

UC Irvine

UC Irvine Previously Published Works

Title

The reaction of hydrogen atoms with ozone as a source of vibrationally excited OH($X\ 2\pi\ i$) $v = 9$ for kinetic studies

Permalink

<https://escholarship.org/uc/item/28m9v5x8>

Journal

The Journal of Chemical Physics, 74(10)

ISSN

00219606

Author

Finlayson-Pitts, B. J

Publication Date

1981

DOI

10.1063/1.440928

Peer reviewed

The reaction of hydrogen atoms with ozone as a source of vibrationally excited OH(X 2Π i) v = 9 for kinetic studies

B. J. FinlaysonPitts and T. E. Kleindienst

Citation: *The Journal of Chemical Physics* **74**, 5643 (1981); doi: 10.1063/1.440928

View online: <http://dx.doi.org/10.1063/1.440928>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/74/10?ver=pdfcov>

Published by the AIP Publishing

Articles you may be interested in

[Collision dynamics of OH\(X 2Π, v=9\)](#)

J. Chem. Phys. **99**, 5807 (1993); 10.1063/1.465932

[Formation and vibrational relaxation of OH \(X 2Π i ,v\) by O2 and CO2](#)

J. Chem. Phys. **95**, 5752 (1991); 10.1063/1.461597

[Vibrational energy transfer in OH X 2Π i , v=2 and 1](#)

J. Chem. Phys. **92**, 7258 (1990); 10.1063/1.458211

[Vibrational relaxation of OH\(X 2Π i , v=1–3\) by O2](#)

J. Chem. Phys. **92**, 3387 (1990); 10.1063/1.457849

[Vibrational relaxation of OH \(X 2Π i , v=2\)](#)

J. Chem. Phys. **90**, 2174 (1989); 10.1063/1.456671

A banner for AIP The Journal of Chemical Physics. It features the AIP logo and the text 'The Journal of Chemical Physics' in white on a dark blue background. Below this, it says 'Meet The New Deputy Editors' in white. There are three circular portraits of the new deputy editors: Peter Hamm, David E. Manolopoulos, and James L. Skinner. The background of the banner is decorated with colorful, abstract, starburst-like patterns in green, yellow, and blue.

AIP | The Journal of Chemical Physics

Meet The New Deputy Editors

 **Peter Hamm**

 **David E. Manolopoulos**

 **James L. Skinner**

The reaction of hydrogen atoms with ozone as a source of vibrationally excited $\text{OH}(X^2\pi_i)_{v=9}$ for kinetic studies

B. J. Finlayson-Pitts^{a)} and T. E. Kleindienst^{b)}

Department of Chemistry, California State University, Fullerton, Fullerton, California 92634
(Received 22 July 1980; accepted 3 February 1981)

The reaction of measured initial concentrations of hydrogen atoms with ozone was used to produce vibrationally excited $\text{OH}(X^2\pi_i)_{v=9}$ in a fast flow discharge system at 1.1 ± 0.1 Torr total pressure in argon at 300 ± 3 °K. The kinetic behavior of the highest vibrational level of OH^* produced ($v = 9$) [designated $\text{OH}^*(9)$] was characterized by a variety of experiments including (1) determination of both its rates of formation and decay under conditions of excess H, as well as excess O_3 , (2) examination of the effects of added quencher/reactants, and (3) determination of the absolute concentrations of $\text{OH}^*(9)$ using published Einstein A factors. In addition, the change in these concentrations of $\text{OH}^*(9)$ for a given set of initial conditions was examined when the total pressure, nature of the carrier gas, coating of the flow tube walls, and concentration of initial, excess hydrogen atoms were varied. The results of these studies indicate that $\text{OH}^*(9)$ is removed sufficiently rapidly from the system that pseudo-first-order kinetics cannot be applied to obtain absolute rate constants for its reactions and energy transfer processes. However, relative rate constants can be obtained and are reported for CO_2 , Ar, and N_2 relative to O_2 . These data are interpreted in light of the two published sets of values for the Einstein A factors, which differ by more than an order of magnitude. The need for accurate values of these A factors in order to convert our relative rate constants into absolute values, as well as to use in understanding the chemistry of the upper atmosphere, is discussed. The rotational temperature of OH^* is shown to be 308 ± 18 °K in both excess H and excess O_3 .

INTRODUCTION

The rates and mechanisms of interaction of vibrationally excited species are of current interest for a number of reasons. Thus, in a chemical reaction, elucidation of the effects of reactant vibrational excitation may help to clarify the detailed nature of the potential energy hypersurface on which the reaction occurs.¹⁻⁶ Additionally, experimentally determined quenching rates of vibrationally excited species can be used to test current theories of energy exchange.⁵⁻¹² Finally, both these reactive and nonreactive rates of removal of vibrationally excited species are of interest in determining the feasibility of development of certain lasers,¹³⁻¹⁸ and of their proposed applications to such areas as isotope separation and catalysis.¹⁸

The hydroxyl radical OH, in both the ground and vibrationally excited states,¹⁹ is of particular interest because of its importance as a chain carrier in a number of systems. These include hydrocarbon combustion,²⁰ as well as the low (296 °K) temperature oxidation of olefins by O_3 ²¹ and $\text{O}(^3P)$.²² In addition, it plays an important role in the chemistry of both the lower^{23,24} and upper atmosphere.²⁴⁻³⁰ Indeed, atmospheric OH in the ground state ($v = 0$) has been measured³¹ recently and vibrationally excited OH has been identified in the upper atmosphere,^{24,32-34} in auroras,³⁵ and in the Comet Kohoutek.³⁶

The reaction of hydrogen atoms with ozone



produces OH primarily in its upper vibrational levels, efficiently channeling ~ 90% of the reaction exothermic-

ity into vibration.³⁷⁻³⁹ The exothermicity ($\Delta H_{298}^\circ = -76.8$ kcal/mole) is just sufficient to populate $v = 9$ at 74.9 kcal above the ground ($v = 0$) state but not $v = 10$ at 80.7 kcal.³⁴ Indeed, this reaction was first discovered three decades ago from the chemiluminescent emission of the vibrationally excited OH [designated here as $\text{OH}^*(v)$] observed³² by Meinel in the spectrum of the night sky. The source of the emission, now known as the Meinel bands, was subsequently shown^{32,40-45} to be Reaction (1), which occurs in the mesosphere.

Several groups of workers^{38,46-50} have used Reaction (1) as a source of highly vibrationally excited OH^* to study its reaction kinetics. The rate constants obtained by the various groups, however, differed substantially. For example, while the rate constants for removal of $\text{OH}^*(9)$ by O_3 ^{38,46,47} differed by only 30%, for all other molecules they differed by at least one order of magnitude (e.g., for O_2)^{38,48} and often by two (e.g., for N_2).^{38,49}

These discrepancies for such simple quenchers are so large that it appeared essential to first characterize the behavior of $\text{OH}^*(9)$ formed by Reaction (1) before investigating the effects of added quenchers/reactants. The present work was therefore undertaken to define the formation and loss processes of $\text{OH}^*(9)$ in a conventional fast flow discharge system and then to extend this work to kinetic studies of the reactions and deactivation processes of $\text{OH}^*(9)$ by a variety of atoms and small molecules. In these and associated⁵¹⁻⁵⁴ studies, we have directly measured as many reactants, intermediates, and products as possible, including H, O_3 , $\text{O}(^3P)$, and HO_2 , and the absolute as well as the relative emission intensities from two of the Meinel bands originating in $v = 9$. In addition, the effects on the absolute $\text{OH}^*(9)$ emission intensities of changes

^{a)} Author to whom correspondence should be addressed.

^{b)} Present address: Statewide Air Pollution Research Center
University of California, Riverside, Cal. 92521.

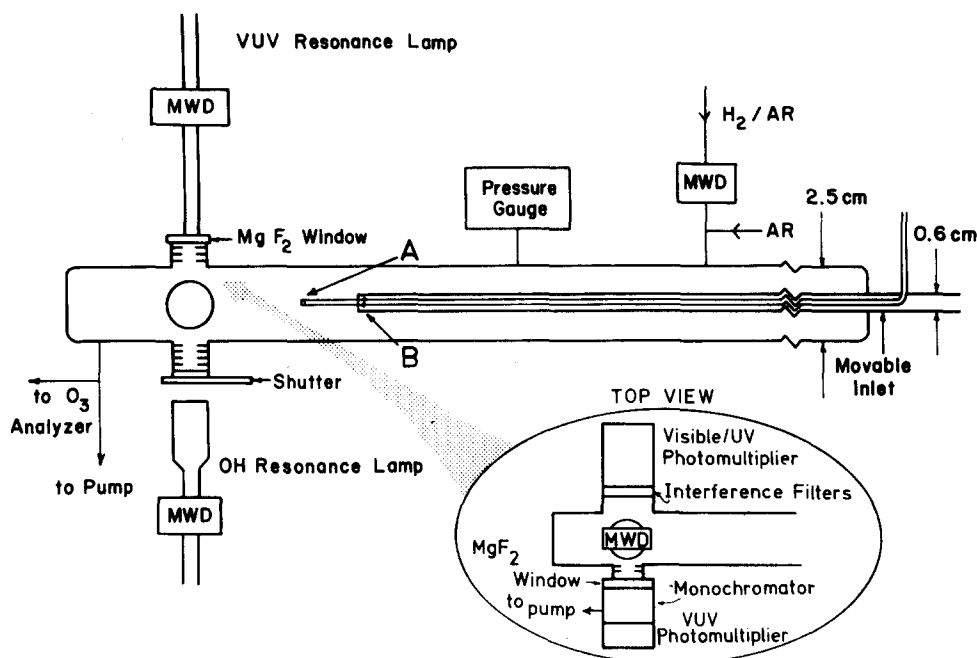


FIG. 1. Schematic diagram of fast flow discharge system. MWD=microwave discharge.

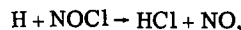
in the total pressure, nature of the inert gas, and the type of coating of the flow tube walls have been examined.

We show here that $\text{OH}^{\dagger}(9)$ is removed very rapidly from the system compared to its rate of formation in Reaction (1) so that pseudo-first order kinetics cannot be applied to obtain absolute rate constants. However, accurate relative rate constants can be obtained and several are reported here. To convert these to absolute rate constants, the radiative lifetime of $\text{OH}^{\dagger}(9)$ (i.e., the Einstein A factors)⁵⁵ must be accurately known. The implications of the two published sets of A factors, one experimental^{46,47} and one theoretical,⁵⁶ for this work are discussed.

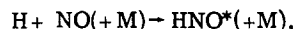
EXPERIMENTAL

The fast flow discharge system is shown in Fig. 1. It consists of a 2.5 cm diam. flow tube with a double concentric movable inlet whose two ports A and B are separated by 3.3 cm. The two detection systems, operating in the vacuum ultraviolet (VUV) and the visible/near UV, respectively, are fixed at the downstream end of the flow tube. The visible/near UV photomultiplier (EMI 9659QB) used to measure ground state OH by resonance fluorescence^{57,58} is also equipped with interference filters to isolate the Meinel band emissions from the (9,3) transition of $\text{OH}(X^2\pi_i)_{v=9}$ at 626 nm (half-bandwidth of 3 nm) and the (9,2) transition at 519 nm (half-bandwidth of 3 nm). The data on $\text{OH}^{\dagger}(9)$ reported here were all recorded using the more intense (9,3) band; however, the (9,2) band was also followed in selected runs to ensure that no interfering emissions were present at 626 nm. This photomultiplier viewed a circular area of 6 mm diam. in the center of the flow tube, corresponding to ~ 0.6 msec reaction time. The Meinel band emissions were generally followed from 4 to 40 msec depending on the rate of decay and thus the signal intensity.

A third interference filter at 762 nm (half-bandwidth of 5 nm) was used with this photomultiplier in the determination of initial hydrogen atom concentrations $> 5 \times 10^{12}$ atoms cm^{-3} by titration with NOCl .⁵⁹ (Unless otherwise stated, all concentrations and rate constants are given in units of molecules cm^{-3} and cm^3 molecule $^{-1}$ s $^{-1}$, respectively, throughout.) This reaction produces NO:



which then reacts with the excess H:



producing electronically excited HNO^* which is detected by its emission at 762 nm.⁶⁰ A plot of $I_{762}/[\text{NOCl}]$ vs $[\text{NOCl}]$, where I_{762} is the emission intensity from HNO^* , extrapolates to zero at $[\text{NOCl}] = [\text{H}]_0$.

