_D/k_O = 8.4 \pm 1$ at 1072 K.


In Reference [14a] results are presented from a study in which the concentration of CO and H are measured as they decay toward the water-gas equilibrium in the post-flame gases from rich $H_2/O_2$ flames containing added CO$_2$, [CO], [CO$_2$], [H$_2$], and [H$_2$O] were measured. If $H$ is known then $k_{32}(H+O_2)$ can be determined. In this study $H$ was estimated from the rate of formation of HD produced by the reaction of H with added D$_2$. The direct experimental result then is really a measurement of $k_{32}/k_{32}(H+D_2)$. In Reference [14b] the expression $k_{32}/k_{32}(H+D_2)$ is given for the results of [14a].

Reference [14b] also reports a study of the relative rates of disappearance of $H_2$ and CO in a $H_2/O_2/Ar$ flame which gives 7-9 for $k_{5}(k_{5}(k_{5}(H_2))$ in the 1200 to 1200 K region.

In [14c] the results of [14a] are given as $k_{5}(H_2) = 0.00$ at 1200 to 1350 K. This gives 12.5 for $k_{5}(H_2)$. Fenimore and Jones assume no change in rates due to isotopic substitution.

In reference [2] the $k_{32}/k_{32}(H+O_2)$ ratio given in reference [14b] is used in a calculation of $k_{5}(H_2)/k_{5}$ by making corrections for changes in rate due to isotopic substitution.


The spatially integrated radiation emitted by the CO + O recombination in reflected shock waves was measured in $H_2-O_2- CO-Ar$ mixtures covering the range 10.0 < $T_0$ < 1.0 and 1000 < $T_0$ < 2500 K. For the induction region the intensity grows exponentially, $I(t) \sim I_0 \exp(\alpha t)$, and values of $\alpha$ are obtained whose dependence on $[H_2], [O_2]$ and $T$ determined. $k_1(H + O_2)$ and the product $k_1(O + H_2)$ both results indicate that the values of $k_1(O + H_2)$ and $k_1(O + H_2)$ are comparable (factor of 3) within the range studied and suggest upper and lower limits for $k_2$. The authors give $k_2(O + H_2)/k_2(H + O_2)$ = 1.6 $10^{17}$ (2.0 $10^{19}$) $[1/(T - 1000)/R]^{3/2}$ mol$^{-3/2}$ cm$^{-2}$ s$^{-2}$ and $k_2(O + H_2)/k_2(H + O_2)$ = (2.16 $10^{17}$) $10^{25}$ exp$^{-14.8 \pm 0.7}$ $[1/(T - 1000)/R]^{3/2}$ mol$^{-3/2}$ cm$^{-2}$ s$^{-2}$.

More recent work by Schott [15b] in which $\alpha$ was determined by thermal IR emission from $H_2O$ formed by reaction 3 gave lower values $\alpha$ resulting in a value of $k_1(O + H_2)$ only 1/4 that determined from the CO + O continuum. The lower bound on the graph has accordingly been shown with this factor of four uncertainty. A value of $k_2$ has been obtained using I/4 the authors $k_2(O + H_2)k_2$ and a value of $k_2(O + H_2)$ from Westenberg and DeHaas [28].

B3.2.d Rate Evaluations


They used a value of $k_1 = 1.48 \times 10^{14}$ exp$^{-63400/RT}$ cm$^{-3}$ mol$^{-1}$ s$^{-1}$ derived from references [3, 7, and 9].


B3.2e. General References


measurements of the temperature dependence of $k_i$ and $k_2$ is shown [4b]. The room temperature points [4a, 5, B2–1], the ratio due to Baldwin et al. [7], and the average of the flame data [8, 9, 10, 11] form a very nice straight line. This line is chosen as the suggested value for the rate ratio. The direct measurement of Dixon-Lewis and Williams [6], combined with the value of $k_3$ suggested in this report, gives a rate ratio which is in good agreement with the suggested value.

The recommended value for $k_4$ is shown in figure B6 with several data items not used in obtaining the rate ratio, $k_4/k_2$. In the high temperature region Mayer's calculated value [16] and Fristrom's compilation [2] are shown. In the low temperature region the measurements of Greiner [4], Horne and Norrish [1], and Wilson and Westenberg [5] are shown. The shaded area is fixed by the error limits of $k_4/k_2$ over the range in which it has been measured and the error limits of $k_2$.

As can be seen there is an appreciable uncertainty over the entire temperature range with no information between 500 and 775 K or above 2000 K. The range of values in the flame temperature region is not unreasonable considering the required assumptions and the experimental difficulties. The divergence of Greiner's values [4b] from those of Horne and Norrish [1] and the interpolation between flame temperature and room temperature is a more serious problem. However, until the role of HO$_2$ is more clearly understood and additional experimental measurements of $k_4$ become available, the suggested value, with the relatively large uncertainties given, would appear to be adequate.

Numerical data are summarized in table IV and a suggested value for $k_4$ is given. The individual studies are discussed in the References and Comments section.

**B4.1b. Other Evaluations**

Schofield [17] has also presented an analysis of this reaction. His value $k = 1.2 \times 10^{-10}$ exp (–29800/T) cm$^3$ molecules$^{-1}$ s$^{-1}$, is a least squares fit to the data of references [2, 5, 6, 9, 11, 12, and 14]. Only the data from references [5 and 6] may be considered valid. References [12 and 14] may be rejected because of interference from HO$_2$. References [2, 9, and 11] are actually measurements of the ratio $k_4/k_2$. The values of $k_4$ given in the original papers were based on values of $k_2$ now known to be incorrect.

Most of the data in the intermediate temperature range are appreciably lower than the suggested value. These measurements were all made in systems in which HO$_2$ is likely to have been present and are, therefore, considered unreliable. The reasons for this have been discussed previously in Section A2.1c.

It is difficult to find serious fault with Greiner's measurements [4]. However, the ratios measured in flames are 3 to 6 times higher than those obtained by extrapolation of his rate equations.
HYDROXYL RADICAL REACTION KINETICS

TABLE IV. CH₄ + OH \rightarrow CH₃ + H₂O

<table>
<thead>
<tr>
<th>A Mol units</th>
<th>A Particle units</th>
<th>B</th>
<th>C</th>
<th>T range K</th>
<th>Ref.</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1 \times 10^{10}</td>
<td>1.83 \times 10^{-14}</td>
<td>0.675</td>
<td>1.100</td>
<td>1000–5000</td>
<td>16</td>
<td>Calculation.</td>
</tr>
<tr>
<td>1.1 \times 10^{13}</td>
<td>1.8 \times 10^{-13}</td>
<td>0</td>
<td>3.270</td>
<td>1350–1850</td>
<td>2</td>
<td>Flame.</td>
</tr>
<tr>
<td>2.4 \times 10^{14}</td>
<td>4.0 \times 10^{-13}</td>
<td>0</td>
<td>4.250</td>
<td>400–600</td>
<td>3</td>
<td>NR*.</td>
</tr>
<tr>
<td>1.8 \times 10^{14}</td>
<td>3.0 \times 10^{-12}</td>
<td>0</td>
<td>1.725</td>
<td>300–500</td>
<td>4b</td>
<td>FP-KS**, NR*.</td>
</tr>
<tr>
<td>4.9 \times 10^{13}</td>
<td>8.2 \times 10^{-11}</td>
<td>0</td>
<td>2.500</td>
<td>300–425</td>
<td>1</td>
<td>FP-KS**.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>k, mol units</th>
<th>k, particle units</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.33 \pm 0.21 \times 10^{9}</td>
<td>8.8 \pm 0.3 \times 10^{-15}</td>
</tr>
<tr>
<td>6.5 \pm 1.5 \times 10^{10}</td>
<td>10.8 \pm 2.5 \times 10^{-15}</td>
</tr>
<tr>
<td>2 to 4 \times 10^{11}</td>
<td>3.3 to 6.6 \times 10^{-12}</td>
</tr>
<tr>
<td>3.0 \pm 0.6 at 773 K</td>
<td>Slow reaction.</td>
</tr>
<tr>
<td>1/4 at 1746, 24 at 1892 K</td>
<td>Flame.</td>
</tr>
<tr>
<td>38 at 1709, 27 at 1743, 33 at 1797 K</td>
<td>Flame.</td>
</tr>
<tr>
<td>15.2 exp (650/T) at 1500–1800 K</td>
<td>Flame.</td>
</tr>
<tr>
<td>1.8 \pm 0.9 at 773 K</td>
<td>Flame.</td>
</tr>
<tr>
<td>2.1 at 1763 K, 1.5 at 723 K</td>
<td>NR*.</td>
</tr>
<tr>
<td>0.83 at 673 K, 1.10 at 723 K, 2.1 at 798 K</td>
<td>Combustion</td>
</tr>
<tr>
<td>2.7 at 873 K, 3.4 at 923 K</td>
<td>Decomposition.</td>
</tr>
<tr>
<td>2 to 5 at 1200 K</td>
<td>Flame.</td>
</tr>
<tr>
<td>14 exp (1600/T) at 300–500 K</td>
<td>Flame.</td>
</tr>
</tbody>
</table>

Ratio, k₁(CH₄ + OH \rightarrow CH₃ + H₂O)/k₂(CO + OH \rightarrow CO₂ + H)

<table>
<thead>
<tr>
<th>k₁, mol units</th>
<th>k₂, particle units</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0 \pm 0.6 at 773 K</td>
<td>8.8 \pm 0.3 \times 10^{-15}</td>
</tr>
<tr>
<td>20–25 at 1750–2000 K</td>
<td>10.8 \pm 2.5 \times 10^{-15}</td>
</tr>
<tr>
<td>1/4 at 1746, 24 at 1892 K</td>
<td>3.3 to 6.6 \times 10^{-12}</td>
</tr>
</tbody>
</table>

Recommended Values

300–2000 K

<table>
<thead>
<tr>
<th>Rate Ratio, k₁/k₂</th>
<th>Error limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>k₁/k₂ = 92 exp (2200/T)</td>
<td>log k₁/k₂ ± 0.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Units</th>
<th>Rate expression</th>
<th>k₁ at 1000 K</th>
<th>Error limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>cm³ mol⁻¹ s⁻¹</td>
<td>k₁ = 2.85 \times 10^{14} exp (−2,500/T)***</td>
<td>2.34 \times 10^{14}</td>
<td>3.86 \times 10⁻¹</td>
</tr>
<tr>
<td>cm³ particles⁻¹ s⁻¹</td>
<td>k₁ = 4.7 \times 10^{11} exp (−2,500/T)**</td>
<td>3.96 \times 10^{14}</td>
<td>2.12 \times 10⁻¹</td>
</tr>
</tbody>
</table>

* The recommended value for k₁ is determined from the value for the ratio k₁/k₂ recommended above, and the value for k₁ recommended in Section B2.

