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Cite as: Journal of Physical and Chemical Reference Data **1**, 535 (1972); https://doi.org/10.1063/1.3253102

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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, H_2, and CH_4. These four reactions are: (1) $OH + OH \rightarrow H_2O + O$; (2) $CO + OH \rightarrow CO_2 + H$; (3) $H_2 + OH \rightarrow H_2O + H$; (4) $CH_4 + OH \rightarrow CH_3 + H_2O$.

Values are recommended for k_1 and k_2 and for the ratio k_3/k_2 and k_4/k_2. These rate ratios are used with the previously established value of k_2 to obtain recommended values for k_3 and k_4.

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

$k_1 = 1.55 \times 10^{12}$, 300 K, $\log k^{+.1}_{-.5}$

$k_2 = 3.1 \times 10^{11} \exp(-300/T)$, 300–2000 K, $\log k \pm .3$

$k_3/k_2 = 73 \exp(2300/T)$, 300–2000 K, $\log k_3/k_2 \pm .3$

$k_3 = 3.8 \times 10^{13} \exp(-2600/T)$, 300–2000 K, $\log k \pm .3$

$k_4/k_2 = 92 \exp(2200/T)$, 300–2000 K, $\log k_3/k_2 \pm .3$

$k_4 = 2.85 \times 10^{13} \exp(-2500/T)$, 300–2000 K, $\log k \pm .7$.

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.

Contents

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List of Figures

List of Tables

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 chniques, with emphasis on the methods of proucing 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), $H_2+OH \rightarrow H_2O+H$ is identified as $k_3(H_2+OH)$. This rule is relaxed in Section B where e reaction being discussed is identified by its umber 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 $k_+ = K_{eq}k_-$ 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 author appear 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 moles^{-1} · seconds^{-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),

$$CO + OH \rightarrow CO_2 + H \qquad (2)$$

has varied by a factor of 10^3 over the last 10 years. As discussed in Section D, the 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 recombustion 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* CO_2. The reaction with OH is the major pathway for converting CO to CO_2 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.

A.1.2. 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

$$H + OH + M \rightarrow H_2O + M \qquad (21)$$

may dominate. This rate, and other recombination rates, are needed for calculation of the specific impulse of propulsion devices based on $H_2 - O_2$ 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][1] in 1961. A number of reactions which might produce OH were postulated. These included photodissociation of H_2O_2, HNO_2, or HNO_3, decomposition of peroxyalkyl and peroxyformyl radicals, the reaction of alkoxyl radicals with oxygen, the reaction of hydrogen atoms with O_2 and NO_2, the reaction of electronically excited oxygen atoms (from the photodissociation of ozone) with water [$O('D) + H_2O \rightarrow 2OH$], $HO_2 + NO \rightarrow OH + NO_2$, and $HNO + O_2 \rightarrow OH + NO_2$.

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.

	Relative rate	
		OH
C_2H_6	1	200
C_2H_4	450	3000
C_2H_2	50	200.

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.

$$CO + OH \rightarrow CO_2 + H$$
$$H + O_2 + M \rightarrow HO_2 + M$$
$$HO_2 + NO \rightarrow NO_2 + OH$$

$$NO_2 \quad NO + O$$
$$O + O_2 \rightarrow O_3.$$

The cycle will continue until the CO is all converted to CO_2 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 NO_2 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 CO_2 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).

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[1] Figures in brackets indicate the literature references at the end of Section A.

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

$$H+O_3 \rightarrow OH^* + O_2.$$

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 $OH+NO_2 \rightarrow HNO_3$ [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 Avramenko and Kolesnikova [B2–14a] gives a good description of the extensive studies by Avramenko and coworkers 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, $k_7(OH+OH+M)=3.2\times 10^{-32}$ T cm^6 molecule$^{-2}\cdot$s^{-1} and wall loss, k (wall)$=1.5\times 10^3$ exp $(-5{,}000/RT)$ cm^{-1}. The value for k_7 of 9.6×10^{-30} at 300 K may be compared with 18×10^{-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 (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, $H+NO_2 \rightarrow NO+OH$

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

$$H+NO_2 \rightarrow NO+OH \qquad (5)$$

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

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[2] Electron spin resonance.

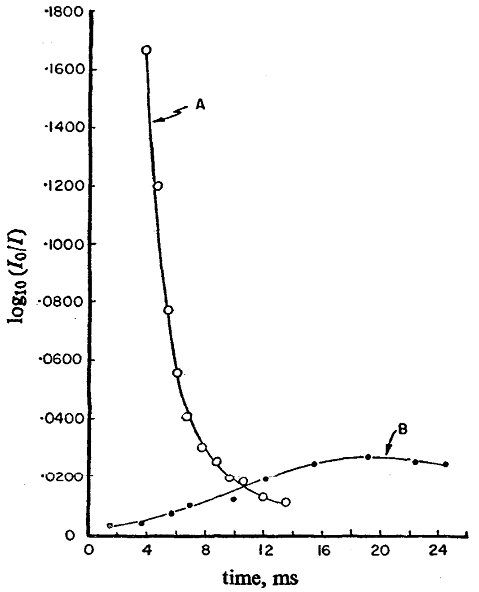

FIGURE A1. *Experimental decay profiles of hydroxyl radicals.*

A. Generated by $H+NO_2 \rightarrow \dot{N}O+OH$.
B. Generated by discharge through water vapor.
Flows in mmol/s, pressure in torr:
A. 0.33 H_2, 3.30 He, 1.94 torr.
B. 0.28 H_2O, 3.70 He, 2.18 torr.
Reference [B3–3b].

vapor, although producing OH, are not suitable sources of OH for kinetic studies. The OH is produced by secondary reactions, probably $H+O_2+M \rightarrow HO_2+M$ and $HO_2+H \rightarrow 2OH$. 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 H_2 in an inert carrier gas. It is possible to obtain 100 percent dissociation of the H_2 if traces of water vapor or O_2 are present.[3] A small amount of NO_2 is added and the following sequence of reactions take place:

$$H+NO_2 \rightarrow OH+NO \qquad (5)$$

$$OH+OH \rightarrow H_2O+O \qquad (1)$$

$$O+OH \rightarrow O_2+H. \qquad (6)$$

Since NO_2 will react with both H and O which are generated in the reaction, the stoichiometry of the overall reaction depends on the H/NO_2 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.

A2.3. H_2O_2 Decomposition: The Problem of HO_2

There are a large number of references in which rate ratios and direct rate measurements have been made in systems in which H_2O_2 was present. In some instances dissociation of H_2O_2, either thermally or photochemically, was the source of OH. In other cases, H_2O_2 was formed by recombination of OH. Unfortunately, the presence of H_2O_2 makes the system unsuitable for simple kinetic analysis and all rate measurements made in systems containing H_2O_2 must be viewed with suspicion.

In a series of papers Greiner [20, 21] has shown that photolysis of H_2O_2 occurs primarily by reaction

$$H_2O_2 = 2OH(^2\Pi)$$

but that this reaction is followed by the rapid reaction

$$OH+H_2O_2 \rightarrow H_2O+HO_2 \qquad (17)$$

with $k_{17}=5.67\times10^{11}$ cm^3 mol^{-1}·s^{-1} at 303 K. Therefore, any system in which OH is produced by dissociation of H_2O_2 (or for that matter in which H_2O_2 is formed by recombination of OH) will contain substantial quantities of HO_2.

The reactions of HO_2 therefore become of considerable importance in such systems. Greiner has investigated the reactions of H_2, CH_4, and CO in photolyzed H_2O_2. When 1.0 torr H_2O_2 + 100 torr Ar was flash photolyzed, the OH disappeared by a mechanism first order in [OH] at a rate of $\sim 4\times10^4$ s^{-1}. When 200 torr H_2, or 50 or 100 torr CH_4, was added, the rate for OH disappearance did not change appreciably from 4×10^4 s^{-1} although OH must have been reacting with H_2 or CH_4 with a rate much greater than 4×10^4 s^{-1}. Evidently some additional reaction was regenerating OH nearly as fast as it reacted. Greiner suggested the following sequence for regeneration of OH:

$$OH+HR \rightarrow H_2O+R,$$

$$R+H_2O_2 \rightarrow ROH+OH.$$

For the addition of CO, Greiner reports, "When 10 torr of CO was added in the H_2O_2 photolysis, [OH], after about 50×10^{-6} s, appeared to be larger than when H_2O_2 was photolyzed alone. This would require that even some of the OH that reacts with H_2O_2 be regenerated. The reaction

$$HO_2+CO \rightarrow CO_2+OH,$$

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 H_2 with OH could also regenerate OH directly

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[3] Traces of N_2, however, are thought to lead to the production of NH_3 and subsequent deposition of NH_4NO_3 on the tube surface. This causes rapid and unreproducible surface recombination of OH.

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] ($136.5 < \lambda < 186.0$ 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.

$$H_2O \xrightarrow{h\nu} OH\ (^2\Pi)+H\ (^2S).$$

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;

$$\begin{gathered} OH+OH+M \rightarrow H_2O_2+M \qquad (22) \\ H+H_2O_2 \rightarrow H_2O+OH \\ H+H_2O_2 \rightarrow HO_2+H_2 \\ H+HO_2 \rightarrow 2OH \\ OH+HO_2 \rightarrow H_2O+O_2. \end{gathered}$$

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_2 or H_2O formed by Reactions (1) and (6) may be used to give $[OH]_0$. This has been used to calibrate the "f" number [B3–30] and $k_3(OH+H_2)$ determinations by Kaufman [B3–3] and the determination of rate ratios involving $k_2(CO+OH)$ by others [B1–5, B1–6, B1–7]. It is not completely satisfactory however because the predicted $[OH]_0$ 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 7.1×10^{-4} [B3–30] and 14.8×10^{-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 H_2O 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 O_2 or H_2O, 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 Λ doublet in the $J=3/2$, $^2\pi_{3/2}$ state. The sensitivity, with standard instrumentation, is approximately 10^{11} molecules/cm^3. 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 broading 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: $N+NO \rightarrow N_2+O$ for both N and O and $O+NO_2 \rightarrow NO+O_2$ for O. The study indicated that ESR measurements of O and N, using 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, H_2-O_2 flames. The techniques have been extended to lean flames by McEwan and Phillips [40]. The most frequently used technique, the Li/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

$$H_2O+H \rightleftarrows H_2+OH$$

which are balanced in the flame gases.

The Li/LiOH method is based on the balanced reaction

$$Li+H_2O \rightleftarrows LiOH+H$$

Flame photometric techniques (either emission [31, 39] or absorption [40, 41, 42]) are used to measure the concentration of free Li atoms. The 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

$$Na+OH \rightarrow NaOH+h\nu.$$

For lean flames a correction must be made for the proportion of Na that combines as Na_2O [40].

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

$$Na+HCl \rightleftarrows NaCl+H.$$

The absolute techniques depend on a knowledge of the equilibrium constant which is fairly well known for the Li/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 $-dB/dt$, dC/dt, and dD/dt, and (2) in a constant concentration of B, measure $-dA/dt$, dC/dt, and dD/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 OH is measured in a large excess (and therefore relatively constant concentration) of reactant. In flames and shock tubes, the 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

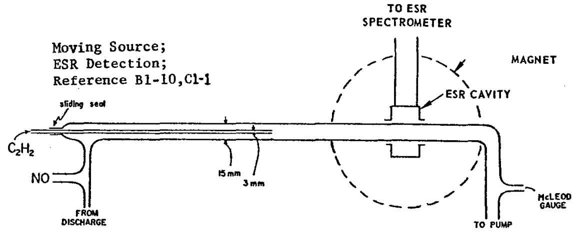
The simple discharge-flow system is being used by many workers to measure reactions of ions, atoms, and radicals. Schematics of several systems used to study OH reactions are shown in figure A2. This technique requires a source of radicals, a mixing zone, a long, cylindrical flow tube, a radical detector,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

In studies of hydroxyl radicals, the OH is generated by introducing NO_2 into a flowing gas stream containing H atoms. These are generated by a microwave discharge (~100 W at 2450 Mc/s) through Ar or He containing a few percent of H_2. A trace of H_2O or O_2 is frequently added to insure complete dissociation of the H_2. This avoids problems that might be caused by vibrationally excited H_2 [45].

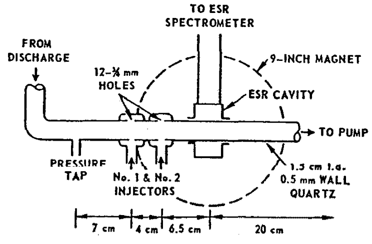
The pressure in the system is normally a few torr and mixing is rapid. The flow tube, usually quartz, is several centimeters in diameter and perhaps a meter long. Reaction time may be varied by moving the NO_2 inlet or the detector. Electron spin resonance and ultraviolet absorption have been used to measure 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.

Moving Source;
ESR Detection;
Reference B1-10,C1-1



Stationary Source; ESR Detection,
References B1-1, B2-1, B3-2, B4-5.



Stationary Source;
Ultraviolet Absorption Detection;
References B1-2, B3-3.

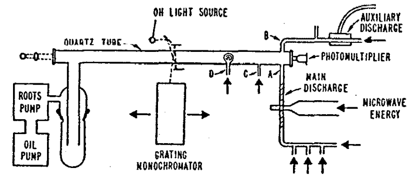


FIGURE A2. *Schematics of experimental apparatus used to measure* OH *kinetics in discharge-flow tubes.*

Reference [B3].

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 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 H_3BO_3 [B1–10] or H_3PO_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 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

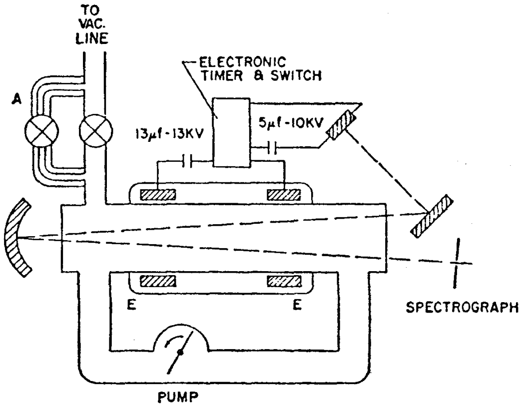


FIGURE A3. *Experimental arrangement.*

References [B2–2, B3–4, B4–4, C4–1, C6.1–1, 20, and 21].

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: $2OH \rightarrow H_2O + O$ or $2OH \rightarrow H_2O_2$. If O is produced, it will react with OH radicals in the gas phase. If H_2O_2 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 spectrograph, with the 250 J spectroscopic flash lamp providing the continuum.

H_2O 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 ($\leq 200 \times 10^{-6}$ 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

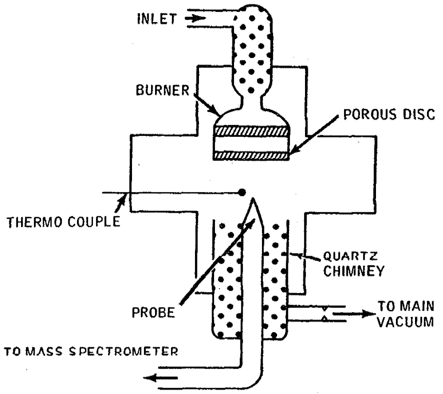


FIGURE A4. *Apparatus used to measure temperature and species profiles in low pressure flames.*

References [25 and 26].

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. Radical 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,

$$K_i=\frac{\rho_0\nu_0}{M_i}\frac{dG_i}{dz}$$

where ρ_0 is density, ν_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).

$$G_i=\frac{N_iM_i(\nu+V_i)}{\rho\nu}$$

where N_i is the number of moles of species, i, m_i the molecular weight of species i, ν 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 ν. In some cases V_i for atomic or radical species may be negative and larger than ν. The lack of experimental measurements of diffusion coefficients at high temperature and the computational difficulties of treating multicomponent 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 [4]

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].

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].

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B. Evaluation of Rate Constants

B1. k_1, Rate Constant for the Reaction, $OH+OH \rightarrow H_2O+O$

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 concentration 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 I. $OH+OH \rightarrow H_2O+O$

Equilibrium constant, $K_{eq}=0.108 \quad \exp(8{,}580/T)$, 600–5000 K $\quad \Delta H^\circ_{298}/R=8.49\times10^3$

$K_{eq}=4.27\times10^{11}$ at 300K

Rate constant. $-d[OH]/dt=2k_1[OH]^2$

$k=AT^B \exp(C/T)$ cm³ concentration units⁻¹ · s⁻¹

$cm^3\ mol^{-1}\cdot s^{-1}$	$cm^3\ particles^{-1}\cdot s^{-1}$	T(K)	Ref.	Comment
$1.55\pm0.15\times10^{12}$	$2.57\pm0.25\times10^{-12}$	300	1	ESR.
$.75\pm.20\times10^{12}$	$1.40\pm.30\times10^{-12}$	300	2	Abs. spec.
$.50\pm.16\times10^{12}$	$.84\pm.26\times10^{-12}$	300	10	ESR.
$.43\times10^{12}$	$.72\times10^{-12}$	300	20	Calculation.
$\geqslant0.1\times10^{12}$	$\geqslant0.17\times10^{-12}$	300	4	Surface recombination of H atoms.
10×10^{12}	1.7×10^{-11}	1600	9	Shock tube reverse.
190×10^{12}	32×10^{-11}			
For reverse $\Delta E/R\sim8$			8	Combustion studies.
Several mass-spectrometric studies support the higher value of k_1 if k_2 $(CO+OH\rightarrow CO_2+H)=10\pm2\times10^{10}$ cm³ mol⁻¹ · s⁻¹ is accepted.			5 6 7	
Recommended value at 300 K			Error limits	
1.55×10^{12} $cm^3\ mol^{-1}\cdot s^{-1}$	2.57×10^{-12} $cm^3\ particles^{-1}\cdot s^{-1}$		$\log k \begin{smallmatrix}+0.1\\-\ .5\end{smallmatrix}$	

is the same in both cases, the reactions involved being

$$H+NO_2 \rightarrow NO+OH \qquad (5)$$

$$OH+OH \rightarrow H_2O+O \qquad (1)$$

$$O+OH \rightarrow O_2+H. \qquad (6)$$

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

$$(-d[OH]/dt)_1=k_1[OH]^2,$$

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 $k_3(H_2+OH)$ by both groups is in agreement. An examination of the relevant equations shows that the only explanation for this agreement on k_3 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_3.

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 ±10 percent with the values determined by chemical titration. The absolute OH measurements should also be good to ±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, $k_5=2.9\times10^{13}$ cm^3 mol$^{-1}\cdot$s^{-1}, for B, $k_5=1\times10^{12}$. 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 $[NO_2]_0=3\times10^{-10}$ mol cm^{-3}, $k_1=1.5\times10^{12}$, $k_6=1\times10^{13}$, and $k(O+NO_2\rightarrow NO+O_2)=1.5\times10^{12}$, all in cm^3 mol$^{-1}\cdot$s^{-1}. The latter reaction was too slow to be significant. The Kaufman and Del Greco assumption [2] requires that the OH concentration be 3×10^{-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 3×10^{-10}. Assuming that mixing is instantaneously complete, a peak value of 2.9×10^{-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 $[OH]^2$. 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

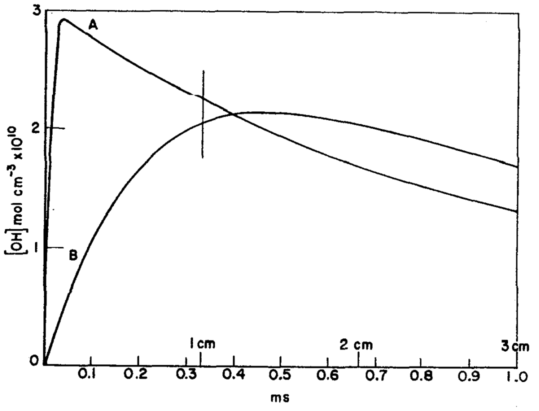


FIGURE B1. *Calculated decay profiles in hydroxyl radicals.*

Curve A: Instantaneous mixing assumed.
Curve B: Finite mixing time of 0.3 ms approximated by lowering value of $k_5(H+NO_2)$.

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_2O_2 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_2O 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 $k_2(CO+OH)/k_1$ indicate that if a value of $k_2=(10\pm2)\times10^{10}$ is accepted (and this value seems fairly reliable) the value of k_1 must be near 1.55×10^{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 the OH radical 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 $OH+OH\rightarrow H_2O+O$ 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. $E_2=18$ kcal/mol is cited, in passing, by Voevodsky and Kondratiev [8] from preliminary work by Azatyan. Kaufman and Del Greco [2] suggested $E_1=1$ kcal/mol. Neither is certain, but both are probably reasonable.

B1.2 References and Comments

B1.2a. Experimental Measurements

[1] Dixon-Lewis, G., Wilson, W. E., and Westenberg, A. A., Studies of hydroxyl radical kinetics by quantitative ESR, J. Chem. Phys. **44**, 2877 (1966).

The OH was generated by $H+NO_2\rightarrow NO+OH$. 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 ≈ 1 torr.

[2] Del Greco, F. P., and Kaufman, F., Lifetime and reactions of OH radicals in discharge flow systems, Disc. Faraday Soc. **33**, 128 (1962); F. Kaufman and F. P. Del Greco, Fast reactions of OH radicals, Symp. Combust. 9th, p. 659 (1963); F. Kaufman, Aeronomic reactions involving hydrogen. A review of recent laboratory studies, Ann. Geophys. **20**, 106 (1964).

The OH was generated by $H+NO_2\rightarrow NO+OH$ and the second order decay measured by absorption spectroscopy near 300 nm. The initial OH concentration [OH] was determined by

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

$OH+OH\rightarrow H_2O+O$ k_1			$H_2O+O\rightarrow OH+OH$ k_{-1}			Temp. range, K	Reference
A	B	C	A	B	C		
−11.59 ± 0.07 (log k)			−23.15 (log k)			300	This work.
−11.02 ± 0.45*		0.39 ± 0.25	−10.02 ± 0.45*		9.06 ± 0.25	300–3000	Baulch et al. [19].
−10.860		.5	−9.85		9.1	300–900	Schofield [15].
−10.90 ± 0.3		.50 ± 0.25	−9.86 ± 0.8		9.1 ± 0.5	300–2000	Kaufman & Del Greco [2].
−11.28 ± 0.21		.5 ± 0.1	−10.16 ± 0.19		9.1 ± 0.1	300–3000	Bascombe [17].
−10.96	+0.0165	.474					Cherry et al. [13].
−11.0 ± 0.7		.5				1000–3500	Jensen & Kurzius [18].
−10.90		.5	−9.94		8.93		Kaskan & Browne [16].
			−10.16		9.1		Tunder et al. [12].

