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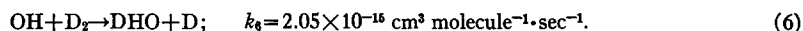
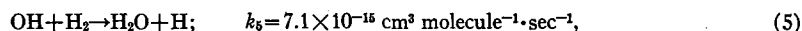
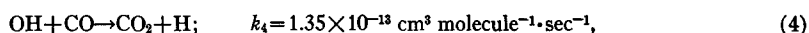
Pulsed Vacuum-uv Photochemical Study of Reactions of OH with H₂, D₂, and CO Using a Resonance-Fluorescent Detection Method

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Resonance fluorescence ($A^2\Sigma^+; v'=0 \rightarrow X^2\Pi; v''=0$) was used to monitor OH radicals in the pulsed vacuum-uv photolysis of H₂O. From the exponential decays of OH radicals in the presence of a large excess of added reactants, absolute rate constants of the following reactions were determined at 298°K:



The over-all uncertainty of these rate constants was estimated to be $\pm 15\%$. The methods for production and detection of OH were discussed in detail.

INTRODUCTION

Hydroxyl radicals play an important role generally in atmospheric chemistry^{1,2} and, in particular, in photochemical smog formation.³ A new method has been developed to study OH reactions that combines repetitive production of OH radicals by low intensity flash photolysis of H₂O with the detection of OH by resonance fluorescence. Resonance fluorescence has been used previously in kinetic studies to monitor low concentrations of atomic species such as H,^{4,5} O,^{6,7} and I,⁸ but has not been applied to the study of reactions of diatomic radicals such as OH. Prior to this work, OH radicals have been monitored by ESR, mass spectroscopy, and absorption spectroscopy in the concentration range, 10^{13} – 10^{14} cm⁻³.⁹ With the present technique, OH radicals were generated and monitored at concentrations ranging from approximately 5×10^{12} down to 1×10^{10} cm⁻³.

The major advantages of this technique are that reactions involving OH radicals can be studied under a wide range of pressures of diluent gas, e.g., 5–100 torr He and Ar, in the absence of wall reactions and that because of the low concentrations of OH involved, complications due to secondary reactions are avoided. Consequently, rate constants are determined with high accuracy because of the inherent simplicity of this method, which requires only time and pressure measurements. Furthermore, at these low concentrations of OH, reactions of OH with OH and with O atoms produced are minimized. This increases the inherent chemical lifetime of OH in this system (up to 0.1 sec) and correspondingly allows use of a larger time constant for the detection of OH which improves the signal to noise ratio. The high detection sensitivity can also be used to study reactions which generate low concentrations of OH as an intermediate.

In the present study, this method has been applied to the reactions of OH with H₂, D₂, and CO.

EXPERIMENTAL

Hydroxyl radicals were generated by pulsed vacuum-uv photolysis of H₂O and were monitored by resonance fluorescence. The apparatus consisted of a pulsed light source, a reaction chamber, an OH emission lamp, and a resonance fluorescence detection system, which is shown schematically in Fig. 1. The photolysis apparatus was identical to that described previously,^{10,11} and only major features will be mentioned here. The resonance fluorescence technique for the detection of OH radicals was developed for the present work and will be described in detail.

Vacuum-uv light pulses (half-width $\sim 2 \mu\text{sec}$) were generated by discharging a capacitor (20 J) with a repetition frequency of 1 Hz. The reactor was separated from the flash lamp by a LiF window. The light intensity per flash transmitted through this LiF window was estimated to be 2×10^{14} photons cm⁻² in the wavelength region between 1050 and 1700 Å.¹⁰ The interior walls of the reaction chamber were painted black with Nextel coating. Three light traps (not shown in Fig. 1) were attached to this reactor to minimize scattered light. Prior to each run, the reaction chamber was evacuated to less than 10^{-6} torr. The leak rate of the chamber was about 3×10^{-7} torr sec⁻¹. The mixtures were prepared by adding the individual gases (H₂, D₂, CO, H₂O, He) to the reactor without premixing. The pressure manometers were calibrated to better than $\pm 5\%$ for all gases except H₂O. In the case of H₂O, the pressure could be estimated only to $\pm 20\%$ because of adsorption effects.