** Using k₂ = 5.1 \times 10⁻¹³ exp (−300/T).
*** Using k₂ = 3.1 \times 10⁻¹³ exp (−300/T).

Therefore, pending further clarification of the water vapor photolysis technique, these measurements will not be used in determining the suggested value for k₁/k₂. (See discussion in Section A2.1d.)

B4.2. References and Comments CH₄ + OH \rightarrow CH₃ + H₂O Reaction 4

B4.2a. Direct Determinations of k₁

[1] Horne, D. G., and Norrish, R. G. W., Rate of H-abstraction by OH from hydrocarbons, Nature 215, 1373 (1967). Hydroxyl radicals were generated by the flash photolysis of water vapor and the OH decay followed by absorption spectroscopy for time periods of about one ms. The reaction mixture contained 8 torr H₂O and 300 torr Ar. In the absence of CH₄ the OH decay was second order. The addition of < 1 torr CH₄ led to a greatly increased, almost first order, OH decay. When d [OH] / dt is plotted against [OH], the gradient yields the second order rate constant and the intercept the first order rate constant. In this treatment the second order rate constant, measured separately at each temperature, was used to fix the gradient thus reducing the error in determining the intercept. Therefore, it was not necessary to measure the absolute OH concentration. k₁ was reported to be log₁₀k₁ = 13.7–5,000/2,303 RT cm³ mol⁻¹ s⁻¹ in the temperature range 300 to 425 K. Due to a very limited
number of experiments, the authors call this an "approximate estimate." Although there is some uncertainty in the absolute value, the temperature dependence should be more reliable. It seems likely that reaction (4) is followed immediately by 

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

The products, probably formaldehyde, would be relatively inert on the time scale over which OH decay was measured. The actual rate of OH decay observed then would be twice that due to Reaction (4). The authors' rate equation (for use in table and graph) has therefore been reduced by a factor of two bringing their value at 300° into excellent agreement with that of refs. [4a, 4b, and 5]. The activation energy, however, is appreciably higher than that determined by Greiner in a similar system in flames with only 1 torr of water vapor [4h].


A least squares fit of the data from several flame studies gave 

\[
\log k_2 = 14.15 - 1.37 \times 10^2 \times T/17 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}.
\]

This is based on the experimental determination of \(k_2/k_0\) and the use of a value of \(k_0\) now known to be incorrect. An experimental measurement of [OH] by absorption spectroscopy was reported for a flame similar to one of the flames studied. The value of [OH] does not change much in the temperature range studied. The author's rate equation has, therefore, been multiplied by 0.8 to account for the difference between the experimental value of [OH] and that calculated from the value of \(k_2\) used in the paper.


This article gives a review of the Russian work in which \(k_2\) is generated by an electric discharge in water vapor and the decay of [OH] in a flow tube is measured by absorption spectroscopy. The article cites L. I. Avramenko, Ph.D. Thesis, Moscow, 1963, as the source for \(k_2 = 7 \times 10^{-14} \text{ exp}(-8300/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}\).

It is now known that an electric discharge is not a satisfactory source of OH in kinetic studies. OH is believed to be generated along the flow tube by reactions involving HO₂. The problems inherent in this technique of generating OH are discussed in Section A2.1b. This measurement was for years the only value at a temperature lower than those in flames and is largely responsible for the many erroneous rate equations found in the literature with activation energies of 6 to 10 kcal. This value should no longer be considered reliable and was not used in obtaining the suggested value of the rate equation.


The OH was generated by flash photolysis of H₂O and the decay was followed by kinetic spectroscopy in a static system over a pressure range of 20 to 200 torr. Because of the short time of reaction (<300×10⁻⁶ s) and the large rate of reaction to OH the reaction could be treated as first order in OH and wall reactions would not be significant.


The flash photolysis-kinetic spectroscopy technique was used to measure the rate of \(k_2\) over the 300 to 500° K range. Values of \(k_2\) at various temperatures were 290 K, 5.51 ± 0.51 × 10⁻¹²; 533 K, 9.25 ± 0.35 × 10⁻¹¹; 730 K, 2.12 ± 0.04 × 10⁻¹⁰; 424 K, 3.68 ± 0.14 × 10⁻¹⁰; and 495 K, 7.18 ± 0.16 × 10⁻¹⁰. The rate expression \(k_2 = 3.31 \times 10^{-19} \exp(-3752/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}\) was obtained. The ratio \(k_2/k_0\) was obtained from this rate equation and the rate equation obtained by Greiner for \(k_0\). Although the room temperature value is in good agreement with those of Wilson and Wooten (5) and of Horne and Norrish (1), the activation energy is lower that of Horne and Norrish. The extrapolated value at flame temperature is almost an order of magnitude lower than that obtained in flame studies. As shown on the \(k_2/k_0\) ratio graph (Fig. 86), Greiner's values are lower, both in magnitude and temperature dependence, than the recommended value. The extrapolated value, however, is in fair agreement with the set of points determined in systems in which HO₂ is thought to be responsible for the low values. In Greiner's system, the same gas mixture is exposed to eight flashes in order to obtain adequate light for the photographic plate. Measurements of OH decay are made of a single flash. The extent of reaction in this case is not sufficient to change the concentration of the stable reactant. However, if any H₂O₃ or O₂ were to form from OH decay the reaction rate H to form first NO and subsequently OH would lead to an understimation of the OH decay rate. If the activation energy for this process were positive, a lower activation energy would also be observed. Greiner's points were not considered in determining the suggested value because of the extremely low extrapolated value at flame temperature and because of their agreement with measurements in systems known to be complicated by HO₂. However, it should be noted that Greiner's work provides the most straightforward measurement now available of OH rates over a temperature range. Until the anomaly between his measurements and the experimental results are resolved there will remain an uncertainty about OH rates.


The OH was generated by H + NO₂ → NO + OH. Quantitative electron spin resonance was used to determine the initial concentration and to follow the hydroxyl decay in a fast time system at ~1 torr pressure. The large error limits give the the limits set by several possible reaction mechanisms involving OH reactions subsequent to the initial reaction.


The methane concentration [CH₄] and chemical reaction rate of (CH₄)/dt (chem) were measured in a fuel-rich CH₃OH/N₂ flame at atmospheric pressure. The maximum flame temperature was 1528 K, burning velocity was 5.2 ± 0.2 cm s⁻¹, and the composition was 5.03 percent CH₄, 19.94 percent O₂, and 75.03 percent N₂. The hydroxyl radical concentration was measured by absorption spectroscopy (maximum was 2.4 × 10⁻¹⁸ mol cm⁻³). \(k_2\) was calculated from 

\[
d(\text{CH}_4)/dt\text{(chem)} = k_2\text{[CH}_4][\text{OH}]\]

This measurement assumes that the only CH₄ reaction is with OH. Reaction with H may be neglected because the H concentration will be very low in the fuel-rich flame and the reaction rate is low. In this flame the [OH] would be approximately \(5\%\) of the [OH] and the rate for O + CH₄ is only \(1\%\) of that measured for \(k_2\) in the flame. No consideration was given to possible reactions with HO₂. A value of \(k_2 = 3.1 ± 10^{-12} \text{ cm}^{-3} \text{ mol}^{-1} \text{ s}^{-1}\) at 1285 K was reported.

B4.2b. Rate Ratio Determinations


Small quantities of CH₄ (ca. 1%) were added to slowly reacting mixtures of H₂ + O₂ in N₂, aged boric-acid-coated vessels at 773 K. The pressure change was used to measure the amount of H₂ oxidized. The amount of CH₄ consumed was determined by catalytic conversion of H₂O and CO to CO₂ and subsequent measurement of CO₂. By examining the variation of the relative rates of consumption of CH₄ and H₂ with mixture composition and total pressure, a value for the ratio \(k_2/\text{OH} + \text{CH}_3/\text{OH} - \text{H} + \text{H} = 1.0\) was obtained at \(1.0\) atm at 733 K. This ratio is independent of the amount of 3.2 to 6. In the earlier measurements \(k_2/\text{OH} - \text{H} + \text{H} + \text{H} + \text{OH} + \text{H} = 9.5\).

It was concluded that Reactions (2) (CO + OH) and (18) (CO + HO₂) were equally important in the production of CO₂ and the following relationships were obtained

\[
\begin{align*}
\text{OH} + \text{H} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}_2 \quad (17) \\
\text{CO} + \text{H}_2 \rightarrow \text{CO}_2 + \text{OH} \quad (18) \\
\text{H}_2 + \text{H}_2 \rightarrow \text{H}_2 + \text{H} \quad (19)
\end{align*}
\]

In the CH₄ study, Reactions (17) and (19) were neglected. Reaction of H₂O with CH₃ was considered but it was concluded that the mechanism was best represented by Reaction (4) (CH₃ + OH). Greiner [4–20, A–21] in a study of the flash photolysis of H₂O with added H₂, CO, and CH₃, has shown that OH is regenerated by secondary reactions with H₂O or HO₂. It would, therefore, seem likely that in the present case the amounts of H₂O₂, the Reactions (17), (19), and (20) would need to be included to form an adequate reaction mechanism. This ratio therefore is probably not adequate evidence for choosing between the two possible rate ratio equations and thereby supporting or rejecting Greiner's activation energy results.