$k=10^{A}\ T^{B}\ \exp[-C(1000/T)]$ cm³ particles⁻¹·s⁻¹, $-d[OH]/dt=2k_1[OH]^2$

*Overall uncertainty in log k: ±0.1 at 300 K, ±0.2 at 2000 K.

assuming (1) that there was a region where $H+NO_2 \rightarrow NO+OH$ had gone to completion and $OH+OH \rightarrow H_2O+O$ had not yet begun, and (2) that [OH] in this region was given by the NO_2 flow rate. The light absorption path integrated 1/3 ms of reaction time and mixing required 1 ms. It appears that the initial OH concentration was overestimated because both the finite mixing time and the overlapping of the formation and decay reactions would lead to a lower actual [OH] then given by the NO_2 flow rate. If the actual [OH] were one-half of the anticipated [OH] the derived k would agree with that from reference [1].

Experimental procedures and results are described in the first two papers. The value quoted here is taken from the last. (The definition of k in these papers is $d[OH]/dt=-k[OH]^2$. That used here is $d[OH]/dt=-2k[OH]^2$.)

[3] Westenberg, A. A., and De Hass, N., Quantitative ESR measurements of gas phase H and OH concentrations in the $H-NO_2$ reaction, J. Chem. Phys. **43**, 1550 (1965).

A study of H and OH concentrations as a function of H and NO_2 flow rates showed the occurence of $OH+OH \rightarrow H_2O+O$ and $O+OH \rightarrow H+O_2$. The value quoted in this study was considered by the authors to be an estimate. The value quoted in the table is the revised one given in reference [1].

[4] Wise, H., Ablow, C. M., and Sancier, K. M., Diffusion and heterogeneous reaction. VI. Surface recombination in the presence of distributed atom sources, J. Chem. Phys. **41**, 3569 (1964).

Only a lower limit for the rate coefficient was obtained.

[5] Reference [1] also reports a mass-spectrometric study of the $CO-OH$ reaction in which the ratio O_2/CO_2 (O_2 formed via $OH+OH=H_2O+O$ and $O+OH=O_2+H$ and CO_2 formed via $CO+OH=CO_2+H$) supports the higher value of k.

[6] Herron, J. T., Mass spectrometric study of the rate of reaction of CO with OH, J. Chem. Phys. **45**, 1845 (1966).

If the rate of $CO+OH$ is assumed to have the value suggested in this report, Herron's measurements, corrected for the effect of NO_2 on the rate, support the suggested value for k_1. See reference [7].

[7] Wilson, Wm. E., and O'Donovan, J. T., Mass spectrometric study of the reaction rate of OH with itself and with CO, J. Chem. Phys. **47**, 5455 (1967).

A repetition of the experiments of reference [6] showed that the $CO+OH$ rate depends upon the NO_2 concentration. (The reaction $NO_2+H \rightarrow NO+OH$ was used to produce hydroxyl.) The suggested value for $OH+OH$ given in the table is shown to be consistent with the recommended $CO+OH$ rate.

[8] Voevodsky, V. V., and Kondratiev, V. N., Progr. Reaction Kinetics **1**, 41 (1961).

This article cites preliminary work of Azatyan and gives an activation energy for k_1 of 18.0±0.2 kcal/mol.

[9] Brokaw, R. S., Ignition kinetics of the carbon monoxide-oxygen reaction. Symp. Combust., 11th (The Combustion Institute, 1969) p. 1063.

A study of shock-tube induction times on reportedly dry $CO-O_2$ mixtures could be explained if a water vapor content of 20 ppm was assumed. From the CO_2 growth rate it was possible to calculate a water vapor content and a value for k_{-1}. Two different methods led to 8×10^{11} and 1.5×10^{12} $cm^3mol^{-1}\cdot s^{-1}$. The smaller value, when combined with the room temperature k_1 of Kaufman, gave an activation energy for the reverse reaction of 19.5 kcal.

[10] Breen, J. E., and Glass, G. P., The rate of some hydroxyl radical reactions, J. Chem. Phys. **52**, 1082 (1970).

The experiment was similar to that of reference [1], except that Breen and Glass observed a first order wall decay. In order to maintain a constant surface condition, they coated the flow tube with boric acid. No wall losses were evident in references [1] or [2]. First-order wall losses should have been observable. Second order wall losses cannot be separated from the homogeneous OH but large losses should have been observable from differences in the measured k_1 as a function of pressure and carrier gas. However, the first-order loss was clearly evident in this study and provides an alternate explanation for the differences in the room temperature values of k_1.

B1.2b. Evaluations

[11] Bahn, G. S., Chemical kinetics. Reactions among H_2O, HO_2, H_2O_2, and O_3, also involving H_2, O_2, OH, H and O, Pyrodynamics **3**, 245 (1965).

[12] Tunder, R., Mayer, S., Cook, E., and Schieler, L., Aerospace Corp., Thermochemistry Research Dept., Report No. TR–1001(9210–02)–1 (1967).

Quoting from R. M. Fristrom and A. A. Westenberg, Flame Structure. (McGraw-Hill Book Co., New York, 1965) p. 367.

[13] Cherry, S. S., Gold, P. I., and Van Nice, L. J., TRW Systems, Redondo Beach, California, Report 08832–600–T000–AD 828–794.

[14] Langan, W. T., Cresswell, J. D., and Browne, W. G., Effects of ablation products on ionization in hypersonic wakes, J. Am. Inst. Aeron. Astronaut. **3**, 2211 (1965).

A secondary source for rate data. The report of these authors, General Electric Technical Information Series 65SD208 (January 1965), same title, is stated to contain the detailed analysis. (Not examined).

[15] Schofield, K., An evaluation of kinetic rate data for reactions of neutrals of atmospheric interest, Plant. Space Sci. **15**, 643 (1967); Erratum: Planet Space Sci. **15**, 1336 (1967).

[16] Kaskan, W. E., and Browne, W. G., General Electric Co. Space Sciences Laboratory Report R64SD37, July 1964.

[17] Dascombe, K. H., Reaction rate data: the hydrogen/oxygen system, Ministry of Aviation, Explosives Research and Development Establishment, Waltham Abbey, Essex, England, E.R.D.E. 1/S/65.

[18] Jensen, D. E., and Kurzius, S. C., Rate constants for calculations on nozzle and rocket exhaust flow fields, AeroChem Research Laboratories, Princeton, New Jersey, March 1967. Report TP–149.

[19] Baulch, D. L., Drysdale, D. D., and Lloyd, A. C., Critical evaluation of rate data for homogeneous, gas-phase reactions of interest in high-temperature systems, Dept. of Physical Chemistry, The University, Leeds, England, High Temperature Reaction Rate Data Report No. 2, November 1968.

B1.2c. Calculations

[20] Mayer, S. W., and Schieler, L., Activation energies and rate constants computed for reactions of oxygen with hydrocarbons, J. Phys. Chem. **72**, 2629 (1968).

The activation energy and rate constant for k_{-1} was calculated using the Johnston-Parr bond-energy method modified to account for spin repulsion. The activation energy was reported as 18.9 $kcal\ mol^{-1}$ with rate constants of 1.0 at 300 and 1.0×10^{10} at 1000 K. Using $k_1=Kk_{-1}$ and $\log K=11.630$, $k_1=4.27\times10^{11}$ somewhat lower than the direct measurement.

B1.2d. General References

[21] Gardiner, W. C., Jr., Morinaga, K., Ripley, D. L., and Takeyama, T., Transition from branching-chain kinetics to partial equilibrium in the combustion of lean hydrogen-oxygen mixtures in shock waves, J. Chem. Phys. **48**, 4 (1968).

Concentration profiles of the OH radical in the shock-initiated combustion of lean hydrogen-oxygen-argon mixtures at low pressures (~200 torr) and temperatures (~1400 K) are found to exhibit pronounced spikes prior to attainment of partial equilibrium. The authors show that this effect is not encompassed within the accepted mechanism for the H_2-O_2 reaction. Possible reconciliations are presented and discussed.

[22] Barrett, J. M., and Walker, R. W., Aged boric-acid-coated silica reaction vessels, Comb. and Flame **12**, 501 (1968).

B2. k_2, Rate Constant for the Reaction, $CO+OH \rightarrow CO_2+H$

B2.1 General Discussion

B2.1a. Rate Constant Measurements

The reaction of CO with OH is an important one for several reasons. This is the primary means of converting CO to CO_2 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 H_2+OH and CH_4+OH are best determined from measurements of rate ratios to $CO+OH$ 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 $H_2+OH \rightarrow H_2O+H$. There are three reasons for preferring $CO+OH$: (1) The available data on H_2+OH suitable for setting an absolute value for the rate constant, including its temperature dependence, are less extensive and probably less reliable than those for $CO+OH$. (2) The activation energy of the $CO+OH$ reaction is lower.

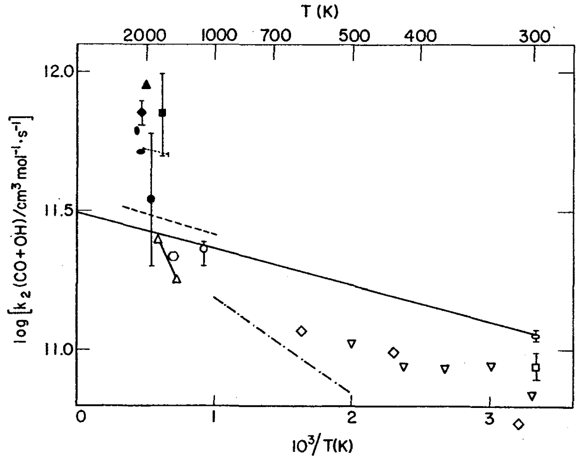


FIGURE B2. *Arrhenius plot of* k_2(CO + OH).

⊖	Dixon-Lewis, Wilson, Westenberg, reference [1];
□	Greiner, reference [2a];
▽	Greiner, reference [2b];
ο	Hottel et al., reference [3];
○	Dixon-Lewis, et al., reference [4];
△	Jost, Scheckner, and Wagner, reference [7];
◇	Wong and Belles, reference [15];
—·—·	Bonne, reference [8];
.....	Browne et al., reference [12];
--	Gardiner, Takeyama, Walker

solid symbols refer to flame structure studies using equilibrium assumption for OH concentration.

▲	Westenberg and Fristrom, reference [6a] and Wilson. O'Donovan and Fristrom reference [9c]:
●	Westenberg and Fristrom, reference [6b1];
■	Westenberg and Fristrom, reference [6b2];
◆	Wilson, O'Donovan, and Fristrom, reference [9a];
⬬	Wilson, O'Donovan, and Fristrom, reference [9b];
⬮	Wilson, O'Donovan, and Fristrom, reference [9d].
———	Recommended value

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_2 is not used here but is considered in later sections in which rate ratio information involving k_3(H_2 + OH) and k_4(CH_4 + 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 $k_2 = 9.8 \pm 0.2$ $T^{1/2}$ cm^3 mol^{-1} · s^{-1} with zero activation energy.

The large variation in the points obtained from flames requires some discussion. In the determination of k_2 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_2 is obtained from $R_{CO_2} = k_2[CO][OH]$. 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_2 would be too high. It is usually possible to make adequate corrections for k_{-2}, H + CO_2 → CO + OH.

The flame structure studies which yielded the higher values for k_2 (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 final 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_2. The values of k_2 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., $k_{-2} = -R_{CO_2}/[H][CO_2]$. Most frequently [H] is obtained by adding D_2O, measuring the rate of formation of HD, R_{HD}, and [D_2O], and using a value of k_{-3D} (H + D_2O) 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_{-2}(H + CO_2). The forward rate constant may then be obtained via the equilibrium constant, $k_2 = K_{eq} \cdot k_{-2}$. In several rate evaluations, a determination of k_{-3D}/k_{-2} by Fenimore and Jones [5] has been used with various values of k_3(H_2 + OH) to obtain k_2. Since this is really a rate ratio measurement, it has been used in determining the value of k_3/k_2 [B3–14] but not for determining k_2.

Dixon-Lewis [4] et al. have also reported values of k_{-3D}/k_{-2} and have used them to obtain a value of k_2. However, their value of k_2 was not based on an assumed value of k_3 since the parameters from which k_{-3D} could be calculated were all measured in the same flame system. Their value of k_2 depends ultimately on k_7(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.

TABLE II. $CO+OH \rightarrow CO_2+H$

Equilibrium $K_{eq}=2.34\times10^{-3}$ exp $(12{,}400/T)$ 300–1000K
Constant, $K_{eq}=8.26\times10^{-3}$ exp $(11{,}135/T)$ 1000–2500 K $\Delta H^{\circ}_{298}/R=-12.5$
Rate constant, $k=A$ exp (C/T) cm^3 concentration units$^{-1}\cdot$ s^{-1}.

A		C	T range K	Ref.	Comment
Mol units	Particle units				
1.3×10^{11}	2.16×10^{-13}	115	300–500	2b	Flash photolysis-kinetic spectroscopy.
3.55×10^{11}	5.9×10^{-13}	800	500–1000	8	Flame absorption spectroscopy.
3.7×10^{11}	6.15×10^{-13}	350	1000–3000	12	Flame-absorption spectroscopy.
6.2×10^{11}	1.0×10^{-12}	300	1500–2200	13	Shock tube.
		500		16	Calculation.
3.5×10^{11}	5.8×10^{-13}	600	300–600	15	Stirred reactor.

Rate constant				
k_2 in 10^{10} cm^3 mol$^{-1}\cdot$ s^{-1}	k_2 in 10^{-13} cm^3 particles$^{-1}\cdot$ s^{-1}			
1.15 ± 0.05	1.91 ± 0.08	300	1	Electron spin resonance.
$0.89\pm.09$	$1.48\pm.15$	300	2	Flash photolysis-kinetic spectroscopy.
2.21	3.67	1400	3	Well-stirred reactor.
2.3	3.8	1072	4	Flame, reverse.
1.0	1.66	1200	5a	Flame, reverse.
1.26	2.09	1350		
1.5 ± 2	2.5 ± 3	1000–1200	5b	Flame, reverse.
9	15	1950	6a	Flame.
2–6	3–10	1850	6b1	Flame.
5–10	8–16	1650	6b2	Flame.
1.8	3.0	1380	7	CO reactor.
2.55	4.2	1720		
$7.5\pm.75$	11.5 ± 1.5	2000	9a	CH_4 flame.
$5.1\pm.1$	$8.3\pm.2$	2150	9b	Same, inhibited with CH_3Br.
$9.0\pm.1$	$15\pm.2$	2000	9c	Same, inhibited with HCl.
$7.75\pm.25$	$12.5\pm.5$	2150	9d	Same, inhibited with CH_3Cl.
$0.51\pm.2$	$.85\pm.3$	300	10	Mass spectroscopic analysis of CO_2 formed.
$1.04\pm.01$	$1.73\pm.02$	300	11	
5.6	9.3	310	15	Stirred reactor, mass spectroscopic analysis for CO_2 and H_2O.
10.1	16.8	440	15	
13.6	21.7	610	15	

Recommended values 300–2000 K

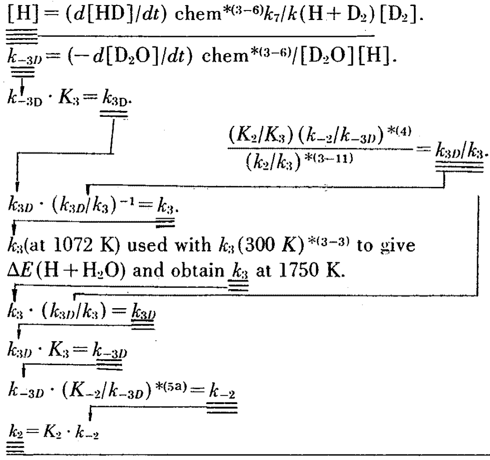
Units	Rate expression	k_2 at 1000 K	Error limits
cm^3 mol$^{-1}\cdot$ s^{-1}	$k_2=3.1\times10^{11}$ exp $(-300/T)$	2.3×10^{11}	$\log_{10}k_2\pm0.3$
cm^3 particles$^{-1}\cdot$ s^{-1}	$k_2=5.1\times10^{-13}$ exp $(-300/T)$	3.8×10^{-13}	

The room temperature measurements of k_2 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 k_2/k_1 which confirm a value of this order of magnitude from measurements of the initial OH and the amount of CO_2 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 k_2 at room temperature. Greiner [2b] has recently measured k_2 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 k_2 which was quoted in the literature. As can be seen from the data chain this value of k_2 was really based on a measurement of $k_{-2}(H+CO_2)/k_{-3D}(H+D_2O)$. A rather complicated sequence was used to establish the relation between $k_{-3D}(H+D_2O)$ and $k_{-3}(H+H_2O)$. This value of k_2 depends ultimately on the value of $k_7(H+D_2)$. The value used was 4.2×10^{11} cm^3 mol$^{-1}\cdot$s^{-1} at 900 K. The most recent experimental

TABLE IIa. *Data chain for the evaluation of a value of* $k_2(CO+OH)$ *found in the literature*

k = Rate constant
K = Equilibrium constant
ΔE = Activation energy
*Indicates an experimental rate measurement, the reference is given in parentheses
Arrows indicate transfer of numerical values
$CO + OH \rightarrow CO_2 + H$ Reaction (2)
$H_2 + OH \rightarrow H_2O + H$ Reaction (3)
$HD + OD \rightarrow D_2O + H$ Reaction (3D)
$k_7(H+D_2)$ at 1000 K*(27) used with
$\Delta E(H+D_2)^{*(28)}$ to give $k_7(H+D_2)$ at 1072 K.



$\underline{\underline{[H]}} = (d[HD]/dt)\ \mathrm{chem}^{*(3-6)} k_7/k(H+D_2)[D_2].$

$\underline{\underline{k_{-3D}}} = (-d[D_2O]/dt)\ \mathrm{chem}^{*(3-6)}/[D_2O][H].$

$k_{-3D} \cdot K_3 = \underline{\underline{k_{3D}}}.$

$\frac{(K_2/K_3)(k_{-2}/k_{-3D})^{*(4)}}{(k_2/k_3)^{*(3-11)}} = \underline{\underline{k_{3D}/k_3}}.$

$k_{3D} \cdot (k_{3D}/k_3)^{-1} = \underline{\underline{k_3}}.$

k_3(at 1072 K) used with $k_3(300\ K)^{*(3-3)}$ to give $\Delta E(H+H_2O)$ and obtain $\underline{\underline{k_3}}$ at 1750 K.

$k_3 \cdot (k_{3D}/k_3) = \underline{\underline{k_{3D}}}$

$k_{3D} \cdot K_3 = \underline{\underline{k_{-3D}}}$

$k_{-3D} \cdot (K_{-2}/k_{-3D})^{*(5a)} = \underline{\underline{k_{-2}}}$

$\underline{\underline{k_2}} = K_2 \cdot k_{-2}$

value is 2.6×10^{11} 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_2. Schofield [23] gives $6.6 \times 10^{11} \exp(-1030/RT)$ $cm^3\ mol^{-1} \cdot s^{-1}$ (1.1×10^{-12} in particle units) and Baulch et al. give $5.6 \pm 0.8 \times 10^{11} \exp(-1080 \pm 500/RT)$ $cm^3\ mol^{-1} \cdot s^{-1}$ ($9.3 \pm 1.3 \times 10^{-13}$ 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_2/k_3, k_{-2}/k_{-3}, or k_{-2}/k_{-3D}.[5] A value must be assumed for k_3, k_{-3}, or k_{-3D} and used to calculate k_2 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 $k_3 = 10^{13.8 \pm 0.7} \exp(-5.900 \pm 1000/RT)$ but have not indicated the uncertainty suggested by Kaufman. This rate expression is based on Kaufman's room temperature rate for k_3[B3–3c] and a value for 1500 K calculated from a rate expression due to Fenimore and Jones. [B3–7], Baulch et al., also graph points (their references [3] and [7]; this report references [B3–14a] and [B3–13]) in which the original authors calculated k_2 from an experimental k_2/k_3 and a k_3 which they had determined experimentally.

The higher activation and frequency factor obtained by Baulch et al. [24b] depends partly on their use of Kaufman's [B3–3c] value for k_3. In a later review they recommend a value for k_3 of $2.19 \times 10^{13} \exp(-5150/RT)$ $cm^3\ mol^{-1} \cdot s^{-1}$ [cf. Kaufman's [B3–3c] $6.3 \times 10^{13} \exp(-5900/RT)$]. If their recommended value of k_3 were to be used to recalculate 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_3 or k_{-3}. His evaluation of k_3 is based on Kaufman's room temperature point [B3–3] and the shock tube results of Ripley and Gardiner [B3–8a]. The latter are no longer considered reliable [B3–8b]. Schofield's [B2–3] higher activation energy for k_2 is due largely to his use of a high value of k_3 in the calculation of k_2 points from k_3/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, $CO + OH \rightarrow H + CO_2$, Reaction 2

B2.2a. Experimental Measurements

[1] Dixon-Lewis, C., Wilson, W. E., and Westenberg, A. A., Studies of hydroxyl radical kinetics by quantitative ESR, J. Chem. Phys. **44**, 2877 (1966).

The OH was generated by $H + NO_2 \rightarrow NO + OH$. Quantitative electron spin resonance was used to determine the initial concentration and to follow the hydroxyl radical decay in a fast flow system at ~1 torr.

[2a] Greiner, N. R., Hydroxyl radical kinetics by kinetic spectroscopy. I. Reactions with H_2, CO and CH_4 at 300 K, J. Chem. Phys. **46**, 2795 (1967).

The OH was generated by flash photolysis of H_2O and the decay followed by kinetic spectroscopy (absorption, static system, pressure 20 to 200 torr). Because of the short time of reaction ($< 200 \times 10^{-6}$ 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.