The OH resonance fluorescence lamp is schematically shown in Fig. 2. The OH emission was generated by passing a small flow of H₂O vapor through a microwave discharge at 0.2 torr. The lamp was made of a Pyrex tube with a quartz window attached to one end. The major emission observed between 2000 and 7000 Å was the 3064 Å system of OH ($A^2\Sigma^+; v'=0 \rightarrow X^2\Pi; v''=0$).

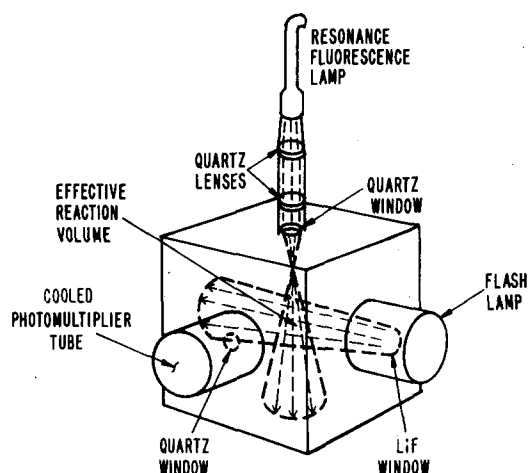


FIG. 1. Schematic diagram of the pulsed photolysis apparatus. The total volume of the reactor is $1.7 \times 10^4 \text{ cm}^3$. The effective reaction volume was estimated to be about 80 cm^3 .

This band recorded in the second order of a 1-m Czerny-Turner monochromator is shown in Fig. 3. Besides the (0; 0) band, the only other detectable emissions between 2600 and 3600 Å were the (1; 1) band and the (1; 0) band. The intensities of these bands were about 20 times weaker than that of the (0; 0) band. The positions of the bandheads of the R_1 , R_2 , and Q_2 branches of the (1; 1) band are also indicated in Fig. 3. The rotational distribution in the (0; 0) band corresponded to a temperature of 600 to 700°K which gives sufficient overlap with the absorption of "room temperature" OH. The resonance light was collimated and focussed into the reaction chamber at right angles to the flash light beam (Fig. 1). Thus, an effective reaction volume was formed in the middle of the reaction chamber and wall reactions were avoided. In some experiments, an interference filter (Baird Atomic; 3155 Å peak wavelength, 190 Å bandwidth, and 19.5% transmission) was placed in the path of the resonance light. The wavelength in the region of the OH resonance emission was scanned by tilting this filter.

Resonance fluorescence from hydroxyl radicals was detected photoelectrically at right angles to the incident flash light and the OH resonance light. It was monitored through an interference filter (Corion Instrument) by a cooled photomultiplier tube of Type EMI 9558QA. The relative transmission of this filter (peak wavelength 3080 Å, bandwidth 40 Å, transmission maximum 19%) is shown in Fig. 3 by the dashed curve. The signal from the photomultiplier was amplified and fed to a multichannel analyzer. The signals generated from 100 consecutive flashes were collected to enhance the signal to noise ratio and also to average fluctuations in the OH lamp intensity. Decays of OH were taken with an RC time constant of 100 μsec, which is 16 times shorter than the fastest decay time used in this study. The signals were usually taken

with a delay of 700 μsec after the flash. This delay was required to minimize interference from light emitted from excited $\text{OH}(A^2\Sigma^+)$, which is produced by H_2O photolysis at short wavelengths.¹²

The gases used in this study had the following stated (Matheson) minimum purities: He, 99.9999%, H_2 , 99.999%, CO, 99.8%, D_2 , 99.5% (isotope purity). The stated impurities in the H_2 sample were N_2 (5 ppm), O_2 (1 ppm), and CH_4 (<0.2 ppm) and in the CO sample were N_2 (303 ppm), hydrocarbons (<330 ppm), CO_2 (90 ppm), and O_2 (76 ppm). The CO sample was stored over liquid N_2 and was used immediately after the initial fraction of the vapor phase was pumped off. This procedure was used to remove hydrocarbons (except CH_4) and carbonyl compounds. The H_2O samples were thoroughly degassed prior to use.