In addition, Cullis, Fish, and Gibson have obtained evidence that the reaction of HO₂ with alkane has a low activation energy which is consistent with the reaction of HO₂ with methane might be of some importance [18].
HYDROXYL RADICAL REACTION KINETICS


The determination of $k_d/k_i$ from flame structure studies of (9) 1/10 and (10) 1/20 atm CH$_4$–O$_2$ flames are reported. It was assumed that only reactions (4) and (2) consumed CH$_4$ and CO. Diffusion corrections were made using binary diffusion coefficients.


Temperature range

<table>
<thead>
<tr>
<th>Temperature range</th>
<th>Suggested values</th>
<th>Error limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>300–1000 K</td>
<td>1.2 $\times$ 10$^4$</td>
<td>$\log_{10} k_d \pm 0.3$</td>
</tr>
<tr>
<td>1000–1600 K</td>
<td>6 $\times$ 10$^4$ exp ($-3,500/\theta$)</td>
<td>$\log_{10} k_a \pm 1$</td>
</tr>
</tbody>
</table>

Some numbers are not considered reliable because of the reasons given under reference [12].

B4.2c. Rate Calculations


The thermal decomposition of H$_2$O$_2$ was used as a source of OH. The OH formed reacts rapidly with H$_2$O to form H$_2$O$_2$ which complicates the reaction mechanism. Because of the presence of H$_2$O$_2$ which also reacts with CO and possibly with CH$_4$, these numbers are not considered reliable.

A thermal reactor was used. This measurement is complicated by wall and H$_2$O reactions and is not considered reliable.

B4.2d. Rate Evaluations


C. Hydroxyl Radical Reactions With Less-Well-Established Rate Parameters

C1. $k_8$, Rate Constant for the Reaction, C$_2$H$_4$ + OH → Products

Breen and Glass studied this reaction using quantitative ESR for measurement of the OH decay and mass spectroscopy to determine the reaction mechanism. They present ample evidence for the initial reaction being OH + C$_2$H$_4$ → H$_2$ + HC$_2$O which is followed by the very rapid reaction OH + HC$_2$O → C$_2$H$_4$ + H$_2$. A value of $k_8 = 2.2 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (1.2 ± 0.4 × 10$^{11}$ cm$^3$ mol$^{-1}$ s$^{-1}$) at 300 K was obtained using a stoichiometric factor of two. It has generally been considered that the reaction path at flame temperatures is OH + C$_2$H$_4$ → C$_2$H$_3$ + H$_2$. The measured rate at 300 K however is comparable to that calculated at 1000 K using the rate expression obtained by Browne et al. [3], for the 1000 to 1600 K region.

Therefore, both reaction mechanisms may occur in flames and the radical may play a role in a chemiluminescence and chem-ionization. Because of the possibility of different reaction paths at different temperatures, rate expressions are given for two temperature ranges. Since the rate measurements at 300 K and 1000 K gave approximately the same result, the rate constant of Breen and Glass[1] with zero activation energy is suggested for the low temperature reaction. The expression of Browne et al. [3], may be used for the higher temperature range.

C1.2. $k_9$, Rate Constant for the Reaction, OH + H$_2$ → Products

The reaction of OH with acetylene was studied in a discharge flow system at room temperature using ESR to follow the OH concentration and mass spectrometry to determine the reaction products after complete reaction. The results of the study were consistent with the following mechanism

\[ \text{OH} + \text{C}_2\text{H}_4 \rightarrow \text{H}_2 + \text{HC}_2\text{O} \quad (8) \]

\[ \text{OH} + \text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O} \]

The C$_2$H$_4$ formed was largely removed by reaction with nitric oxide yielding N$_2$, N$_2$O, CO, and CO$_2$. The NO was introduced into the system during the generation of OH from the atomic hydrogen titration reaction

\[ \text{NO}_2 + \text{H} \rightarrow \text{NO} + \text{OH} \]

A computer analysis of the OH decay profiles, which took into account OH + OH → HO$_2$ + O, O + OH → O$_2$ + H, and OH + HO$_2$ → products. The expression of Browne et al. [3], may be used for the higher temperature range.


The reaction of OH with acetylene was studied in a discharge flow system at room temperature using ESR to follow the OH concentration and mass spectrometry to determine the reaction products after complete reaction. The results of the study were consistent with the following mechanism

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\[ \text{OH} + \text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O} \]

The C$_2$H$_4$ formed was largely removed by reaction with nitric oxide yielding N$_2$, N$_2$O, CO, and CO$_2$. The NO was introduced into the system during the generation of OH from the atomic hydrogen titration reaction

\[ \text{NO}_2 + \text{H} \rightarrow \text{NO} + \text{OH} \]

A computer analysis of the OH decay profiles, which took into account OH + OH → HO$_2$ + O, O + OH → O$_2$ + H, and OH + HO$_2$ → products.
Two studies at higher temperatures give upper limits only. Greiner's negative activation energy (300–500 K) probably should not be extrapolated to higher temperatures. A value of \( k_0(\text{C}_2\text{H}_4 + \text{OH}) \) of between 2 and 3, as indicated by the work of Breen and Glass, refers to a rate constant of radical recombination of \( 10^{14} \text{cm}^3\text{mol}^{-1}\text{s}^{-1} \). Values obtained for \( k_0(\text{C}_2\text{H}_4 + \text{OH}) \) were \( 3.21 \pm 0.39 \times 10^{12} \) at 299 K, \( 2.46 \pm 0.16 \) at 374 and \( 1.86 \pm 0.11 \) at 497 K. The best fit to an Arrhenius plot was log \( \Delta \) (cm$^3$ mol$^{-1}$ s$^{-1}$) = 11.88 ± 0.09 and \( E = 903 \pm 136 \text{cal} \text{mol}^{-1} \).


The reaction was assumed to be \( \text{C}_2\text{H}_4 + \text{OH} \rightarrow \text{C}_2\text{H}_3\text{O} + \text{H} \), and the OH decay was corrected for reactions of the \( \text{C}_2\text{H}_3\text{O} \) with \( \text{OH} \) assuming a rate constant for radical recombination of \( 10^{14} \text{cm}^3\text{mol}^{-1}\text{s}^{-1} \). Values obtained for \( k_0(\text{C}_2\text{H}_3\text{O} + \text{OH}) \) were \( 3.21 \pm 0.39 \times 10^{12} \) at 299 K, \( 2.46 \pm 0.16 \) at 374 and \( 1.86 \pm 0.11 \) at 497 K. The best fit to an Arrhenius plot was log \( \Delta \) (cm$^3$ mol$^{-1}$ s$^{-1}$) = 11.88 ± 0.09 and \( E = 903 \pm 136 \text{cal} \text{mol}^{-1} \).


The reaction of \( \text{C}_2\text{H}_4 + \text{OH} \), which was also studied, was too rapid for accurate measurement but a value of \( k_0(3 \times 10^4) \text{cm}^3\text{mol}^{-1}\text{s}^{-1} \) was estimated. The value of \( n \), which refers to the number of \( \text{OH} \) radicals reacting for each \( \text{C}_2\text{H}_4 \) molecule, was not determined. Assuming a stoichiometry of \( n=2 \), as indicated by the work of Brown and Glass, a value of \( k_0=2 \times 10^{10} \text{cm}^3\text{mol}^{-1}\text{s}^{-1} \) is good agreement with their value of \( k_0=1.2 \pm 0.4 \times 10^{12} \text{cm}^3\text{mol}^{-1}\text{s}^{-1} \).


The slight dependence on \( \text{H}_2 \) concentration of the efficiency of inhibition is explained by an abstraction reaction of either \( \text{O} \) or \( \text{OH} \) with \( \text{C}_2\text{H}_4 \). The ratio of this reaction to \( k_0(\text{H}_2 + \text{OH}) \) is 6.7 at 813 K. Although the authors prefer the reaction of \( \text{OH} \) with \( \text{C}_2\text{H}_4 \), they state that a reaction of \( \text{O} + \text{C}_2\text{H}_4 \) is also consistent with the results. Using the \( k_0 \) recommended in this report, a value of \( k_0(\text{OH} + \text{C}_2\text{H}_4) \) of \( 3.6 \times 10^{12} \text{cm}^3\text{mol}^{-1}\text{s}^{-1} \) is obtained. Since the value of \( \text{O} + \text{C}_2\text{H}_4 \) is in 4 \times 10^2 \text{cm}^3\text{mol}^{-1}\text{s}^{-1} \) at this temperature [28–28] this value of \( k_0 \) might be considered an upper limit.