[2b] Greiner, N. R., Hydroxyl radical reactions by kinetic spectroscopy. V. Reactions with H_2 and CO in the range 300–500 K, J. Chem. Phys. **51**, 5049 (1969).

The FP-KS apparatus was adapted so that the temperature could be varied from 300 to 500 K. The data reported for k_2 in $cm^3\ mol^{-1} \cdot s^{-1}$ are: average of 4 measurements at 300 K, $8.56 \pm 0.43 \times 10^{10}$; 334 K, $9.80 \pm 0.53 \times 10^{10}$; 373 K, $8.84 + 0.27 = 10^{10}$; 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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[5] k_3 is the rate constant for $H_2 + OH \rightarrow H_2O + H$.

squares fit gives log A (cm^3 mol^{-1}·s^{-1})$=11.10\pm.07$ and $E=230\pm140$ (cal/mol). 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. [B3–4, B4–4] and Section D.) These points do fall within the uncertainty limits of log $k\pm0.3$ given with th suggested rate equation.

[3] Hottel, H. C., Williams, G. C., Nerheim, N. M., and Schneider, G. R., Kinetic studies in stirred reactors: combustion of carbon monoxide and propane, Symp. Combust. 10th (The Combustion Institute, 1965), p. 111.

k_2 was calculated from a study of CO combustion rates in a well stirred reactor.

[4] Dixon-Lewis, G., Sutton, M. M., and Williams, A., Reactions contributing to the establishment of the water gas equilibrium when carbon dioxide is added to a hydrogen-oxygen flame, Trans. Faraday Soc. **61**, 255 (1965).

Addition of both D_2O 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, $k_{-3D}(H+D_2O)/k_{-2}(H+CO_2)=4.3\pm0.5$. The value of k_2 given, 2.3×10^{10} cm^{3}mol^{-1}·s^{-1}, was calculated from the equilibrium constant and $k_{-3D}=9.4\times10^{13}$ given in reference [25]. However, in the flame study R_{HD}, the rate of formation of HD from $H+D_2O$, and $[D_2O]$, the concentration of D_2O were measured experimentally. The derived k_2, therefore, does not require the use of k_{-3D} but only a value of [H] since $k_{-3D}=R_{HD}/[H][D_2O]$. The value of [H] used in determining k_{-3D} and ultimately in determining k_2 is traceable to the rate constant used for $H+D_2=HD+D$ [B3–6]. A recent determination of this rate [26] indicates that the value used was high by a factor of 1.8. The resulting value of k_2 may also be high by a factor of as much as 1.8.

[5a] Fenimore, C. P., and Jones, G. W., The reaction of hydrogen atoms with carbon dioxide at 1200–1350 K, J. Phys. Chem. **62**, 1578 (1958).

[5b] Fenimore, C. P., and Jones, G. W., Rate of reaction in hydrogen, nitrous oxide and in some other flames, J. Phys. Chem. **63**, 1154 (1959).

Reference [5a] reports work in which $k_{-2}(H+CO_2)/k_{-3D}(H+D_2O)$ was measured. In reference [5b] the ratio is given as 0.33 exp $(7800/RT)$. This is not a direct measurement of k_2. The references are given here because they have frequently been used with a value for $k_{-3D}(H+D_2O)$ or $k_{-3}(H+H_2O)$ to obtain a value of k_{-2} from which k_2 is calculated and shown on Arrhenius plots. In addition to the uncertainty due to use of a value for $k_{-3D}(H+D_2O)$ the derived k_2 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_3/k_2 [B3–14].

[6a] Westenberg, A. A., and Fristrom, R. M., Methane-oxygen flame structure. IV. Chemical kinetics considerations, J. Phys. Chem. **65**, 591 (1961).

[6b] Westenberg, A. A., and Fristrom, R. M., H and O atom profiles measured by ESR in C_2 hydrocarbon flames, Symp. Combust., 10th (The Combustion Institute, 1965), p. 473.

k_2 was determined in low pressure (1/10 atm) flames [(6a): CH_4+O_2, (6ba):$C_2H_6+O_2$, (6b2):$C_2H_4+O_2$] from the measured [CO], [d CO/dt] chem, and assuming [OH] at hot boundary is given by chemical equilibrium conditions. Since [OH] may well exceed equilibrium values these rates may be too high.

[7] Jost, W., Schecker, H. G., and Wagner, H. Gg., Z. Physik, Chem. (Frankfurt) **45**, 47 (1965).

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 ascertained, first, that the flame gases 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 3 cm of the long tube. Investigation of the reaction of the added CO with OH gave $k_2=10^{12}$ exp $(-4700/RT)$ for $\Delta H_f^\circ(OH)=9.3$ kcal mol^{-1}. As the authors stress, the apparent activation energy is a small difference between large numbers involved in the experiment itself and in the OH equilibrium. Other unpublished results from their laboratory would indicate a smaller E_2. At the end points of their temperature range, $k_2=1.8\times10^{11}$ cm^3 mol^{-1}·s^{-1} at 1380 K and 2.55×10^{11} at 1720 K.

[8] Bonne, Ulrich, Inst. Phys. Chemie., Univ. Göttingen, private communication.

A flame structure study of a $2\,CO+O_2$ flame (with a trace of water) at 20 torr. CO and CO_2 were measured by gas chromatography, [OH] was measured by absorption spectroscopy of the Q, 6 line in the (0,0) band of $^2\Sigma^+\longleftarrow{}^2\pi_1$ using $f=10\times10^{-4}$ (Anketell and Pery-Thorne [B3–31] found $f=12.8\times10^{-4}$ for this line). Bonne reports $k_2=10^{11.55}$ exp$(-1600/RT)$ cm^{3}mol^{-1}·s^{-1}. Use of the higher f number would increase Bonne's rate constant by 1.28 and bring it into better agreement with other work. His activation energy of 1600 cal is further evidence that the high activation energies obtained in some flame studies are erroneous.

[9] Wilson, Wm. E., O'Donovan, J. T., and Fristrom, R. M., Flame inhibition by halogen compounds, Symp. Combust., 12th (The Combustion Institute, 1969), p. 929.

(a): CH_4+O_2 uninhibited, (b): inhibited with CH_3Br, (c): inhibited with HCl, (d): inhibited with CH_3Cl. CH_3Br is the most effective inhibitor and Br is probably a good catalyst for recombination so 9a should have [OH] nearest the equilibrium value and does have the lowest rate. See comments following reference [6] and reference [B4–5].

[10] Herron, John T., Mass-spectrometric study of the rate of the reaction of CO+OH, J. Chem. Phys. **45**, 1854 (1966).

The OH was generated by $H+NO_2\rightarrow NO+OH$. Since the NO_2 was in excess, the H generated by $CO+OH\rightarrow CO_2+H$ regenerated a OH and $d(OH)/dt$ was not effected by the CO reaction. From a measurement of the initial [OH], the [CO] formed as a function of [CO], and k_1 for the OH disproportionation it is possible to calculate k_2. Herron used $k_1=0.75\times10^{12}$ due to Kaufman [B1–2]. If $k_1=1.55\times10^{12}$ due to Dixon-Lewis, Wilson, Westenberg [B1–1] is used Herron's results give $k_2=0.45-0.92\times10^{11}$ (cm^3 mol^{-1} · s units). The low value and large scatter are the result of reaction of OH with NO_2 which was not recognized by Herron. This value was not used in determining the suggested values.

[11] Wilson, Wm. E., and O'Donovan, J. T., Mass-spectrometric study of the reaction rate of OH with itself and with CO, J. Chem. Phys. **47**, 5455 (1967).

See 10. When Herron's experiment was repeated, it was discovered that the value of k_2 obtained was a function of the $[NO_2]$. The reaction was studied as a function of $[NO_2]$ and $[NO_2]$ extrapolated to 0 to obtain the value shown.

[12a] Porter, R. P., Clark, A. H., Kaskan, W. E., and Browne, W. G., A study of hydrocarbon flames, Symp. Combust., 11th (The Combustion Institute, 1967), p. 907.

[12b] Browne, W. G., Porter, R. P., Verlin, J. D., and Clark, A. H., A study of acetylene-oxygen flames, Symp. Combust., 12th (The Combustion Institute, 1969), p. 1035.

The 11th Symposium paper gave preliminary results of a study of a number of low pressure flames. A value of $k_2=5.3\times10^{11}$ cm^3 mol^{-1} · s^{-1} at 1600 K was reported. Measurements of this reaction over a temperature range in a given flame gave activation energies ranging from 6 to 10 kcal. For the 12th Symposium acetylene flame paper a computer program had been used to solve the flame equations, consisting of the species continuity equations and the multicomponent diffusion equations over the 1000 to 1700 K range. The experimental temperature and OH profiles (measured by absorption spectroscopy, Kaskan's technique) [B3–29] were used in the analysis. A set of kinetic coefficients, including $k_2=3.7\times10^{11}$ exp $(-700/RT)$ cm^3 mol^{-1} · s^{-1}, were presented which gave adequate agreement with the experimental profiles of the major stable species. The authors felt that the higher activation energies obtained in the earlier analysis were due to the use of binary diffusion coefficients instead of multicomponent diffusion coefficients which were used in the later computer studies. This observation may provide a partial explanation for the high activation energies which have been suggested by flame studies.

[12c] Browne, W. G., White, D. R., and Smookler, G. R., A study of the chemical kinetics of shock heated $H_2/CO/O_2$ mixtures, Symp. Combust., 12th (The Combustion Institute, 1969), p. 557.

The density field behind a normal shock wave in H_2-O_2, $H_2-N_2-O_2$, and H_2-CO-O_2 mixtures diluted with argon was measured by optical interferometry. H_2/O_2 was varied from 8/1 to 1.5/48.5, added N_2 or CO from 0 16 percent; temperature from 1400 to 3000 K. A set of kinetic coefficients were presented which could be used to calculate density profiles which gave good agreement with the experimental profiles. For mixtures with added CO the k_2 determined in [12b] was satisfactory.

[13] Gardiner, W. C., Jr., Takeyama, T., and Walker, B. F., Shock tube measurement of the $CO+OH\rightarrow CO_2+H$ reaction rate, paper No. 341, Southwest Regional meeting of the American Chemical Society, Austin, Texas, Dec. 1968.

k_2 and k_{-2} $(H+CO_2)$ were measured in shock waves through $H_2/O_2/CO/Ar=1/5/3/91$ and $H_2/O_2/CO_2/Ar=5/1/4/90$ at an initial pressure of 10 torr and final temperatures from 1500 to 2200 K. Reaction process in the partial equilibrium region was monitored using ultraviolet absorption of OH, IR emission of

CO_2, and the visible continum 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_2 is about twice the value calculated from the rate equation suggested in reference [1].

[14] Avramenko, K. I., and Kolesnikova, R. V., Z. Fiz. Khim. **24**, 207 (1950).

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 $\Delta E \sim 10$ kcal/mol found in the early literature. The experimental technique is discussed in reference [14a], a review in English

[14a] Avramenko, K. I., and Kolesnikova, R. V., Mechanisms and rate constants of elementary gas phase reactions involving hydroxyl radical and oxygen atoms, Advances in Photochemistry Vol. **2** (Interscience, N.Y., 1964), p. 25.

[15] Wong, E. L., and Belles, F. E., Activation energies for reactions of hydroxyl radicals with hydrogen and carbon monoxide, NASA TN D-5707, March, 1970.

A mass-spectrometer stirred reactor study was used to obtain $k_2 = 5.6 \times 10^{10}$ at 310 K, 10.1×10^{10} at 440 K and 13.6×10^{10} at 610 K in $cm^3\ mol^{-1} \cdot s^{-1}$, a least-squares fit gave $k_2 = (3.5 \pm 1.1) \times 10^{11} \exp[-(1220 \pm 80)/RT]$ $cm^3\ mol^{-1} \cdot s^{-1}$. In the analysis $[OH]_0$ is assumed equal to $[NO_2]_0$ 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 $[OH]_0$ 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 O_2, N_2, NO, N_2O, NO_2, and CO_2, 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

[17] Bahn, G. S., Pyrodynamics **6**, 101 (1968).

[18] Cherry, S. S., Gold, P. I., and Van Nice, L. J., TRW Systems, Redondo Beach, California, Report 08832-6001-T000 (AD828-794).

[19] Tunder, R., Mayer, S., Cook, E., and Schieler, L., Aerospace Corporation, Thermochemistry Reseach Department, Report No. TR-1001(9210-03)-1 (1967).

[20] Jensen, D. E., and Kurzius, S. C., Aerochem Research Laboratories, Princeton, N.J., March 1967. Report TP-149.

[21 Fristrom, R. M., and Westenberg, A. A., Flame Structure (McGraw-Hill Book Co., New York, 1965), p. 367.

[22] Kaskan, W. E., and Browne, W. G., General Electric Co., Space Sciences Laboratory Report R64SD37, July 1964.

[23] Schofield, K., An evaluation of kinetic rate data for reactions of neutrals of atmospheric interest, Planet. Sci. **15**, 643 (1967). Reaction 4, table 1; table 5; figure 2c, figure 5. Erratum: Planet. Space Sci. **15** 1336 (1967).

[24] Baulch, D. L., Drysdale, D. D., and Lloyd, A. C., High temperature reaction rate data, Dept. of Physical Chemistry, The University, Leeds, England.

[24a] Report No. 1, May, 1968.

[24b] Report No. 2, November, 1968.

B2.2d. General References

[25] Dixon-Lewis, G., Sutton, M. M., and Williams, A., The reactions of hydrogen atoms with nitrous oxide, J. Chem. Soc., 5724 (1965).

Quotes $k_{3D}(H + D_2O) = 9.4 \times 10^{-13} \exp(-21{,}800/RT)$ $cm^3\ mol^{-1} \cdot s^{-1}$ from M. M. Sutton's thesis.

[26] Westenberg, A. A., and De Haas, N., Atom-molecule kinetics using ESR detection. II. results for $D + H_2 \rightarrow HD + H$ and $H + D_2 \rightarrow HD + D$, J. Chem. Phys. **47**, 4 (1967).

A value of $k_7(H + D_2) = 4.9 \times 10^{13} \exp(-9390/RT)$ $cm^3\ mol^{-1} \cdot s^{-1}$ was obtained which gives $k_7(H + D_2) = 2.6 \times 10^{11}$ at 900 K. This may be compared with the value of $k_7 = 4.2 \times 10^{11}$ used by Dixon-Lewis and Williams [B3-6a] in calculating [H] and ultimately k_2 and k_3. Had they used the most recent value, their k_2 and k_3 would have been lower, although not by the full 4.2/2.6 ratio. To obtain $k_7 = 4.2 \times 10^{11}$ at 900 K, Dixon-Lewis and Williams [6a] used a value at 1000 K, due to Boato et al. [27], and an activation energy from Van Meerssche [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**, 783 (1956).

$k_7(H + D_2)$ at 1000 K is given as 6.1×10^{11} $cm^3\ mol^{-1} \cdot s^{-1}$.

[28] Van Meerssche, Bull. Soc. Chem. Belg. **60**, 99 (1951). The activation energy for $k_7(H + D_2)$ is given as 6.65 kcal/mol.

B3. k_3, Rate Constant for the Reaction, $H_2 + OH \rightarrow H_2O + H$

B3.1. General Discussion

B3.1a. Rate Constant Determinations

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_3 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 $CO + OH \rightarrow CO_2 + H$, has been established first. This value is then used with rate ratio data to establish other OH rate constants. Alternatively the rate for $H_2 + OH$ could have been established first and used as a base. Reasons for preferring Reaction (2) are given in Section A.

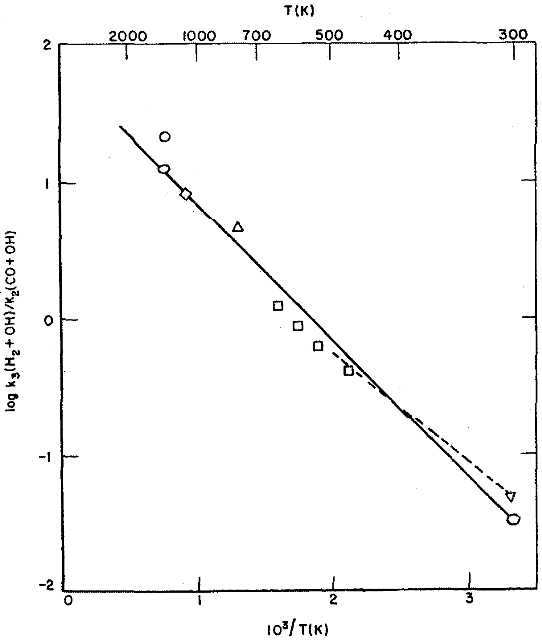

FIGURE B3. *Rate ratio data* $k_3(H_2 + OH)/k_2(CO + OH)$.

○ Fenimore and Jones, reference [14], using data analysis of reference [2]:
⬭ Fenimore and Jones, reference [14].
◇ Dixon-Lewis, et al., reference [13] and Fenimore and Jones, reference [14b];
△ Baldwin, et al., reference [12]:
□ Ung and Back, reference [11]:
○ Dixon-Lewis, Wilson, Westenberg, reference [2];
▽ Greiner, reference [4a];
– – Greiner, reference [4b]:
— recommended value.

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_2 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 $k_3 = 2.19 \times 10^{13} \exp(-5150/RT)$ cm^3 mol^{-1} · 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_2 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][6] to obtain values for k_2 at several temperatures. These points were then used to establish the temperature dependence of k_2. In the later review of $H_2 + OH$ rate measurements Baulch, Drysdale, and Lloyd [24b] use their evaluation of k_2 and the k_3/k_2 ratios of Baldwin et al. [12],[7] 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.[8] The resulting value $k_3 = 2.19 \times 10^{13} \exp(-5150/RT)$ cm^3 mol^{-1} · s^{-1} is inconsistent with Kaufman's expression [3c] of $k_3 = 6.3 \pm 5 \times 10^{13} \exp(-5900 \pm 1000/RT)$ cm^3 mol^{-1} · s^{-1}, which was used to calculate the points on which their value for k_3 is based.

B3.2. References and Comments, $H_2 + OH \rightarrow H_2O + H$, Reaction 3

B3.2a. Determinations of k_3

[1] Wise, H., Ablow, C. M., and Sancier, K. M., Diffusion and heterogeneous reaction, VI. Surface recombination in the presence of distributed atom sources, J. Chem. Phys. **41**, 3569 (1964).

A theoretical analysis is made of the simultaneous removal of atoms by a first-order heterogeneous reaction and their generation by a second-order gas-phase reaction. Such a model is found to apply to a system in which hydrogen atoms and hydroxyl radicals are generated by a 14 Mc/s discharge in wet H_2. The hydrogen atoms recombine on the walls of a cylindrical quartz tube in the presence of hydroxyl radicals which produce hydrogen atoms by reaction with H_2. The [H] is measured by electron-spin resonance spectroscopy. The perturbation of the [H] profile due to $OH + OH \rightarrow H_2O + H$ is employed to calculate k_3. Diffusion coefficients for H and OH in H_2 and surface recombination coefficients must be used in the data analysis. Two measurements were made which allowing for a range in the OH diffusion coefficient give $k_3 = 6 \pm 3 \times 10^9$ cm^3 mol^{-1} · s^{-1} at 300 K.

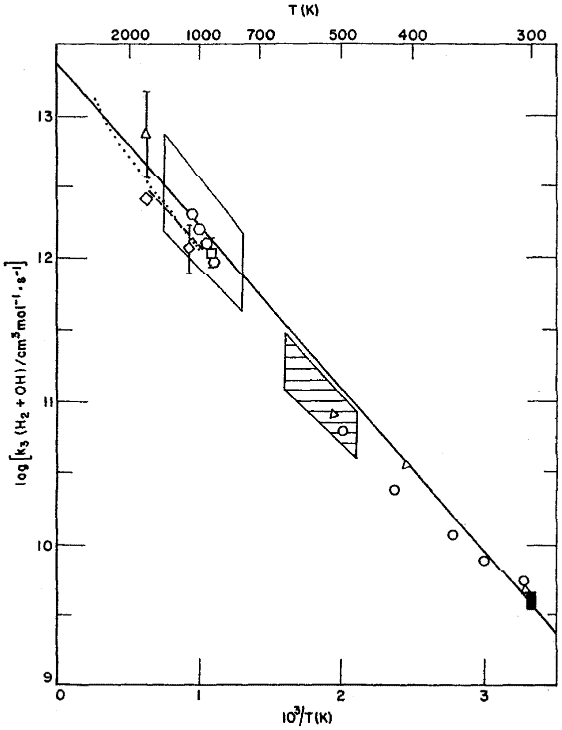

FIGURE B4. *Arrhenius plot of* $k_3(H_2 + OH)$.

▮	Dixon-Lewis, Wilson, and Westenberg, reference [2], Del Greco and Kaufman, reference [3], Greiner, reference [4a];
○	Greiner, reference [4b];
□, ◇	Dixon-Lewis, Sutton, and Williams, reference [6]. □ is direct measurement with OH measured by absorption spectroscopy, ◇ is from reverse;
◇, △	Schott, reference [15], ◇ k_2 from reference [28a] and $k_2 \cdot k_4$, △ upper bound for k_4;
——	Browne et al., reference [5];
. . .	Mayer, Schieler, and Johnston, reference [10];
▧	Ung and Back, reference [11], k_3/k_2 ratio used with upper limit of k_2, (this paper, sec. B2) to give upper bound, and Greiner k_2, reference [4b], to give lower bound;
▱	k_2/k_4 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_2 limits (this paper, sec. B2);
△	Wong and Belles, reference [9c];
⬡	Balakhin et al., reference [9e];
——	Recommended value.

[2] Dixon-Lewis, G., Wilson, W. E., and Westenberg, A. A., Studies of hydroxyl radical kinetics by quantitative ESR, J. Chem. Phys. **44**, 2877 (1966).

The OH was generated by $H + NO_2 \rightarrow NO + OH$. Quantitative electron spin resonance was used to determine the initial concentration and to follow the hydroxyl radical decay in a fast-flow system at ~ 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_1 ($OH + H_2O \rightarrow H_2O + O$), which requires absolute measurements of [OH].

[3a] Kaufman, F., and Del Greco, F. P., Formation, lifetime, and decay of OH radicals in discharge-flow systems, J. Chem. Phys. **35**, 1895 (1961).