RESULTS

Detection of OH by Resonance Fluorescence

Figure 4 displays the signal of the fluorescence decay of OH in the photolysis of 0.05 torr H_2O and 20 torr He. This curve was read out from the memory of the multi-channel analyzer by a chart recorder. A sufficiently fast time constant was used for the chart recorder output to display the counts in each channel. Several experiments were conducted to verify that the observed signal originates only from OH and not from other species. When the OH lamp was turned off, no signal was detected and possible interference from chemiluminescence emission can therefore be disregarded. When the interference filter of the OH lamp was tilted to scan the OH spectrum, the stray light from the lamp

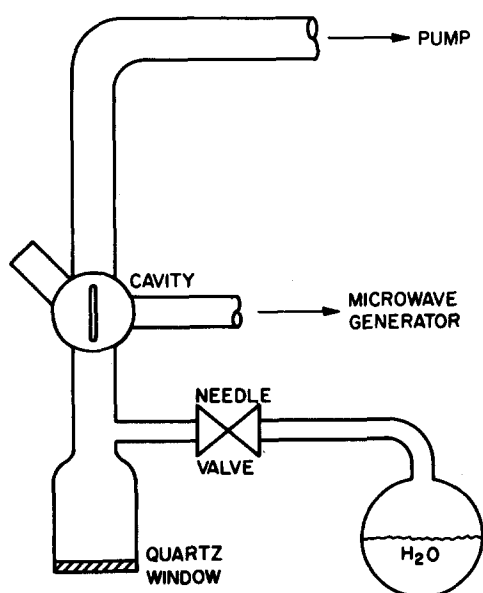
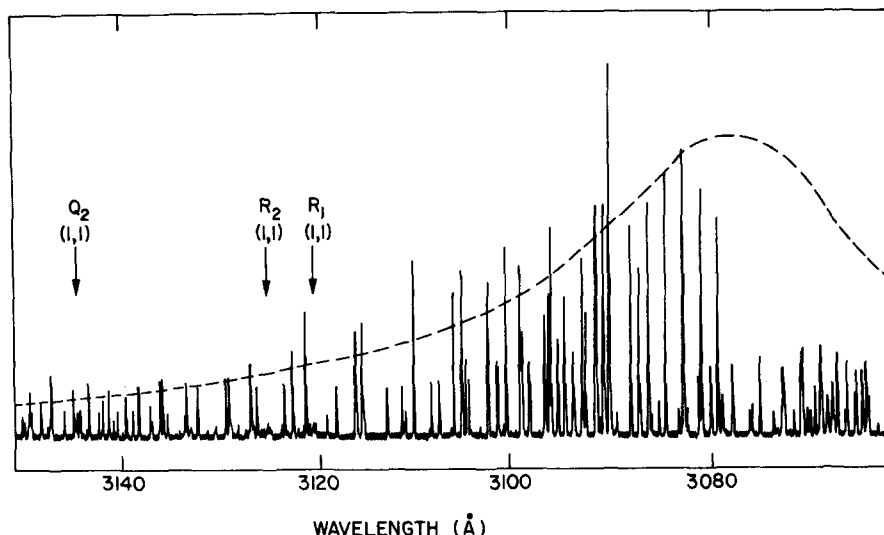
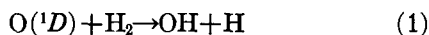


FIG. 2. Schematic diagram of the OH resonance fluorescence lamp.

FIG. 3. Emission spectrum of the OH resonance fluorescence lamp in the wavelength region from 3060 to 3150 Å taken in the second order with a Czerny-Turner 1 m monochromator. The dashed curve represents the relative transmission of the interference filter (maximum transmission 19%) used to monitor the OH fluorescence. The ordinate represents either emission intensity or transmission of the filter (in arbitrary units).



changed to the same extent as the fluorescence intensity. This indicates the similarity of the spectrum of the fluorescence to that of the lamp. Two other chemical processes for the generation of OH by the fast reactions,^{13,14}



and



were found to produce similar fluorescence. In this experiment, O(¹D) was generated by the photolysis of O₂. Furthermore, when D₂ was used instead of H₂ and D₂O instead of H₂O, the fluorescence signal was reduced by a factor of about 20. The remaining intensity is probably due to residual H₂O present in this system and/or to possible coincidence of some OH emission lines with OD lines.