Standard flame structure techniques were used to determine the concentration profiles of \( \text{C}_2\text{H}_4 \), \( \text{CO} \), and \( \text{CO}_2 \) through a 76 torr flat flame and the concentration rate profiles of \( \text{C}_2\text{H}_4 \) and \( \text{CO} \). Taking a known value of \( k_0(\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}) \), the CO concentration, and the \( \text{CO}_2 \) formation rate, a concentration profile may be calculated for \( \text{OH} \). This is then used with the \( \text{C}_2\text{H}_4 \) concentration and rate of decay to determine \( k_0(\text{C}_2\text{H}_4 + \text{OH}) \). The assumption must be made that \( \text{OH} \) is the only species attacking \( \text{C}_2\text{H}_4 \). In the \( \text{O}_2 \)-rich flames used the \( \text{H} \) atom concentration would be very low but the \( \text{C}_2\text{H}_4 \) concentration is approximately half of the \( \text{OH} \) radical concentration at the hot boundary and might be expected to be an appreciable fraction of \( \text{OH} \) throughout the flame. The authors' assumption that \( \text{OH} \) is the primary attacking species is based on the ESR analysis of samples extracted from the flames by a microprobe and conducted through an ESR cavity. \( \text{H} \) and \( \text{O} \) were not found early in the flame and were observed only in the region of the flame after the \( \text{C}_2\text{H}_4 \) had completely disappeared. The electric dipole spectrum of \( \text{OH} \) could not be observed with the cavity used. The most reasonable explanation for the unexpected profiles of \( \text{H} \) and \( \text{O} \) is that the rapid reaction of \( \text{O} + \text{OH} \) in the tube from the probe to the cavity removed \( \text{O} \) and generated \( \text{H} \) and that much of the \( \text{H} \) was lost by wall recombination. This possibility was suggested in the discussions following the paper. The reaction time available, 25 ms, would be ample for the complete reaction of \( \text{O} + \text{OH} \). The reaction rate constant for \( \text{O} + \text{OH} \) is about 10^12 in the temperature range considered. The authors reported value of \( k_0(\text{C}_2\text{H}_4 + \text{OH}) \) = 1 \times 10^{14} \text{cm}^3\text{mol}^{-1}\text{s}^{-1} \) in the range 1250 to 1400 K must therefore be considered an upper limit. A recalciulation of \( k_0 \) from the author's reported data using \( k_0(\text{CO} + \text{OH}) \) from this report gave the following values, \( \log k_0 = 12.5 \) at 1240 K, 12.7 at 1368 K, 13.2 at 1447 K, and 13.9 at 1491 K in cm$^3$ mol$^{-1}$ s$^{-1}$ units.


The reaction of \( \text{OH} \) with ethylene was studied in a low-pressure discharge-flow system with mass spectrometric detection. OH
was generated by $H + NO_2 \rightarrow NO + OH$. The rate constant was determined by two methods. The pseudo first order decay of $OH$ as a function of reactant concentration under OH lean conditions gave $k_{OH} = 4.2 \times 10^{17} \text{cm}^{-3} \text{mol}^{-1} \cdot \text{s}^{-1}$. The ethylene decay in an OH rich system gave $k_3 = 3.0 \times 10^8$. $n$ is the number of OH reacting per ethylene molecule reacting.

C3. $k_{10}$ Rate Constant for the Reaction, $C_2H_6 + OH \rightarrow C_2H_5 + H_2O$

The experimental points are shown on an Arrhenius plot in figure C3. The two measurements of the rate of $k_{10}$ of $(CH_3+OH)$ in the 300 to 500 K range agree fairly well in absolute magnitude but the indicated activation energies are appreciably different [1, 2]. As usual, Greiner’s [2] activation energy is lower but the extrapolation to flame temperature is in agreement with the $k_{10}$ reported by Westenberg and Fristrom [4]. The flame temperature point of Fenimore and Jones [5] is in better agreement with the activation energy of Horne and Norrish [1]. The studies of Baldwin et al. [6, 7] give some information on the ratio of $k_{10}(C_2H_6+OH)$ to $k_{10}(H_2+OH)$. If the $k_3$ expression recommended in this report is used, the derived $k_{10}$ agrees with the higher activation energy. However, if Greiner’s expression for $k_{10}(H_2+OH)$ is used, the resulting $k_{10}$ is in agreement with the extrapolation of Greiner’s expression for $k_{10}$. Unfortunately neither of the flame temperature points are reliable enough to establish the proper activation energy. The recommended expression is $k_{10} = 6.5 \pm 0.5 \times 10^{13} \exp (-1,800 \pm 300/T)$. The choice is based on considerations discussed in Section D and references [B2–2, B3–4, and B4–4].

[3.1] Horne, D. G., and Norrish, R. C. W., Rate of H-abstraction by OH from hydrocarbons, Nature 215, 1373 (1967). Hydroxyl radicals were generated by flash photolysis of water vapor and the OH decay followed by absorption spectroscopy for time periods of about 1 ms. The expression, $log k_{10} = (14.1 + 0.7) - (3,600 \pm 600)/(2,303 RT)$, $cm^3 \text{mole}^{-1} \cdot \text{s}^{-1}$ was reported. The experimental technique is described in reference [B4–1] and reasons are given for believing their value should be divided by two to account for subsequent reactions of C$_2$H$_6$ radicals with OH. When this is done the room temperature value agrees with that of references [3.2 and 3.3].


[3.3] Wilson, W. E., and Westenberg, A. A., Study of the reaction of hydroxyl radical with methane by quantitative ESR, Symp. Combust., 11th (The Combustion Institute, 1967), p. 1143. The reaction of C$_2$H$_6 + OH$ was also studied. A value $k_{10} = (6 \times 10^{13})/n \text{cm}^3 \text{mole}^{-1} \cdot \text{s}^{-1}$ was obtained. The value of $n$, which refers to the number of OH radicals reacting for each C$_2$H$_6$ molecule that reacts, was not determined. Assuming a stoichiometry of between 2 and 3, a value of 2-3 $\times 10^{13}$ is obtained, in good agreement with the values from references [3.1 and 3.2].

[3.4] Westenberg, A. A., and Fristrom, R. M., H and O atom profiles measured by ESR in C$_2$ hydrocarbon–O$_2$ flames, Symp. Combust., 10th (The Combustion Institute, 1965), p. 473. Standard flame structure techniques were applied to a 26 torr C$_2$H$_6$–O$_2$ flame. (See reference [2-4]). The authors report $k_{10} = 3.5 \times 10^{16} \text{cm}^{-3} \text{mole}^{-1} \cdot \text{s}^{-1}$ in the range 1500 to 1520 K. $k_{10}$ was assumed to be the only reaction removing C$_2$H$_6$. In this flame [O] = 1/2 [OH] and the rate of O + C$_2$H$_6$ at 1500 may be estimated as $2.3 \times 10^{13}$ at 1500 K [B3–28b]. As much as 25 percent of the C$_3$H_8 disappearance might be due to attack by O leading to a slightly smaller value for $k_{10}$.


Flame structure techniques were applied to C$_3$H$_8$–O$_2$ flames of varying mixture ratios enabling the rate of both H and OH + C$_2$H$_6$ to be determined. Initial attack by O atoms was not thought to be important. The authors report $k_{10} = 3 \times 10^{10} \text{cm}^3 \text{mole}^{-1} \cdot \text{s}^{-1}$ in the 1400 to 1600 K range.


The inhibition of the second limit of the H$_2$O$_2$ reaction by C$_2$H$_6$ was studied. (See discussion following ref. [B3–1]) From the dependence of the inhibition on the mol fraction of H$_2$O$_2$, the following relationship was obtained where $k_{10} = k_{10}(CH_3OH)/k_{10}(OH)$ and $R_{OH} = k_{10}(CH_3OH)/k_{10}(OH)$. (R$+13.1$) (R$+2.98$) = 201 at 813 K. Thus, if $k_{10}$, $k_{14}$, and $k_3$ are known, $k_{10}$ may be calculated. The following values are assumed: $k_1 = 1.8 \pm 0.2 \times 10^{13} \exp (-5100/RT)$ [3–28b] $k_3 = 3.2 \times 10^{10} \exp (-10200/RT)$ [3–28b], and $k_{12} = 2.3 \times 10^{10} \exp (-2600/RT)$ [this report]. At 793 K the corresponding values are $k_1 = 4.10 \times 10^{12}$, $k_3 = 5.76 \times 10^{10}$, and $k_{12} = 9.38 \times 10^{10}$. The authors relationship yields $k_{10} = 6.3 \times 10^{10}$. This point falls very close to the extension of Horne and Norrish’s rate expression (Figure C3). Alternately Greiner’s expression, $log k_1 = 12.61 - 4020/2303RT$, may be used. In this case $k_3 = 3.39$ and $k_{10} = 2.35 \times 10^{10}$ (all in $cm^3 \text{mole}^{-1} \cdot \text{s}^{-1}$). This point falls very close to the extension of Greiner’s expression for $k_{10}$. The rate ratio studies, therefore, do not help in the selection of an activation for OH abstraction reactions.


When traces of ethane ($\sim 0.001$ mol fraction) are added to slowly reacting mixtures of H$_2$–O$_2$ near 773 K, information on the relative rates of attack of H, O, OH, and HO$_2$ on the additive can be obtained by determining the relative rates of consumption of H$_2$ and additive as a function of pressure and mole fractions of the three components. Under slow reaction conditions, the additive is removed mainly by attack of OH radicals. Hence the rate constants for OH reactions can be determined more accurately than in studies of inhibition of the
second limit. The ratio \( k_n (OH + CH_3H)/k_2 (OH + H_2) = 9.5 \) was obtained at 773 K. Using the value of \( k_3 \) recommended in this report, \( k_n = 8.5 \times 10^{11} \text{ cm}^2 \text{ mol}^{-1} \text{ s}^{-1} \).

**C4. Reactions of OH With Alkanes, Olefins, and Miscellaneous Compounds**


The flash-photolysis kinetic-spectroscopy technique was used to study the reactivity of OH radicals toward a representative set of ten alkanes. It was found that primary, secondary, and tertiary hydrogen atoms behaved differently but that there was a generally applicable frequency and activation energy for each of the three types of hydrogen atoms. (Methane and ethane were exceptions.) The following formula reproduced accurately the observed rate constants for all ten model alkanes (cm\(^{-3}\) mol\(^{-1}\) s\(^{-1}\) units).

\[
k_{\text{OH}} = 6.15 \times 10^{13} N_p \exp (-1635/RT) + 14.1 \times 10^{11} N_q \exp (-850/RT) + 12.6 \times 10^{11} N_p \exp (+190/RT),
\]

where \( N_p, N_q, \) and \( N_r \) are the respective numbers of primary, secondary, and tertiary H atoms in the alkane, and \( k_{\text{OH}} \) is the total rate constant for abstraction of H atoms from the alkane. The activation energies obtained by Greiner are in general lower than those of other workers but his room temperature rate constants are in good agreement (See discussion Sec. D).