The VUV detection system, consisting of a Minuteman model 302VM 0.25 m evacuated vacuum monochromator with a 600 grooves/mm grating (40 Å/mm) and a EMR solar blind photomultiplier (model 541G-09-18), was used to measure initial $\text{H}(^2\text{S})$ concentrations $< 5 \times 10^{12}$ by resonance fluorescence at 121.6 nm during its titration with NO_2 . In addition, concentrations of $\text{O}(^3\text{P})$ formed from the reaction of nitrogen atoms with nitric oxide (see below) were measured by resonance fluorescence of the triplet around 130 nm.⁶¹ A slit width of 0.4 mm was used in all runs.

Emission spectra when H and O_3 were mixed were scanned from 200 to 700 nm in the presence of Ar only, and with added O_2 , H_2 , and CO_2 , respectively, using a Jarrell-Ash monochromator (model 82-410, 1180 grooves/mm, resolution 6 Å) and the EMI 9659QB photomultiplier. Comparison to literature spectra confirmed that $\text{OH}(X^2\pi_i)_{v \leq 9}$ was the only emitting species present.

The rotational distribution of the vibrationally ex-

cited $\text{OH}^\dagger$ was determined from the (8, 3) and (7, 2) overtone bands. The intensities of the peaks were corrected for the spectral response of the detection system determined using an NBS 1000 W quartz iodine lamp (Epply Laboratory, Inc.) for which the absolute spectral irradiance was known.

Mixtures of O_3 in O_2 were generated by passing O_2 through a commercial ozonizer and further diluting with O_2 prior to entering the flowmeter and O_3 measurement system. O_3 in He was generated by trapping the O_3 from an O_3 - O_2 mixture on silica gel (Davison PA-400, Grade 407, mesh size 8-20) at -77°C . The O_2 was pumped off and the O_3 eluted by passing He through the trap at 1 atm pressure. The composition of the mixture was determined from its absorbance at 253.7 nm using published extinction coefficients.⁶²

The Ar, O_2 , and H_2/Ar mixture were all U.H.P. grade ($\geq 99.9999\%$) while the N_2 and CO_2 were 99.98% and 99.95%, respectively. The Ar and O_2 were used as received while the H_2/Ar mixture and the N_2 were passed through a catalyst (BASF Corp. Catalyst R3-11) to remove O_2 prior to entering the discharge. The CO_2 was passed through a glass-wool-packed trap at -60°C before use.

Mixtures of NO_2 in Ar were made as needed and stored in the dark to prevent photolysis by room lights. The NO_2 ($\geq 99.5\%$) was first purified by trap-to-trap distillation (-78°C) until only a white solid remained. This was then allowed to evaporate to a known pressure in a 5 liter mixing bulb and Ar was added to the desired total pressure. The composition of the mixture, calculated from the pressure measurements, was corrected for the $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ equilibrium as described elsewhere.⁵⁸ The composition of selected mixtures was checked by measuring the absorbance due to NO_2 at 400 nm using a Cary 15 spectrophotometer; the results of the two methods were always within 1%. The flow rate of this mixture was determined by measuring its pressure drop in a calibrated volume.

NO/Ar mixtures were made by passing NO through a molecular sieve (Linde 13X) to remove NO_2 , CO_2 , and H_2O and then through either a glass-wool-packed trap at -160°C or a silica gel trap at -77°C into a mixing bulb. Argon was added to give the desired concentration. The flow rate of this mixture was also determined by the pressure drop in a calibrated volume.

NOCl/Ar mixtures were similarly prepared and the flow rates measured after trapping the NOCl ($>97\%$) in a liquid nitrogen trap and diluting with Ar.

All studies were carried out at $300 \pm 3^\circ\text{K}$ and, except as described below, at 1.1 ± 0.1 Torr in Ar. The flow tube was coated with a halocarbon wax, except for one study in which a boric acid coated wall was used.

The linear flow speed was typically 1000 cm sec^{-1} . Corrections were made to the observed first order rates of decay k' of $\text{OH}^\dagger(9)$ for deviation from plug flow^{63,64} and for the effects of axial diffusion.⁶⁴ Correction factors for the former were estimated from the literature⁶³ using calculated values of $\alpha = D/k'R^2$,

where D , the diffusion coefficient, was estimated⁶⁵ to be $219 \text{ cm}^2 \text{ sec}^{-1}$ at 1 Torr and R is the flow tube radius; this correction was $\leq 14\%$. The correction⁶⁴ for axial diffusion was $\leq 20\%$. Because the rate constant for wall removal of $\text{OH}^\dagger(9)$, i.e., k_w , could not be determined independent of quenching by Ar (see below) and because these corrections may be sensitive to the absolute value of k_w ,⁶⁶ they must be considered approximate. However, the absolute values of the first order rate constants reported here are not used to derive absolute rate constants, but rather as confirmation of the type of kinetic analysis which is applicable in this system. Since the appropriateness of the kinetics applied here is supported by other experimental evidence as well (see below), any errors in the magnitude of the corrections made will not alter the conclusions or the relative rate constants derived in this paper.

RESULTS

Rotational temperature

The emission intensity of a vibration-rotation line for a Boltzmann distribution of multiplet levels is given by⁵⁶

$$I(J', v', i' - J'', v'', i'') \\ = N_{v'} A \frac{2(2J' + 1)}{Q_{v'}} \exp \left[\frac{-E_{J', v'}(J')}{kT_R} \right].$$

I is the emission intensity, $N_{v'}$ is the total concentration of molecules in the v' vibrational level, A is the Einstein coefficient for that transition, $Q_{v'}$ is the electronic-rotational partition function for the v' level which depends on T_r , $E_{J', v'}(J')$ is the rotational energy of the emitting state, and T_R is the rotational temperature for this distribution. Thus, if the rotational distribution is Boltzmann, a plot of $\ln[I/A(2J'+1)]$ against the rotational energy should be linear with a negative slope of $(kT_R)^{-1}$. The rotational energies used here were those summarized by Krassovsky *et al.*³⁴

Six experiments were carried out in which the P_1 - P_5 lines of the (8, 3) or (7, 2) band of the $\text{OH}(X^2\pi_{3/2})$ state were scanned. Using the most recent theoretical values of the A factors,⁵⁶ $\ln[I/A(2J'+1)]$ was found to vary linearly with the rotational energy. (Although, as discussed below, there is considerable disagreement between the theoretical⁵⁶ and experimental^{46,47} absolute values of the A factors, the relative values predicted theoretically⁵⁶ appear to be in good agreement with a variety of experimental data in the literature and hence were used here.) A typical plot is shown in Fig. 2 and the reaction conditions and results are summarized in Table I, where the average rotational temperature is shown to be $308 \pm 18^\circ\text{K}$.

Reaction scheme

Table II shows a simplified reaction scheme for the production and loss of $\text{OH}^\dagger(9)$ in the $\text{H} + \text{O}_3$ system. Removal of $\text{OH}^\dagger(9)$ by interaction with the initial reactants H and O_3 is included because of the results of initial studies of the $\text{OH}^\dagger(9)$ decay at a constant, initial hydrogen atom concentration. As the concentration of an

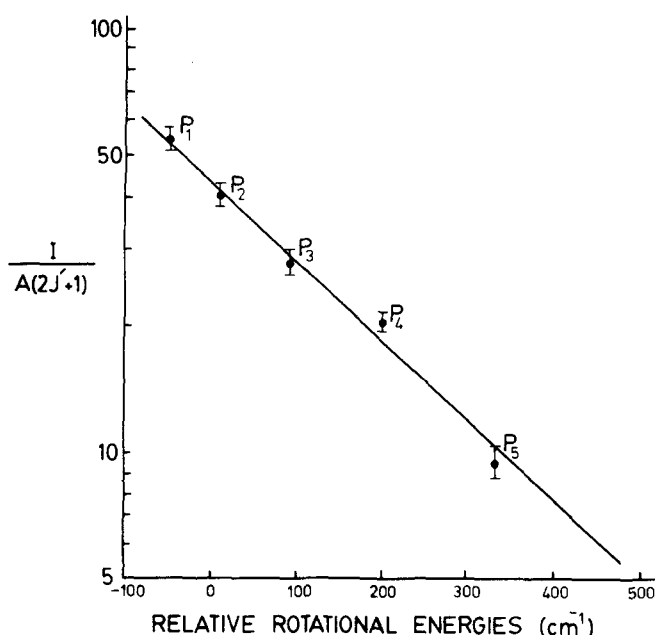


FIG. 2. Typical rotational distribution of the (8,3) band of OH($X^2\pi_{3/2}$); $[H]_0 = 2.7 \times 10^{12}$; $[O_3]_0 = 2.6 \times 10^{13}$, reaction time ~ 0.4 msec. From slope, $T_R = 337 \pm 43$ °K ($2\sigma_s$).

added O_3-O_2 mixture increased, the (9,3) band emission intensity first increased rapidly to a peak. Increasing the O_3-O_2 flow further resulted in slowly decreasing signal intensities. These observations are qualitatively consistent with a rapid removal of $OH^+(9)$ by H and a slower removal by O_3-O_2 .

Kinetic analysis

From the reaction scheme in Table II, the following kinetic expression for removal of $OH^+(9)$ is derived:

$$d[OH^+(9)]/dt = k_1[H][O_3] - B[OH^+(9)]. \quad (I)$$

B is the sum of the first order removal rates, i. e.,

$$B = k_2[H] + k_3[O_3] + k_4[Ar] + k_5[O_2] + k_6[H_2] + k_{rad} + k_w + k_9[OH^+(0-9)] + k_{10}[X] \quad (II)$$

and $k_2 = (k_{2a} + k_{2b})$, etc.

TABLE I. Summary of experiments to determine rotational distribution of OH($X^2\pi_{3/2}$) $_{v=9}$.

Vibrational band	$10^{-12} [H]_0$ (cm^{-3})	$10^{-13} [O_3]_0$ (cm^{-3})	Reaction time (msec)	$T_R (\pm 2\sigma_s)^a$ (°K)
(8,3)	2.5	2.5	0.4	281 ± 58
(8,3)	2.7	2.6	0.4	337 ± 43
(8,3)	2.7	2.6	3.9	283 ± 60
(8,3)	2.5	2.5	0.4	302 ± 28
(7,2)	2.5	2.5	0.4	297 ± 42
(8,3)	15	0.15	0.5	306 ± 66
Weighted mean ^b :				308 ± 18 °K ($2\sigma_s$)

^a σ_s is the external consistency value⁶⁷⁻⁶⁹ of the standard deviation of the slope of plots such as Fig. 2.

^bEach T_R was weighted (Refs. 67-69) by $w = 1/\sigma_s^2$.

TABLE II. Reaction scheme for $OH^+(9)$ produced in H + O_3 system.