[3b] Del Greco, F. P., and Kaufman, F., Lifetime and reactions

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[6] 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.

[7] The value of $k_3/k_2 = 3.0$ was first reported in Baldwin and Cowe [27] and attributed to unpublished work of Baldwin and Doran. This estimate was later confirmed by Baldwin et al. [12a]. The original value was used in the evaluation of k_2 and a revised value, [12b], $k_3/k_2 = 4.5$, used in the evaluation of k_3.

[8] 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].

TABLE III. $H_2+OH \rightarrow H_2O+H$

Equilibrium constant, $K_{eq}=0.211 \exp(7640/T)$, 1000–6000 K $\Delta H^\circ_{293}/R=-7.56$
Rate constant, $k=AT^B \exp(C/T)$ cm^3 concentration units$^{-1}\cdot$s^{-1}

A	A	B	C	T range K	Ref.	Comment
Mol units	Particle units					
2.2×10^{11}	3.65×10^{-13}	0.56	2,200	1000–4000	10	Calculation.
2.8×10^{12}	4.67×10^{-13}	0	1,960	300– 500	4b	Flash photolysis-kinetic spectroscopy.
1.5×10^{13}	2.5×10^{-11}	0	2,500	1000–1700	5	Flame.
2.5×10^{14}	4.2×10^{-10}	0	5,000	1285–1700	7	Flame.
4×10^{13}	7×10^{-11}	0	2,850	1400–2500	8	Shock tube, not reliable.
4.2×10^{12}	7.0×10^{-12}	0.5	5,000	378– 489	9	H_2O discharge, not reliable.
4.7×10^{12}	7.8×10^{-12}	0	2,100	300– 500	9c	Stirred reactor.

k, mol units	k, particle units	T K	Ref.	Comment
$3.9\pm0.2\times10^{9}$	$6.5\pm0.3\times10^{-15}$	300	2	Electron spin resonance.
$4.3\pm1.0\times10^{9}$	$7\pm2\times10^{-15}$	300	3	Absorption spectroscopy.
$4.0\pm0.2\times10^{9}$	$6.6\pm0.3\times10^{-15}$	301	4a	Flash photolysis-kinetic spectroscopy.
$6\pm3\times10^{9}$	$10\pm5\times10^{-15}$	300	1	Electron spin resonance of H.
1.1×10^{12}	1.8×10^{-12}	915	6	Flame, OH absorption spectroscopy.
1.75×10^{12}	2.9×10^{-12}	1072	6	Flame, reverse.
$5.0\pm3.0\times10^{9}$	$8.3\pm5.0\times10^{-15}$	304	9c	Stirred reactor with mass spectroscopic analysis for H_2O.
$3.6\pm0.4\times10^{10}$	$6.0\pm.7\times10^{-14}$	403	9c	
$6.5\pm1.1\times10^{10}$	$1.8\pm.2\times10^{-13}$	504	9c	
9.6×10^{11}	1.6×10^{-12}	900	9e	Flame reactor—electron spin resonance analysis.
1.3×10^{12}	2.1×10^{-12}	943	9e	
1.6×10^{12}	2.6×10^{-12}	993	9e	
2.0×10^{12}	3.4×10^{-12}	1052	9e	

Rate ratio: $k_3\ (H_2+OH \rightarrow H_2O+H)/k_2(CO+OH \rightarrow CO_2+H)$

Rate ratio	T K	Ref.	Comment
0.034 ± 0.003	300	2	Direct studies.
0.045 ± 0.006	301	4	Both k's.
0.429	473	11	H_2O photolysis.
0.615	523		
0.875	573		
1.221	623		
4.5 ± 0.5	773	12	Explosion limits.
8.4	1072	13	Flame, reverse.
7–9	1000–1200	14b	Flame.
12.5	1200–1350	14a & c	Flame, reverse.
22.3	1200–1350	14a & c	Flame, calculation of reference 2, reverse.

Recommended Values

300–2000 K

Rate ratio, k_3/k_2	Error limits
$k_3/k_2=73 \exp 2300/T$	$\log k_3/k_2$ ±0.3

k_3, rate constant for the Reaction $H_2+OH \rightarrow H_2O+H$*

Units	Rate expression	k_3 at 1000 K	Error limits
cm^3 mol$^{-1}\cdot$s^{-1}	$k_3=2.3\times10^{13} \exp(-2600/T)$***	1.7×10^{12}	$\log k_3\pm0.3$
cm^3 particles$^{-1}\cdot$s^{-1}	$k_3=3.8\times10^{-11} \exp(-2600/T)$**	2.8×10^{-12}	

*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 $k_2=5.1\times10^{-13} \exp(-300/T)$.

***Using $k_2=3.1\times10^{11} \exp(-300/T)$.

TABLE IIIA. *Evaluations of the rate of hydrogen with hydroxyl*

$H_2+OH\rightarrow H_2O+H$ k_3			$H_2O+H\rightarrow H_2+OH$ k_{-3}			Temp. range, K	Reference
A	*B*	*C*	*A*	*B*	*C*		
$-10.43\begin{Bmatrix}+0.3\\-0.7\end{Bmatrix}$		2.6	$-9.75\begin{Bmatrix}+0.3\\-0.7\end{Bmatrix}$		10.0	300–1500	This work.
-10.44 ± 0.14		2.59 ± 0.07	-9.86 ± 0.14		10.12 ± 0.25	300–3000	Baulch. et al. [24b].
-10.20		2.76	-9.52		10.40	300–2500	Schofield [19].
-10.4 ± 0.5		2.77					Jensen & Kurzius [21].
-10.85		2.43 ± 0.3	-10.18		10.0 ± 0.3	300–3000	Bascombe [18].
-9.98		2.97	-9.40		10.42	300–2000	Kaskan & Browne [17].
-12.0	$+0.5$	2.5	-12.32	0.7	9.1		Tunder [23].

$k=10^A\,T^B\exp[-C(1000/T)]$ cm^3 particle$^{-1}\cdot$s^{-1} units.

of OH radicals in discharge flow systems, Dis. Faraday Soc. **33,** 128 (1962).

[3c] Kaufman, F., and Del Greco, F. P., Fast reactions of OH radicals, Symp. Combust., 9th (Academic Press, 1963), p. 659.

[3d] Kaufman, F., Aeronamic reactions involving hydrogen. A review of recent laboratory studies, Ann. Geophys. **20,** 106 (1964).

The OH was generated by $H+NO_2\rightarrow NO+OH$. Absorption spectroscopy was used to determine the initial concentration and to follow the OH decay in a fast flow-low pressure system. In the experiments H_2+OH and $OH+OH$ are competitive. The first three papers describe the experimental work. The value is quoted from the last. In [3a] the authors fit an Arrhenius expression to their room temperature value for k_2 and a value for k_3 at 1500 K calculated from an expression due to Fenimore and Jones [7]. The rate expression obtained, $k_3=6.3\times10^{13}\exp(-5900/RT)$ cm^3 mol$^{-1}\cdot$s^{-1}, has been widely quoted, usually without the uncertainty values given later in the paper, ±0.7 for log *A* and ±1000 for *E* [$k=A\exp(-E/RT)$].

[4a] Greiner, N. R., Hydroxyl radical kinetics by kinetic spectroscopy. I. Reactions with H_2, CO, and CH_4 at 300 K, J. Chem. Phys. **46,** 2795 (1967).

The OH was generated by flash photolysis of H_2O 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 ($<200\times10^{-6}$ 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.

[4b] Greiner, N. R., Hydroxyl reactions by kinetic spectroscopy. V. Reactions with H_2, CO, and CH_4 in the range 300–500 K. J. Chem. Phys. **51,** 5049 (1969).

The flash photolysis-kinetic spectroscopy technique (FP-KS) was extended to higher temperatures. The H_2 points (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 k_3/k_2 was formed using the individual equations determined by a least squares fit of the k_3 and k_2 data points (fig. B3). The k_3/k_2 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 Greiner measurements, made in systems in which OH is generated by photolysis of H_2O vapor, give activation energies for k_3 and k_3/k_2 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_2 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 gas mixture is flashed eight times to obtain sufficient OH absorption and background intensity. It is possible that some H_2O_2 or O_2 could be formed and produce HO_2 or OH by reaction with H. The HO_2 might interfere by the reaction $H+HO_2\rightarrow 2\,OH$. Another possible argument is that HO_2 is present in the high temperature systems and reacts with H_2 leading to an erroneously high reaction rate. These measurements were not used in establishing the suggested value. However, this anomoly between FP-KS using water vapor and other measurements must be resolved before the reliability of k_3 can be considered well established. (See Sec. D.)

The data reported for k_3 in cm^3 mol$^{-1}\cdot$s^{-1} units are: average of 8 measurements at 300 ± 5 K, $4.75\pm0.23\times10^{9}$; 332 K, $8.57\pm1.42\times10^{9}$; 358 K, $1.40\pm0.03\times10^{10}$; 420 K, $3.40\pm0.09\times10^{10}$; average of 5 measurements at 495 K, $6.89\pm0.32\times10^{10}$ cm^3 mol$^{-1}\cdot$s^{-1}.

[5] Browne, W. G., Porter, R. P., Verlin, J. D., and Clark, A. H., A study of acetylene-oxygen flames, Symp. Combust., 12th (The Combustion Institute, 1969), p. 1035.

A set of kinetic coefficients are presented which satisfactorily characterize several low-pressure $C_2H_2-O_2$ flames, some with added CO and H_2. 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. k_3 was reported to be $1.5\times10^{13}\exp(-5000/RT)$ cm^3 mol$^{-1}\cdot$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.

[6a] Dixon-Lewis, G., and Williams, A., Some observations on the structure of a slow burning flame supported by the reaction between hydrogen and oxygen at atmospheric pressure, Symp. Combust., 9th (Academic Press, 1963), p. 576.

[6b] Dixon-Lewis, G., Sutton, M. M., and Williams, A., Some reactions of hydrogen atoms and simple radicals at high temperatures, Symp. Combust., 10th (The Combustion Institute, 1965), p. 495.

These papers report studies of the structure of a flat $H_2-N_2-O_2$ flame with a final temperature of 1072 K at atmospheric pressure. Measurements were obtained for k_3, $k_{-3D}(D_2O)$, and $k_{-3D}(D_2O)/k_{-2}$. The rate ratio is discussed in reference [13].

k_3. Assuming all H_2 reacts by reaction 3, a measurement of $(d[H_2]/dt)$ chem, $[H_2]$, and [OH] yields a direct value of $k_3=1.1\times10^{12}$ cm^3 mol$^{-1}\cdot$s^{-1} at 915 K. The measurement of [OH] was made using absorption spectroscopy. The technique and *f* number of Kaskan [29] were used (absorption by the broad 0,0 band at 306.4 nm in the flame of the narrow emission line from a cooled water discharge lamp). Kaskan used $f_{00}=12.3\times10^{-4}$ based on ΔH^0_{298} (OH) = 10 kcal. A correction factor of 1.34 is introduced in revising ΔH^0_{298} to 9.33 kcal in agreement with the JANAF tables. This gives $f_{00}=9.2\times10^{-4}$. Golden, Del Greco, and Kaufman [30] obtained $f_{00}=7.1\pm1.1\times10^{-4}$ 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 $f_{00}\approx14\times10^{-4}$ in agreement with the recent determination of Anketell and Pery-Thorne [31] of $14.8\pm1.3\times10^{-4}$. An uncertainty of log $k\pm0.2$ is therefore introduced to account for the *f* number uncertainty with the lower value of *k* being considered more likely.

k_{-3}. This rate measurement requires an absolute value of [H]. The D_2O 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 D_2 and measurement of $(d[HD]/dt)$ chem. Since the measurement regions overlap this absolute value of [H] could be used to scale the others. A measurement of $(d[D_2O]/dt)$ chem with the [H] gave $k_{-3D}(H+D_2O)$. In [6b] a revised value of [H] was used to obtain $k_{-3D}(H+D_2O)=3.6\times10^{9}$ cm^3 mol$^{-1}\cdot$s^{-1} at 1072 K. Due to uncertainties in equilibration conditions, upon which [H] depends, the authors state [6a] that "this may be an upper limit." The [H] also depends on the value of $k_7(H+D_2\rightarrow HD+D)$ used. Recent studies of this reaction [B2–26] indicate that the k_7 used by Dixon-Lewis et al., may be high by a factor of two. This would give a low [H] concentration resulting in $k_{-3}(H+D_2O)$ and k_3 being high by something less than a factor of two.

To obtain a value of $k_{-3}(H+H_2O)$ it is necessary to make some assumptions about the ratio $k_{-3}(H+H_2O)/k_{-3D}(H+D_2O)$. In reference [2] a ratio of 1.84 was obtained by assuming $k_{-3}(H_2O)$ to be larger than $k_{-3}(D_2O)$ by a factor determined by the zero point energy difference between single OH and OD bonds ($\approx$ 1.3 kcal mol^{-1}).

Using the equilibrium constant this yields $k_3=1.75\times10^{12}$ cm^3 mol$^{-1}\cdot$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].

[7a] Fenimore, C. P., and Jones, G. W., Determination of hydrogen atoms in rich, flat, premixed flames by reaction with heavy water, J. Phys. Chem. **62**, 693 (1958).

[7b] Fenimore, C. P., and Jones, G. W., Rate of Reaction, $O+H_2\rightarrow OH+H$, 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 $(d\ HD/dt)_{chem}$ from $H+D_2O\rightarrow HD+OD$ determined. The temperature range was 1285 to 1500 K in H_2 flames and 1345 to 1850 K in hydrocarbon flames. The Avramenko and Lorentso [9] value for k_3 and the equilibrium constant were used to obtain k_{-3}. This value was then increased by a factor of two and used to determine [H]. (All isotopic rates 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 $[H]/[H]_{eq}$ being linear with $1/T$ for both sets of flames. Considering the number and extent of assumptions made and that Avramenko and Lorentso's rate 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 $(d[D_2O]/dt)_{chem}$ was also measured in rich hydrocarbon flames. A value of $k_{-3D}(H+D_2O)=10^{12}$ used earlier gave [H] equal to the equilibrium concentration. This is better evidence for k_3 but still can hardly be considered to be of better than order of magnitude accuracy.

In the second paper, the rate equation $k_3=2.5\times10^{14}$ exp $(-5000/T)$ cm^3 mol$^{-1}\cdot$s^{-1} 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 $k=10^{13.8\pm0.7}$ exp $(-2950\pm500/T)$. This value has been widely quoted in the literature, usually without the large uncertainty given by Kaufman.

[8a] Ripley, D. L., and Gardiner, W. C., Jr., Shock-tube study of the hydrogen-oxygen reaction. II. Role of exchange initiation, J. Chem. Phys. **44**, 2285 (1966).

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

Induction time measurements on the H_2/O_2 reaction ($\sim$ 1400–2500 K) were interpreted in terms of hydrogen and oxygen dissociation, $k_{11}(H+O_2)$, $k_{12}(O+H_2)$, 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 $[k_{12}(O+H_2)k_3]$. The equation given in this reference, $k_3=10^{13.6}$ exp $(-5700/RT)$/cm^3 mol$^{-1}\cdot$s^{-1}, 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.

[9a] Avramenko, K. I., and Lorentso, R. V., Z. Fiz. Khim. **24**, 207 (1950).

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 $\Delta E\sim10$ kcal/mol found in the early literature. The experimental technique is discussed in [9b], a review in English.

[9b] Avramenko, K. I., and Kolesnikova, R. V., Mechanisms and rate constants of elementary gas phase reactions involving hydroxyl radical and oxygen atoms, Advances in Photochemistry **2**, (Interscience, N.Y., 1964), p. 25.

[9c] Wong, E. L., and Belles, F. E. Activation energies for reactions of hydroxyl radicals with hydrogen and carbon monoxide, NASA TN D-5707, March, 1970.

A mass-spectrometric stirred reactor technique was used to obtain $k_3=5.0\pm3.0\times10^9$ at 304 K, $36\pm4\times10^9$ at 403 K, and $65\pm11\times10^9$ at 504 in cm^3 mol$^{-1}\cdot$s^{-1}, a least squares fit gave $k_3=(4.7\pm1.2)\times10^{12}$ exp $[-(4200\pm300)/RT]$ cm^3 mol$^{-1}\cdot$s^{-1}. In the analysis $[OH]_0$ is assumed equal to $[NO_2]_0$ and k_3 is calculated from the reaction time (obtained from flow rates and reactor volume) and the concentration of water formed by the reaction (obtained from mass-spectrometric analysis). As discussed in Sections A3.1 and B1.1a, this can give a$[OH]_0$ which is too high. In the data analysis used in this study, this would cause k_3 to be low. This apparently was the case in a similar measurement of $k_2(CO+OH)$ [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. Since k_3 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_3PO_4.)

[9d] Azatyan, V. V., Romanovich, L. B., and Sysolva, S. G., Determination of the reaction rate constant of the hydroxyl radical and hydrogen, Phys. of Comb. and Explosion **3** (1), 77–85 (1967), in Russian.

Values of $k_3=5.3$, 5.5, and 6.0×10^{11} cm^3 mol$^{-1}\cdot$s^{-1} at 813, 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.

[9e] Balakhin, V. P., Gershenzon, Y. M., Kondrat'ev, V. N., and Nalbandyan, A. B., A quantitative study of the mechanism of hydrogen combustion close to the lower explosive limit. Dok. Akad. Nauk. SSSR **170**, 1117 (1966).

Quantitative ESR was used to follow the concentration of H, O, O_2, and OH as a function of flow rate in a flame-type reactor at 2.86 torr for a $H_2:O_2$ mixture ratio of 1:1. Water concentration was measured by freeze-out techniques. Values obtained were $k_3=2.7$, 3.3, 4.3, and 5.7×10^{12} cm^3 mol$^{-1}\cdot$s^{-1} at 900, 943, 993, and 1052 K. The Arrhenius expression obtained, $k_3=(3\pm1)\times10^{14}$ exp $[(-8600\pm1200)/RT]$, gives too high an activation energy but the experimental points are in good agreement with the recommended value.

B3.2b. Rate Calculations

[10] Mayer, S. W., Schieler, L., and Johnston, H. S., Computation of high-temperature rate constants for bimolecular reactions of combustion products, Symp. Combust., 11th (The Combustion Institute, 1967), p. 837.

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

B3.2c. Rate Ratio Determinations

[11] Ung, A. Y. M., and Back, R. A., The photolysis of water vapor and reactions of hydroxyl radicals, Can. J. Chem. **42**, 753 (1964).

The OH was generated by photolysis of water, CO_2 was formed when CO was present. The rate ratio, k_3/k_2, was determined from the decrease in CO_2 formed when H_2 was added. Evidently the three-body recombination to form H_2O_2 was sufficiently fast to interfere at lower temperatures.

[12a] Baldwin, R. R., Jackson, D., Walker, R. W., and Webster, S. J., The use of the hydrogen-oxygen reaction in evaluating velocity constants, Symp. Combust., 10th (The Combustion Institute, 1965), p. 423.

[12b] Baldwin, R. R., and Walker, R. W., personal communication.

The k_3/k_2 ratio 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_2 and H_2O when CO was added to a slowly reacting H_2–O_2 mixture at 773 K. The $[H_2O]/[CO_2]$ 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 HO_2 and H_2O_2, led to the following conclusions:

(1) Neither $CO+O$ or $CO+O+M$ produce appreciably CO_2,
(2) $CO+OH$ and $CO+HO_2$ contribute roughly equally to the production of CO_2, and
(3) the ratio $k_3(H_2+OH)/k_2(CO+OH)=4.5\pm0.5$.

A particularly important aspect of this work is the indication that $CO+HO_2$ is an important source of CO_2 during slow combustion at 773 K.

[13] Dixon-Lewis, G., Sutton, M. M., and Williams, A., Reactions contributing to the establishment of the water gas equilibrium when carbon dioxide is added to a hydrogen-oxygen flame. Trans. Faraday Soc. **61**, 255 (1965).

The addition of both D_2O 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 measurment of the ratio, $k_{-3D}(H+D_2O)/k_{-2}(H+CO_2)=4.3\pm0.5$. Assuming $k_{-3}(H+H_2O)/k_{-3D}(H+D_2O)=1.84$ (as in ref. [6]) $k_{-3}(H+H_2O)/k_{-2}(H+CO_2)=7.9\pm1$ and using the equilibrium constant of the water gas reaction, $CO_2+H_2\rightarrow CO+H_2O$, $k_3/k_2=8.4\pm1$ at 1072 K.

[14a] Fenimore, C. P., and Jones, G. W., The reaction of hydrogen atoms with carbon dioxide at 1200–1350 K., J. Phys. Chem. **62,** 1578 (1958).

[14b] Fenimore, C. P., and Jones, G. W., Rate of reaction in hydrogen, nitrous oxide and in some other flames, J. Phys. Chem. **63,** 1154 (1959).

[14c] Fenimore, C. P., and Jones, G. W., Destruction of acetylene in flames with oxygen, J. Chem. Phys. **39,** 1514 (1963).

In Reference [14a] results are presented from a study in which the concentration of CO_2 and H_2 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_2O] were measured. If [H] is known then $k_{-2}(H+CO_2)$ 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_2O. The direct experimental result then is really a measurement of $k_{-2}/k_{-3D}(H+D_2O)$. In Reference [14b] the expression $k_{-2}/k_{-3}=3\ \exp\ (-7800/RT)$ 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 $H_2/CO/O_2/Ar$ flame which gives 7–9 for k_3/k_2 in the 1000 to 1200 K region.

In [14c] the results of [14a] are given as $k_2/k_3=0.08$ at 1200 to 1350 K. This gives 12.5 for k_3/k_2. Fenimore and Jones assume no change in rates due to isotopic substitution.

In reference [2] the k_{-2}/k_{-3} ratio given in reference [14b] is used to calculate a value of $k_3/k_2=22.3$ by making corrections for changes in rate due to isotopic substitution.

[15a] Schott, G. L., Chain branching and initiation rates measured by spatially integrated light emission during reflected shock wave ignition. Symp. Combust., 12th (The Combustion Institute, 1969), p. 569.

[15b] Schott, G. L., Los Alamos Scientific Laboratory, Los Alamos, N.M., personal communication.