Detailed investigations of the inhibition of the hydrogen-oxygen reaction by a number of hydrocarbons and related compounds have been made. With formaldehyde, ethane, propane, \( n \)- and \( i \)-butane, the features of the inhibition of the second limit in KCl-coated vessels at 773 K can be accounted for by a mechanism in which Reactions (14), (15), and (16) are added to the basic Reactions (3), (11), (12), and (13) of the \( HO_2 \) reaction.

\[
\begin{align*}
&k_{14} = k_{1} [OH + RH] + k_{16} [OH + RH] + k_{18} [OH + O_2]
&k_{15} (OH + RH) / k_{11} (H + O_2)
&k_{16} (OH + RH) / k_{11} (H + O_2)
&k_{17} (OH + RH) / k_{11} (H + O_2)
\end{align*}
\]

The rate constant for \( k_{11} (O + n-C_3H_8) \) has been measured and can be used with \( k_3 \) and \( k_4 \) to determine \( k_{16} (OH + CH_3H) \). As in the case of \( C_3H_8 \), if Greiner’s value of \( k_3 \) is used, the \( k_{16} \) agrees with the value calculated from Greiner’s expression for \( k_{16} \). If the \( k_3 \) recommended in the report is used, a higher value is obtained for \( k_{16} \).


The reaction of \( OH \) with propylene and acetaldehyde was studied in a low-pressure fast-flow system with mass spectrometric detection. \( OH \) was generated by \( H + NO_2 \rightarrow NO + OH \). The rate constants were determined by two techniques. The first-order decay of hydrocarbon under OH-rich conditions gave \( k = 11.0 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) for propylene and \( k_4 = 9.0 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) for acetaldehyde. The pseudo first-order decay of \( OH \) as a function of reactant concentration under OH-lean conditions gave \( k/n \) and \( n \) was determined by product analysis, isotopic studies, and experiments under OH-rich conditions.

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>( k_{14} (O + RH) = 0 )</th>
<th>( k_{16} (OH + RH) = 0 )</th>
<th>( B )</th>
<th>( C )</th>
<th>( D )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>813</td>
<td>38</td>
<td>12</td>
<td>32</td>
<td>54</td>
</tr>
<tr>
<td>Propane</td>
<td>793</td>
<td>77</td>
<td>27</td>
<td>62</td>
<td>124</td>
</tr>
<tr>
<td>( n )-Butane</td>
<td>793</td>
<td>83</td>
<td>36</td>
<td>53</td>
<td>250</td>
</tr>
<tr>
<td>( i )-Butane</td>
<td>793</td>
<td>153</td>
<td>20</td>
<td>147</td>
<td>56</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>813</td>
<td>326</td>
<td>42</td>
<td>309</td>
<td>150</td>
</tr>
<tr>
<td>Tetraethylsilane</td>
<td>793</td>
<td>374</td>
<td>74</td>
<td>341</td>
<td>254</td>
</tr>
</tbody>
</table>

C5. \( k_{16} \), Rate Constant for the Reaction, \( O + OH \rightarrow O_2 + H \)

There are four experimental studies of this reaction [1, 2, 3, 4, 5] and a number of suggested and estimated values which are discussed in a recent review [6]. The experimental values, \((3 \pm 1) \times 10^{13}\)
HYDROXYL RADICAL REACTION KINETICS

\[ \text{H}_2\text{O}_2 + \text{M} \rightarrow \text{OH} + \text{M} \]
\[ \text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2 \]
\[ \text{H}_2\text{O} + \text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2 \]

and that in the presence of \( \text{H}_2 \) the decomposition of \( \text{H}_2\text{O}_2 \) is sensitized by the chain process
\[ \text{H}_2\text{O}_2 + \text{M} \rightarrow 2\text{OH} + \text{M} \]

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

Therefore the ratio \( \text{k}_{17}/\text{k}_3 \) and a number of other ratios could be obtained from these studies. A value for \( \text{k}_{17} \) may be obtained by using \( \text{k}_3 \) either that recommended in this report or that obtained by Greiner. The results, compared with Greiner’s direct measurement of \( \text{k}_{17} \), are shown below.

<table>
<thead>
<tr>
<th>( \text{k}_{17} ) in 10^{12} cm^3 mol^{-1} s^{-1}</th>
<th>773 K</th>
<th>715 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Using ( \text{k}_3 ), Greiner [B3–4])</td>
<td>1.0</td>
<td>0.77</td>
</tr>
<tr>
<td>(Using ( \text{k}_3 ), this report)</td>
<td>3.8</td>
<td>2.6</td>
</tr>
<tr>
<td>(Extrapolation of Greiner’s measurement over 300–458 K)</td>
<td>3.1</td>
<td>2.8</td>
</tr>
</tbody>
</table>

C6. \( \text{k}_{17} \), Rate Constant for the Reaction, \( \text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2 + \text{HO}_2 \)

The extrapolation of Greiner’s expression is in agreement with the rate ratio measurements of Baldwin et al. [2]. Baulch [C5.6] et al. have also reviewed this reaction. Their expression of \( 1 \times 10^{-13} \exp(-1800/RT) \) cm^3 mol^{-1} s^{-1} over the temperature range 300 to 1000 K with error limits \( \log \text{k}_{17} \pm 0.7 \) is recommended. This expression also provides an adequate fit of Greiner’s experimental measurements. This reaction is fast, \( \text{k}_{17} = 8.3 \times 10^{11} \) cm^3 mol^{-1} s^{-1} at room temperature. Therefore, substantial amounts of \( \text{HO}_2 \) will be found in systems in which \( \text{H}_2\text{O}_2 \) is formed by recombination of \( \text{OH} \) or in systems in which \( \text{OH} \) is generated by the thermal decomposition of \( \text{H}_2\text{O}_2 \). Such systems, therefore, are not satisfactory for studying \( \text{OH} \) reactions unless the role of \( \text{HO}_2 \) is considered.

C7. \( \text{k}_{12} \), Rate Constant for the Reaction, \( \text{OH} + \text{H} \rightarrow \text{H}_2 + \text{O} \)

There are no direct measurements of this reaction; all rate constants are based on measurements of the forward reaction and calculation of the reverse rate via the equilibrium constant. The two most recent considerations of \( \text{k}_{12} \) (\( \text{O} + \text{H}_2 \)) are discussed below. The recommended value, \( \text{k}_{12} = 1.35 \times 10^{14} \exp(-9.0500/RT) \) cm^3 mol^{-1} s^{-1}, error limits \( \log k \pm 0.3 \), 500 to 3000 K, is based on \( \text{k}_{13} \) from reference [C.5.2] and \( \text{K}_4 \) from reference [C.5.1].

[7.1] Baulch, D. L., Drysdale, D. D., and Lloyd, A. C., High temperature reaction rate data, No. 2, November, 1968, Department of Physical Chemistry, The University, Leeds 2, England. The available information on \( \text{k}_{12} \) was reviewed and a value of \( \text{k}_{12} = 1.74 \times 10^{13} \exp(-9.4500/RT) \) cm^3 mol^{-1} s^{-1} was recommended with error limits of \( \pm 30 \) percent. Using \( \text{K}_4 = 2.38 \exp(-2150/RT) \) they obtained \( \text{k}_{12} = 7.33 \times 10^{14} \exp(-7.3000/RT) \) cm^3 mol^{-1} s^{-1}.


A reinvestigation of these reactions over the temperature range of 500 to 900 K using a low pressure-flow tube and quantitative electron spin resonance for the detection of \( \text{H}_2 \) atoms yielded \( \text{k}_{12} = 3.2 \times 10^{14} \exp(-10.9000/RT) \) cm^3 mol^{-1} s^{-1}. The rates measured in this study were uniformly lower than those reported earlier and included in the review of Baulch et al [7.1]. The new data are in very good agreement with that of other workers.
and give a better fit to the high temperature data. Below 500 K the measured values of $k_2$ were greater than predicted by the Arrhenius expression.

C8. Miscellaneous Bimolecular OH Reactions

C8.1. Ammonia: $k_{32}$ (NH$_3$ + OD → Products)


Preliminary results are reported which give $k_{32}$(OD + NH$_3$)/$k_{32}$(NH$_3$ + H$_2$) = 0.5 at 500 K or $k_{32}$(OD + NH$_3$) = $10^{11}$ cm$^3$ mol$^{-1}$ s$^{-1}$.

C8.2. Formaldehyde: $k_{34}$ (OH + H$_2$CO → H$_2$O + HCO)

Four measurements have been reported for $k_{34}$(OH + H$_2$CO). The values at 773 K and the upper limit at 813 K, derived from rate ratio measurements, are in agreement. Both these, and the lower limit at 300 K, are higher than calculated from the rate expression derived from flames. In view of the general problem of extrapolating flame data to lower temperatures, a temperature-independent rate of $k_{34}$(OH + H$_2$CO) = 5 × 10$^{10}$ cm$^3$ mol$^{-1}$ s$^{-1}$ with an uncertainty of log $k_{34}$ = 1 is recommended.


Studies of the slow oxidation of methane yielded $k_{34}$(OH + H$_2$CO)/(OH + H$_2$) = 33 ± 5 at 773 K, or $k_{34}$ = 4.3 × 10$^{10}$ cm$^3$ mol$^{-1}$ s$^{-1}$ at 773 K (using $k_4$ from this review).