Since electronically excited OH(A ²Σ⁺, v'=0) has a long lifetime of 8×10⁻⁷ sec,¹⁵ the resonance fluorescence is susceptible to quenching by gases present in the reaction system. It was observed, however, that the addition of up to 150 torr He and Ar did not quench the OH fluorescence significantly. On the other hand, the addition of H₂ to this system decreased the OH fluorescence intensity. From this decrease, the rate constant for the quenching of OH(A ²Σ⁺) by H₂ was

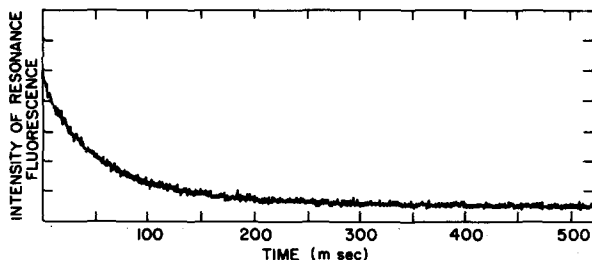
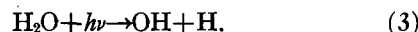


FIG. 4. Time dependence of the intensity of the OH resonance fluorescence (in arbitrary units) in the pulsed photolysis of 0.05 torr H₂O and 20 torr He. The decay curve is the average of 100 runs and was read out by a chart recorder (see text).

estimated to be approximately 10⁻¹⁰ cm³ molecule⁻¹·sec⁻¹. The quenching by H₂O could not be readily estimated in the present study, since variation in the H₂O pressure also changes the concentration of photochemically generated OH. In the experiments with CO (up to 0.13 torr) the attenuation of the OH fluorescence was too small to be measured reliably.

The initial concentration of OH radicals was calculated from the vacuum-uv flash light intensity in the effective reaction volume,^{10,11} and absorption characteristics of H₂O,¹⁶ and the quantum yield (assumed to be one) for the photodissociation,



On this basis, the initial concentration of OH in the photolysis of 0.05 torr H₂O was estimated to be (3±2)×10¹¹ cm⁻³. This corresponds in Fig. 4 to a signal to noise ratio of one at approximately 10¹⁰ OH cm⁻³. At these low concentrations of OH, the resonance fluorescence intensity can be expected to depend linearly on the concentration, since the electronic transition probability for OH is relatively small.

Rate Constants

Rate constants for reactions of OH with CO, H₂, and D₂ were determined from first order decays of OH in the presence of a large excess of the reactant and diluent He. As described elsewhere,¹¹ the decay of OH radicals can be represented by

$$\ln([\text{OH}]_{t_2}/[\text{OH}]_{t_1}) = (\tau_0^{-1} + k[\text{R}]) (t_1 - t_2), \quad (I)$$

where [OH]_t is the OH concentration at time t, [R] the concentration of the reactant, and τ₀ the decay time of OH in the absence of R. The bimolecular rate constant for the reaction of OH with R is represented by k. The observed lifetime, τ, of the OH radicals is then given by

$$\tau^{-1} = \tau_0^{-1} + k[\text{R}]. \quad (II)$$

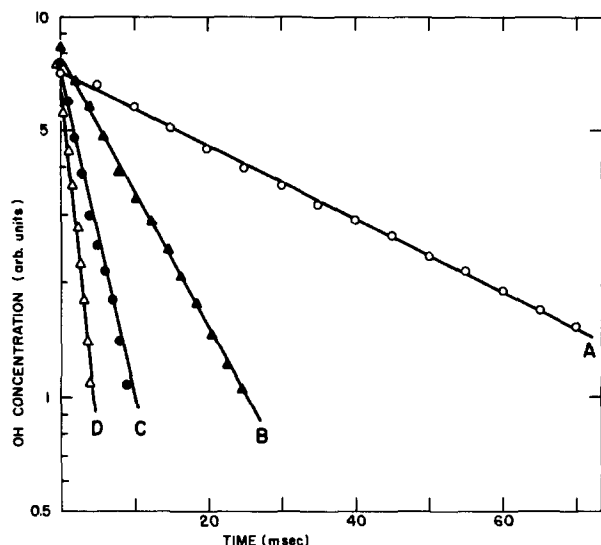


FIG. 5. Time dependence of the OH resonance fluorescence intensity for the addition of 0 torr CO, A; 0.015 torr CO, B; 0.04 torr CO, C; 0.09 torr CO, D. The average fluorescence intensity is plotted for every tenth channel of the multichannel analyzer. Hydroxyl radicals were produced by the photolysis of 0.05 H_2O and 20 torr He and 100 runs were averaged for each CO pressure.