- (1) $H + O_3 \xrightarrow{a} OH^+(9) + O_2$
 $\xrightarrow{b} OH^+(1-8) + O_2$
- (2) $OH^+(9) + H \xrightarrow{a} OH^+(0-8) + H$
 $\xrightarrow{b} H_2 + O(^3P)$
- (3) $OH^+(9) + O_3 \xrightarrow{a} HO_2 + O_2$, $v \geq 0$
 $\xrightarrow{b} H + 2O_2$, $v \geq 1$
 $\xrightarrow{c} O + O_2 + OH$, $v \geq 3$
- (4) $OH^+(9) + Ar \rightarrow OH^+(0-8) + Ar$
- (5) $OH^+(9) + O_2 \xrightarrow{a} OH^+(0-8) + O_2$
 $\xrightarrow{b} HO_2 + O(^3P)$
- (6) $OH^+(9) + H_2 \xrightarrow{a} OH^+(0-8) + H_2$
 $\xrightarrow{b} H_2O + H$
- (7) $OH^+(9) \xrightarrow{k_{rad}} OH^+(0-8) + h\nu$
- (8) $OH^+(9) \xrightarrow{k_w} \text{wall loss}$
- (9) $OH^+(9) + OH^+(v) \xrightarrow{a} H_2O + O$
 $\xrightarrow{b} HO_2 + H$
 $\xrightarrow{c} OH^+(0-8) + OH^+(v' > v)$
- (10) $OH^+(9) + X \xrightarrow{a} OH^+(0-8) + X$
 $\xrightarrow{b} \text{products}$

Assuming that the formation term $k_1[H][O_3]$ is negligible compared to the loss term $B[OH^+(9)]$ after most of the limiting reagent in Reaction (1) is consumed, and that the bimolecular reaction (9) can be ignored (see below), Eq. (I) can be integrated to yield the following:

$$\ln[OH^+(9)] = -Bt + \text{const.} \quad (III)$$

To test whether such an analysis was appropriate, we evaluated the two terms in Eq. (I) representing formation and loss, respectively. The rate constant k_1 is known from studies in this⁵³ and other⁷⁰⁻⁷³ laboratories. Furthermore, a number of groups³⁷⁻³⁹ have determined the initial vibrational distribution of $OH^+(v)$ from Reaction (1). From the work of Polanyi *et al.*,³⁷ we estimate that $\sim 45\%$ of the reaction produces OH^+ in $v = 9$. Thus, $k_{1a} = 0.45k_1 = 1.08 \times 10^{-11}$, assuming⁵³ $k_1 = (2.4 \pm 0.4) \times 10^{-11}$. In a great excess of H, $[H] = [H]_0$, and $[O_3]$ at a particular reaction time t can be calculated from k_1 and $[H]_0$. This then gives the formation term $k_1[H][O_3]$ at time t .

The concentration of $OH^+(9)$ was estimated using Eq. (AIII) (derived in the Appendix):

$$[OH^+(9)] = 2.73 \times 10^{-18} \frac{[O][NO]}{I_{NO_2}^*} \frac{I_{9,3}}{A_{9,3}}. \quad (AIII)$$

$I_{NO_2}^*$ is the signal from the O + NO reaction observed through the 626 nm filter when known concentrations of O and NO are present, $I_{9,3}$ is the signal observed from the $OH^+(9)$ through the same filter, and $A_{9,3}$ is the Einstein A factor for the (9,3) transition. [As discussed in the Appendix, the (9,2) transition and the 519 nm filter were also used in some runs as a check.] The results from a typical experiment to determine $([O][NO]/I_{NO_2}^*)$ are shown in Fig. 3.

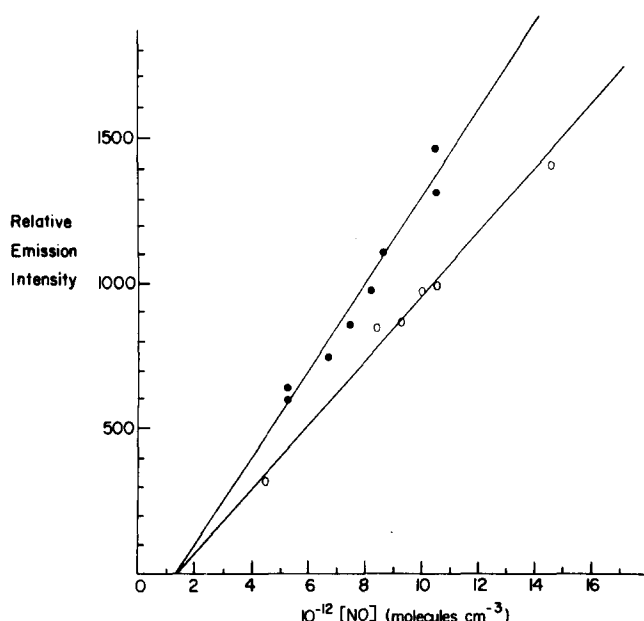


FIG. 3. Relative NO_2^* emission intensities through 626 nm filter (●) and through 519 nm filter (○) when excess NO is added to N atoms. $[\text{N}]_0 = [\text{O}]$ measured simultaneously by resonance fluorescence was 1.6×10^{12} atoms cm^{-3} .

Two values of $A_{9,3}$ are reported in the literature. One is derived from the studies of Potter and co-workers,^{46,47} who experimentally determined the radiative lifetime (τ_9) of $\text{OH}^\dagger(9)$ and used Cashions' tabulations⁷⁴ of relative transition probabilities for $\text{OH}^\dagger$ (corrected to more recent band origin frequencies) to obtain the lifetimes of various $\text{OH}^\dagger$ transitions. From this work, $A_{9,3} = 3.9 \times 10^{-3} \text{ sec}^{-1}$ was derived.

Mies calculated⁵⁶ A factors for the various vibrational transitions using a theoretically derived dipole moment function. The relative values of the thermally averaged A factors obtained are in reasonable agreement with the results of a number of experimental studies, but the absolute values are much larger than those derived by Potter *et al.* Thus, Mies reports $A_{9,3} = 0.13 \text{ sec}^{-1}$ at room temperature, a factor of 33 larger than the experimentally determined value.

Throughout the following discussion, our data are treated in terms of each value of $A_{9,3}$ individually and the implications of each discussed. However, this is merely to illustrate the consequences of each value and should not be taken to imply that either one or the other is necessarily correct. Indeed, the true value may not necessarily even lie between these two published values.

Using each value of $A_{9,3}$, then, the measured calibration factors $[\text{O}][\text{NO}]/I_{\text{NO}_2^*}$ and the observed emission intensities $I_{9,3}$, concentrations of $\text{OH}^\dagger(9)$ were calculated from Eq. (AIII). A typical semilog plot of $[\text{OH}^\dagger(9)]$ against reaction time is shown in Fig. 4, where the left axis gives the concentrations derived using $A_{9,3} = 3.9 \times 10^{-3} \text{ sec}^{-1}$ (Refs. 46 and 47) and the right axis gives those obtained using $A_{9,3} = 0.13 \text{ sec}^{-1}$.⁵⁶

Given k_{1a} , k_{1b} , $[\text{H}]_0$, and $[\text{O}_3]_0$, the first order loss

B needed to match the observed absolute concentrations of $\text{OH}^\dagger(9)$ can then be calculated (see below). For the conditions of Fig. 4, $B = 1.4 \times 10^3$ and $4.2 \times 10^4 \text{ sec}^{-1}$ gave the best fit to the data for $A_{9,3} = 3.9 \times 10^{-3}$ and 0.13 sec^{-1} , respectively. Comparing the formation and loss terms at 8 msec, for example, $k_{1a}[\text{H}][\text{O}_3] \approx 10^{13}$ and $B[\text{OH}^\dagger(9)] \approx 10^{13}$. Thus, the formation term cannot be ignored and both formation and decay are occurring simultaneously. As a result, one cannot assume the simplified pseudo-first order kinetic analysis of Eq. (III).

Because of the variety of reaction paths available when $\text{OH}^\dagger$ reacts with O_3 , and the possible complications this introduces (see below), the kinetic scheme and analysis for the system is simpler under conditions of excess H. Considering then only conditions where $[\text{H}]_0 \geq 10[\text{O}_3]_0$ and where $[\text{O}_3]_0$ is sufficiently small that bimolecular reactions of $\text{OH}^\dagger$ such as (9) can be ignored (see below), a simplified reaction scheme consisting of Reactions (1), (2), and (4)–(8) is obtained. The differential equations describing these reactions can then be integrated to yield the time dependence of $[\text{OH}^\dagger(9)]$ in the absence of added quencher/reactants X:

$$[\text{OH}^\dagger(9)] = \frac{k_{1a}[\text{H}][\text{O}_3]_0}{B - k_1[\text{H}]} (e^{-k_1[\text{H}]t} - e^{-Bt}). \quad (\text{IV})$$

If $Bt > 2.5$ and $k_1[\text{H}] < 0.1B$, then $e^{-Bt} < 0.1e^{-k_1[\text{H}]t}$ and Eq. (IV) reduces to

$$[\text{OH}^\dagger(9)] = \frac{k_{1a}[\text{H}][\text{O}_3]_0}{B} e^{-k_1[\text{H}]t}. \quad (\text{V})$$

As discussed below, in all experiments $B \geq 5 \times 10^2 \text{ sec}^{-1}$,

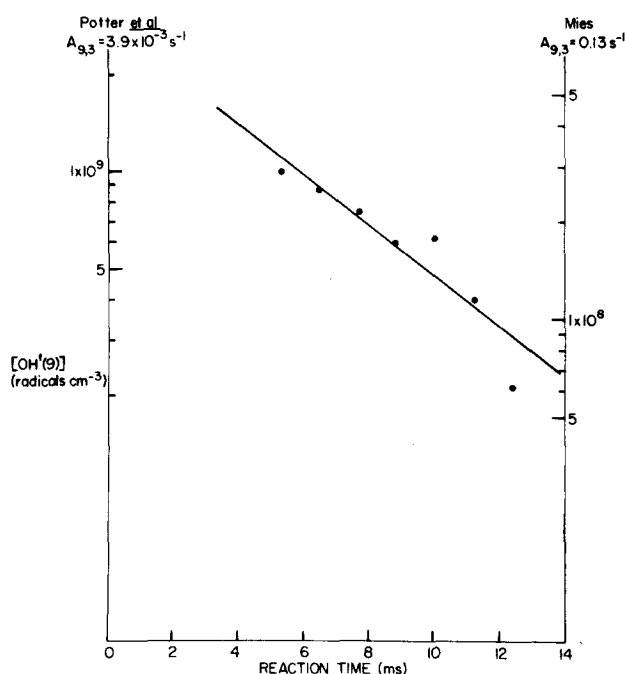


FIG. 4. Concentrations of $\text{OH}^\dagger(9)$ as a function of reaction time when $[\text{H}]_0 = 7.5 \times 10^{12}$ atoms cm^{-3} , $[\text{O}_3]_0 = 4.3 \times 10^{11}$ molecules cm^{-3} , $[\text{O}_2]_0 = 0$, total pressure 1.1 Torr in Ar. Line is calculated best fit with $B = 1.4 \times 10^3 \text{ sec}^{-1}$ for $A_{9,3} = 3.9 \times 10^{-3}$ or $4.2 \times 10^4 \text{ sec}^{-1}$ for $A_{9,3} = 0.13 \text{ sec}^{-1}$ (see the text).

TABLE III. Typical values of R (sec^{-1}) for $\text{OH}^\dagger(9)$ decay at various initial, excess hydrogen atom concentrations (halo-carbon wax coated tube).

Experi- ment number	$10^{-13} [\text{H}]_0$ (atoms cm^{-3})	$10^{-12} [\text{O}_3]_0$ (molecules cm^{-3})	$R \pm 2\sigma_s^a$ (sec^{-1})	$R \pm 2\sigma_0$ (sec^{-1})
1	4.3	2.9	1074 ± 16	1082 ± 28
		2.3	1169 ± 73	
		1.3	1101 ± 38	
2	3.4	2.1	639 ± 76	698 ± 69
		1.3	767 ± 37	
		1.1	673 ± 49	
		0.5	602 ± 52	
		0.2	813 ± 151	
3	2.6	2.4	730 ± 7	679 ± 43
		2.3	632 ± 7	
		1.6	664 ± 6	
		0.3	752 ± 10	
		0.1	646 ± 9	
4	1.7	2.1	319 ± 14	310 ± 35
		1.4	275 ± 20	
		1.2	353 ± 33	
5	0.75	0.85	136 ± 4	132 ± 14
		0.61	108 ± 10	
		0.43	154 ± 43	

^aStatistical weighting of the data was done using recommended procedures.⁶⁷⁻⁶⁹ Thus, the semilog plots of intensity vs time were treated by weighting each point by the factor $(I_T - I_B)^2 / (I_T + I_B)$, where I_T is the total light intensity and I_B is the background signal with only H present. A weighted least squares of the $\ln(\text{intensity})$ vs reaction time was then calculated and the slope of this plot, i.e., the decay rate R , assigned the weighting factor $w_i = 1/\sigma_s^2$, where σ_s is one standard deviation of the slope. (Because the external consistency values of the standard deviations were generally greater than the internal consistency values, these were used throughout the data analysis.) These weighting factors were then used in least squares analyses of R against $[\text{H}]_0$.

so that Eq. (V) is always valid for $t \geq 5$ msec; for larger values of B , it is applicable at even shorter reaction times. The reaction times studied in all experiments were such that the condition $Bt \geq 2.5$ was satisfied.