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 $0.1\leqslant H_2:O_2\leqslant 10.0$ and $1000\leqslant T\leqslant 2500$ K. For the induction region the intensity grows exponentially, $I(t)=i_0\ \exp\ (\alpha t)$, and values of α are obtained whose dependence on [H_2], [O_2], and T determine $k_{11}(H+O_2)$ and the product $k_{12}(O+H_2)k_3$. Their results indicate that the values of $k_{12}(O+H_2)$ and $k_3(OH+H_2)$ are comparable (factor of 3) within the range studied and suggest upper and lower limits for k_3. The authors give $k_{12}(O+H_2)\ k_3=1.5\times10^{25}\ \exp-(20\pm4)[(1/T-1/1600)/R]\ cm^6\ mol^{-2}\cdot s^{-2}$ and k_3 or $k_{12}(O+H_2)\geqslant(2.16\pm0.7)\times10^{25}\ \exp-(14.8\pm0.7)[(1/T-1/1600)/R]\ cm^3\ mol^{-1}\cdot s^{-1}$.

More recent work by Schott [15b] in which α was determined by thermal IR emission from H_2O formed by reaction 3 gave lower values for α resulting in a value of $k_{12}(O+H_2)k_3$ 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_3 has been obtained using 1/4 the authors $k_{12}(O+H_2)k_3$ and a value of $k_{12}(O+H_2)$ from Westenberg and DeHaas [28].

B3.2d Rate Evaluations

[16] Bahn, G. S., Pyrodynamics **3,** 245 (1965).

[17] Kaskan, W. E., and Browne, W. G., General Electric Co. Space Sciences Laboratory Report R64SD37, July 1964.

[18] Bascombe, K. N., Reaction rate data: the hydrogen/oxygen system, Ministry of Aviation, Explosives Research and Development Establishment, Waltham Abbey, Essex, England, E.R.D.E. 1/65.

[19] Schofield, K., An evaluation of kinetic rate data for reactions of neutrals of atmospheric interest, Planet. Space Sci. **15,** 643 (1967), Erratum: Planet. Space. Sci. **15,** 1336 (1967).

[20] Fristrom, R. M., and Westenberg, A. A., Flame Structure (McGraw-Hill Book Co., New York, 1965), p. 367.

[21] Jensen, D. E., and Kurzius, S. C., Aerochem Research Laboratories, Princeton, N.J., March 1967. Report TP–149.

[22] Skinner, G. B., and Ringrose, G. H., Ignition delays of a hydrogen-oxygen-argon mixture at relatively low temperatures, J. Chem. Phys. **42,** 2190 (1965).

They used a value of $k_3=1.48\times10^{14}\ \exp-6430/RT\ cm^3\ mol^{-1}\cdot s^{-1}$ derived from references [3, 7, and 9].

[23] Tunder, R., Mayer, S., Cook, E., and Schieler, L., Aerospace Corp., Thermochemistry Research Dept., Report No. TR–1001(9210–02)–1 (1967).

[24] Baulch, D. L., Drysdale, D. D., and Lloyd, A. C., Critical evaluation of rate data for homogeneous, gas-phase reactions of interest in high-temperature systems. Department of Physical Chemistry, The University, Leeds 2, England.

[24a] Part 1. May 1968.

[24b] Part 2. November 1968.

[25] Cherry, S. S., Gold, P. I., and Van Nice, L. J., TRW Systems, Redondo Beach, California, Report 08832–6001–T0000.

B3.2e. General References

[26] Johnston, H. S., Gas phase reaction kinetics of neutral oxygen species, National Standard Reference Data Systems, National Bureau of Standards, Publication No. 20, September 1968.

[27] Baldwin, R. R., and Cowe, D. W., The inhibition of the hydrogen and oxygen reaction by formaldehyde, Trans. Far. Soc. **58,** 1768 (1962).

Original reference for rate ratio information reported in more detail in reference [12a].

[28a] Westenberg, A. A., and De Hass, N., Atom-molecule kinetics at high temperature using ESR detection. Technique and results for $O+H_2$, $O+CH_4$, and $O+C_2H_6$, J. Chem. Phys. **46,** 490 (1967).

[28b] Westenberg, A. A., and de Hass, N., Reinvestigation of the rate coefficients for $O+H_2$ and $O+CH_4$, J. Chem. Phys. **50,** 6 (1969).

[29a] Kaskan, W. E., Line widths and integrated absorption coefficients for the ultraviolet bands of OH, J. Chem. Phys. **29,** 1420 (1958).

[29b] Kaskan, W. E., Abnormal excitation of OH in $H_2/O_2/N_2$ flames, J. Chem. Phys. **31,** 944 (1959).

[30] Golden, D. M., Del Greco, F. P., and Kaufman, F., Experimental oscillator strength of OH, $^2\Sigma^+\rightarrow{}^2\Pi$, by a chemical method, J. Chem. Phys. **39,** 11 (1963).

A value of $f_{00}=7.1\pm1.1\times10^{-4}$ was obtained. The OH was made by $H+NO_2\rightarrow NO+OH$ and the concentration of OH was assumed equal to the NO_2 added to an excess of H. In Section B1 reasons are given for believing this value might be low.

[31] Anketell, J., and Pery-Thorne, Anne, Oscillator strengths in the $^2\Sigma^+$—$^2\Pi$ band system of OH by the hook method, Proc. Roy. Soc. A. **301,** 343–353 (1967).

$f_{00}=(14.8\pm1.3)\times10^{-4}$ was obtained. The hook method has the advantage of being independent of both the line shape and the instrumental width of the spectrograph. For this study OH was obtained by heating a mixture of oxygen and water vapor to 1800 to 1950 K. The OH concentration was calculated using a dissociation energy of 101.36 kcal/mol.

B4. k_4, Rate Constant for the Reaction $CH_4+OH\rightarrow CH_3+H_2O$

B4.1. General Discussion

B4.1a. Rate Constant Measurements

There are three independent and direct measurements of k_4, the rate of reaction of methane and hydroxyl radical, at room temperature. The results are in good agreement with each other. The room temperature rate, therefore, may be considered fairly well established. However, there is only one direct measurement of this rate at flame temperatures. There are a large number of studies, from 750 to 2000 K, in which the ratio of k_4 to some other reaction involving OH has been measured. The competing reaction has most frequently involved CO, although in a few instances the rate has been measured relative to that with H_2. The rate equation for k_4 has, therefore, been derived by first establishing the ratio k_4/k_2 and then using the value previously established for k_2, the rate constant for the reaction $CO+OH\rightarrow CO_2+H$.

The rate ratio data are shown in figure B5. The two points for the ratio at 300 K were derived from the direct measurements at room temperature [5, B2–1, 4a]. The ratio line derived from Greiner's

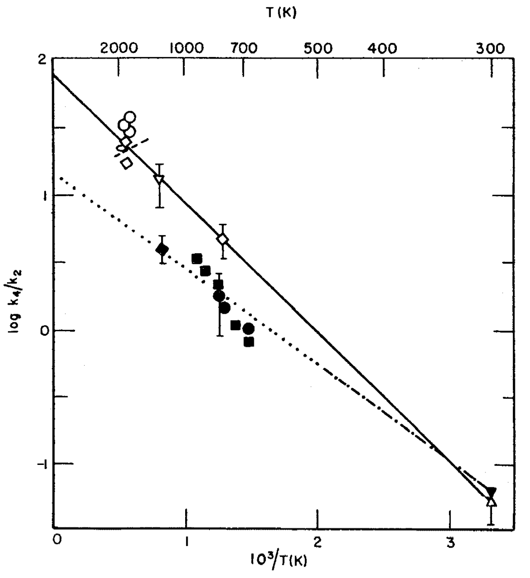

FIGURE B5. *Rate ratio data for* $k_4(CH_4 + OH)/k_2(CO + OH)$.

△	Calculated from electron spin resonance studies of k_4 and k_2: k_2, reference [5], Wilson and Westenberg, and k_4, reference [B2–1], Dixon-Lewis, Wilson and Westenberg;
▼	Calculated from reference [4a], Greiner;
—·—·	Calculated from experimental values, reference [4b], Greiner;
......	Extrapolation of rate equation, reference [4b], Greiner;
◇	Reference [7], Baldwin, Norris and Walker;
▽	Calculated from k_4 of reference [6], Dixon-Lewis and Williams and the value of k_2 suggested in this report;
○	Reference [8], Wilson, O'Donovan, and Fristrom;
○	Reference [9], Westenberg and Fristrom;
◇	Reference [10], Westenberg and Fristrom;
●	Reference [12], Blundell et al.;
■	Reference [14], Hoare;
◆	Reference [15], Pratt;
———	Recommended value.

Figure reproduced from Symp. Combust. 11th, p. 1148 (1967) by permission of the Combustion Institute. Point and line from references [4a and 4b] added.

measurements of the temperature dependence of k_4 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_2 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.

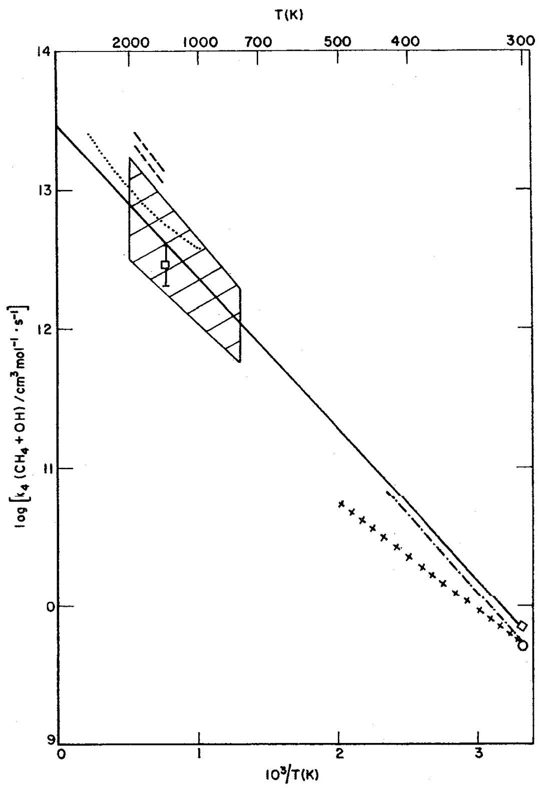

FIGURE B6. *Arrhenius plot of* k_4 $(CH_4 + OH)$

—·—·	Horne and Norrish, reference [1];
+++	Greiner, reference [4b];
○	Greiner, reference [4a];
◇	Wilson and Westenberg, reference [5];
□	Dixon-Lewis and Williams, direct measurement in a flame, reference [6];
...	Mayer and Schieler, calculation, reference [16];
----	Fristrom, compilation from flame studies, for the lower line a spectroscopic measurement of OH was used, reference [2];
▨	Region in which ratio k_4/k_2 has been determined, range due to error limits of k_4/k_2 and k_2;
———	Recommended value.

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 $(-2980/T)$ cm³ 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.

TABLE IV. $CH_4+OH \rightarrow CH_3+H_2O$

Equilibrium constant, $K_{eq}=5.87 \exp(8{,}600/T)$, 300 to 2500 K $\Delta H^{\circ}_{298}/R=-8.1$
Rate constant, $k=AT^{B} \exp(C/T)$ cm^3 concentration $units^{-1} \cdot s^{-1}$

A Mol units	*A* Particle units	*B*	*C*	*T* range K	Ref.	Comment
1.1×10^{10}	1.83×10^{-14}	0.675	1,100	1000–5000	16	Calculation.
1.1×10^{13}	1.8×10^{-11}	0	3,270	1350–1850	2	Flame.
2.4×10^{14}	4.0×10^{-10}	0	4,250	400–600	3	NR*.
1.8×10^{12}	3.0×10^{-12}	0	1,725	300–500	4b	FP-KS**, NR*.
4.9×10^{13}	8.2×10^{-11}	0	2,500	300–425	1	FP-KS**.
k, mol units	*k*, particle units					
$5.33\pm0.21\times10^{9}$	$8.8\pm0.3\times10^{-15}$			300	4a	FP-KS**.
$6.5\pm1.5\times10^{9}$	$10.8\pm2.5\times10^{-15}$			300	5	ESR***.
2 to 4×10^{12}	3.3 to 6.6×10^{-12}			1290	6	Flame.
Ratio, $k_4(CH_4+OH \rightarrow CH_3+H_2O)/k_2(CO+OH \rightarrow CO_2+H)$						
3.0 ± 0.6 at 773 K					7	Slow reaction.
20–25 at 1750–2000 K					8	Flame.
17 at 1748, 24 at 1789 K					9	Flame.
38 at 1709, 27 at 1743, 33 at 1797 K					10	Flame.
15.2 exp (650/*T*) at 1500–1800 K					11	Flame.
1.8 ± 0.9 at 773 K					12	NR* Slow.
1.0 at 673 K, 1.5 at 773 K					13	Combustion
0.83 at 673 K, 1.10 at 723 K, 2.1 at 798 K					14	NR*, H_2O_2.
2.7 at 873 K, 3.4 at 923 K						Decomposition.
3–5 at 1200 K					15	NR*.
14 exp (1600/*T*) at 300–500 K					4b	NR*.

*NR = not reliable, these values are not considered reliable and were not used in determining the recommended value.

**Flash photolysis—kinetic spectroscopy.

***Electron spin resonance.

Recommended Values

300–2000 K

Rate Ratio, k_4/k_2

	Error limits
$k_4/k_2=92 \exp(2200/T)$	log $k_4/k_2 \pm 0.3$

k_4, Rate Constant for the Reaction $CH_4+OH \rightarrow CH_3+H_2O$*

Units	Rate expression	k_4 at 1000 K	Error limits
cm^3 $mol^{-1} \cdot s^{-1}$	$k_4=2.85\times10^{13} \exp(-2{,}500/T)$***	2.34×10^{12}	log $k_4 \pm 0.7$
cm^3 $particles^{-1} \cdot s^{-1}$	$k_4=4.7\times10^{-11} \exp(-2{,}500/T)$**	3.86×10^{-12}	

* The recommended value for k_4 is determined from the value for the ratio k_4/k_2 recommended above, and the value for k_2 recommended in Section B2.

** Using $k_2=5.1\times10^{-13} \exp(-300/T)$.

*** Using $k_2=3.1\times10^{11} \exp(-300/T)$.

Therefore, pending further clarification of the water vapor photolysis technique, these measurements will not be used in determining the suggested value for k_4/k_2. (See discussion in Section A2.1d.)

B4.2. References and Comments $CH_4+OH \rightarrow CH_3+H_2O$ Reaction 4

B4.2a. Direct Determinations of k_4

[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 H_2O and 300 torr Ar. In the absence of CH_4 the OH decay was second order. The addition of <1 torr CH_4 led to a greatly increased, almost first order, OH decay.

When $\frac{d \ln [OH]}{dt}$ 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. k_4 was reported to be $\log_{10}k_4=13.7-5{,}000/2.303\,RT$ cm^3 $mol^{-1} \cdot s^{-1}$ 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 $CH_3 + OH \rightarrow$ products. 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 at 100 torr with only 1 torr of water vapor [4b].

[2] Fristrom, R. M., Radical concentrations and reactions in a methane-oxygen flame. Sym. Combust., 9th (Academic Press, 1963), p. 560.

A least squares fit of the data from several flame studies gave $\log k_4 = 14.154 - 1.37 \times 10^3 \times 1/T$ $cm^3\ mol^{-1} \cdot s^{-1}$. This is based on the experimental determination of k_4/k_2 and the use of a value of k_2 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.

[3] Avramenko, L. I., and Kolesnikova, R. V., Mechanisms and rate constants of elementary gas phase reactions involving hydroxyl radical and oxygen atoms, Advances in Photochemistry **2,** (Interscience, N.Y., 1964), p. 25.

This article gives a review of the Russian work in which OH 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, P.h.D. Thesis, Moscow, 1952, as the source for $k_4 = 7 \times 10^{14} \exp(-8300/RT)$ $cm^3\ mol^{-1} \cdot s^{-1}$. It is now known that an electric discharge is not a satisfactory source of OH for kinetic studies. OH is believed to be generated along the flow tube by reactions involving HO_2. 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.

[4a] Greiner, N. R., Hydroxyl radical kinetics by kinetic spectroscopy. I. Reactions with H_2, CO, and CH_4 at 300 K, J. Chem. Phys. **46,** 2795 (1967).

The OH was generated by flash photolysis of H_2O 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 ($< 200 \times 10^{-6}$ s) and the large ratio of reactant to OH the reaction could be treated as first order in OH and wall reactions would not be significant.

[4b] Greiner, N. R., Hydroxyl radical kinetics by kinetic spectroscopy VI. Reactions with alkanes in the range 300–500 K, J. Chem. Phys. **53,** 1070 (1970).

The flash photolysis-kinetic spectroscopy technique was used to measure the rate of k_4 over the 300 to 500 K range. Values of k_4 at various temperatures were 298 K, $5.51 \pm 0.51 \times 10^9$; 333 K, $9.26 \pm 0.35 \times 10^9$; 370 K, $2.12 \pm 0.04 \times 10^{10}$, 424 K, $3.68 \pm 0.14 \times 10^{10}$; 495 K, $7.18 \pm 0.16 \times 10^{10}$. The rate expression $k_4 = 3.31 \times 10^{12} \exp(-3732/RT)$ $cm^3\ mol^{-1} \cdot s^{-1}$ was obtained. The ratio k_4/k_2 was obtained from this rate equation and the rate equation obtained by Greiner for k_2. Although the room temperature value is in good agreement with those of Wilson and Westenberg [5] and of Horne and Norrish [1], the activation energy is lower that 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_4/k_2 ratio graph [fig. B6], 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 HO_2 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 only during the first 100 μs. The extent of reaction is not sufficient to change the concentration of the stable reactant. However, if any H_2O_2 or O_2 were to form from OH decay the reaction with H to form first HO_2 and subsequently OH would lead to an underestimation 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 HO_2. 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 those based on flame results are resolved there will remain an uncertainty about OH rates.

[5] Wilson, W. E., and Westenberg, A. A., Study of the reaction of hydroxyl radical with methane, Symp. Combust., 11th (The Combustion Institute, 1967), p. 1143.

The OH was generated by $H + NO_2 \rightarrow NO + OH$. Quantitative electron spin resonance was used to determine the initial concentration and to follow the hydroxyl decay in a fast flow 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.

[6] Dixon-Lewis, G., and Williams, A., Some observations on the combustion of methane in premixed flames, Symp. Combust., 11th (The Combustion Institute, 1967), p. 951.

The methane concentration $[CH_4]$ and chemical reaction rate $d[CH_4]/dt$ (chem) were measured in a fuel-lean $CH_4/O_2/N_2$ 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 CH_4, 19.94 percent O_2, and 75.03 percent N_2. The hydroxyl radical concentration was measured by absorption spectroscopy (maximum was 2.4×10^{-9} mol cm^{-3}). k_4 was calculated from

$$d[CH_4]/dt\,(chem) = k_2[CH_4][OH].$$

This measurement assumes that the only CH_4 reaction is with OH. Reaction with H may be neglected because the H concentration will be very low in the fuel-lean flame and the reaction rate is low. In this flame the [O] would be approximately 1/7 of the [O] and the rate for $O + CH_4$ is only 1/5 of that measured for k_4 in the flame. No consideration was given to possible reactions with HO_2. A value of $k_2 = 3 \pm 1 \times 10^{12}$ $cm^3\ mol^{-1} \cdot s^{-1}$ at 1285 K was reported.

B4.2b. Rate Ratio Determinations

[7] Baldwin, R. R., Norris, A. C., and Walker, R. W., Reactions of methane in slowly reacting hydrogen-oxygen mixtures, Symp. Combust., 11th (The Combustion Institute, 1967), p. 889.

Small quantities of CH_4 (ca 1%) were added to slowly reacting mixtures of $H_2 + O_2$ in N_2 in aged boric-acid-coated vessels at 773 K. The pressure change was used to measure the amount of H_2 oxidized. The amount of CH_4 consumed was determined by catalytic conversion of H_2CO and CO to CO_2 and subsequent measurement of CO_2. By examining the variation of the relative rates of consumption of CH_4 and H_2 with mixture composition and total pressure, a value for the ratio $k_4(OH + CH_4)/k_3(OH + H_2)$ of 1.0 ± 0.2 at 773 K was obtained. This value may be combined with the earlier value [B3–12] for $k_2(OH + CO)/k_3(OH + H_2)$ of 0.33 (later adjusted to 0.2–0.25) to obtain a range for $k_4(OH + CH_4)/k_2(CO + OH)$ of 3.2 to 6. In the earlier measurement of k_2/k_3 in slowly reacting $H_2/CO/O_2$ mixtures, it was necessary to consider the reactions

$$OH + H_2O_2 \rightarrow HO_2 + H_2O \qquad (17)$$

$$CO + HO_2 \rightarrow CO_2 + OH \qquad (18)$$

$$H_2 + HO_2 \rightarrow H_2C_2 + H. \qquad (19)$$

It was concluded that Reactions (2) (CO + OH) and (18) ($CO + HO_2$) were equally important in the production of CO_2 and the following relationships were obtained

$$k_{18}(HO_2 + CO)/k_{19}(HO_2 + H_2) = 9.5.$$

In the CH_4 study, Reactions (17) and (19) were neglected. Reaction of HO_2 with CH_4 was considered but it was concluded that the mechanism was best represented by Reaction (4) ($CH_4 + OH$). Greiner [A–20, A–21] in a study of the flash photolysis of H_2O_2 with added H_2, CO, and CH_4, has shown that OH is regenerated by secondary reactions with HO_2 or H_2O_2. It would, therefore, seem likely that in the presence of large amounts of H_2O_2 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 HO_2 with alkanes has a low activation energy which suggests that reaction of HO_2 with methane might be of some importance [18].

[8] Wilson, Wm. E., Jr., O'Donovan, J. T., and Fristrom, R. M., Flame inhibition by halogen compounds, Symp. Combust., 12th (The Combustion Institute, 1969), p. 929.

k_4/k_2 ratios were determined in the temperature range 1750 to 2000 K from flame structure studies of a number of flames inhibited with halogen compounds. It was assumed that only reactions (4) and (2) consumed CH_4 and CO. Diffusion corrections were made using binary diffusion coefficients.