In this study, the values of the rate constant, k , were determined from the slope of a linear plot of τ^{-1} vs $[\text{R}]$.

Figure 5 illustrates the relationship given in Eq. (1) for the reaction $\text{OH} + \text{CO}$. The time dependence of the OH concentration is shown in a semilogarithmic plot as a function of the amount of added CO at 20 torr He, i.e., curve A for no CO, B for 0.015 torr CO, C for 0.04 CO, and D for 0.09 torr CO. In this figure, the counts of several channels were averaged and plotted at every 5 msec. It should be noted in this figure, that the decays of OH can be well represented by exponential curves. Figure 6 shows a linear plot of τ^{-1} vs $[\text{CO}]$ for CO pressures up to 0.137 torr. In this experiment,

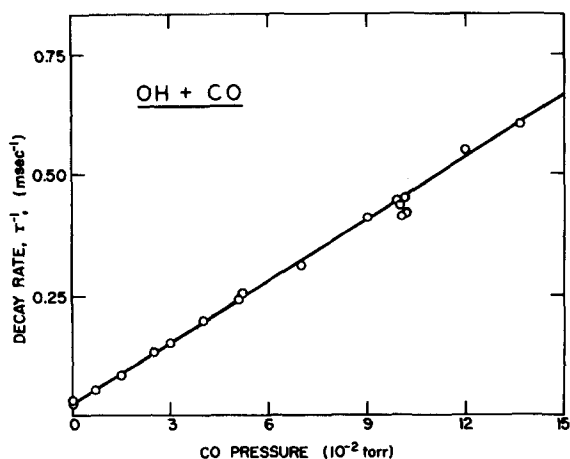


FIG. 6. Decay rates of the OH resonance fluorescence intensity as a function of CO pressure. The pressures of H_2O and He were constant at 0.05 and 20 torr.

the CO pressure was varied by approximately a factor of 20 in the presence of 0.05 torr H_2O and 20 torr He. From the slope of this figure, the rate constant k_4 for the reaction,



was determined to be $1.35 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \cdot \text{sec}^{-1}$. The intercept, τ_0^{-1} , in Fig. 6 corresponds to a lifetime $\tau_{1/0} = 47 \text{ msec}$ (or $\tau_{1/2} = 33 \text{ msec}$) which is identical to the lifetime obtained from Fig. 4 and from curve A in Fig. 5. In several experiments, τ_0 was determined as a function of the pressure (5–80 torr) of diluent He and also Ar. Under otherwise identical conditions, with Ar, τ_0 was longer than with He. It was also observed that τ_0 increased with increasing pressure until it reached a plateau at about 30 torr for Ar and at about 70 torr for He. The longest lifetime, τ_0 , thus obtained in these experiments was 0.1 sec. These results will be discussed later.

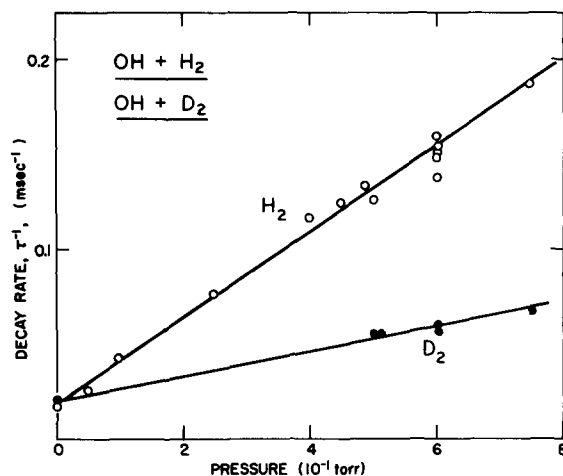
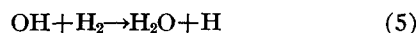
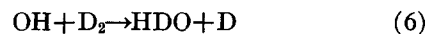


FIG. 7. Decay rates of the OH resonance fluorescence intensity as a function of H_2 and D_2 pressure. The pressures of H_2O and He were constant at 0.05 and 20 torr.