Equation (V) shows that if $\text{OH}^\dagger(9)$ is removed rapidly relative to its rate of formation in Reaction (1), then in a great excess of H, $\text{OH}^\dagger(9)$ should decay exponentially with time with an observed first order rate constant (R) given by $k_1[\text{H}] \approx k_1[\text{H}]_0$. A plot of R vs $[\text{H}]_0$ should thus be a straight line with slope k_1 and an intercept of zero.

In addition, if some quencher/reactant X is added, Eq. (V) is modified to

$$[\text{OH}^\dagger(9)]^X = \left[\frac{k_{1a}[\text{H}][\text{O}_3]_0}{B + k_{1a}[\text{X}]} \right] e^{-k_1[\text{H}]t}. \quad (\text{VI})$$

Thus, addition of X should lower the concentration of $\text{OH}^\dagger(9)$ at all reaction times but should not change its observed first order rate constant R . As discussed below, both expectations are consistent with our experimental observations.

Kinetic behavior observed experimentally

The first order rate constants for decay of $\text{OH}^\dagger(9)$ in excess H ($[\text{H}]_0 \geq 10[\text{O}_3]_0$) were studied as a function of $[\text{H}]_0$ at concentrations from 2×10^{12} to 4×10^{13} . A total of 46 runs with 15 different initial hydrogen atom concentrations were carried out. Some typical data are given in Table III.

It is seen that for one value of $[\text{H}]_0$, R does not vary significantly with $[\text{O}_3]_0$, consistent with Eq. (V). Thus, the observed values of R at one $[\text{H}]_0$ were averaged and plotted in Fig. 5.

In these studies, the increasingly rapid decay of $\text{OH}^\dagger(9)$ as $[\text{H}]_0$ increased necessitated the addition of larger concentrations of the limiting reagent O_3 to produce a detectable signal over measurable reaction times. This produced larger quantities of $\text{OH}^\dagger$, and increased the possibility that bimolecular reactions such as Reaction (9) are important. Thus, at the lower values of $[\text{H}]_0$, and hence $[\text{O}_3]_0$, $\text{OH}^\dagger$ - $\text{OH}^\dagger$ interactions will be minimized and the kinetic analysis leading to Eq. (V) will be most valid. A weighted least squares analysis of the data in Fig. 5 for which $[\text{H}]_0 \leq 1 \times 10^{13}$ and $[\text{O}_3]_0 \leq 1 \times 10^{12}$ leads to a slope of $(2.4 \pm 0.8) \times 10^{-11}$ and an intercept of $(-12 \pm 38) \text{sec}^{-1}$. This is in excellent agreement with Eq. (V), which predicts a slope⁵³ of $k_1 = (2.4 \pm 0.4) \times 10^{-11}$ and an intercept of zero. (The errors quoted here and throughout the paper are two standard deviations.)

The effect on the decay of $\text{OH}^\dagger(9)$ of adding increasing concentrations of the deactivator $\text{X} = \text{CO}_2$ is shown in Fig. 6. It is seen that, consistent with Eqs. (V) and (VI), the intensity of the (9,3) band [i.e., the concentration of $\text{OH}^\dagger(9)$] decreases as increasing concentrations of CO_2 are added, but the observed slope, i.e., R , remains essentially unchanged.

In summary, under conditions of a great excess of

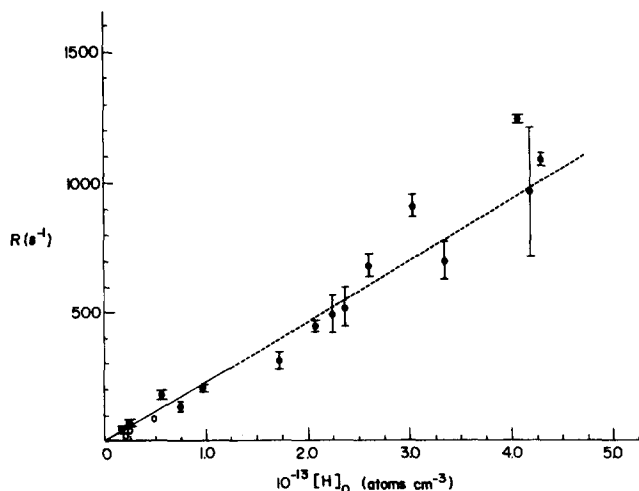


FIG. 5. Observed values of R (see the text) as a function of initial, excess hydrogen atom concentration. Error bars are $2\sigma_s$; where no error bars appear, they are contained within the points. ●, Halocarbon wax coated tube; ○, boric acid coated flow tube. Line is weighted least square line for $[\text{H}]_0 \leq 1 \times 10^{13}$ atoms cm^{-3} .

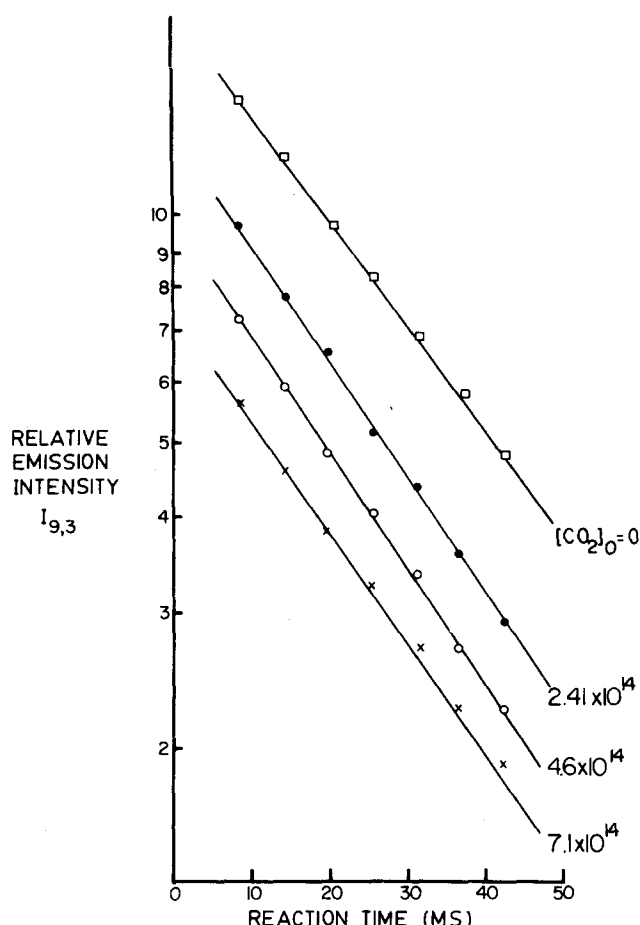


FIG. 6. Relative emission intensity of the $\text{OH}^\dagger(9,3)$ band as a function of added CO_2 concentration. $[\text{H}]_0 = 1.6 \times 10^{12}$ atoms $\times \text{cm}^{-3}$, $[\text{O}_3]_0 = 2.5 \times 10^{11}$ molecules cm^{-3} , total pressure 1.05 Torr in Ar.

hydrogen atoms, a variety of experiments including determination of (1) absolute concentrations of $\text{OH}^\dagger(9)$, (2) first order rate constants for decay of $\text{OH}^\dagger(9)$ as a function of $[\text{H}]_0$, and (3) effects of added quenchers all indicate that even though Reaction (1a) forming $\text{OH}^\dagger(9)$ is fast, the removal of $\text{OH}^\dagger(9)$ is also rapid. Thus, a pseudo-first order kinetic analysis cannot be used and expressions such as Eqs. (V) and (VI) must be applied.

Relative rate constants for removal of $\text{OH}^\dagger(9)$

Equations (V) and (VI) can be combined to yield

$$\frac{[\text{OH}^\dagger(9)]}{[\text{OH}^\dagger(9)]^x} = \frac{I_0}{I_0^x} = 1 + \frac{k_{10}}{B}[\text{X}], \quad (\text{VII})$$

where I_0^x and I_0 are the observed emission intensities from $\text{OH}^\dagger(9)$ at a particular reaction time in the presence and absence, respectively, of a known concentration $[\text{X}]$ of the deactivator/reactant X. A plot of I_0/I_0^x against $[\text{X}]$ should thus be linear with a slope of (k_{10}/B) and an intercept of 1.0. Figure 7 shows such plots for $\text{X} = \text{CO}_2$ and $\text{X} = \text{O}_2$, respectively, for (a) two different O_3 concentrations and (b) for the (9,3) and (9,2) bands.

To obtain absolute rate constants k_{10} from the slope of the lines in Fig. 7, B must be known. As discussed

in detail below, this depends on the value of the Einstein A factors and is highly uncertain. As a result we prefer to use the data in Fig. 7 to obtain accurate *relative* rate constants. Taking O_2 as the reference, the average ratio of the slopes of plots such as Fig. 7 gives $k_{10}(\text{CO}_2)/k_{10}(\text{O}_2) = 2.7 \pm 0.4$, where the quoted error is our estimate of the total possible errors due to both systematic and random errors. Upper limits have also been placed on this ratio for $\text{X} = \text{Ar}$ and N_2 . The results are given in Table IV.

Reaction(s) removing $\text{OH}^\dagger(9)$ in the absence of X

Although it is clear that $\text{OH}^\dagger(9)$ is being removed rapidly compared to its rate of formation in the absence of an added quencher/reactant, it is of interest to determine what reactions are responsible. Because initial studies indicated that H_2 was much less efficient than O_2 in deactivating $\text{OH}^\dagger(9)$, and the concentrations of H_2 remaining after the discharge were $\leq 10^{13}$, Reaction (6) was ignored. Similarly, if mixtures of O_3 in He are used, the concentration of O_2 is sufficiently small that Reaction (5) must be negligible.

As discussed above, H is much more effective in removing $\text{OH}^\dagger(9)$ than O_3 and O_2 . In a great excess of H, then, Reaction (3) can also be ignored. For reasons discussed in detail below, the bimolecular reactions of $\text{OH}^\dagger(v)$ either leading to loss or production of $\text{OH}^\dagger(9)$ were also assumed to be negligible.

This leaves the interaction with H and Ar as well as radiation and wall loss as candidates for the removal of $\text{OH}^\dagger(9)$. (Even though Ar is a relatively inefficient quencher of $\text{OH}^\dagger(9)$ as seen in Table IV, it is present in such large concentrations ($\sim 3 \times 10^{18}$) compared to all other species that even a low value of k_4 may lead to substantial first order removal rates, $k_4[\text{Ar}]$).

To test the relative contributions of Reactions (2), (4), (7), and (8) to the removal of $\text{OH}^\dagger(9)$, studies were

TABLE IV. Comparison of relative rate constants $k_{10}(\text{X})/k_{10}(\text{O}_2)$ to literature values.

Quencher	Relative rate constants		
	This work	Refs. 46-49 ^a	Ref. 38 ^a
O_2	1.0	1.0	1.0
CO_2	2.7 ± 0.1^b	2.4	n.d.
Ar	≤ 0.02	negligible	0.3
N_2	< 0.05	0.4	1.3

^aThe relative rate constants were obtained by dividing the absolute values reported by the value for O_2 obtained by that group.

^bError is two standard deviations of the weighted mean of seven experiments carried out at different initial hydrogen atoms and ozone concentrations; the weighting factors used were $\omega_i = 1/\sigma_i^2$, where σ_i is the standard deviation of the ratio of the slopes of plots such as Fig. 7. Total error including systematic and random errors is estimated to be $\pm 15\%$.