Inhibition studies of the H$_2$-O$_2$ reaction yield an upper limit of $k_{34}k_4$ = 42 at 813 K or $k_{34}$ = 6.5 × 10$^{10}$ cm$^3$ mol$^{-1}$ s$^{-1}$ at 813 K. (See 4.2.)


Flame structure studies of C$_3$ hydrocarbon flames yielded $k_{34}$(OH + H$_2$CO) = 5 × 10$^{10}$ exp(-6500/T) cm$^3$ mol$^{-1}$ s$^{-1}$ at 1600 K this gives $k_{34}$ = 8.5 × 10$^{10}$ at 773 K, $k_{34}$ = 1.1 × 10$^{10}$.


The reaction of OH + HCHO was studied in a low-pressure flow reactor. Based on the consumption of HCHO and the initial concentration of OH a lower limit of $k_{34}$ = 4 × 10$^{12}$ cm$^3$ mol$^{-1}$ s$^{-1}$ at 300 K was obtained.

C8.3. Nitric Acid: $k_{35}$ (HNO$_3$ + OH → H$_2$O + NO$_3$)


Values of $k_{35}$ = 0.9 and 1.1 × 10$^{10}$ cm$^3$ mol$^{-1}$ s$^{-1}$ were obtained at 300 K from $-d$[OH]/$dt$ at $d$[H]. The formation of NO$_3$ and the disappearance of OH were observed.

C8.4. Nitroxy1: $k_{36}$ (HNO + OH → Products)


Studies of the decay of H and OH in the burn gas region of fuel-rich flames of H$_2$, O$_2$ at atmospheric pressure indicate that NO is an effective homogeneous catalyst. The results were consistent with the mechanism

\[
\begin{align*}
\text{H + NO + M} & \rightarrow \text{HNO + M} \\
\text{H + HNO} & \rightarrow \text{H}_2 + \text{NO} \\
\text{OH + HNO} & \rightarrow \text{H}_2 + \text{NO} \text{ or } \text{H}_2 + \text{NO}_2 \\
\end{align*}
\]

$k_{36}$ = $1.5 \pm 0.5 \times 10^{18}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ with no significant temperature effect from 1600 to 2000 K.


C8.5 Methyl Radical: $k_5$ (CH$_3$ + OH → Products)


The slow decay of CH$_4$ in the postflame gas from fuel-rich, methane-oxygen flames was measured. The balancing reactions between H, OH, O, O$_2$, H$_2$, and H$_2$O were shown to be in equilibrium. Since the rate of decay of CH$_4$ was much lower than the calculated rate for H + CH$_4$ → CH$_3$ + H$_2$, it was assumed that this reaction and the reactions OH + CH$_4$ → CH$_3$ + H$_2$ and O + CH$_4$ → CH$_3$ + H$_2$ were also equilibrated. The rate of decay of CH$_4$ could, therefore, be attributed to CH$_3$ + OH → products with CH$_3$ and OH both being in quasi-equilibrium. The calculated rate constant was $k_5$ = $(4.2 \pm 1) \times 10^{10}$ cm$^3$ mol$^{-1}$ s$^{-1}$ in the region 1970 to 2190 K.

C8.6. C$_2$ Radical: $k_6$ (C$_2$ + OH → CO + CH)


Flame structure studies, in which $C_2$ and OH concentrations, in both ground and excited states were measured, yielded the following rates which showed no trend with temperature from 875 to 1665 K.

$C_2 + OH + CO + CH^* \rightarrow C^* \rightarrow 6 \times 10^{10}$ cm$^3$ mol$^{-1}$ s$^{-1}$.

$k_6$ = $5 \pm 2 \times 10^{10}$ cm$^3$ mol$^{-1}$ s$^{-1}$ at 2200 K.

C8.7. Halogenated Compounds: HCl, HBr, CHCl, and CHBr + OH → Products


From flame structure studies of low pressure, inhibited CH$_3$ + OH flames, the following rate constants were obtained. OH concentrations were estimated from CH$_4$ and CO decay rates and the corresponding rate constants.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate in 10$^{18}$ cm$^3$ mol$^{-1}$ s$^{-1}$</th>
<th>Temperature, K</th>
<th>Error limits on log k</th>
</tr>
</thead>
<tbody>
<tr>
<td>HBr + OH</td>
<td>$k_{32}$ = 1.6</td>
<td>1875-1975</td>
<td>± 1</td>
</tr>
<tr>
<td>HCl + OH</td>
<td>$k_{33}$ = 0.77</td>
<td>1920-1940</td>
<td>± 1</td>
</tr>
<tr>
<td>CH$_2$Br + OH</td>
<td>$k_{34}$ = 1.5</td>
<td>1775-1825</td>
<td>± 0.5</td>
</tr>
<tr>
<td>CH$_3$Cl + OH</td>
<td>$k_{35}$ = 1.3</td>
<td>1850-2190</td>
<td>± 0.5</td>
</tr>
</tbody>
</table>

C8.8. $k_5$ (N + OH → NO + H)


The effect of adding H$_2$ to active N$_2$ was studied. There was no primary reaction, but when the nitrogen atoms were partially titrated with NO, a catalytic removal of atoms was induced involving the reactions

\[
\begin{align*}
O + H_2 & \rightarrow OH + H \\
N + OH & \rightarrow NO + H \\
N + NO & \rightarrow N + O \\
O + OH & \rightarrow O + H \\
\end{align*}
\]

The consumption of both nitrogen atoms and oxygen atoms were followed photometrically and the results yield a ratio $k_5$(N + OH)/$k_5$(O + OH) of 1.5 ± 0.1 at 320 K. Using $k_5$(O + OH) = $2.5 \times 10^{10}$ cm$^3$ mol$^{-1}$ s$^{-1}$ (this review, C3), $k_5$(N + OH) = $3.5 \times 10^{10}$ cm$^3$ mol$^{-1}$ s$^{-1}$.
C8.9. \( k_{21}(SO + OH + SO_2 + H) \)


The reaction of \( H \) with \( H_2S \) in a discharge flow system yields \( S \) atoms which react rapidly with molecular oxygen to yield \( SO \). When excess \( O_2 \) is present, \( SO \) is removed by \( H \) formed in the reaction sequence,

\[
\begin{align*}
&H + O_2 + M \rightarrow HO_2 + M + H \\
&H + HO_2 \rightarrow OH + OH \\
&SO + OH \rightarrow SO_2 + H.
\end{align*}
\]

A value of \( k_{21}(SO + OH)/k_{20}(OH+OH) = 2.5 \) at 298 K was obtained. Using \( k_{20} \) from this review (C5), \( k_{21}(SO+OH)/(6.2 \pm 3) \times 10^{-13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \).

C9. \( k_{22} \), Rate Constant for the Reaction \( OH + OH + M \rightarrow H_2O + M \)

There are two experimental measurements of the forward reaction [1, 2]. The values of Baulch et al. [3] based on their evaluation of the reverse reaction, and the relative third-body efficiencies of Black and Porter [1] are recommended.


The absorption spectrum of \( OH \) was recorded at intervals of 60 to 700 \( \mu s \) after flash photolysis of cells containing 14 torr \( H_2O \) with 100 to 800 torr of various third-body gases. The decay of \( OH \) was second order in \( OH \) and first order in the added inert gas. Decay of \( OH \) was attributed to the three-body reactions

\[
\begin{align*}
&H + OH + M \rightarrow H_2O + M \quad (21) \\
&OH + OH + M \rightarrow H_2O_2 + M. \quad (22)
\end{align*}
\]

The \( OH \) decay is given by

\[
\frac{d[OH]}{dt} = -k_{21}[OH][H][M] + 2k_{22}[OH^+M].
\]

At the beginning of the reaction \([H] = [OH]\), and

\[
-\frac{d[OH]}{dt} = k_{22}[OH^+M].
\]

where \( k_{21} = 2k_{22} \). Black and Porter assume that both reactions (21) and (22) go through a hydroxyl-third-body complex, i.e., \( OH + M \rightarrow OH \cdot M \) followed by reaction of \( OH \cdot M \) with \( H \) (Reaction 21) or \( OH \) (Reaction 22). The ratio of \( k_{21}/k_{22} \) will depend on the difference in the rate of \( OH \cdot M \) complex with \( H \) and the \( OH \) in the reactor. The authors then calculate \( k_{21}/k_{22} \) from kinetic theory on the basis of a reaction on every collision. This ratio was 2.55 for He and 3.6 ± 2.0 for the other species studied. A knowledge of the absolute \( OH \) concentration is needed to calculate \( k_{22} \). Using the pressure rise to give an indication of \( OH \) and \( H \) formed, an upper limit of \( k_{21} = 3 \times 10^{-13} \) was obtained for \( M = H_2O \). The authors, however, used Oldenberg and Necké's [A-5] value of 1 x 10^{-13} to scale their values. Since that work is now considered to be in error, it is now considered that the \( OH \) was prepared by an electric discharge in water, see Section A2.1). This study can only provide relative efficiencies for various \( M \). The relative efficiencies obtained are: \( H_2O, 1.00; CO_2, 0.45; H_2, 0.25; N_2, 0.20; \) and \( Ar, H_2, \) and \( Xe \) all 0.06. Subsequent to this review, Homer and Hurle [10.2] have reported a shock tube study of the dissociation of water vapor. Their results, with argon as the third body, are in reasonable agreement with those of Olschewski, Troe, and Wagner [10.3]. The reverse rate, calculated from these results and the equilibrium constant, and measurements of the recombination in flames and shock tubes are plotted in figure C4.

C10. \( k_{21} \), Rate Constant for the Reaction \( H + OH + M \rightarrow H_2O + M \)

In spite of many studies in flame and shock tubes the rate for this reaction remains uncertain. Many studies have been made in the post-reaction zones of laminar flames using the flame photometric techniques, largely developed by Sugden and coworkers, to follow the coupled decay of \( H \) and \( OH \) (see Sec. A3-6). While the measurement of \( H \) and the inference of \( OH \) appear valid, the neglect of the reverse, dissociation reaction has apparently led to the unusually high activation energies observed and has caused the measured reaction rates to be low.