Figure 7 shows a linear plot of τ^{-1} vs $[\text{H}_2]$ and vs $[\text{D}_2]$. The H_2 pressure was varied by a factor of 15 (up to 0.75 torr) in the presence of 0.05 torr H_2O and 20 torr He. For D_2 , five data points are given in Fig. 7. From the slopes, the rate constants k_5 and k_6 for the reactions



and



were determined to be $k_5 = 7.1 \times 10^{-15}$ and $k_6 = 2.05 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \cdot \text{sec}^{-1}$.

The standard deviations of the slopes in Figs. 6 and 7 were computed to be 3%, 4%, and 6% for the reactions with H_2 , CO, and D_2 , respectively. The pressure and time measurements were calibrated to $\pm 5\%$ and $\pm 1\%$, respectively. Secondary products are known to react inefficiently (H_2O , CO_2) or very slowly (H) with

OH under the present conditions and should not interfere with the measured decay times. Thus, by adding these known errors, an uncertainty of about 10% is obtained. However, because of unknown impurity and mixing effects, the over-all uncertainty is conservatively estimated to be $\pm 15\%$.

A few additional experiments were performed with OH concentrations ranging from 1 to 10×10^{11} radicals cm^{-3} and at higher pressures of He (up to 70 torr). The rate constants obtained under these conditions are well within $\pm 12\%$ of the values determined above and, thus, support the relation given by Eq. (II). However, it should be noted that, in these experiments, τ_0 was dependent on $[\text{He}]$ because of diffusion losses and on $[\text{H}_2\text{O}]$ because of the different initial concentrations of OH.

DISCUSSION

Production and Detection of OH

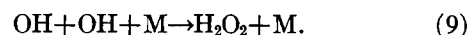
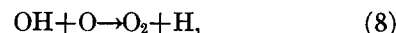
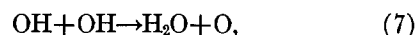
In both flash and continuous photolysis of water, OH and H are the major primary photodissociation products.⁹ The formation of OH in the flash photolysis of H₂O has been studied previously using both fused quartz windows ($\lambda > 1500\text{--}1600 \text{ \AA}$)¹⁷⁻²⁰ and LiF windows ($\lambda > 1050 \text{ \AA}$).^{21,22} In all these studies, OH radicals have been produced in the concentration range from 2×10^{13} to $3 \times 10^{14} \text{ cm}^{-3}$ using high intensity flash lamps ($> 1000 \text{ J}$) and have been monitored by absorption spectroscopy. It has also been shown that $\text{OH}(X^2\Pi; v''=0)$ is formed with virtually no excess rotational energy.²² A small fraction of OH has been observed in the first vibrational state ($v''=1$) at short delay times (up to 5 μsec) which is subsequently deactivated by about 100 collisions with H₂O.²¹ Thus, at 0.05 torr H₂O used in this study, the relaxation time is approximately 100 μsec , which is sufficiently short compared with the initial delay time of 700 μsec .

There is also evidence for a minor production of $\text{O}(^1D)$ and H₂ in the vacuum-uv photolysis of H₂O.^{23,24} However, $\text{O}(^1D)$ reacts rapidly with H₂O [Reaction (2)] to form OH radicals¹⁴ and also with other gases (CO and H₂) added to this system.²⁵ The quenching efficiency of $\text{O}(^1D)$ by He at 30 torr has been reported to be small,²⁶ in agreement with the present observation in the H₂-O₂ system. The formation of excited $\text{OH}(A^2\Sigma^+)$ radicals also occurs in the photolysis of H₂O at wavelengths below 1350 \AA with a low quantum yield ($\sim 5\%$).¹² This gives plausible explanations for the strong light emission observed during the flash.

All the results obtained in this study support the presumption that the observed fluorescence signal is due to the presence of OH radicals. Particularly, the formation of OH by different chemical systems [Reactions (1)–(3)] and the remarkable decrease of the signal when OH was replaced by OD (in the experiments with D₂ and D₂O) demonstrate that OH is selectively monitored by this technique. A quantitative compari-

son of the quenching of the observed fluorescence signal with the data for the quenching of $\text{OH}(A^2\Sigma^+)$ can be, in principle, used for the identification of OH radicals. Unfortunately, the literature values exhibit marked disagreement²⁷⁻³⁰ and are difficult to judge.