[9, 10] Westenberg, A. A., and Fristrom, R. M., Methane oxygen flame structure. IV. chemical kinetic considerations, J. Phys. Chem. **65**, 591 (1961).

The determination of k_4/k_2 from flame structure studies of (9) 1/10 and (10) 1/20 atm CH_4-O_2 flames are reported. It was assumed that the only reactions consuming CH_4 and CO were (4) and (2). Diffusion corrections were made using binary diffusion coefficients.

[11] Fenimore, C. P., and Jones, G. W., Rate of reaction of methane with H atoms and OH radicals, J. Chem. Phys. **65**, 2200 (1961).

Flame structure studies of several flames. Ratio quoted in table IV calculated (ref. [5]) from the rate constants given by Fenimore and Jones. Note that the activation energy has the opposite sign from the suggested equation, but that absolute values agree within the range of experimental measurements.

[12] Blundell, R. V., Cook, W. G. A., Hoare, D. E., and Milne, G. S., Rates of radical reactions in methane oxidation, Symp. Combust., 10th (The Combustion Institute, 1965), p. 445.

Slow combustion of CH_4 with analysis of CO, CO_2, and H_2CO at times up to 750 s., pressure 60 to 450 mm, temperature 773 to 998 K. Catalytic oxidation of CO on the surface and reaction with HO_2 probably cause this value to be low. Because of expected errors this number is not considered reliable.

[13] Slow combustion studies by a variety of workers. Discussion and references are given in reference [12] above. These numbers are not considered reliable because of the reasons given under reference [12].

[14] Hoare, D. E., Reactions of gaseous hydroxyl radicals, Nature **194**, 283 (1962); Hoare, D. E., Studies of the reactions of hydroxyl radicals. I, Proc. Roy. Soc. **A291**, 73 (1966); Hoare, D. E., and Peacock, G. B., Studies of the reactions of hydroxyl radicals. II, Proc. Roy. Soc. **A291**, 85 (1966).

The thermal decomposition of H_2O_2 was used as a source of OH. The OH formed reacts rapidly with H_2O_2 to form HO_2 which complicates the reaction mechanism. Because of the presence of HO_2 which also reacts with CO and possibly with CH_4 these numbers are not considered reliable.

[15] Pratt, N. H., Symp. Combust., 11th (The Combustion Institute, 1967), p. 1150, and Ph.D. Thesis, University of London, 1962.

A thermal reactor was used. This measurement is complicated by wall and HO_2 reactions and is not considered reliable.

B4.2c. Rate Calculations

[16] Mayer, S. W., and Schieler, L., Computed high-temperature rate constants for polyatomic combustion products, to be published.

B4.2d. Rate Evaluations

[17] Schofield, K., An evaluation of kinetic rate data for reactions of neutrals of atmospheric interest, Planet. Space Sci. **15**, 643 (1967). Erratum: Planet. Space. Sci. **15**, 1336 (1967).

B4.2e. General References

[18] Cullis, C. F., Fish, A., and Gibson, J. F., Quantitative aspects of free radical reactions in combustion, Symp Combust., 10th (The Combustion Institute, 1965) p. 411.

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

C1. k_8, Rate Constant for the Reaction, $C_2H_2 + OH \rightarrow$ 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 $OH + C_2H_2 \rightarrow H_2 + HC_2O$ which is followed by the very rapid reaction $OH + HC_2O \rightarrow C_2O + H_2O$. A value of $k_8 = 2 \pm 0.6 \times 10^{-13}$ cm³ molecule⁻¹ · s⁻¹ ($1.2 \pm 0.4 \times 10^{11}$ cm³ 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 $OH + C_2H_2 \rightarrow C_2H + H_2O$. 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 chemi-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.

Temperature range	Suggested values	Error limits
	k_8 in cm³ mol⁻¹ · s⁻¹	
300–1000 K	1.2×10^{11}	$\log_{10} k_8 \pm 0.3$
1000–1600 K	$6 \times 10^{12} \exp(-3{,}500/T)$	$\log_{10} k_8 \pm 1$

[1.1] Breen, J. E., and Glass, G. P., The reaction of the hydroxyl radical with acetylene, Int. J. Chem. Kinetics **3**, 145 (1970).

The reaction of OH with acetylene was studied in a discharge flow system at room temperature using E.S.R. 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

$$OH + C_2H_2 \rightarrow H_2 + HC_2O \tag{8}$$

$$OH + HC_2O \rightarrow C_2O + H_2O.$$

The C_2O formed was largely removed by reaction with nitric oxide yielding N_2, N_2O, CO, and CO_2. The NO was introduced into the system during the generation of OH from the atomic hydrogen titration reaction

$$NO_2 + H \rightarrow NO + OH.$$

A computer analysis of the OH decay profiles, which took into account $OH + OH \rightarrow H_2O + O$, $O + OH \rightarrow O_2 + H$, and OH

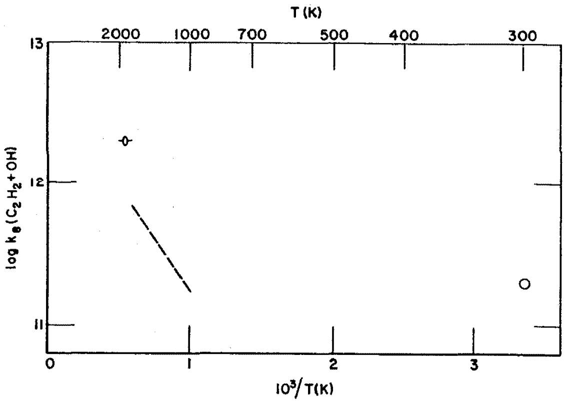

FIGURE C1. *Arrhenius plot for* $k_8(C_2H_2 + OH)$.

----	Browne et al.,
⦶	Fenimore and Jones,
○	Breen and Glass.

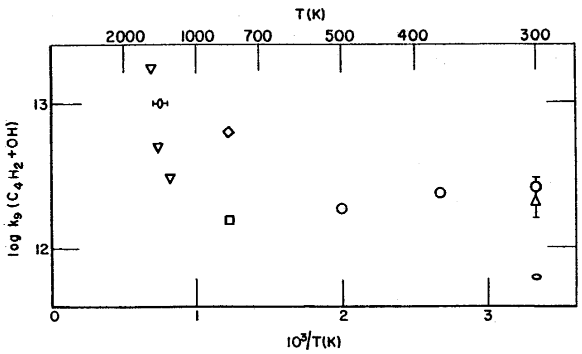

FIGURE C2. *Arrhenius plot of* $k_9(C_2H_4+OH)$.

○ Greiner, reference [1];
△ Wilson and Westenberg, reference [2];
◇ Baldwin et al., k_9/k_3, with Greiner's k_3, reference [3];
□ Baldwin et al., k_9/k_3, with k_3 from this report;
0 Westenberg and Fristrom, reference [4];
▽ Westenberg and Fristrom, recalculated values using k_2 from this report;
⬭ Morris, Stedman, Niki, reference [5].

+wall → products, yielded $k_8=2.0\pm0.6\times10^{-13}$ cm^3 molecule$^{-1}\cdot$s^{-1} for the first, rate controlling step.

[1.2] 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_2H_2+OH was also studied. A value $k_8=(6\times10^{11})/n$ cm^3 mol$^{-1}\cdot$s^{-1} was obtained. The value of n, which refers to the number of OH radicals reacting for each C_2H_2 molecule that reacts, was not determined. Assuming a stoichiometry of between 2 and 3, as indicated by the work of Breen and Glass, a value of $k_8=2$–3×10^{11} is obtained in good agreement with their value of $k_8=1.2\pm0.4\times10^{11}$ cm^3 mol$^{-1}\cdot$s^{-1}.

[1.3] Browne, W. G., Porter, R. P., Verlin, J. D., and Clark, A. H., A study of acetylene-oxygen flames, Sym. Combust., 12th (The Combustion Institute, 1969), p. 1035.

Five $C_2H_2-O_2$ flames, for which concentration and temperature profiles had been measured, were analyzed by integrating numerically the one-dimensional flame equations. Multicomponent diffusion equations and experimental temperature and OH profiles were used in the analysis. In lean flames up to 25 percent of the C_2H_2 reacted with OH. A value of $k_8=6\times10^{12}$ exp $(-7000/RT)$ cm^3 mol$^{-1}\cdot$s^{-1} was found to give satisfactory results in fitting data between 1000 and 1600 K. This is probably the best value available for this rate at flame temperatures but because of the small extent of reaction with OH and the involvement of other reactions in the analysis, the value and especially the activation energy is still somewhat uncertain. The reaction mechanism at flame temperatures is thought to be $C_2H_2+OH\rightarrow C_2H+H_2O$. Browne et al., also give values for H and $O+C_2H_2$.

[1.4] Fenimore, C. P., and Jones, G. W., Rate of destruction of acetylene in flame gases, J. Chem. Phys. **41**, 1887 (1964).

The rate of decay of C_2H_2 in the burnt gas from fuel-rich $C_2H_2-O_2$ flames was measured. Equilibrium amounts of H, OH, O, and O_2 were present in the ratio $[H]:[OH]:[O]:[O_2]=15:1:10^{-3}:3\times10^{-4}$. The concentration of C_2H_2 was greater than equilibrium and its rate of consumption could be measured. Assuming that the reaction, $C_2H_2+OH\rightarrow$ products, is irreversible, the rate of decay of C_2H_2 in the burnt gas environment could be represented by $-d[C_2H_2]/dt=2\times10^{12}[OH][C_2H_2]$ mol cm$^{-3}\cdot$s^{-1}, but could not be represented by $k[X][C_2H_2]$ where X was H, O, or O_2. This led to the suggestion of 2×10^{12} cm^3 mol$^{-1}\cdot$s^{-1} for the reaction of C_2H_2 with OH with an activation energy estimate of 7 kcal. However, the work of Browne et al, indicates that the rate of $H+C_2H_2$ in the 1700 to 2000 K range is comparable to that of $OH+C_2H_2$. Since the decay could not be correlated with [H], it follows that the reaction $C_2H_2+H=C_2H+H_2$ was equilibrated. If, as is now thought, the product of the reaction of both H and OH with C_2H_2 is C_2H, both reactions will be equilibrated. Fenimore and Jones recognized this possibility and pointed out that unless OH oxidized a carbon atom in C_2H_2, the reaction followed in the burnt gas would not be C_2H_2+OH but $C_2H+H_2O\rightarrow$ products. This apparently was the case.

C2. k_9, Rate Constant for the Reaction, $C_2H_4+OH\rightarrow$ Products

Two measurements by different techniques are in reasonable agreement at room temperature. 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 $k_9(C_2H_4+OH)\rightarrow 3\pm2\times10^{12}$ cm^3 mol$^{-1}\cdot$s^{-1} with no activation energy is recommended. Experimental points are shown on an Arrhenius plot in figure C2.

[2.1] Greiner, N. R., Hydroxyl radical kinetics by kinetic spectroscopy VII. The reaction with ethylene in the range 300–500 K, J. Chem. Phys. **53**, 1284 (1970).

The flash-photolysis, kinetic-spectroscopy technique was used. The reaction was assumed to be $C_2H_4+OH\rightarrow C_2H_4OH$ and the OH decay was corrected for reactions of the C_2H_4OH radical with OH assuming a rate constant for radical recombination of 10^{14} cm^3 mol$^{-1}\cdot$s^{-1}. Values obtained for $k_9(C_2H_4+OH)$ were $3.21\pm0.39\times10^{12}$ at 299 K, 2.46 ± 0.16 at 374 and 1.86 ± 0.11 at 497 K. The best fit to an Arrhenius plot was log A (cm^3 mol$^{-1}\cdot$s^{-1}) $=11.88\pm0.09$ and $E=-903\pm136$ cal mol^{-1}.

[2.2] 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_2H_4+OH, which was also studied, was too rapid for accurate measurement but a value of $k_9=(3\times10^{12})/n$ cm^3 mol$^{-1}\cdot$s^{-1} was estimated. The value of n, which refers to the number of OH radicals reacting for each C_2H_4 molecule that reacts, was not determined. This value, within experimental error, is in agreement with Greiner's room temperature value.

[2.3] Baldwin, R. R., Simmons, P. F., and Walker, R. W., Inhibition of the hydrogen plus oxygen reaction with ethylene. Part 2. Discussion and evaluation of velocity constants, Trans. Far. Soc. **62**, 2486 (1966).

The slight dependence on H_2 concentration of the efficiency of inhibition is explained by an abstraction reaction of either O or OH with C_2H_4. The ratio of this reaction to $k_3(H_2+OH)$ is 6.7 at 813 K. Although the authors prefer the reaction of OH with C_2H_4, they state that a reaction of $O+C_2H_2$ could also satisfy the results. Using the k_3 recommended in this report, a value of $k_9(OH+C_2H_4)$ of 6.3×10^{12} cm^3 mol$^{-1}\cdot$s^{-1} is obtained. Since the rate of $O+C_2H_4$ is about 4×10^{12} at this temperature [B3–28] this value of k_9 might be considered an upper limit.

[2.4] 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 used to determine the concentration profiles of C_2H_4, CO, and CO_2 through a 76 torr flat flame and the reaction rate profiles of C_2H_4 and CO_2. Taking a known value of $k_2(CO+OH\rightarrow CO_2+H)$, the CO concentration, and the CO_2 formation rate, a concentration profile may be calculated for OH. This is then used with the C_2H_4 concentration and disappearance rate to determine k_9 (C_2H_4+OH). The assumption must be made that OH is the only species attacking C_2H_4. In the O_2-rich flames used the H atom concentration would be very low but the O atom concentration is approximately half of the OH radical concentration at the hot boundary and might be expected to be an appreciable fraction of OH throughout the flame. The author's assumption that OH is the primary attacking species was based on the ESR analysis of samples extracted from the flames by a microprobe and conducted through an ESR cavity. H and O were not found early in the flame and were observed only in the region of the flame after the C_2H_4 had completely disappeared. The electric dipole spectrum of OH could not be observed with the cavity used. The most reasonable explanation for the unexpected profiles of H and O is that the rapid reaction of $O+OH$ in the tube from the probe to the cavity removed O and generated H and that much of the 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 O with OH. The reaction rate constant for $O+C_2H_4$ is about 10^{13} in the temperature range considered. The authors reported value of $k_9(C_2H_4+OH)=1\times10^{13}$ in the range 1250 to 1400 K must therefore be considered an upper limit. A recalculation of k_9 from the author's reported data using $k_2(CO+OH)$ from this report gave the following values, log $k_9=12.5$ at 1240 K, 12.7 at 1368 K, 13.2 at 1447 K, and 13.8 at 1491 K in cm^3 mol$^{-1}\cdot$s^{-1} units.

[2.5] Morris, E. D., Jr., Stedman, D. H., and Niki, H., Mass spectrometric study of the reactions of the hydroxyl radical with ethylene, propylene, and acetaldehyde in a discharge-flow system, J. Am. Chem. Soc. **93**, 3570 (1971).

The reaction of 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 $nk_9=4.2\times10^{12}$ cm³ mol⁻¹ · s⁻¹. The ethylene decay in an OH rich system gave $k_9=3.0\times10^{12}$. *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 $k_{10}(C_2H_6+OH)$ 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 $k_3(H_2+OH)$. 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 $k_3(H_2+OH)$ is used, the resulting k_{10} is in agreement with the extrapolation of Greiner's measurement of k_{10}. Unfortunately neither of the flame temperature points are reliable enough to establish the proper activation energy. The recommended expression is $k_{10}=6.5\pm0.5\times10^{13}\exp(-1{,}800\pm300/T)$. 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. G. 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, $\log_{10} k_{10}=(14.1\pm0.7)-(3{,}600\pm600)/2.303\ RT$ cm³ mol⁻¹·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_2H_5 radicals with OH. When this is done the room temperature value agrees with that of references [3.2 and 3.3].

[3.2a] Greiner, N. R., Hydroxyl radical kinetics by kinetic spectroscopy. II. Reactions with C_2H_6, C_3H_8, and *iso*-C_4D_{10} at 300 K, J. Chem. Phys. **46,** 3389 (1967).

[3.2b] Greiner, N. R., Hydroxyl radical kinetics by kinetic spectroscopy. VI. Reactions with alkanes in the range 300–500 K, J. Chem. Phys. **53,** 1070 (1970).

Measurements were made by the flash photolysis-kinetic spectroscopy technique in the temperature range 300 to 500 K. In this range the rate constant may be expressed as $k_{10}=1.12\times10^{13}\exp(-2447/RT)$ cm³ mol⁻¹ · s⁻¹. Individual values are: 1.76±0.23 at 302 K, 2.75±0.06 at 335 K, 4.52±0.30 at 369 K, 5.64±0.35 at 424 K, and 9.35 at 4.93. Corrections of the order of 10 percent were made for the subsequent reaction of C_2H_5 with OH. Experimental techniques and a discussion of the difference in activation energies obtained by Greiner and other workers may be found in reference [4–4] and Section D.

[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_2H_6+OH was also studied. A value $k_{10}=(6\times10^{11})/n$ cm³ mol⁻¹ · s⁻¹ was obtained. The value of *n*, which refers to the number of OH radicals reacting for each C_2H_6 molecule that reacts, was not determined. Assuming a stoichiometry of between 2 and 3, a value of $2\text{–}3\times10^{11}$ 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 76 torr $C_2H_6-O_2$ flame (See reference [2.4]). The authors report $k_{10}=5\times10^{12}$ cm³ mol⁻¹ · s⁻¹ in the range 1300 to 1550 K. k_{10} was assumed to be the only reaction removing C_2H_6. In this flame $[O]\approx1/2\ [OH]$ and the rate of $O+C_2H_6$ at 1500 may be estimated as 2.3×10^{12} at 1500 K [B3–28b]. As much as 25 percent of the C_2H_6 disappearance might be due to attack by O leading to a slightly smaller value for k_{10}.

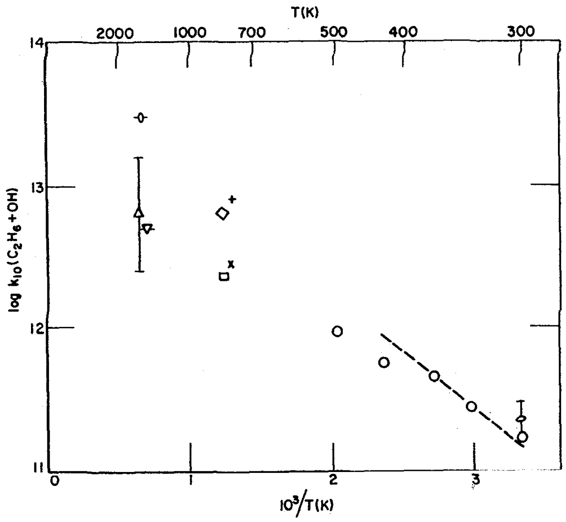

FIGURE C3. *Arrhenius plot of* $k_{10}(C_2H_6+OH)$.

---- Horne and Norrish (their expression ÷ 2), reference [1];
○ Greiner, reference [2];
⊖ Wilson and Westenberg, reference [3];
□, ◇ Baldwin et al., k_{10}/k_3 (ref. [6] inhibition); □ with Greiner's k_3,
◇ with k_3, this report;
X, + Baldwin et al., k_{10}/k_3 (ref. [7] slow reaction); X with Greiner's k_3,
+ with k_3, this report;
▽ Fristrom and Westenberg, reference [4];
△ Fristrom and Westenberg, recalculation with k_2 from this report;
0 Fenimore and Jones, reference [5].

[3.5] Fenimore, C. P., and Jones, G. W., The decomposition of ethylene and ethane in premixed hydrocarbon-oxygen-hydrogen flames, Symp. Combust., 9th (Academic Press, 1963), p. 597.

Flame structure techniques were applied to $C_2H_6-O_2$ flames of varying mixture ratios enabling the rate of both H and OH $+C_2H_6$ to be determined. Initial attack by O atoms was not thought to be important. The authors report $k_{10}=3\times10^{13}$ cm³ mol⁻¹ · s⁻¹ in the 1400 to 1600 K range.

[3.6] Baldwin, R. R., Jackson, D., Walker, R. W., and Webster, S. J., The use of the hydrogen-oxygen reaction in evaluating velocity constants, Symp. Combust., 10th (The Combustion Institute, 1965), p. 423.

The inhibition of the second limit of the H_2/O_2 reaction by C_2H_6 was studied. (See discussion following ref. [B3–12]) From the dependence of the inhibition on the mol fraction of H_2 the following relationship was obtained where $R_0=k_{14}(O+C_2H_6)/k_{12}(O+H_2)$ and $R_{OH}=k_{10}(OH+C_2H_6)/k_3(OH+H_2)$: $(R_0+13.1)(R_{OH}+2.98)=201$ at 813 K. Thus, if k_{14}, k_{12}, and k_3 are known, k_{10} may be calculated. The following values are assumed: $k_{14}=1.8\pm0.2\times10^{13}\exp(-6100/RT)$ [3–28a], $k_{12}=3.2\times10^{13}\exp(-10{,}200/RT)$ [3–28b], and $k_3=2.3\times10^{13}\exp(-2600/T)$ [this report]. At 793 K the corresponding values are $k_{14}=4.10\times10^{11}$, $k_{12}=5.76\times10^{10}$, and $k_3=9.38\times10^{11}$. The authors relationship yields $k_{10}=6.5\times10^{12}$. This point falls very close to the extension of Horne and Norrish's rate expression. (Figure C3.) Alternately Greiner's expression, $\log k_3=12.61-4020/2.303RT$, may be used. In this case $k_3=3.39$ and $k_{10}=2.35\times10^{12}$ (all in cm³ mol⁻¹ · 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.

[3.7] Baldwin, R. R., Hopkins, D. E., and Walker, R. W., Addition of ethane to slowly reacting mixtures of hydrogen and oxygen at 500 C, Trans. Faraday Soc. **66,** 189 (1970).

When traces of ethane (~ 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_{10} $(OH+C_2H_6)/k_3(OH+H_2)=9.5$ was obtained at 773 K. Using the value of k_3 recommended in this report, $k_{10}=8.5\times 10^{12}$ cm^3 mol$^{-1}\cdot$ s^{-1}.