In their review Baulch, Drysdale, and Lloyd [10.1] suggest \( k_{21} = 1.17 \times 10^{17} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) at 2040 K for \( M = H_2O \) with an uncertainty of ±50 percent. Their suggested 3d body efficiencies are \( H_2O, 1.00; CO_2, 0.45; H_2, 0.25; N_2, 0.20; \) and \( Ar, H_2, \) and \( Xe \) all 0.06. Subsequent to this review, Homer and Hurle [10.2] have reported a shock tube study of the dissociation of water vapor. Their results, with argon as the third body, are in reasonable agreement with those of Olschewski, Troe, and Wagner [10.3]. The reverse rate, calculated from these results and the equilibrium constant, and measurements of the recombination in flames and shock tubes are plotted in figure C4.

The rate expressions of Homer and Hurle [10.2] given by the extrapolated line in figure C4, are recommended with error limits of log \( k \) ± 0.5. They should be valid over the temperature range 1000 to 3300 K.
The overall rate equation can be expressed as

\[ k_{21, Ar} = 7.5 \times 10^{23} T^{-2.6} \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1} \]
\[ k_{21, H_2O} = 1.5 \times 10^{23} T^{-2.6} \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1} \]


The dissociation of water vapor in dilute (<7%) mixtures with argon was studied behind shock waves. The growth of OH concentration in the initial stages of dissociation was followed using a short-duration flash-absorption technique which recorded the OH(0,0) band with high resolution.

Profiles of OH concentration were constructed for various conditions of temperature and concentration and a computer analysis was used to match these profiles to a proposed reaction sequence. The results indicate that basically the decomposition proceeds by the reaction

\[ H_2O + M \rightarrow H + OH + M. \]

and rate constants for this reaction were determined over a temperature range of 2570 to 3290 K with M = Ar and H_2O. The overall rate equation can be expressed as

\[ k_{21, M}(M) = A [Ar] + \eta [H_2O] T^{N-\eta}/RT \]

with \( A \) being 494 KJ mol\(^{-1}\) (118 kcal mol\(^{-1}\)) and the calculated parameters being:

\[ A = (4.0 \pm 0.5) \times 10^{23} \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1} \]
\[ \eta = 29 \pm 7, \quad N = 2.2 \pm 0.8. \]

This result, together with the equilibrium constant of the reaction, provides an assessment of the rate of the reverse process, the recombination of H and OH, which in conjunction with previous assessments in flames and shock tubes presents a consistent set of rate data over a wide temperature range.


### C11. Summary of Recommended Rate Constants for Reactions in Section C.

<table>
<thead>
<tr>
<th>Section number</th>
<th>Reaction</th>
<th>Rate expression in cm(^3)mol(^{-1})s(^{-1})</th>
<th>Temperature range, K</th>
<th>Error bounds on log ( k )</th>
</tr>
</thead>
</table>
| C1 \( k_6 \)  | \( C_2H_4 + OH \rightarrow \) products | \( 1.2 \times 10^{11} \)
|              |  \( 6 \times 10^{12} \exp \left(-3500/T\right) \)
| C2 \( k_8 \)  | \( C_2H_4 + OH \rightarrow \) products | \( 3 \times 10^{11} \)
| C3 \( k_{a\beta} \) | \( C_2H_4 + OH \rightarrow \) H, CH\(_3\), CH\(_2\), H\(_2\O\) | \( 6.5 \times 10^{13} \exp \left(-1800/T\right) \)
| C4 \( k_{b\gamma} \) | \( H_2O + RH \rightarrow \) products (number of carbon atoms: \( N_\gamma = \) primary, \( N_\delta = \) secondary, \( N_\epsilon = \) tertiary), \( N_\delta \) | \( 6.5 \times 10^{11} \exp \left(-820/T\right) \)
|              |  \( + 14.1 \times 10^{11} \exp \left(-425/T\right) \)
|              |  \( + 12.6 \times 10^{11} \exp \left(+65/T\right) \)
| C5 \( k_{c\delta} \) | \( O + OH \rightarrow O_2 + H \) | \( 2.5 \times 10^{13} \)
| C6 \( k_{d\epsilon} \) | \( OH + H_2O \rightarrow H_2 + H_2O \) | \( 1 \times 10^{10} \exp \left(-1800/T\right) \)
| C7 \( k_{e\zeta} \) | \( OH + H \rightarrow H_2 + O \) | \( 1.35 \times 10^{10} \exp \left(-4000/T\right) \)
| C8.1 \( k_{f\eta} \) | \( NH_3 + OD \rightarrow \) products | \( 10^{11} \)
| C8.2 \( k_{g\nu} \) | \( H_2O + OH \rightarrow \) H, OH\(_2\), HCO \(_2\), HCO \(_3\), CO \(_2\) | \( 5 \times 10^{11} \exp \left(-6500/T\right) \)
| C8.3 \( k_{h\xi} \) | \( HNO_2 + OH \rightarrow NO_2 + H_2O \) | \( 1 \times 10^{11} \)
| C8.4 \( k_{i\zeta} \) | \( HNO + OH \rightarrow \) products | \( 1 \times 10^{10} \)
| C8.5 \( k_{j\eta} \) | \( CH_3 + OH \rightarrow \) products | \( 4 \times 10^{13} \)
| C8.6 \( k_{k\zeta} \) | \( C_2 + OH \rightarrow \) CO + CH \(_4\) + CH \(_2\) + CH \(_3\) \(_2\) + CH \(_2\) \(_3\) \ | \( 5 \times 10^{12} \)
|              |  \( 4 \times 10^{10} \)
|              |  \( 4 \times 10^{10} \)
| C8.7 \( k_{l\eta} \) | \( HBr + OH \rightarrow \) H, OH + Br | \( 1.6 \times 10^{13} \)
|              |  \( 1.6 \times 10^{13} \)
|              |  \( 0.8 \times 10^{13} \)
|              |  \( 1.5 \times 10^{13} \)
|              |  \( 1.3 \times 10^{13} \)
| C8.8 \( k_{m\xi} \) | \( N + OH \rightarrow NO + H \) | \( 3.5 \times 10^{13} \)
| C8.9 \( k_{n\zeta} \) | \( SO + OH \rightarrow SO_2 + H \) | \( 7 \times 10^{13} \)
| C9 \( k_{o\eta} \) | \( OH + OH + N_2 \rightarrow H_2O + N_2 \) | \( 8.4 \times 10^{14} \exp \left(-2650/T\right) \)
| C10 \( k_{p\zeta} \) | \( H + OH + H_2O \rightarrow H_2 + H_2O \) | \( 1.5 \times 10^{13} \)
|              |  \( 7.5 \times 10^{13} \)

D. Present Status and Recommendations for Further Study

The knowledge of OH kinetics has improved greatly in the last few years. At the present time experimentalists are concerned about differences of a factor of two which not many years ago would have been considered in agreement. However, there are still a number of puzzling features about OH kinetics.

The assignment of a suitable activation energy (ΔE) for hydroxyl radical reactions has been a longstanding problem in chemical kinetics. In the last ten years recommended values of ΔE have encompassed the following ranges:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Number</th>
<th>1961</th>
<th>1966</th>
<th>1969</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO + OH → CO₂ + H</td>
<td>(2)</td>
<td>7.7⁺⁻</td>
<td>0.6⁻⁰</td>
<td>0.2⁻³</td>
</tr>
<tr>
<td>H₂ + OH → H₂O + H</td>
<td>(3)</td>
<td>11.0⁻⁰</td>
<td>5.2⁻²</td>
<td>4.6⁻³</td>
</tr>
<tr>
<td>CH₄ + OH → H₂O + CH₃</td>
<td>(4)</td>
<td>9.0⁻¹</td>
<td>5.0⁻¹</td>
<td>3.7⁻⁷</td>
</tr>
</tbody>
</table>

A major revision in ΔE for these reactions, shown in the middle column, occurred following room temperature measurements in three laboratories which agreed among themselves [2, 6, 8, 9] and the explanation for the source of error in Avrumenko's earlier work [10] advanced by Kaufman and Del Greco [9]. Arrhenius plots using rate constants measured at room temperature and flame temperature, and rate constants derived from rate constant ratios at intermediate temperatures, all gave good agreement and it appeared that OH kinetics were in good condition. However, the question of activation energy was reopened by Greiner's recent measurements [3, 7] of these and other reactions in the temperature range 300 to 500 K, which give the lower activation energies shown in the third column.

During the preparation of this report, a careful consideration of sources of error in kinetic studies of hydroxyl radical reactions was made. It is concluded that Greiner's flash photolysis-kinetic spectroscopy technique [3,7,8] provides the most straightforward, and presumably most reliable method for measuring hydroxyl radical kinetics. However, possible sources of error in the flame temperature studies do not seem large enough to explain the order of magnitude differences between the reaction rates measured in flames and those obtained from an extrapolation of Greiner's measurements at lower temperatures. There appear to be four possible explanations for the wide variation in experimental activation energies:

1. OH reactions do not follow an Arrhenius temperature dependence.
2. There are errors in the analytical techniques which are not properly appreciated.
3. There are competing reactions which have not been properly accounted for in the analysis, or
4. An appreciable part of the CO₂ production in flames is by reaction with an excited hydroxyl radical.

There are two alternatives to an Arrhenius temperature dependence. There could be two reaction mechanisms, one important at high temperatures and the second important at low temperatures. In such a case the log k versus 1/T² plot might show two lines of different slope. Another possibility is to include a Tⁿ term in the rate constant. When this is done, a quite reasonable plot is obtained for k₁ (CO + OH) with T⁴. For k₂ and k₃ the inclusion of T gives a better correlation but Greiner's points still extrapolate lower than the flame-temperature measurements.