The observed decay of OH in the pure H₂O-He system can be due to diffusional losses from the effective reaction volume, to reactions with impurities and to the reaction sequence,



For the typical concentrations used in these experiments ($3 \times 10^{11} \text{ OH cm}^{-3}$; 20 torr He), the half-lifetime of OH determined by Reactions (7)–(9) was computed to be 450 msec.⁹ This calculated lifetime is much longer than the measured lifetime ($\tau_{1/2} = 33 \text{ msec}$). Therefore, the observed decay must be attributed to other processes. The most likely reasons for this observation are diffusion of OH from the reaction volume and reactions of OH with impurities. The dependence of τ_0 on the pressure of diluent He and Ar indicates that the diffusive loss rate of OH in 20 torr He is about 10 sec^{-1} in this system. This appears to be a reasonable rate according to a rough estimate. Since, at higher pressures of He and Ar, τ_0 becomes almost independent of pressure, it is likely that the presence of reactive impurities limits the lifetime of OH in this system. Whether impurities are contained in the He, Ar, or H₂O samples or whether the reactor is contaminated with a highly reactive impurity is not known. At any rate, this effect, which determines τ_0 in this study, can be considered to remain constant for the addition of small amounts of reactants. This is also strongly suggested by the good linearity of the plots τ^{-1} vs $[\text{R}]$.

Rate Constants; Comparison with Previous Work

In Tables I and II, the rate constants of OH with CO, H₂, and D₂ determined in previous studies are compared with the present experiments at 300°K. While the reactions with CO and H₂ have been studied by a number of authors, only one investigation has been reported for D₂. As can be seen in Tables I and II, the present data obtained by pulsed photolysis using resonance fluorescent detection are in reasonable agreement with the majority of the recent studies. All the previous studies used either discharge flows or high intensity flash photolyses. The flow systems were coupled with ESR, mass spectrometric, or optical absorption detectors. The most successful technique to generate OH radicals in these flow systems has been shown to be the conversion of H atoms into OH radicals by the fast reaction $\text{H} + \text{NO}_2 \rightarrow \text{OH} + \text{NO}$.³¹ Avramenko *et al.*,^{32,33} who studied Reactions (3) and (4) at room temperature, applied a discharge in H₂O to produce

TABLE I. Summary of rate constants for $\text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H}$ at 300°K.

Investigators (year)	Method	Rate constant ($\times 10^{-13} \text{ cm}^3$ $\text{molecule}^{-1} \cdot \text{sec}^{-1}$)	Remarks
Avramenko (1947) ³²	Discharge flow; uv absorption	0.0046	Production of OH in H ₂ O discharge (see text)
Avramenko (1950) ³³	Discharge flow; uv absorption	0.0024	Production of OH in H ₂ O discharge (see text)
Dixon-Lewis, Wilson, and Westenberg (1966) ³⁶	Discharge flow; ESR of OH	1.9($\pm 4.4\%$)	Standard deviation
Herron (1966) ³⁴	Discharge flow; mass spectrometry	0.85($\pm 39\%$)	Probably over-all accuracy ^a
Greiner (1967) ¹⁸	Flash photolysis; uv absorption	1.5($\pm 10\%$)	Standard deviation
Wilson and O'Donovan (1967) ³⁸	Discharge flow; mass spectrometry	1.5($\pm 3\%$)	Standard deviation
Greiner (1969) ¹⁹	Flash photolysis; uv absorption	1.43	Average of data between 300 and 305°K. Standard deviation for each datum is about $\pm 5\%$
Wong and Belles (1970) ^b	Stirred flow; production of CO ₂ , mass spectrometry	0.9	Based on author's value for k_b ; uncertainty probably large
Mulcahy and Smith (1971) ^c	Discharge flow; mass spectrometry	1.65($\pm 30\%$)	Probably range of experimental data
This work	Pulsed photolysis; resonance fluorescence	1.35($\pm 15\%$)	Estimated over-all accuracy

^a Reference 35.^b E. L. Wong and F. E. Belles, NASA Tech. Note D5707 (1970).^c M. F. R. Mulcahy and R. H. Smith, J. Chem. Phys. **54**, 5215 (1971).TABLE II. Summary of rate constants for $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$ and $\text{OH} + \text{D}_2 \rightarrow \text{DHO} + \text{D}$ at 300°K.