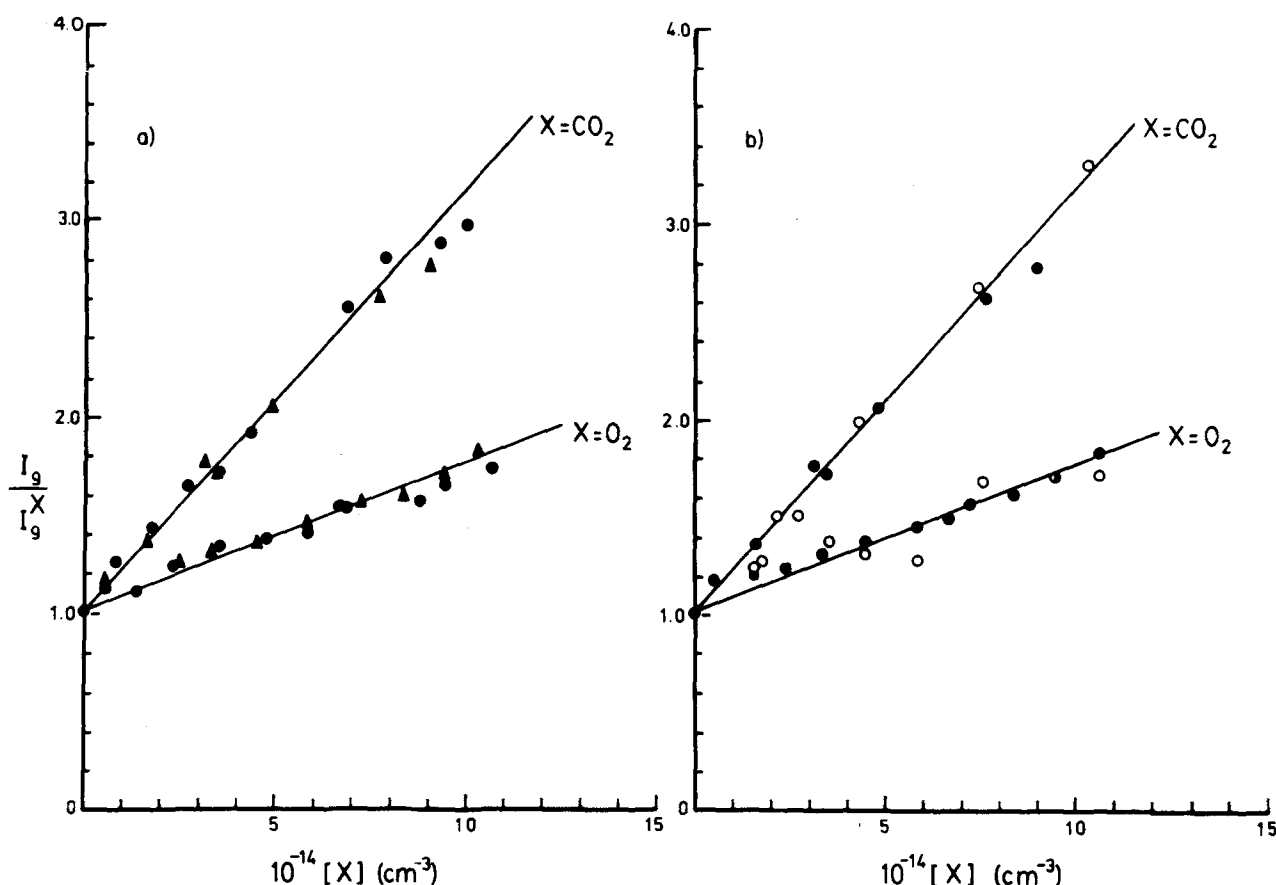


FIG. 7. Relative emission intensities of $\text{OH}^{\dagger}(9)$ bands at a fixed reaction time as O_2 and CO_2 are added (see the text for definitions of I_9/I_9^X). $[\text{H}]_0 = 1.6 \times 10^{12} \text{ atoms cm}^{-3}$, total pressure 1.05 Torr in Ar (a) (9,3) band and $\bullet$, $[\text{O}_3]_0 = 1.7 \times 10^{11}$; $\blacktriangle$, $[\text{O}_3]_0 = 2.9 \times 10^{11} \text{ molecules cm}^{-3}$; (b) $[\text{O}_3]_0 = 2.9 \times 10^{11}$ and $\bullet$, (9,3) band at 626 nm; $\circ$, (9,2) band at 519 nm.

carried out to obtain absolute concentrations of $\text{OH}^{\dagger}(9)$ as a function of reaction time under various conditions. For each of these runs, where the initial concentrations of H, O_3 , and Ar were measured, the simultaneous first order differential equations describing the concentration of each species as a function of reaction time were solved by numerical integration. Hammings' modified predictor-corrector method,⁷⁵ in which the four preceding points are used to compute the next, was used. The initial increment is adjusted, and the starting values computed using a fourth order Runge-Kutta method. An integration step of $1 \times 10^{-5} \text{ sec}$ was used to ensure an absolute precision of $1 \times 10^6 \text{ molecules cm}^{-3}$ in the predicted concentrations of reactants and products; lowering the step size by a factor of 10 did not significantly change these predicted concentrations. Results using this integration technique were compared to those using the Gear algorithm^{76,77} and were found not to differ significantly.

This numerical integration technique was used to find a best match to the $[\text{OH}^{\dagger}(9)]$ data as a function of reaction time for the initial conditions of each run by varying the first order loss of $\text{OH}^{\dagger}(9)$, i.e., B , which is now given by

$$B = k_2[\text{H}] + k_4[\text{Ar}] + k_{\text{rad}} + k_w. \quad (\text{VIII})$$

The effect on the "best fit" value of B of changing the

following parameters was then measured: (1) initial concentration of hydrogen atoms, (2) total pressure, (3) nature of the carrier gas, and (4) coating of the flow tube walls. The results are shown in Tables V and VI for the two assumptions $A_{9,3} = 3.9 \times 10^{-3}$ and 0.13 sec^{-1} , respectively.

For unknown reasons, the scatter in the values of B obtained for one value of $[\text{H}]_0$ but different $[\text{O}_3]_0$ is unexpectedly large, especially since all other experimental observations on the system are highly reproducible. This may be partly due to the fact that the observed rates of decay were not always exactly $2.4 \times 10^{-11}[\text{H}]_0$ (Fig. 5) as predicted by Eq. (V). The best match then depends on which of the $\text{OH}^{\dagger}(9)$ data, i.e., at short or long reaction times, one fits. In these studies B was varied until the predicted $\text{OH}^{\dagger}(9)$ concentration matched that at the midpoint (in time) of our observations.

However, within the uncertainty the scatter imposes on the results, the following observations can be made: First, the initial concentration of H markedly changes B . As shown in Table V, as $[\text{H}]_0$ increases from 1×10^{12} to 2×10^{13} , B increases from $\sim 0.5 \times 10^3$ to $\sim 4 \times 10^3 \text{ sec}^{-1}$ if $A_{9,3} = 3.9 \times 10^{-3} \text{ sec}^{-1}$, or from $\sim 1 \times 10^4$ to $\sim 1 \times 10^5 \text{ sec}^{-1}$ if $A_{9,3} = 0.13 \text{ sec}^{-1}$. Figure 8 shows B as a function of $[\text{H}]_0$ for the case where $A_{9,3} = 3.9 \times 10^{-3} \text{ sec}^{-1}$. A least squares analysis of the data of

TABLE V. Values of B (sec^{-1}) giving best fit to observed $\text{OH}^\dagger(9)$ concentrations in 1.1 ± 0.1 Torr Ar.

Experiment number	$10^{-12} [\text{H}]_0$ (atoms cm^{-3})	$10^{-11} [\text{O}_3]_0$ (molecules cm^{-3})	Best fit $10^{-3} B$ (sec^{-1}) for $A_{3,3} =$		Average $10^{-3} B$ (sec^{-1}) for $A_{3,3} =$	
			$3.9 \times 10^{-3} \text{ sec}^{-1}$	0.13 sec^{-1}	$3.9 \times 10^{-3} \text{ sec}^{-1}$	0.13 sec^{-1}
1	1.0	1.9	0.60	16	0.5	14
2		2.9	0.43	11		
3	1.9	2.4	1.20	32	0.9	25
4		5.2	0.55	18		
5	2.6	1.7	0.70	21		
6		3.8	0.35	10	0.5	14
7		4.9	0.35	10		
8	5.7	4.2	1.20	35	1.2	35
9	7.5	8.5	1.00	35		
10		6.1	1.10	42	1.2	40
11		4.3	1.40	42		
12	9.7	8.5	1.10	32	1.1	32
13		3.8	1.10	32		
14	17.2	20.6	1.95	66		
15		14.3	1.90	56	2.6	80
16		11.6	3.90	118		
17	20.4	11.6	5.20	166	4.3	128
18		7.0	3.30	90		
19	22.5	26.4	3.50	114	3.5	114

TABLE VI. Values of B (sec^{-1}) giving best fit to observed $\text{OH}^\dagger(9)$ concentrations when total pressure, nature of carrier gas, and wall coating are changed.

Experiment number	$10^{-12} [\text{H}]_0$ (atoms cm^{-3})	$10^{-11} [\text{O}_3]_0$ (molecules cm^{-3})	Best fit $10^{-3} B$ (sec^{-1}) for $A_{3,3} =$		Average $10^{-3} B$ (sec^{-1}) for $A_{3,3} =$	
			$3.9 \times 10^{-3} \text{ sec}^{-1}$	0.13 sec^{-1}	$3.9 \times 10^{-3} \text{ sec}^{-1}$	0.13 sec^{-1}
Halocarbon wax coated walls						
$P_{\text{tot}} = 0.56 \text{ Torr Ar}$						
1	1.2	1.9	0.45	12	0.45	12
2		5.0	0.45	12		
$P_{\text{tot}} = 2.5 \text{ Torr Ar}$						
3	1.9	2.1	0.60	17	0.55	16
4		4.8	0.50	14		
$P_{\text{tot}} = 1.1 \text{ Torr He}$						
5	1.5	1.9	0.90	24	0.75	20
6		3.6	0.80	21		
7		5.7	0.55	15		
Boric acid coated walls, 1.1 Torr Ar						
8	2.2	5.9	1.23	39	1.6	53
9		5.0	2.20	72		
10		2.7	1.50	48		
11	4.9	6.6	1.10	33	2.0	67
12		4.8	1.18	35		
13		2.4	3.60	133		
14	2.5	3.9	1.00	31	1.5	49
15		2.3	2.05	67		

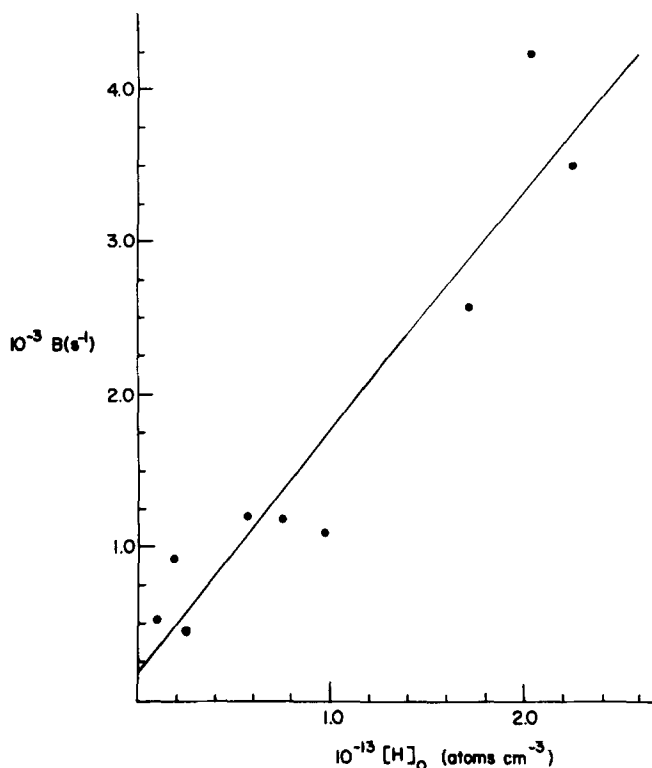


FIG. 8. Values of B (see the text) needed to match observed concentrations of $\text{OH}^\dagger(9)$ in excess H at known initial concentrations of H and O_3 assuming $A_{9,3} = 3.9 \times 10^{-3}$.