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

[4.1] Greiner, N. R., Hydroxyl radical kinetics by kinetic spectroscopy. VI. Reactions with alkanes in the range 300–500 K, J. Chem. Phys. **53**, 1070 (1970).

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$^{-1}\cdot$ s^{-1} units).

$$k_{\text{total}} = 6.15\times 10^{11}\,N_P \exp(-1635/RT) + 14.1\times 10^{11}\,N_S \exp(-850/RT) + 12.6\times 10^{11}\,N_T \exp(+190/RT),$$

where N_P, N_S, and N_T are the respective numbers of primary, secondary, and tertiary H atoms in the alkane, and k_{total} 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).

[4.2] Baldwin, R. R., Jackson, D., Walker, R. W., and Webster, S. J., The use of the hydrogen-oxygen reaction in evaluating velocity constants, Symp. Combust., 10th (The Combustion Institute, 1965), p. 423.

Detailed investigations of the inhibition of the hydrogen-oxygen reaction by a number of hydrocarbons and related compounds have been made. With formaldelyde, 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 H_2/O_2 reaction.

$$OH+H_2\rightarrow H_2O+H \quad (3)$$

$$H+O_2\rightarrow OH+O \quad (11)$$

$$O+H_2\rightarrow OH+H \quad (12)$$

$$H+O_2+M\rightarrow HO_2+M \quad (13)$$

$$O+RH\rightarrow OH+R \quad (14)$$

$$H+RH\rightarrow H_2+R \quad (15)$$

$$OH+RH\rightarrow H_2O+R. \quad (16)$$

It is assumed that the HO_2 radicals are destroyed without continuing the chain, and it appears that the alkyl radicals R react predominantly with O_2 to form an olefin (CO in the case of the HCO radical) and the HO_2 radical. Because of the almost linear decrease in the second limit pressure with mol fraction of inhibitor, the efficiency of inhibition is conveniently assessed in terms of $i_{1/2}$, the mol fraction of inhibitor required to halve the second limit. From the above mechanism, $i_{1/2}$ is given by

$$1/i_{1/2}=(k_{15}/k_{11}y)+[2k_{16}/(k_3x+k_{16}i_{1/2})] + [k_{14}/(k_{12}x+k_{14}i_{1/2})], \quad \text{(i)}$$

where x, y are the mol fractions of H_2, O_2.

The marked dependence of $i_{1/2}$ on y, found experimentally, indicates uniquely the importance of Reaction (15), the dependence on x does not enable Reactions (14) and (16) to be distinguished. Use of eq (i) with either $k_{14}=0$ or $k_{16}=0$ enables an accurate prediction to be made of the variation of $i_{1/2}$ with x and y over a wide range (x/y varying from 6:1 to 1:8), with a rms deviation of a few percent between calculated and experimental values of $i_{1/2}$. The values for k_{16}/k_3 assuming $k_{14}=0$ and for k_{14}/k_{12} assuming $k_{16}=0$ are given below. Both k_{16} and k_{14} undoubtedly play a role in the inhibition. If either ratio is known the other may be determined from the empirical relation:

$$\left(\frac{k_{14}(O+RH)}{k_{12}(O+H_2)}+B\right)\left(\frac{k_{16}(OH+RH)}{k_3(OH+H_2)}+C\right)=D.$$

The values of B, C, and D are given below.

Hydrocarbon	Temp, K	$k_{14}(O+RH)=0$		$k_{16}(OH+RH)=0$		B	C	D
		$\frac{k_{15}(H+RH)}{k_{11}(H+O_2)}$	$\frac{k_{16}(OH+RH)}{k_3(O+H_2)}$	$\frac{k_{15}(H+RH)}{k_{11}(H+O_2)}$	$\frac{k_{14}(O+RH)}{k_{12}(O+H_2)}$			
Ethane	813	38	12	32	54	13.1	2.98	201
Propane	793	77	27	62	124	26.3	5.70	857
n-Butane	793	83	36	53	250	20.6	3.00	811
i-Butane	793	153	20	147	56	38.3	13.40	1,267
Formaldehyde	813	326	42	309	130	68.0	22.7	4,200
Tetraethylsilane	793	374	74	341	254	101.6	29.5	10,480

The rate constant for k_{14} $(O+n{-}C_4H_{10})$ has been measured and can be used with k_{12} and k_3 to determine k_{16} $(OH+n{-}C_4H_{10})$. As in the case of C_2H_6, 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}.

[4.3] Morris, E. D., Jr., Stedman, D. H., Niki, H., Mass spectrometric study of the hydroxyl radical with ethylene, propylene, and acetaldehyde in discharge-flow systems, J. Am. Chem. Soc. **93**, 3570 (1971).

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 $k_{23}=11.0\times 10^{12}$ cm^3 mol$^{-1}\cdot$ s^{-1} for propylene and $k_{24}=9.0\times 10^{12}$ cm^3 mol$^{-1}\cdot$ 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.

	k/n	Observed stoichiometry	k
C_3H_6	3.0×10^{13}	3.2	9.6×10^{12}
CH_3CHO	1.8×10^{13}	1.9	9.6×10^{12}

C5. k_6, 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, $(3\pm 1)\times 10^{13}$

[1–4] and $(2.6\pm0.8)\times10^{13}$ [5], and $(2.0\pm0.3)\times10^{13}$ $cm^3\ mol^{-1}\cdot s^{-1}$ are in reasonable agreement with the value of 1.3×10^{13} $cm^3\ mol^{-1}\cdot s^{-1}$ obtained from the rate of the reverse reaction. A value of $(2.5\pm1)\times10^{13}$ $cm^3\ mol^{-1}\cdot s^{-1}$, with zero activation energy, is recommended.

[5.1] Kaufman, F., Aeronamic reactions involving hydrogen. A review of recent laboratory studies, Ann. Geophys. **20**, 106 (1964).

[5.2] Kaufman, F., and Del Greco, F. P., Fast reactions of OH radicals, Symp. Combust., 9th (Academic Press, 1963), p. 659.

[5.3] Clyne, M. A. A., and Thrush, B. A., Rates of elementary processes in the chain reaction between hydrogen and oxygen. I. Reactions of oxygen atoms, Proc. Roy. Soc. **A275**, 544 (1963).

[5.4] Clyne, M. A. A., Rates of some atomic reactions involving hydrogen and oxygen, Symp. Combust., 9th (Academic Press, 1963), p. 211.

[5.5] Breen, J. E., and Glass, G. P., Rates of some hydroxyl radical reactions, J. Chem. Phys. **52**, 1082 (1970).

[5.6] Baulch, D. L., Drysdale, D. D., and Lloyd, A. C., High temperature reaction rate data, No. 3, Dept. Phys. Chem. The University, Leeds 2, England, April 1969.

[5.7] Westenberg, A. A., de Haas, N., and Roscoe, J. M., Radical reactions in an electron spin resonance cavity homogeneous reactor, J. Phys. Chem. **74**, 3431 (1970).

C6. k_{17}, Rate Constant for the Reaction, $OH+H_2O_2\rightarrow H_2O+HO_2$

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 1×10^{13} $\exp(-1800/RT)$ $cm^3\ mol^{-1}\cdot s^{-1}$ over the temperature range 300 to 1000 K with error limits log k_{17} ±0.7 is recommended. This expression also provides an adequate fit of Greiner's experimental measurements. This reaction is fast, $k_{17}=8.3\times10^{11}$ cm^3 $mol^{-1}\cdot s^{-1}$ at room temperature. Therefore, substantial amounts of HO_2 will be found in systems in which H_2O_2 is formed by recombination of OH or in systems in which OH is generated by the the thermal decomposition of H_2O_2. Such systems, therefore, are not satisfactory for studying OH reactions unless the role of HO_2 is considered.

[6.1.1] Greiner, N. R., Hydroxyl radical kinetics by kinetic spectroscopy. III. Reactions with H_2O_2 in the Range 300–458K, J. Phys. Chem. **72**, 406 (1968).

Gas-phase reactions of OH radicals in the presence of H_2O_2 and various amounts of Ar were studied in the region 300 to 458 K by flash photolysis-kinetic spectroscopy. The results were interpreted in terms of Reaction (17),

$$OH+H_2O_2\rightarrow H_2O+HO_2 \qquad (17)$$

with $\log k_{17}=(11.39\pm0.05)+1/2\log T-1200/2.303\ RT$ cm^3 $mol^{-1}\cdot s^{-1}$. A reaction second order in OH with $k=3.9\pm1.5\times10^{13}$ $cm^3\ mol^{-1}\cdot s^{-1}$ was observed at 300 K but not at higher temperatures. An unsucessful search was made for an absorption spectrum of HO_2 in the region 250 to 1000 nm. There was evidence that one of the products of the reaction was vibrationally excited. (An absorption attributed to HO_2 has been observed in shock tube studies at 230 nm [9].)

[6.1.2] Baldwin, R. R., Jackson, D., Walker, R. W., and Webster, S. J., The use of the hydrogen-oxygen reaction in evaluating velocity constants, Symp. Combust., 10th (The Combustion Institute, 1965), p. 423

Studies of the slow H_2O_2 reaction in aged boric-acid-coated vessels yielded a value of $k_{17}/k_3=4.7$ at 773 K. The original treatment [3, 4] was refined by using an improved experimental technique and using a computer program to calculate rate ratios. Studies of decomposition of H_2O_2 in the presence of H_2 in an aged boric-acid-coated flow system at atmospheric pressure yielded $k_{17}/k_3=4.3\pm0.3$ at 713 K. The analysis assumes that the decomposition of H_2O_2 is a nonchain process [5, 6, 7, 8] represented by the sequence

$$H_2O_2+M\rightarrow 2\,OH+M$$

$$OH+H_2O_2\rightarrow H_2O+HO_2 \qquad (17)$$

$$2\,HO_2\rightarrow H_2O+O_2$$

and that in the presence of H_2 the decomposition of H_2O_2 is sensitized by the chain process

$$H_2O_2+M\rightarrow 2\,OH+M$$

$$OH+H_2\rightarrow H_2O+H \qquad (3)$$

$$H+H_2O_2\rightarrow H_2O+OH.$$

Therefore the ratio k_{17}/k_3 and a number of other ratios could be obtained from these studies.

A value for k_{17} may be obtained by using k_3, either that recommended in this report or that obtained by Greiner. The results, compared with Greiner's direct measurement of k_{17}, are shown below.

k_{17} in 10^{12} $cm^3\ mol^{-1}\cdot s^{-1}$	773 K	713 K
(Using k_3, Greiner [B3–4])	1.0	0.77
(Using k_3, this report)	3.8	2.6
(Extrapolation of Greiner's measurements over 300–458 K)	3.1	2.8

[6.1.3] Baldwin, R. R., and Mayor, L., Trans. Faraday Soc. **56**, 80, 103 (1959).

[6.1.4] Baldwin, R. R., Doran, P., and Mayor, L., Trans. Faraday Soc. **56**, 93 (1959).

[6.1.5] Giguere, P. A., and Liu, I. D., Can. J. Chem. **35**, 283 (1957).

[6.1.6] Frost, W., Can. J. Chem. **36**, 1308 (1958).

[6.1.7] Hoare, D. E., Prothero, J. B., and Walsh, A. D., Trans. Faraday Soc. **56**, 548 (1959).

[6.1.8] Baldwin, R. R., Booth, D., and Brattan, D., Can. J. Chem. **39**, 3120 (1961).

[6.1.9] Meyer, E., Olschewski, H. A., Troe, J., and Wagner, Gg. H., Investigation of N_2H_4 and H_2O_2 decomposition in low and high pressure shock waves, Symp. Combust., 12th (The Combustion Institute, 1969), p. 345.

[6.1.10] Frost, W., and Giguere, P. A., J. Phys. Chem. **62**, 340 (1958). A value of k_{17}/k_3 of 4.8 to 5.7 at 447 K was derived from a study of H_2/O_2 ignition.

C7. k_{-12}, Rate Constant for the Reaction, $OH+H\rightarrow H_2+O$

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 k_{12} $(O+H_2)$ are discussed below. The recommended value, k_{-12} $(OH+H)=1.35\times10^{13}\exp(-8{,}050/RT)$ $cm^3\ mol^{-1}\cdot s^{-1}$, error limits log $k\pm0.3$, 500 to 3000 K, is based on k_{12} from reference [C.5.2] and K_{eq} 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 k_{12} was reviewed and a value of $k_{12}=1.74\times10^{13}\exp(-9{,}450/RT)$ $cm^3\ mol^{-1}\cdot s^{-1}$ was recommended with error limits of ±30 percent. Using $K_{eq}=2.38\exp(-2150/RT)$ they obtained $k_{-12}=7.33\times10^{12}\exp(-7{,}300/RT)$ $cm^3\ mol^{-1}\cdot s^{-1}$.

[7.2] Westenberg, A. A., and deHaas, N., Reinvestigation of the rate coefficients for $O+H_2$ and $O+CH_4$, J. Chem. Phys. **50**, 6 (1969).

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 H atoms yielded $k_{12}=3.2\times10^{13}\exp(-10{,}200/RT)$ $cm^3\ mol^{-1}\cdot s^{-1}$. 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_{12} were greater than predicted by the Arrhenius expression.

C8. Miscellaneous Bimolecular OH Reactions

C8.1. Ammonia: k_{23D} ($NH_3+OD \rightarrow$ Products)

[8.1.1] Albers, E. A., Hoyermann, K., Wagner, Gg. H., and Wolfrum, J., Study of the reaction of ammonia with oxygen atoms, Symp. Combust. **12** (The Combustion Institute, 1969), p. 313.

Preliminary results are reported which give $k_{23D}(OD+NH_3)/k_{3D}(OD+H_2)=0.5$ at 500 K or $k_{23D}(OD+NH_3)\approx 10^{11}$ cm³ mol⁻¹ · s⁻¹.

C8.2. Formaldehyde: $k_{20}(OH+H_2CO \rightarrow H_2O+HCO)$

Four measurements have been reported for $k_{20}(OH+H_2CO)$. The values at 773 K and the upper limit at 813 K, derived from rate ratio measurments, 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 $k_{20}(OH+H_2CO)=5\times 10^{13}$ cm³ mol⁻¹ · s⁻¹ with an uncertainty of log $k_{20}\pm 1$ is recommended.

[8.2.1] Blundell, R. V., Cook, W. G. A., Hoare, D. E., and Milne, G. S., Rates of radical reactions in methane oxidation, Symp. Combust., 10th (The Combustion Institute, 1965), p. 445.

Studies of the slow oxidation of methane yielded $k_{20}(OH+H_2CO)/k_3(OH+H_2)=33\pm 3$ at 773 K, or $k_{20}=4.3\times 10^{13}$ cm³ mol⁻¹ · s⁻¹ at 773 K (using k_3 from this review).

[8.2.2] Baldwin, R. R., Jackson, D., Walker, R. W., and Webster, S. J., The use of the hydrogen-oxygen reaction in evaluating velocity constants, Symp. Combust., 10th (The Combustion Institute, 1965), p. 423.

Inhibition studies of the H_2-O_2 reaction yield an upper limit of $k_{20}/k_3=42$ at 813 K or $k_{20}\leq 6.5\times 10^{13}$ cm³ mol⁻¹ · s⁻¹ at 813 K. (See 4.2.)

[8.2.3] 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.

Flame structure studies of C_2 hydrocarbon flames yielded $k_{20}(OH+H_2CO)=5\times 10^{15}\exp(-6500/T)$ cm³ mol⁻¹ · s⁻¹, at 1600 K this gives $k_{20}=8.5\times 10^{13}$, at 773 K, $k_{20}=1.1\times 10^{12}$.

[8.2.4] Herron, J. T., and Penzhorn, R. D., Mass spectrometric study of the reactions of atomic oxygen with ethylene and formaldehyde, J. Phys. Chem. **73**, 191 (1969).

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 $k_{20}\leq 4\times 10^{12}$ cm³ mol⁻¹ · s⁻¹ at 300 K was obtained.

C8.3. Nitric Acid: $k_{24}(HNO_3+OH \rightarrow H_2O+NO_3)$

[8.3.1] Husain, D., and Norrish, R. G. W., The production of NO_3 in the photolysis of nitrogen dioxide and of nitric acid vapor under isothermal conditions. Proc. Royal Soc. **A273**, 165 (1963).

Values of $k_{24}=0.9$ and 1.1×10^{11} cm³ mol⁻¹ · s⁻¹ were obtained at 300 K from $-d[OH]/dt$. Both the formation of NO_3 and the disappearance of OH were observed.

C8.4. Nitroxyl: k_{25}($HNO+OH \rightarrow$ Products)

[8.4.1] Bulewicz, E. M., and Sugden, T. M., Flame photometric studies of reactions induced by nitric oxide in hydrogen-oxygen-nitrogen flames. I. The catalyzed recombination of atomic hydrogen and hydroxyl radicals, Proc. Royal Soc. **A277**, 143 (1964).

Studies of the decay of H and OH in the burnt gas region of fuel-rich flames of H_2, N_2, O_2 at atmospheric pressure indicate that NO is an effective homogeneous catalyst. The results were consistent with the mechanism

$$H+NO+M \rightarrow HNO+M$$
$$H+HNO \rightarrow H_2+NO$$
$$OH+HNO \rightarrow H_2O+NO \text{ or } H_2+NO_2.$$

$k_{25}=1.5\pm 0.5\times 10^{-10}$ cm³ molecule⁻¹ · s⁻¹ with no significant temperature effect from 1600 to 2000 K.

C8.5 Methyl Radical: k_{26} ($CH_3+OH \rightarrow$ Products)

[8.5.1] Fenimore, C. P., Destruction of methane in water gas by reaction of CH_3 with OH radicals, Symp. Combust., 12th (The Combustion Institute, 1969), p. 463.

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_2O were shown to be in equilibrium. Since the rate of decay of CH_4 was much lower than the calculated rate for $H+CH_4 \rightarrow CH_3+H_2$, it was assumed that this reaction and the reactions $OH+CH_4 \rightarrow CH_3+H_2O$ and $O+CH_4 \rightarrow CH_3+OH$ were also equilibrated. The rate of decay of CH_4 could, therefore, be attributed to $CH_3+OH \rightarrow$ products with CH_3 and OH both being in quasi-equilibrium. The calculated rate constant was $k_{26}=(4\pm 2)\times 10^{12}$ cm³ mol⁻¹ · s⁻¹ in the region 1970 to 2190 K.

C8.6. C_2 Radical: $k_{27}(C_2+OH \rightarrow CO+CH)$

[8.6.1] Porter, R. P., Clark, A. H., Kaskan, W. E., and Browne, W. E., A study of hydrocarbon flames, Symp. Combust., 11th (the Combustion Institute, 1967), p. 907.

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.

$$C_2+OH \rightarrow CO+CH^*(^2\Delta)k_{27a}=4\times 10^{11}\ \text{cm}^3\ \text{mol}^{-1}\cdot\text{s}^{-1}$$
$$C_2+OH \rightarrow CO+CH^*(^2\Sigma^-)k_{27b}=4\times 10^{10}\ \text{cm}^3\ \text{mol}^{-1}\cdot\text{s}^{-1}$$

The measured quantity is the ratio of the formation of CH* to the quenching of CH*, lifetimes for CH*, taken from other sources, were used to obtain the values of k.

[8.6.2] Bulewicz, E. M., Padley, P. J., and Smith, R. E., Spectroscopic studies of C_2, CH, and OH radicals in low pressure acetylene+oxygen flames, Proc. Royal Soc. **A315**, 129–148 (1970).

In this study it was possible to measure $d[C_2]/dt$ and [OH] and $[C_2]$ and thus obtain a more direct determination of $k_{27}=5\pm 2\times 10^{12}$ cm³ mol⁻¹ · s⁻¹ at 2200 K.

C8.7. Halogenated Compounds: HCl, HBr, CH_3Cl, and $CH_3Br+OH \rightarrow$ Products

[8.7.1] Wilson, Wm. E., Jr., O'Donovan, J. T., and Fristrom, R. M., Flame inhibition by halogen compounds, Symp. Combust., 12th (The Combustion Institute, 1969), p. 929.

From flame structure studies of low pressure, inhibited CH_4+O_2 flames, the following rate constants were obtained. OH concentrations were estimated from CH_4 and CO decay rates and the corresponding rate constants.

Reaction	Rate in	Temperature, K	Error limits on log k
	10^{13} cm³ mol⁻¹ · s⁻¹		
HBr+OH	$k_{23}=1.6$	1875–1975	±1
HCl+OH	$k_{29}=0.77$	1920–1940	±1
CH_3Br+OH	$k_{30}=1.5$	1775–1825	±0.5
CH_3Cl+OH	$k_{31}-1.3$	1850–2100	±0.5

C8.8. k_{32} ($N+OH \rightarrow NO+H$)

[8.8.1] Campbell, I. M., and Thrush, B. A., Reactivity of hydrogen to atomic nitrogen and atomic oxygen, Trans. Far. Soc. **64**, 1265 (1968).

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

$$O+H_2 \rightarrow OH+H \tag{12}$$

$$N+OH \rightarrow NO+H \tag{32}$$

$$N+NO \rightarrow N_2+O$$

$$O+OH \rightarrow O_2+H. \tag{6}$$

The consumption of both nitrogen atoms and oxygen atoms were followed photometrically and the results yield a ratio $k_{32}(N+OH)/k_6(O+OH)$ of 1.4 ± 0.1 at 320 K. Using $k_6(O+OH)=2.5\times 10^{13}$ cm³ mol⁻¹ · s⁻¹ (this review, C5), $k_{32}(N+OH)=3.5\times 10^{13}$ cm³ mol⁻¹ · s⁻¹.

C8.9. $k_{33}(\text{SO}+\text{OH}\rightarrow\text{SO}_2+\text{H})$

[8.9.1] Fair, R. W., and Thrush, B. A., Reaction of hydrogen atoms with hydrogen sulphide in the presence of molecular oxygen, Trans. Far. Soc., **65**, 1557 (1969).

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 OH formed in the reaction sequence,

$$\begin{gathered}\text{H}+\text{O}_2+\text{M}\rightarrow\text{HO}_2+\text{M}\\ \text{H}+\text{HO}_2\rightarrow\text{OH}+\text{OH}\\ \text{SO}+\text{OH}\rightarrow\text{SO}_2+\text{H}.\end{gathered}$$

A value of $k_{33}(\text{SO}+\text{OH})/k_6(\text{O}+\text{OH})=2.5$ at 298 K was obtained. Using k_6 from this review (C5), $k_{33}(\text{SO}+\text{OH})=(6.2\pm3)\times10^{13}$ cm^3 mol$^{-1}\cdot$ s^{-1}.