Investigators (year)	Method	Rate constant ($\times 10^{-15} \text{ cm}^3$ $\text{molecule}^{-1} \cdot \text{sec}^{-1}$)	Remarks
OH + H₂			
Avramenko (1950) ³³	Discharge flow; uv absorption	0.7	Production of OH in H ₂ O discharge (see text)
Kaufman and Del Greco (1963) ³¹	Discharge flow; uv absorption	7.0($\pm 23\%$)	Over-all accuracy
Wise, Ablow, and Sancier (1964) ^a	Perturbation of H profile; diffusion; ESR of H atoms	9.5	Uncertainty probably large
Dixon-Lewis, Wilson, and Westenberg (1966) ³⁶	Discharge flow; ESR of OH	6.5($\pm 5.1\%$)	Standard deviation
Greiner (1967) ¹⁸	Flash photolysis; uv absorption	6.7($\pm 5\%$)	Standard deviation
Greiner (1969) ¹⁹	Flash photolysis; uv absorption	7.9	Average of data between 295 and 305°K. Standard deviation for each datum is about $\pm 5\%$
Dodonov, Lavroskaya, and Tal'roze (1969) ³⁷	Diffusional-cloud-in-flow; reactions of H with O ₂ ; mass spectrometry	13($\pm 31\%$)	Over-all accuracy
Wong and Belles (1970) ^b	Stirred flow; production of H ₂ O by mass spectrometry	8.3($\pm 60\%$)	Average of room temp data; standard deviation
This work	Pulsed photolysis; resonance fluorescence	7.1($\pm 15\%$)	Estimated over-all accuracy
OH + D₂			
Greiner (1968) ^c	Flash photolysis; uv absorption	2.1($\pm 12.5\%$)	Probably range of data
This work	Pulsed photolysis; resonance fluorescence	2.05($\pm 15\%$)	Estimated over-all accuracy

^a H. Wise, C. M. Ablow, and K. M. Sancier, J. Chem. Phys. **41**, 3569 (1964).^b Footnote b, Table I.^c N. R. Greiner, J. Chem. Phys. **48**, 1413 (1968).

OH, but this method was later shown by Kaufman³¹ to give erroneous results. The flow systems were used mostly at pressures below 5 torr. All studies at higher diluent pressures have been done by high intensity flash photolysis (>1000 J). In these investigations, the reactor and flash lamp were usually separated by fused quartz and OH radicals were formed in the vacuum-uv photolysis ($\lambda > 1500 \text{ \AA}$) of H₂O. Concentrations of OH radicals were recorded on photoplates.

Among the previous values listed in Tables I and II, the rate constant k_4 (8.5×10^{-14}) reported by Herron³⁴ has been shown to be too low by Wilson and O'Donovan.³⁵ Two of the recent values, i.e., k_4 (1.9×10^{-13}) of Dixon-Lewis *et al.*³⁶ and k_5 (1.3×10^{-14}) of Dodonov *et al.*³⁷ do not agree with those of the present work within the combined uncertainties. The value of Dodonov *et al.*³⁷ was obtained in a more complex system (reactions in H+O₂+H₂+He) and might be susceptible to greater mechanistic uncertainty. The uncertainty in the value of Dixon-Lewis *et al.*³⁶ is probably greater than the stated standard deviation of $\pm 4.4\%$.³⁸

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Flash Photochemical Study of the Reaction OH+NO+M Using Resonance Fluorescent Detection of OH

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The kinetic behavior of OH radicals was studied in the presence of a large excess of NO at 5–82 torr He. Hydroxyl radicals were produced by pulsed vacuum-uv photolysis of H₂O and were monitored directly by a resonance fluorescence method. The rate constant for the reaction OH+NO was nonlinearly dependent on the concentration of diluent He in this pressure range. The high pressure limit of the bimolecular rate constant was determined to be $(2 \pm 1) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ at 300°K.

INTRODUCTION

Both OH and NO are important constituents of the atmosphere, that play an important role in the formation of photochemical smog.^{1,2} Recently, we have

developed a kinetic spectroscopic technique for studying reactions involving OH and have reported rate constants for bimolecular reactions of OH with CO, H₂, and D₂.³ For these experiments, hydroxyl radicals were formed by pulsed photolysis of H₂O and were