Fig. 8 and the comparable plot assuming $A_{9,3} = 0.13 \text{ sec}^{-1}$ gives a slope of $(16 \pm 4) \times 10^{-11}$ and an intercept of $(188 \pm 498) \text{ sec}^{-1}$ if $A_{9,3} = 3.9 \times 10^{-3} \text{ sec}^{-1}$, or for $A_{9,3} = 0.13 \text{ sec}^{-1}$, a slope and intercept of $(5 \pm 1) \times 10^{-9}$ and $(4 \pm 14) \times 10^3 \text{ sec}^{-1}$, respectively.

From Eq. (VIII), the slope of Fig. 8 should be k_2 and the intercept $(k_4[\text{Ar}] + k_{\text{rad}} + k_w)$. Thus, $k_2 = (16 \pm 4) \times 10^{-11}$, assuming $A_{9,3} = 3.9 \times 10^{-3} \text{ sec}^{-1}$, or $(5 \pm 1) \times 10^{-9}$, assuming $A_{9,3} = 0.13 \text{ sec}^{-1}$. The errors quoted represent 2σ ; our estimate of the total uncertainty in the slope, however, is approximately a factor of 2.

While the intercept is within two standard deviations of zero, the results of the quenching studies of $\text{OH}^\dagger(9)$ by CO_2 support the existence of a significant intercept. Thus, if $B = k_2[\text{H}]$, corresponding to a zero intercept in Fig. 8, increasing $[\text{H}]_0$ should increase B and hence decrease the slope of plots such as Fig. 7 proportionately [see Eq. (VII)]. However, increasing $[\text{H}]_0$ from 1.6×10^{12} to 3.9×10^{12} did not significantly lower the slope. In addition, when the conditions were reversed so that $[\text{O}_3]_0 \approx 10[\text{H}]_0 \approx 3 \times 10^{12}$, the slope did not change significantly. Only increasing $[\text{H}]_0$ to $\approx 10^{13}$ resulted in a substantially lowered slope. Thus, while the uncertainty in the intercept is large, it does appear to be nonzero.

A nonzero intercept of the line in Fig. 8 implies that one or more of Reactions (4), (7), and (8) must be important as $[\text{H}]_0$ is lowered to $\sim 10^{12}$. There are two observations which must be considered under these conditions, i.e., that changing the pressure of Ar by a fac-

tor of ~ 5 (Table VI, experiments 1–4) and changing the carrier gas from Ar to He (Table V, experiments 1–4 and Table VI, experiments 5–7) did not substantially alter the observed B values. This suggests that either (1) quenching by the carrier gases is negligible and wall loss is relatively slow so that diffusion to the walls is not rate determining, or (2) loss at the walls is relatively fast and is affected by diffusion rates, and quenching by the carrier gas is significant. In the latter case, the net changes in B caused by changing Ar pressure or carrier gas could cancel out.

The net rate of removal at the halocarbon wax coated walls must occur with a surface recombination coefficient γ (defined⁶⁴ as the fraction of the total number of collisions with the surface which lead to deactivation) which is < 1 . Otherwise, the observed B values would not increase when the walls were coated with boric acid as was observed (see Table V, experiments 3–8 and Table VI, experiments 8–15). Boric acid has been shown⁷⁸ to deactivate $\text{OH}^\dagger$ in $v = 1, 2$ relatively rapidly, and Potter and co-workers⁴⁶ suggested that deactivation of $\text{OH}^\dagger(9)$ occurred on every collision with their boric acid coated walls. (A more recent analysis⁷⁹ of these data, however, suggests that only about one collision in 100 leads to relaxation.) In any event, it seems reasonable to assume that wall loss of $\text{OH}^\dagger(9)$ will be substantially increased for a boric acid wall coating where energy transfer to the polar $\text{B}-\text{OH}$ groups can occur. The increase in B observed here in a boric acid tube is consistent with the work of Spencer and Glass⁷⁸ on the lower vibrational levels $v = 1, 2$, where $k_w < 80 \text{ sec}^{-1}$ in a halocarbon wax coated tube but increased substantially in a boric acid coated tube.

While the wall loss of $\text{OH}^\dagger(9)$ is then less than on every collision in the wax coated tube, suggesting explanation (1) above for the lack of effect of P_{Ar} and changing the carrier gas, k_w could not be determined independent of quenching by the carrier gas in these experiments. This, combined with the large uncertainty in the intercept of Fig. 8, precludes further discussion of the loss processes of $\text{OH}^\dagger(9)$ at low $(\leq 10^{12})[\text{H}]_0$.

Removal of $\text{OH}^\dagger(9)$ in excess O_3

Removal of $\text{OH}^\dagger(9)$ in excess O_3 is more complicated than in excess H because even with $[\text{O}_3]_0/[\text{H}]_0 \geq 10$, H can still be a significant quencher of $\text{OH}^\dagger(9)$. Thus, computer kinetic modeling of the system under these conditions suggests that much of the curvature in the plots of $\ln[\text{OH}^\dagger(9)]$ vs reaction time which we observed in excess O_3 can be attributed to a rapid removal by H , the limiting reagent, whose concentration is changing. In addition, however, it is known from studies in this⁵³ and other⁷³ laboratories that H is regenerated in excess O_3 when $[\text{H}]_0 \geq 2.5 \times 10^{11}$ in the absence of O_2 and when $[\text{H}]_0 \geq 4 \times 10^{11}$ in its presence, although the reaction(s) responsible are not clear.

The observed first order rate constants for decay of $\text{OH}^\dagger(9)$ in a great excess of O_3 are plotted against $[\text{O}_3]_0$ in Fig. 9. The slope of the line is $(1.4 \pm 0.8) \times 10^{-11}$,

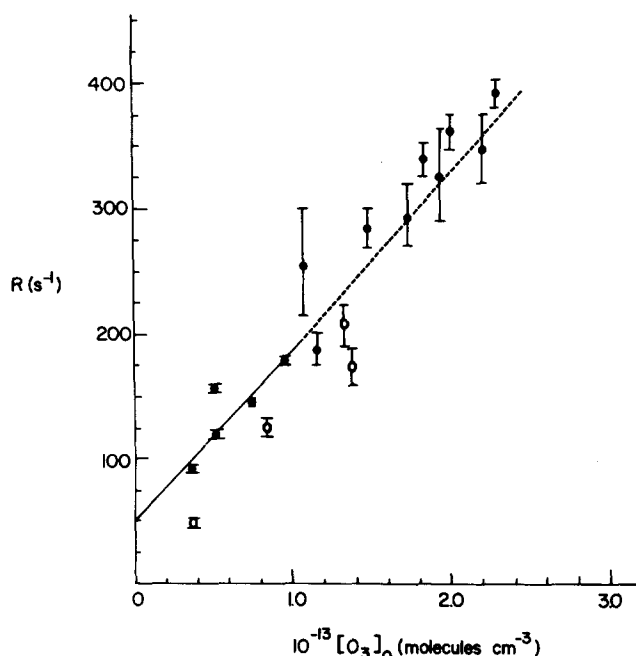


FIG. 9. Observed values of R (see the text) as a function of initial, excess O_3 concentration. $\bullet$, Halocarbon wax coated flow tube, O_3/O_2 mixtures; $\circ$, boric acid coated flow tube and O_3/He mixtures.

significantly less than k_1 . In addition, a nonzero intercept ($51 \pm 44 \text{ sec}^{-1}$) is found. Finally, the rate constants in the boric acid coated flow tube are less than those in the wax coated flow tube.

Because of these indications that a simple reaction scheme analogous to that in excess H may not be applicable in excess O_3 , we have not carried out detailed studies under these conditions. It should be noted, however, that the kinetic behavior observed upon addition of a quencher/reactant was the same as that in excess H , i.e., the concentration of $OH^{\dagger}(9)$ fell, but R remained constant.

DISCUSSION

Possible contribution of bimolecular reactions of $OH^{\dagger}(\nu)$

In the data analysis, the reactions of two $OH^{\dagger}(\nu)$ (often referred to as the bimolecular reaction of $OH^{\dagger}$), leading either to the production or to the loss of $OH^{\dagger}(9)$, were assumed to be negligible. The effect of the bimolecular reaction (9) removing $OH^{\dagger}(9)$ was tested using the computer kinetic model for the conditions of Fig. 4 (experiment 11, Table V) by including the reactions of $OH^{\dagger}(9)$ with itself, with $OH^{\dagger}(1-8)$ (treated as one species), and with ground state OH . No decrease in the $OH^{\dagger}(9)$ concentrations due to Reaction (9) is predicted from this model if k_9 is increased from zero to 1×10^{-10} , assuming the first order rate of removal of $OH^{\dagger}(9)$ by all other processes is 1400 sec^{-1} and using $A_{9,3} = 3.9 \times 10^{-3} \text{ sec}^{-1}$. Even increasing k_9 to the extremely large, and probably unrealistic, value of 1×10^{-9} only lowers the predicted concentrations by 12%. If $A_{9,3} = 0.13 \text{ sec}^{-1}$ and $B = 4.2 \times 10^4 \text{ sec}^{-1}$ is used, increasing k_9 to $1 \times 10^{-9} \text{ sec}^{-1}$ has essentially no effect on the $OH^{\dagger}(9)$

concentrations because of the high rate of removal by other processes needed to match the low $OH^{\dagger}(9)$ concentrations predicted.

For higher concentrations of the limiting reagent O_3 , such bimolecular reactions may become significant. For example, for the conditions of experiment 14, Table V, increasing k_9 from 0 to 1×10^{-10} with a first order rate constant for removal by other processes of 1950 sec^{-1} (i.e., assuming $A_{9,3} = 3.9 \times 10^{-3} \text{ sec}^{-1}$) lowers the predicted $OH^{\dagger}(9)$ concentrations by 14% and increasing it further to 1×10^{-9} decreases it by an additional 29%. While this effect should be manifested in increased B values as $[O_3]_0$ increases at a constant $[H]_0$, the scatter in the results (Tables V and VI) is too large to detect the smaller trend anticipated. Again, little effect ($\leq 2\%$) on the $OH^{\dagger}(9)$ concentrations is predicted if the larger $A_{9,3}$ and corresponding B values are used.

However, the results of the computer kinetic model show that at least for $[O_3]_0 \leq 1 \times 10^{12}$, the contribution of Reaction (9) should be negligible and hence can be ignored.

A similar situation applies to the bimolecular reactions of $OH^{\dagger}(\nu)$ which lead to the production of $OH^{\dagger}(9)$ via energy transfer. Except at the highest concentrations of O_3 used, this source of $OH^{\dagger}(9)$ is expected to be negligible since all vibrational levels of $OH^{\dagger}$ are removed very rapidly by H . In addition, the spacing³⁴ of the vibrational levels rapidly decreases with increasing vibrational level so that in order to be resonant or near resonant, such processes must involve simultaneous multiquantum rotation changes as well, which makes them less probable.⁶⁰ For example, for the conditions of Fig. 4, assuming $A_{9,3} = 3.9 \times 10^{-3} \text{ sec}^{-1}$, the peak concentration of $OH^{\dagger}(1-8)$ predicted for first order rate constants for removal of $OH^{\dagger}(9)$ and $OH^{\dagger}(1-8)$ of 1400 and 700 sec^{-1} , respectively, is $\sim 6 \times 10^{10}$, which occurs at 3 msec. Assuming an extremely large rate constant for the bimolecular reaction to produce $OH^{\dagger}(9)$ of 6×10^{-10} , the instantaneous rate of production of $OH^{\dagger}(9)$ at 3 msec from this reaction is $2 \times 10^{12} \text{ radicals cm}^{-3} \text{ sec}^{-1}$ while its rate of formation from Reaction (1a) at this point is an order of magnitude greater. Only for $[O_3]_0 > 1 \times 10^{12}$ could this reaction become a significant source of $OH^{\dagger}(9)$. If $A_{9,3} = 0.13 \text{ sec}^{-1}$ is assumed, the peak concentration of $OH^{\dagger}(1-8)$ predicted is substantially lower and the bimolecular reaction is predicted to be even less important.