C9. k_{22}, Rate Constant for the Reaction $\text{OH}+\text{OH}+\text{M}\rightarrow\text{H}_2\text{O}_2+\text{M}$

There are two experimental measurements of the forward reaction [1, 2]. The value 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.

[9.1] Black, G., and Porter, G., Vacuum ultraviolet flash photolysis of water vapor, Proc. Roy. Soc. A. **266**, (185) 1962.

The absorption spectrum of OH was recorded at intervals of 60 to 700 μs 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

$$\text{H}+\text{OH}+\text{M}\rightarrow\text{H}_2\text{O}+\text{M}\tag{21}$$

$$\text{OH}+\text{OH}+\text{M}\rightarrow\text{H}_2\text{O}_2+\text{M}.\tag{22}$$

The OH decay is given by $-d[\text{OH}]/dt=k_{21}[\text{OH}][\text{H}][\text{M}]+2k_{22}[\text{OH}]^2[\text{M}]$. At the beginning of the reaction $[\text{H}]=[\text{OH}]$, and $-d[\text{OH}]/dt=k[\text{OH}]^2$, where $k=k_{21}+2k_{22}$. Black and Porter assume that both Reactions (21) and (22) go through a hydroxyl-third-body complex, i.e., $\text{OH}+\text{M}\rightarrow\text{OH}\cdot\text{M}$ followed by reaction of OH · M with H (Reaction 21) or CH (Reaction 22). The ratio of k_{21}/k_{22} will depend on the difference in the rate of reaction of the OH · M complex with H and OH. 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 ± 0.2 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 $k_{22}=3\times10^{17}$ was obtained for $\text{M}=\text{H}_2\text{O}$. The authors, however, used Oldenberg and Rieke's [A–4] value of 1×10^{17} to scale their values. Since that work is now considered to be in error (OH was prepared by an electric discharge in water, see Section A2.1), this study can only provide relative efficiencies for various M's. The relative efficiencies obtained are: H_2O, 1.00; CO_2, 0.23; O_2, 0.29; N, 0.18; Xe, 0.07; Ar, 0.05; He, 0.04.

[9.2] Caldwell, J., and Back, R. A., Combination reactions of hydroxyl radicals in the flash photolysis of water vapor, Trans. Far. Soc. **61**, 1939 (1965).

The yields of H_2 and O_2 from the flash photolysis of water vapor were measured over a range of flash energy, water-vapor pressure, and pressure of added inert gas. Relative rates of $k_1(\text{OH}+\text{OH}\rightarrow\text{H}_2\text{O}+\text{O})$ and $k_{21}(\text{OH}+\text{OH}+\text{M}\rightarrow\text{H}_2\text{O}_2)$ could be estimated from the H_2 and O_2 yields and the ratio $k_{21}[\text{M}]/k_1$ measured. The relative k_{21} values of Black and Porter were used to calculate an effective [M] based on the relative efficiencies. It was necessary to assume that reaction of OH and H with H_2O_2 could be neglected. At higher pressures and flash energies this appeared to be the case. Using Black and Porter's relative efficiencies, the value of k_1 recommended in this review, 1.55×10^{12} cm^3 mol$^{-1}\cdot$s^{-1}, and Caldwell and Back's $k_{21}[\text{M}]/k_1$, the following rates for k_{21} are obtained with an uncertainty of at least $\log k\pm1$ $(-d[\text{OH}]^2[\text{M}]$, k in 10^{18} cm^6 mol$^{-2}\cdot$s^{-1}): He, 0.6; Ar, 0.7; Xe, 1.0; N_2, 2.4; O_2, 3.7; CO_2, 3.0; H_2O, 13.0.

[9.3] Baulch, D. L., Drysdale, D. D., and Lloyd, A. C., Critical evaluation of rate data for homogeneous, gas-phase reactions of interest in high-temperature systems. No. 3. Department of Physical Chemistry, The University, Leeds 2, England. April, 1969.

In this evaluation it is concluded that the data available on Reaction (22) are not adequate to establish a rate constant. From their evaluation of the reverse rate constant, k_{-22} $(\text{H}_2\text{O}_2+\text{N}_2\rightarrow\text{OH}+\text{OH}+\text{N}_2)=1.17\times10^{17}\exp(-45{,}500/RT)$ cm^3 mol$^{-1}\cdot$ s^{-1}, and K_{eq}, they obtain $k_{22}=8.4\times10^{14}\exp(5300/RT)$ cm^6 mol$^{-2}\cdot$ s^{-1}, $\text{M}=\text{N}_2$. At 300 K this gives 5.6×10^{18} in reasonable agreement with the value of 2.4×10^{18} obtained from k_1 (this review), $k_{22}[\text{M}]/k_1$ of Caldwell and Back [2], and the relative third-body efficiencies of Black and Porter [1].

C10. k_{21}, Rate Constant for the Reaction, $\text{H}+\text{OH}+\text{M}\rightarrow\text{H}_2\text{O}+\text{M}$

In spite of numerous 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 $k_{21}=1.17\times10^{17}$ cm^6 mol$^{-2}\cdot$s^{-1} at 2040 K for $\text{M}=\text{H}_2\text{O}$ 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, He, 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 $\log k\pm0.5$. They should be valid over the temperature range 1000 to 3300 K.

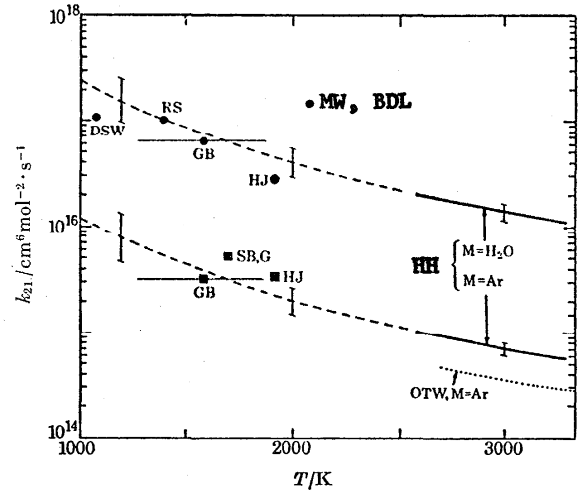

FIGURE C4. *Comparison of rate measurements for* $k_{21}(\text{H}+\text{OH}+\text{M})$.

HH	Homer and Hurle, (stock tube, reverse), reference [10.2]. The error bars indicate the 95 percent confidence limits.
OTW	Olschewski, Troe, and Wagner, (shock tube, reverse), reference [10.3].
DSW	Dixon-Lewis, Sulton, and Williams, (flame), reference [B3–6a].
RS	Rosenfeld and Sugden, (flame), reference [A–34].
GB	Getzinger and Blair, (shock tube), reference [10.4].
HJ	Halstead and Jenkins, (flame), reference [10.5].
MW	McAndrew and Wheeler, (flame), reference [10.6].
SB	Schott and Bird, (shock tube), reference [10.7].
G	Getzinger, (shock tube), reference [10.8].
BDL	Baulch, Drysdale, and Lloyd, (recommended value), reference [10.1].

$$k_{21,\,\mathrm{Ar}} = 7.5 \times 10^{23} T^{-2.6}\ \mathrm{cm}^6\ \mathrm{mol}^{-2} \cdot \mathrm{s}^{-1}.$$

$$k_{21,\,\mathrm{H_2O}} = 1.5 \times 10^{25} T^{-2.6}\ \mathrm{cm}^6\ \mathrm{mol}^{-2} \cdot \mathrm{s}^{-1}.$$

[10.1] 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.

[10.2] Homer, J. B., and Hurle, I. R., The dissociation of water vapour behind shock waves, Proc. Roy. Soc. **314**, 585–598 (1970).

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

$$H_2O + M \xrightarrow{k_{-21,M}} H + OH + M,$$

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

$$k_{-21,\,\mathrm{M}}(\mathrm{M}) = \mathrm{A}\ [\mathrm{Ar}] + \eta[\mathrm{H_2O}])T^{-N} e^{-D_0/RT}$$

with D_0 being 494KJ mol^{-1} (118 kcal mol^{-1}), and the calculated parameters being:

$$A = (4.0 \pm 0.5) \times 10^{23}\ \mathrm{cm}^3\ \mathrm{mol}^{-1} \cdot \mathrm{s}^{-1},$$

$$\eta = 20 \pm 7, \quad N = 2.2 \pm 0.8.$$

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.

[10.3] Olschewski, H. A., Troe, J., and Wagner, H., Symp. Combust., 11th (The Combustion Institute, 1967), p. 155.

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[10.6] McAndrew, R., and Wheeler, R. J., J. Phys. Chem. **66**, 229 (1962).

[10.7] Schott, G. L., and Bird, P. F., J. Chem. Phys. **41**, 2869 (1964).

[10.8] Getzinger, R. W., Symp. Combust., 12th (The Combustion Institute, 1967), p. 117.

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

Section number		Reaction	Rate expression in cm^{3}mol^{-1}·s^{-1}	Temperature range, K	Error limits on log k
C1	k_8	$C_2H_2 + OH \rightarrow$ products	1.2×10^{11} $6 \times 10^{12} \exp(-3{,}500/T)$	300–1000 1000–1600	±0.3 ±1
C2	k_9	$C_2H_4 + OH \rightarrow$ products	3×10^{12}	300–2000	±0.3
C3	k_{10}	$C_2H_6 + OH \rightarrow C_2H_5 + H_2O$	$6.5 \times 10^{13} \exp(-1800/T)$	300–2000	±0.3
C4		$OH + RH \rightarrow$ products (number of carbon atoms: N_P = primary, N_S = secondary, N_T = tertiary)	$6.5 \times 10^{11} N_P \exp(-820/T) + 14.1 \times 10^{11} N_S \exp(-425/T) + 12.6 \times 10^{11} N_T \exp(+85/T)$	300–500	±0.3
C5	k_6	$O + OH \rightarrow O_2 + H$	2.5×10^{13}	300–2000	±0.3
C6	k_{17}	$OH + H_2O_2 \rightarrow H_2O + HO_2$	$1 \times 10^{13} \exp(-1800/T)$	300–1000	±0.7
C7	k_{-12}	$OH + H \rightarrow H_2 + O$	$1.35 \times 10^{13} \exp(-4000/T)$	500–3000	±0.3
C8.1	k_{23D}	$NH_3 + OD \rightarrow$ products	10^{11}	500	±1
C8.2	k_{20}	$OH + H_2CO \rightarrow H_2O + HCO$	$5 \times 10^{15} \exp(-6500/T)$	700–1600	±1
C8.3	k_{24}	$HNO_3 + OH \rightarrow NO_3 + H_2O$	1×10^{11}	300	±0.7
C8.4	k_{25}	$HNO + OH \rightarrow$ products	1×10^{14}	1600–2000	±0.7
C8.5	k_{26}	$CH_3 + OH \rightarrow$ products	4×10^{12}	1970–2190	±0.5
C8.6	k_{27}	$C_2 + OH \rightarrow CO + CH$ $CO + CH^*(^2\Delta)$ $CO + CH^*(^2\Sigma^-)$	5×10^{12} 4×10^{11} 4×10^{10}	2200 875–1665 875–1665	±0.7 ±0.7 ±0.7
C8.7	k_{28} k_{29} k_{30} k_{31}	$HBr + OH \rightarrow H_2O + Br$ $HCl + OH \rightarrow H_2O + Cl$ $CH_3Br + OH \rightarrow$ products $CH_3Cl + OH \rightarrow$ products	1.6×10^{13} 0.8×10^{13} 1.5×10^{13} 1.3×10^{13}	1875–1995 1920–1940 1775–1825 1850–2100	±0.5 ±0.7 ±0.5 ±0.5
C8.8	k_{32}	$N + OH \rightarrow NO + H$	3.5×10^{13}	320	±0.5
C8.9	k_{33}	$SO + OH \rightarrow SO_2 + H$	7×10^{13}	300	±0.5
			Rate expression in cm^{6}mol^{-2}·s^{-1}		
C9	k_{22}	$OH + OH + N_2 \rightarrow H_2O_2 + N_2$	$8.4 \times 10^{14} \exp(-2650/T)$	500–1000	±0.5
C10	k_{21}	$H + OH + H_2O \rightarrow H_2O + H_2O$ $H + OH + Ar \rightarrow H_2O + Ar$	$1.5 \times 10^{25} T^{-2.6}$ $7.5 \times 10^{23} T^{-2.6}$	1000–3300 1000–3300	±0.5 ±0.5

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:

Reaction	Number	1961 1966 1969 Activation energy, ΔE, in kcal
$CO+OH \rightarrow CO_2+H$	(2)	$7.7^{(1)}-0.6^{(2)}-0.23^{(3)}$
$H_2+OH \rightarrow H_2O+H$	(3)	$11.0^{(4)}-5.2^{(2)}-4.02^{(3)}$
$CH_4+OH \rightarrow H_2O+CH_3$	(4)	$9.0^{(5)}-5.0^{(6)}-3.77^{(7)}$

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 Avromenko'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 CO_2 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 $1/T$ plot might show two lines of different slope. Another possibility is to include a T^n term in the rate constant. When this is done, a quite reasonable plot is obtained for k_1 (CO+OH) with $T^{1/2}$. For k_2 and k_3 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, H_2, or CH_4 is OH. It can be shown that O and H would not make significant contributions. However, the possible contribution of conversion of CO to CO_2 by HO_2 has not been considered in flame analyses. This path has been shown to account for about half of the CO_2 formation in explosion limits studies [12] but it was not possible to obtain an absolute rate. Values of k_1, obtained from flame measurements of the reverse reaction, may be appreciably lower than the direct measurements of the forward reaction. However, for H_2+OH the forward and reverse measurements are in good agreement. Such a difference between reactions of H_2 and CO might be expected since $k(CO+HO_2)/k(H_2+HO_2)=9\pm0.5$ at 773 K[11]. However, if HO_2 contributed to CO conversion, then the measurements in flames which determine k_2/k_1 from a comparison of $R_{CO_2}/[CO]$ to $-R_{H_2}/[H_2]$, (where R refers to rate of formation or depletion), assuming *only* OH attack, would be too low because the rate of k_1 would be too large. However, the k_2/k_1 measurements from flames are higher than the value obtained from an extrapolation of the ratio of Greiner's two measurements. Therefore, reaction with HO_2 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 H_2O_2 were produced by recombination of 2 OH. The HO_2, formed by reaction of H with H_2O_2, could react with CO or H_2 resulting in regeneration of OH. Greiner [12] has observed a very rapid recombination of OH in the photolysis of H_2O_2 in addition to decay due to $OH+OH \rightarrow H_2O+O$. When H_2, CO, or CH_4 were added, the OH decay decreased (in the case of CO there was more OH than when H_2O_2 was photolyzed by itself). The formation of H_2O_2 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 $k=10^{14}$ cm^3 mol$^{-1}\cdot$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 HO_2 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, H_2, 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 f number,
(6) any rate measurements in which the role of HO_2 can be clearly established,
(7) reaction of OH with species other than CO, H_2, and CH_4.

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E. Acknowledgements

This review began in 1967 with the preparation, at the request of R. M. Fristrom, of several sample tables of chemical kinetics for use in "Report on the Establishment of Chemical Kinetics Tables," Chemical Propulsion Information Agency, unnumbered report, April 1967, p. 20 and which appeared later in CPIA Publication No. 146, Vol. **1**, p. 147 (May 1967). The sample tables had as their starting point the publication by G. Dixon-Lewis, W. E. Wilson, and A. A. Westenberg, Studies of hydroxyl radical kinetics by quantitative electron spin resonance, J. Chem. Phys. **44**, 2877 (1966). The sample tables of chemical kinetics were expanded and revised and presented as "A Critical Review of the Combustion Reactions of the Hydroxyl Radical" at the 1967 Spring Meeting of the Western States Section, The Combustion Institute, La Jolla, California 24–25 April 1967, Paper WSCI-67–16. The work mentioned above was performed at The Applied Physics Laboratory, the Johns Hopkins University, under Contract NOw62–0604–c with the Bureau of Naval Weapons. A slightly modified version of the Combustion Institute paper appeared as "Kinetic Tables for the Reactions of Hydroxyl Radicals" in National Bureau of Standards Report No. 9884, "A Compendium of Evaluated and Estimated Rate Constants" July 1968, edited by David Garvin.

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 assitance of David Garvin, Chemical Kinetics Information Center, National Bureau of Standards, and Lewis H. Gevantman, Project Monitor, are greatly appreciated.

Appendix A. List of Reactions

1. $OH + OH \rightarrow H_2O + O$
2. $CO + OH \rightarrow CO_2 + H$
3. $H_2 + OH \rightarrow H_2O + H$
4. $CH_4 + OH \rightarrow H_2O + CH_3$
5. $H + NO_2 \rightarrow NO + OH$
6. $O + OH \rightarrow O_2 + H$
7. $H + D_2 \rightarrow HD + D$
8. $C_2H_2 + OH \rightarrow$
9. $C_2H_4 + OH \rightarrow$
10. $C_2H_6 + OH \rightarrow$
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. $OH + RH \rightarrow H_2O + R$
17. $OH + H_2O_2 \rightarrow H_2O + HO_2$
18. $HO_2 + CO \rightarrow CO_2 + OH$
19. $HO_2 + H_2 \rightarrow H_2O + OH$
20. $OH + H_2CO \rightarrow HCO + H_2O$
21. $OH + H + M \rightarrow H_2O + M$
22. $OH + OH + M \rightarrow H_2O_2 + M$
23. $NH_3 + OH \rightarrow$
24. $HNO_3 + OH \rightarrow H_2O + NO_3$
25. $HNO + OH \rightarrow$
26. $CH_3 + OH \rightarrow$
27. $C_2 + OH \rightarrow CO + CH$
28. $HBr + OH \rightarrow H_2O + Br$
29. $HCl + OH \rightarrow H_2O + Cl$
30. $CH_3Br + OH \rightarrow$
31. $CH_3Cl + OH \rightarrow$
32. $N + OH \rightarrow NO + H$
33. $SO + OH \rightarrow SO_2 + H$

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
J	joules
k_1	forward rate constant for reaction 1
k_{-1}	reverse rate constant for reaction 1
K_{eq}	equilibrium constant
UV	ultraviolet
[ ]	concentration
$[\ ]_0$	initial concentration

Appendix C. List of Conversion Factors

Second-order reactions*

A B	$cm^3\ mol^{-1}\ s^{-1}$	$litre\ mol^{-1}\ s^{-1}$	$m^3\ mol^{-1}\ s^{-1}$	$m^3\ particle^{-1}\ s^{-1}$	$(mm\ Hg)^{-1}\ s^{-1}$	$atm^{-1}\ s^{-1}$
$cm^3\ mol^{-1}\ s^{-1}$		10^3	10^6	6.023×10^{23}	$62.40 \times 10^3 T$	$82.10\ T$
$litre\ mol^{-1}\ s^{-1}$	10^{-3}		10^3	6.023×10^{20}	$62.40\ T$	$82.10 \times 10^{-3}\ T$
$m^3\ mol^{-1}\ s^{-1}$	10^{-6}	10^{-3}		6.023×10^{17}	$62.40 \times 10^{-3}\ T$	$82.10 \times 10^{-6}\ T$
$cm^3\ particle^{-1}\ s^{-1}$	0.1660×10^{-23}	0.1660×10^{-20}	0.1660×10^{-17}		$10.36 \times 10^{-20}\ T$	$13.63 \times 10^{-23}\ T$
$(mm\ Hg)^{-1}\ s^{-1}$	$16.03 \times 10^{-6}\ T^{-1}$	$16.03 \times 10^{-3}\ T^{-1}$	$16.03\ T^{-1}$	$96.53 \times 10^{17}\ T^{-1}$		1.316×10^{-3}
$atm^{-1}\ s^{-1}$	$12.18 \times 10^{-3}\ T^{-1}$	$12.18 T^{-1}$	$12.18 \times 10^3\ T^{-1}$	$73.36 \times 10^{20} T^{-1}$	760	

Third-order reactions

A B	$cm^6\ mol^{-2}\ s^{-1}$	$litre^2\ mol^{-2}\ s^{-1}$	$m^6\ mol^{-2}\ s^{-1}$	$cm^6\ particle^{-2}\ s^{-1}$	$(mm\ Hg)^{-2}\ s^{-1}$	$atm^{-2}\ s^{-1}$
$cm^6\ mol^{-2}\ s^{-1}$		10^6	10^{12}	36.28×10^{46}	$38.94 \times 10^8 T^2$	$6.740 \times 10^3 T^2$
$litre^2\ mol^{-2}\ s^{-1}$	10^{-6}		10^6	36.28×10^{40}	$38.94 \times 10^2 T^2$	$6.740 \times 10^{-3} T^2$
$cm^6\ mol^{-2}\ s^{-1}$	10^{-12}	10^{-6}		36.28×10^{34}	$38.94 \times 10^{-4} T^2$	$6.740 \times 10^{-9} T^2$
$cm^6\ particle^{-2}\ s^{-1}$	2.76×10^{-48}	2.76×10^{-42}	2.76×10^{-36}		$1.07 \times 10^{-38} T^2$	$1.86 \times 10^{-44} T^2$
$(mm\ Hg)^{-2}\ s^{-1}$	$2.57 \times 10^{-10}\ T^{-2}$	$2.57 \times 10^{-4}\ T^{-2}$	$2.57 \times 10^2\ T^{-2}$	$93.18 \times 10^{36}\ T^{-2}$		1.73×10^{-6}
$atm^{-2}\ s^{-1}$	$1.48 \times 10^{-4}\ T^{-2}$	$1.48 \times 10^2\ T^{-2}$	$1.48 \times 10^8\ T^{-2}$	$53.82 \times 10^{42}\ T^{-2}$	57.76×10^4	

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 6.023×10^{20}.

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*Data taken from "High Temperature Reaction Rate Data", D. L. Baulch, D. D. Drysdale, and A. C. Lloyd, Dept of Phys. Chem. The University, Leeds 2, England.