It is also possible that there are additional reactions which have not been properly accounted for in the analysis. In flame studies of the forward reaction, it is assumed that the primary reactant removing CO, H₂, or CH₄ is OH. It can be shown that O and H would not make significant contributions. However, the possible contribution of conversion of CO to CO₂ by HO₂ has not been considered in flame analyses. This line has been shown to account for about half of the CO₂ formation in explosion limits studies [12] but it was not possible to obtain an absolute rate. Values of k₁, obtained from flame measurements of the reverse reaction, may be appreciably lower than the direct measurements of the forward reaction. However, for H₂ + OH the forward and reverse measurements are in good agreement. Such a difference between reactions of H₂ and CO might be expected since k₂(CO + HO₂)/k₁(H₂+HO₂) = 9 ± 0.5 at 773 K [11]. However, if HO₂ contributed to CO conversion, then the measurements in flames which determine k₂/k₁ from a comparison of R_CO/[CO] to -R_H₂/[H₂], (where R refers to rate of formation or depletion), assuming only OH attack, would be too low because the rate of k₃ would be too large. However, the k₂/k₁ measurements from flames are higher than the value obtained from an extrapolation of the ratio of Greiner's two measurements. Therefore, reaction with HO₂ in flames does not seem able to account for the entire difference.

In assessing Greiner's work [3, 7], one naturally looks for a three-body combination reaction which might generate OH and become less efficient at higher temperatures. Such a phenomena could be produced if H₂O₂ were produced by recombination of 2 OH. The HO₂, formed by reaction of H with H₂O₂, could react with CO or H₂ resulting in regeneration of OH. Greiner [12] has observed a very rapid recombination of OH in the photolysis of H₂O₂ in addition to decay due to OH + OH → H₂O + O. When H₂, CO, or CH₄ were added, the OH decay decreased (in the case of CO there was more OH than when H₂O₂ was photolyzed by itself). The formation of H₂O₂ seems to be an unlikely, but not impossible, complication and suggests that further studies with a variation in pressure and third bodies might be useful.

In Greiner's study of the reaction of hydroxyl with hydrocarbons, a combination reaction of the radical formed in the initial step with another OH was postulated. A second-order reaction rate of k = 10⁻¹⁴ cm³ mol⁻¹ s⁻¹ was used to correct for this. If this were a normal combination reaction, with a negative temperature coefficient, its contribution might have been overestimated at high temperature leading to a low activation energy. In addition, it
is ordinarily expected that an abstraction reaction would have a positive activation energy. Therefore, the negative activation energy observed by Greiner for abstraction of a tertiary hydrogen by hydroxyl suggests that he may be underestimating the activation energies in the entire series.

Since there is no explanation available at present for this disagreement in activation energies, further experimentation is needed. Especially useful for clarification of the activation energy problem would be (1) repetition of Greiner’s work with different pressures and third bodies, (2) studies in which the role of HO2 can be determined, and (3) additional studies in the subambient, 500 to 1000 K, or < 2000 K temperature regions.

In more general terms the following areas for additional research should yield useful information about hydroxyl radical reactions:

1. High temperature studies capable of measuring OH as well as CO, H2, or other reacting species,
2. Flame studies in which OH is measured by spectroscopic or other direct methods such as molecular beam mass spectroscopy,
3. Studies spanning the intermediate range from 300 to 1000 K,
4. Studies above 2000 K,
5. Improved determinations of the OH/number,
6. Any rate measurements in which the role of HO2 can be clearly established,
7. Reaction of OH with species other than CO, H2, and CH4.


E. Acknowledgements


Support from the National Standard Reference Data System—National Bureau of Standards made it possible to expand the earlier versions of this material and obtain a more complete and current coverage of the literature. The concurrent pursuit of an experimental project in gas phase kinetics, supported through Grant AP 00828 from the National Air Pollution Control Administration, Environmental Health Service, Public Health Service, was found extremely helpful in carrying out the evaluative effort. The reviewer has profited from conversations and correspondence with many of the authors whose work is referenced. The encouragement and assistance of David Garvin, Chemical Kinetics Information Center, National Bureau of Standards, and Lewis H. Gevan, Project Monitor, are greatly appreciated.
Appendix A. List of Reactions

1. OH + OH $\rightarrow$ H$_2$O + O
2. CO + OH $\rightarrow$ CO$_2$ + H
3. H$_2$ + OH $\rightarrow$ H$_2$O + H
4. CH$_4$ + OH $\rightarrow$ H$_2$O + CH$_3$
5. H + NO$_2$ $\rightarrow$ NO + OH
6. O + OH $\rightarrow$ O$_2$ + H
7. H + D$_2$ $\rightarrow$ HD + D
8. C$_2$H$_4$ + OH $\rightarrow$
9. C$_2$H$_5$ + OH $\rightarrow$
10. C$_2$H$_6$ + OH $\rightarrow$
11. H + O$_2$ $\rightarrow$ OH + O
12. O + H$_2$ $\rightarrow$ OH + H
13. H + O$_2$ + M $\rightarrow$ HO$_2$ + M
14. O + RH $\rightarrow$ OH + R
15. H + RH $\rightarrow$ H$_2$ + R
16. OH + RH $\rightarrow$ H$_2$O + R
17. OH + H$_2$O$_2$ $\rightarrow$ H$_2$O + HO$_2$

Appendix B. List of Symbols

chem subscript, refers to change in concentration due to chemical reaction as opposed to that due to diffusion
D subscript, refers to reaction in which one or more H's have been replaced by D
ESR electron spin resonance
FP–KS flash photolysis – kinetic spectroscopy
H's high temperature reaction rate data
J joules
$J$ forward rate constant for reaction 1
$K_{eq}$ equilibrium constant
$k_1$ reverse rate constant for reaction 1
UV ultraviolet
X concentration
$X$ initial concentration

Appendix C. List of Conversion Factors

### Second-order reactions

<table>
<thead>
<tr>
<th>$B$</th>
<th>$A$</th>
<th>cm$^3$ mol$^{-1}$ s$^{-1}$</th>
<th>litre mol$^{-1}$ s$^{-1}$</th>
<th>m$^3$ mol$^{-1}$ s$^{-1}$</th>
<th>m$^3$ particle$^{-1}$ s$^{-1}$</th>
<th>(mm Hg)$^{-1}$ s$^{-1}$</th>
<th>atm$^{-1}$ s$^{-1}$</th>
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<td>cm$^3$ mol$^{-1}$ s$^{-1}$</td>
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<td>$10^6$</td>
<td>6.023 x 10$^{23}$</td>
<td>62.40 x 10$^{-7}$</td>
<td>82.10 T</td>
<td>82.10 x 10$^{-3}$ T</td>
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</tr>
<tr>
<td>litre mol$^{-1}$ s$^{-1}$</td>
<td>$10^{-3}$</td>
<td>$10^6$</td>
<td>6.023 x 10$^{23}$</td>
<td>62.40 T</td>
<td>82.10 x 10$^{-3}$ T</td>
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<tr>
<td>m$^3$ mol$^{-1}$ s$^{-1}$</td>
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<td>$10^{10}$</td>
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<td></td>
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<tr>
<td>cm$^3$ particle$^{-1}$ s$^{-1}$</td>
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<td>0.1660 x 10$^{-3}$</td>
<td>0.1660 x 10$^{-3}$</td>
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<td>13.63 x 10$^{-4}$ T</td>
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<tr>
<td>(mm Hg)$^{-1}$ s$^{-1}$</td>
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<td>16.03 x 10$^{-4}$ T$^{-1}$</td>
<td>16.03 T$^{-1}$</td>
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<td>atm$^{-1}$ s$^{-1}$</td>
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<td>12.18 x 10$^{-2}$ T$^{-1}$</td>
<td>12.18 x 10$^{-2}$ T$^{-1}$</td>
<td>73.36 x 10$^{-3}$ T$^{-1}$</td>
<td>760</td>
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### Third-order reactions

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<th>m$^6$ mol$^{-2}$ s$^{-1}$</th>
<th>m$^6$ particle$^{-2}$ s$^{-1}$</th>
<th>(mm Hg)$^{-2}$ s$^{-1}$</th>
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<tr>
<td>cm$^6$ mol$^{-2}$ s$^{-1}$</td>
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<td>$10^{12}$</td>
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<td>6.740 x 10$^{-7}$ T$^2$</td>
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</tr>
<tr>
<td>litre$^2$ mol$^{-2}$ s$^{-1}$</td>
<td>$10^{-4}$</td>
<td>$10^6$</td>
<td>36.28 x 10$^{36}$</td>
<td>38.94 x 10$^{37}$ T$^2$</td>
<td>6.740 x 10$^{-7}$ T$^2$</td>
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<td></td>
</tr>
<tr>
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<td>$10^{-4}$</td>
<td>36.28 x 10$^{36}$</td>
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<td>6.740 x 10$^{-7}$ T$^2$</td>
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</tr>
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<td>2.76 x 10$^{-48}$</td>
<td>2.76 x 10$^{-48}$</td>
<td>1.07 x 10$^{-38}$ T$^2$</td>
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<tr>
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<td>2.57 x 10$^{-18}$ T$^{-2}$</td>
<td>2.57 x 10$^{-18}$ T$^{-2}$</td>
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<td>1.48 x 10$^{-4}$ T$^{-2}$</td>
<td>1.48 x 10$^{-4}$ T$^{-2}$</td>
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To convert a rate constant from one set of units $A$ to a new set $B$, the conversion factor is found vertically below $A$ and in the horizontal row $B$ of the appropriate Table, e.g. a second-order rate constant in units of cm$^3$ particle$^{-1}$ s$^{-1}$ can be converted to units of litre mol$^{-1}$ s$^{-1}$ by multiplying by 6.023 x 10$^{23}$.

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