At the higher concentrations, the contribution to the production of $OH^{\dagger}(9)$ from the bimolecular energy transfer, if it occurs, should be greatest at the shortest reaction times where the concentrations of $OH^{\dagger}(1-8)$ are the largest. At longer reaction times, the contribution of this process becomes negligible because of the rapid removal of $OH^{\dagger}(1-8)$. Thus, a substantial contribution to the formation of $OH^{\dagger}(9)$ by the bimolecular energy transfer process should lead to increased concentrations of $OH^{\dagger}(9)$ at short reaction times. The apparent rate constant for decay R of $OH^{\dagger}(9)$ should thus be larger if such processes are important. A slight trend to higher values of R at

$[H]_0 \gtrsim 3 \times 10^{13}$ (and $[O_3]_0 \gtrsim 1 \times 10^{12}$) may be present in Fig. 5 due to this reaction. To minimize the possible contribution of such secondary reactions, the studies to determine B (see above) were carried out with $[H]_0 < 3 \times 10^{13}$.

Effect of $O(^3P)$ production on these results

It is known^{51,54} that under these conditions, substantial concentrations of $O(^3P)$ (~30% of the O_3 reacted) are produced. Their source is not known but may be either Reaction (2b) and the analogous reactions of $OH^{\dagger}(1-8)$ or possibly a second channel^{51,51} in the reaction of H with O_3 , forming $HO_2 + O(^3P)$. Because the bulk of the evidence^{52,54,82} at the present time is against the latter possibility, we did not include it in the computer matching studies of $[OH^{\dagger}(9)]$. The results of studies^{76,83} on the lower vibrational levels ($v=1, 2$) of $OH^{\dagger}$ suggest the rate constant for removal of $OH^{\dagger}(9)$ by $O(^3P)$ is likely to be similar to that for removal by H. However, the net contribution of $O(^3P)$ to the observed rate of removal of $OH^{\dagger}(9)$ is expected to be small under our conditions since H is in great excess and the peak $O(^3P)$ concentration is not reached⁵⁴ until the $OH^{\dagger}(9)$ emission intensity is undetectable. As a result, quenching by $O(^3P)$ was ignored. If subsequent studies show that the second reaction channel does exist, the major effect on the results of this work will be to lower the rate of production of $OH^{\dagger}(9)$ by Reaction (1a) in this system. The values of B needed to match the $[OH^{\dagger}(9)]$ data will then decrease by the same factor as the decrease in k_{1a} [see Eq. (V)].

Comparison to other work

In the first kinetic studies⁴⁶⁻⁴⁹ of $OH^{\dagger}(9)$ formed in Reaction (1), Potter, Coltharp, and Worley applied pseudo-first order kinetics to its decay in a fast flow discharge system similar to that used here. By studying the rates of decay of $OH^{\dagger}(9)$ as a function of the added quencher/reactant concentration, they obtained absolute rate constants for deactivation plus reaction, where possible. In addition, as discussed above, the radiative lifetime of $OH^{\dagger}(9)$ was determined^{46,47} and rate constants for the reaction of the lower vibrational levels $v=2-8$ with ozone were obtained.⁴⁷

The experimental system used in the present studies is similar to that of Potter and co-workers, except that the flow tube diameter is smaller (2.5 vs 9.5 cm) and the wall coating for most of our experiments was halocarbon wax rather than boric acid. In addition, their experiments were carried out in excess O_3 and in He carrier gas at total pressures of ~0.3 Torr. The similarity between the two systems, however, is such that it is puzzling that they observed a change in the first order rate constant for decay upon addition of most quencher/reactants, consistent with pseudo-first order kinetics, whereas we find that R remains constant and only the concentrations of $OH^{\dagger}(9)$ decrease. They report behavior similar to that observed here when SO_2 , H_2S , or H_2O were added but attribute it to a reaction with one of the initial reactants, probably ozone. However, all of these species react with O_3 extremely

slowly ($k < 10^{-18}$).⁸⁴ The limiting reagent H also reacts slowly with SO_2 and H_2O and its rate constant for reaction with H_2S is not extremely large ($k_{298} = 7 \times 10^{-13}$).⁸⁵

To test the kinetic behavior expected under their reaction conditions, we input to our computer kinetic model initial concentrations of H and O_3 of 3×10^{12} and 1×10^{13} , respectively, typical of their experiments,⁴⁹ and their rate constant^{46,47} for removal of $OH^{\dagger}(9)$ by O_3 of 7.7×10^{-12} . The effect of an added quencher/reactant was then mimicked by adding various first order rate constants for decay from 0 to 1000 sec^{-1} , on top of that due to its reaction with O_3 . The observed rates of decay of $OH^{\dagger}(9)$ predicted by the computer study increased as the additional first order rate constants for decay R increased from 0 to 100 sec^{-1} ; however, the change in R predicted was less than that used as input. For example, inputs of 10, 23, and 50 sec^{-1} on top of that due to reaction with O_3 gave predicted changes in R of only 8, 18, and 39 sec^{-1} , respectively. With $R \gtrsim 300 \text{ sec}^{-1}$, the predicted first order rate constants for decay essentially remained constant and only the concentrations decreased.

The observation of Potter and co-workers that R changed upon addition of an added quencher/reactant thus implies that, in their system, losses of $OH^{\dagger}(9)$ other than that due to reaction with O_3 were $< 300 \text{ sec}^{-1}$. However, our computer studies indicate that even then their observed changes in R for $OH^{\dagger}(9)$ may be too low. In addition, it should be noted that the changes in R that they observed⁴⁹ were all relatively small ($\leq 23 \text{ sec}^{-1}$) on top of decay rates in the absence of added quencher/reactant of 60–80 sec^{-1} . Such relatively small changes may limit the accuracy of the measurements.

However, it is seen in Table IV that the *relative* rate constants derived here are consistent with those of Potter and co-workers⁴⁶⁻⁴⁹ for $X = CO_2$ and Ar although our value for N_2 is much smaller than theirs.

Our upper limits derived for $X = \text{Ar}$ and N_2 relative to O_2 are much smaller than those of Streit and Johnston,³⁸ however. In the latter study,³⁸ the chemiluminescent emission intensities from various vibrational levels produced when H and O_3 were mixed at low pressures (10^{-3} – 10^{-1} Torr) in a large sphere in the presence of added quenchers/reactants were studied to obtain absolute rate constants for removal of $OH^{\dagger}(4-9)$. The concentration of hydrogen atoms was not measured, and because rapid quenching of $OH^{\dagger}$ by H had not yet been observed,⁷⁸ removal of $OH^{\dagger}$ by this species was not included in the reaction scheme. The results of our studies indicate that it is in fact significant, but why this would lead to high values of the *relative* rate constants is not clear.

The rotational temperature at their relatively low pressures was ~1500 °K whereas ours is room temperature (Table I). While this might account for the differences in absolute values of the rate constants, the discrepancy in the relative values, especially for such simple deactivators as Ar and N_2 , is surprisingly large.

Mechanisms of removal of OH[†](9) by H

Several efficient mechanisms exist for deactivation of OH[†](9) by H. For example, OH[†]($v=1, 2$) has been shown⁷⁸ to be relaxed by H with rate constants of 2.7 and 3.3×10^{-10} , respectively. As discussed above, the rate constant for removal of OH[†](9) by H obtained from the present studies depends on the absolute value of $A_{9,3}$ and for the two particular values considered here one estimates $k_2 \approx 2 \times 10^{-10}$ and 5×10^{-9} assuming $A_{9,3} = 3.9 \times 10^{-3}$ and 0.13 sec^{-1} , respectively. The latter value is approximately ten times the gas kinetic collision frequency. While this is somewhat surprising, extremely large rate constants, faster than diffusion controlled, have also been observed for the deactivation of such species as HF[†] by strongly interacting collision partners.⁸⁶ This unusual result has been proposed to arise from a rapid, collision-induced, $V \rightarrow R$ intramolecular energy redistribution within the vibrationally excited species.⁸⁷ This type of mechanism was suggested⁸⁸⁻⁹⁰ some years ago and has been observed⁹¹ in electronically excited OH ($A^2\Sigma^+$). Of direct relevance to this work, Robinson and co-workers^{13,14} have shown that the relative intensities of pure rotational laser emissions from $v=0-3$ of OH($X^2\Pi_{1/2}$) and from $v=0-2$ of OD($^2\Pi_{1/2}$) are consistent with a rapid transition from lower rotational levels of an upper vibrational state into higher rotational levels of a lower vibrational state, where the two states are close to each other in total energy. Any small energy mismatch between the two levels is thought to be removed by collisional $R \rightarrow T$ processes.

In the case of OH[†](9), several rotational levels of lower vibrational states ($v=0-8$) lie within 30 cm^{-1} of one of the rotational levels $K=1-10$ of $v=9$ which are populated in the initial reaction³⁷ so that such a mechanism, resulting in extremely large values of k_2 , is not implausible.

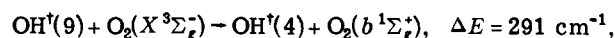
On the other hand, the lower value of k_2 of 2×10^{-10} , which results if $A_{9,3} = 3.9 \times 10^{-3} \text{ s}^{-1}$ is assumed, is approximately equal to that for OH[†]($v=1, 2$) + H⁷⁸ when our estimate of the factor of 2 uncertainty in k_2 is taken into account. A rate constant k_2 of the order of 10^{-10} is reasonable if deactivation occurs via the formation of a bound, highly excited HOH intermediate which would serve to randomize the vibrational energy before re-dissociation. Such a mechanism is consistent with the rapidity with which ground state OH undergoes an exchange reaction with D ($k = 1.3 \pm 0.3 \times 10^{-10}$).⁹² In addition, there is a body of experimental and theoretical evidence^{5-12,93,94} showing that similar deactivating processes, such as O + NO[†] in which intermediate complex formation can occur, generally proceed quite rapidly. A rate constant for relaxation of $v=9$ which is not substantially greater than that for $v=1$ and 2, while somewhat unexpected, might be possible if the highly excited intermediate complex dissociated so rapidly that randomization of the energy was not complete. This has been suggested,⁷⁸ for example, in the relaxation of OH[†](v) by NO.

Range of absolute rate constants

The absolute magnitude of the rate constants for re-

moval of OH[†](9) by O₂ and CO₂ are important in assessing likely mechanisms of energy transfer. As discussed above, absolute values of k_{10} cannot be obtained from this work unless $A_{9,3}$ is known. An estimate of the absolute values of k_{10} assuming each of the two values of $A_{9,3}$ followed in this paper can be calculated from Figs. 7 and 8. For example, the slopes of the lines in Fig. 7(a) for X = CO₂ and O₂ are 2.0 and 0.72×10^{-15} , respectively. From Fig. 8, under these conditions, $B \approx 5 \times 10^2 \text{ sec}^{-1}$ if $A_{9,3} = 3.9 \times 10^{-3} \text{ sec}^{-2}$ and $B \approx 1.2 \times 10^4 \text{ sec}^{-1}$ if $A_{9,3} = 0.13 \text{ sec}^{-1}$. From Eq. (VII), then, $k_{10} = 1 \times 10^{-12}$ ($A_{9,3} = 3.9 \times 10^{-3} \text{ sec}^{-1}$) or 2×10^{-11} ($A_{9,3} = 0.13 \text{ sec}^{-1}$) for CO₂ and $k_{10} = 4 \times 10^{-13}$ ($A_{9,3} = 3.9 \times 10^{-3} \text{ sec}^{-1}$) to 1×10^{-11} ($A_{9,3} = 0.13 \text{ sec}^{-1}$) for O₂. It is stressed, however, that these values may not necessarily even place a limit on the true values of k_{10} since the true value of $A_{9,3}$ may not lie between the two published values used to derive these estimates for k_{10} .

If these estimates do bracket the true values of k_{10} , they imply that energy transfer from OH[†](9) to both O₂ and CO₂ is relatively efficient. In the case of O₂ this may be due to the energy transfer process



which may become near resonant when possible rotational changes are taken into account. No such process is possible for OH[†](1), which has been shown to be only slowly deactivated by O₂ ($k < 4 \times 10^{-13}$).⁹⁵ In the case of CO₂, a one quantum energy transfer from OH[†] in $v=9$ to $v=8$ could produce the (00⁰1) state or the (20⁰0) state, with band center energy defects (i.e., the difference in energy between the quantum being transferred and the vibrational quantum of the acceptor quenching gas, assuming a rotationless transition) of only -112 and $+100 \text{ cm}^{-1}$.⁹⁶ These energy discrepancies may be even smaller when possible simultaneous rotational transitions are taken into account, and thus efficient energy transfer from OH[†](9) is not unreasonable.

CONCLUSIONS

OH[†](9) formed by the reaction of H with O₃ is removed sufficiently rapidly in a fast flow discharge system that the observed exponential decays reflect a combination of continuing formation and decay. Thus, pseudo-first order kinetics cannot be applied to obtain absolute rate constants for removal of this highly vibrationally excited species. However, accurate relative rate constants can be obtained and values are reported for CO₂, N₂, and Ar relative to O₂.

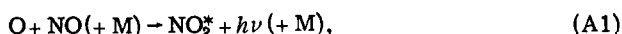
Removal of OH[†](9) by H predominates at higher values of $[\text{H}]_0$ ($\sim 10^{13}$). The absolute rate constant for this process as well as for quenching by O₂, CO₂, etc. depends on the value assumed for the Einstein A factor for the (9,3) transition, which is controversial. Since the Einstein A factors are used in computer kinetic models of the upper stratosphere and mesosphere to determine the role of OH[†] in the chemistry of this region²⁴⁻³⁰ as well as to estimate the concentration of other species such as H,⁹⁷ an independent experimental determination of these A factors is extremely important.

ACKNOWLEDGMENTS

The authors are grateful to the National Science Foundation (Grant No. CHE 76-23577) and to The Donors of the Petroleum Research Foundation administered by the American Chemical Society (Grant No. 3080-G2), for support of this work. We also thank G. C. Pimentel for helpful discussions, R. Ammari for the calculation of the rotational energy levels within each vibrational manifold, W. P. L. Carter and W. Rucker for computer assistance, and J. N. Pitts, Jr. and M. J. Ezell for comments on the manuscript.

APPENDIX

The emission intensity from



follows the relationship

$$I_{\text{NO}_2^*} = \beta T I_0 [\text{O}][\text{NO}], \quad (\text{AI})$$

where β is a geometrical factor taking into account that only a small portion of the total light emitted is detected. This ultimately cancels out in the analysis, as does T which corrects for the fact that the filter does not transmit 100% of the light over its range. (T was, however, estimated to be ≈ 0.36 using the transmittance of the filter measured in this laboratory.)

I_0 has been measured⁹⁸⁻¹⁰¹ from 387.5 nm to 3.3 μ by several groups. Taking $I_0 = 11.2 \times 10^{-17}$ over the entire spectral range,¹⁰⁰ I_0 was estimated to be 1.42×10^{-18} in the region 622.5–630.0 nm, the limits of our 626 nm filter. (The experiments in which I_0 was determined over the entire spectral region were carried out in O_2 , while the carrier gas in these experiments was Ar. However, the values of I_0 in O_2 and Ar are sufficiently similar¹⁰¹ that no correction was made to the literature value of I_0 .)

The emission intensity from $\text{OH}^*(9)$ observed through the 626 nm filter is given by

$$I_{9,3} = I_{9,3}^{\text{true}} \beta T P \\ = A_{9,3} [\text{OH}^*(9)] \beta T P, \quad (\text{AII})$$

where $A_{9,3}$ is the Einstein A factor for the (9,3) transition, β and T are as defined above, and P is the fraction of the total (9,3) band falling within the limits of the filter. P was estimated to be 0.52 from a spectrum of the (9,3) band taken using the Jarrell-Ash monochromator and EMI 9659QB photomultiplier. This spectrum was corrected for the spectral response of the detection system which was measured using an NBS calibrated quartz iodine lamp.

Combining Eqs. (AI) and (AII), one obtains,

$$[\text{OH}^*(9)] = 2.73 \times 10^{-18} \frac{[\text{O}][\text{NO}]}{I_{\text{NO}_2^*}} \frac{I_{9,3}}{A_{9,3}}. \quad (\text{AIII})$$

Thus, if $([\text{O}][\text{NO}]/I_{\text{NO}_2^*})$ and $I_{9,3}$ are measured and $A_{9,3}$ is known, $[\text{OH}^*(9)]$ can be calculated.

The factor $([\text{O}][\text{NO}]/I_{\text{NO}_2^*})$ was determined by measuring the observed emission intensity from NO_2 , i.e., $I_{\text{NO}_2^*}$, at known concentrations of O and NO. The con-

centration of oxygen atoms was determined by calibrating the VUV resonance lamp for $\text{O}(^3P)$ by adding small, known amounts of NO to an excess of N atoms as described in detail elsewhere.^{51,54} The flow of N_2 through the microwave discharge was then lowered until $[\text{N}] \approx (1-3) \times 10^{12}$ and excess NO was added through the moveable inlet to convert all of the N to $\text{O}(^3P)$. Care was taken to ensure that a sufficiently large excess of NO was present to bring



to completion upstream of the detection port. The $\text{O}(^3P)$ signal observed in excess NO could then be converted to a concentration using the calibration curve generated under the reverse conditions. The concentrations of $\text{O}(^3P)$ so obtained generally agreed well with those obtained by extrapolating a plot of $I_{\text{NO}_2^*}$ vs $[\text{NO}]$ back to zero emission intensity, at which point $[\text{N}]_0 = [\text{NO}]_0 = [\text{O}]$ (Fig. 3). The plots of $I_{\text{NO}_2^*}$ against $[\text{NO}]$ were all linear over the range of NO concentrations used since the loss of $\text{O}(^3P)$ due to reactions (A1) and



was always $< 2\%$ and the NO remains essentially constant because it is regenerated by Reaction (A3).

A similar calibration was carried out using the 519 nm filter. The $\text{OH}^*(9)$ data so obtained were used mainly as a check on the 626 nm data since the intensity of the (9,2) band at 519 nm was approximately a factor of 10 weaker than the (9,3) band.

¹J. C. Polanyi, Acc. Chem. Res. 5, 161 (1972) and references therein.

²R. D. Levine and R. B. Bernstein, *Molecular Reaction Dynamics* (Oxford University, New York, 1974) and references therein.

³J. H. Birely and J. L. Lyman, J. Photochem. 4, 269 (1975).

⁴J. Wolfrum, Ber. Bunsenges. Phys. Chem. 81, 114 (1977).

⁵I. W. M. Smith, Acc. Chem. Res. 9, 161 (1976) and references therein.

⁶S. H. Bauer, Chem. Rev. 78, 147 (1978) and references therein.

⁷D. Secrest, Annu. Rev. Phys. Chem. 24, 379 (1973).

⁸C. B. Moore, Acc. Chem. Res. 6, 323 (1973).

⁹E. Weitz and G. Flynn, Annu. Rev. Phys. Chem. 25, 275 (1974).

¹⁰S. Ormonde, Rev. Mod. Phys. 47, 193 (1975).

¹¹J. D. Lambert, *Vibrational and Rotational Relaxation in Gases* (Clarendon, Oxford, 1977) and references therein.

¹²G. A. Fisk and F. F. Crim, Acc. Chem. Res. 10, 73 (1977).

¹³G. D. Downey, D. W. Robinson, and J. H. Smith, J. Chem. Phys. 66, 1685 (1977).

¹⁴J. H. Smith and D. W. Robinson, J. Chem. Phys. 68, 5474 (1978).

¹⁵A. B. Callear and H. E. Van Den Bergh, Chem. Phys. Lett. 8, 17 (1971).

¹⁶E. Vietzke, H. I. Schiff, and K. H. Welge, Chem. Phys. Lett. 12, 429 (1971).

¹⁷I. W. M. Smith, in *Chemiluminescence and Bioluminescence*, edited by M. J. Cormier, D. M. Hercules, and J. Lee (Plenum, New York, 1973), pp. 43–59.

¹⁸See, for example, *Proceedings of the International Conference*

- on *Tunable Lasers and Applications in Optical Science*, edited by A. Mooradian, T. Jaeger, and P. Stokseth (Springer, New York, 1976), Vol. 3.
- ¹⁹Throughout this paper, vibrationally excited OH in level v is written as OH[†](v); OH[†] refers to vibrationally excited OH in all levels $v > 0$ and OH is used to designate ground state OH.
 - ²⁰See, for example, R. Atkinson, K. R. Darnall, A. C. Lloyd, A. M. Winer, and J. N. Pitts, Jr., in *Advances in Photochemistry*, edited by J. N. Pitts, Jr., G. S. Hammond, and K. Gollnick (Wiley, New York, 1979), Vol. 11, pp. 375–488; D. D. Drysdale and A. C. Lloyd, *Oxidation Combustion Review*, edited by C. F. H. Tipper (Elsevier, Amsterdam, 1970), Vol. 4, pp. 157–250; W. E. Wilson, Jr., J. Phys. Chem. Ref. Data 1, 535 (1972) and references therein.
 - ²¹B. J. Finlayson, J. N. Pitts, Jr., and R. Atkinson, J. Am. Chem. Soc. 96, 5356 (1974) and references therein; J. T. Herron and R. E. Huie, J. Am. Chem. Soc. 99, 5430 (1977); H. Niki, in "Chemical Kinetic Data Needs for Modeling the Lower Troposphere," edited by J. T. Herron, R. E. Huie, and J. A. Hodgeson, Natl. Bur. Stand. (U.S.) Spec. Publ. 557 (1979); M. C. Dodge and R. R. Arnts, Int. J. Chem. Kinet. 11, 399 (1979).
 - ²²B. B. Krieger and R. H. Kummier, J. Phys. Chem. 81, 2493 (1977) and references therein.
 - ²³B. J. Finlayson and J. N. Pitts, Jr., Science 192, 111 (1976); B. J. Finlayson-Pitts and J. N. Pitts, Jr., Adv. Environ. Sci. Technol. 7, 75 (1977).
 - ²⁴J. Heicklen, *Atmospheric Chemistry* (Academic, New York, 1976), Chap. 2 and references therein.
 - ²⁵"Chlorofluoromethanes and the Stratosphere," edited by R. D. Hudson, NASA Ref. Publ. 1010 (1977) and references therein.
 - ²⁶A. F. Nagy, S. C. Liu, and D. J. Baker, Geophys. Res. Lett. 3, 731 (1976).
 - ²⁷G. E. Streit, G. Z. Whitten, and H. S. Johnston, Geophys. Res. Lett. 3, 521 (1976).
 - ²⁸E. J. Llewellyn and B. H. Long, Can. J. Phys. 56, 581 (1978) and references therein.
 - ²⁹E. J. Llewellyn, B. H. Long, and B. H. Solheim, Planet. Space Sci. 26, 525 (1978).
 - ³⁰H. Takahashi and P. P. Batista, Planet. Space Sci. 28, 559 (1980).
 - ³¹C. C. Wang and L. I. Davis, Jr., Phys. Rev. Lett. 32, 349 (1974); D. D. Davis, W. Heaps, and T. J. McGee, Geophys. Res. Lett. 3, 331 (1976); J. G. Anderson, *ibid.* 3, 165 (1976); P. M. Selzer and C. C. Wang, J. Chem. Phys. 71, 3786 (1979) and references therein.
 - ³²A. B. Meinel, Astrophys. J. 111, 207, 433, 555 (1950).
 - ³³F. E. Bunn and H. P. Gush, Can. J. Phys. 50, 213 (1972); A. W. Harrison and D. J. W. Kendall, Planet. Space Sci. 21, 1731 (1973); M. V. Shagaev, J. Atmos. Terrest. Phys. 36, 367 (1974); B. P. Potapov, Planet. Space Sci. 23, 1346 (1975); A. W. Peterson and L. M. Kieffaber, Nature (London) 257, 649 (1975).
 - ³⁴V. I. Krassovsky, N. N. Shefov, and V. I. Yarin, Planet. Space Sci. 9, 883 (1962).
 - ³⁵R. L. Gattinger and A. Vallance Jones, Can. J. Phys. 52, 2343 (1974).
 - ³⁶D. D. Meisel and R. A. Berg, Icarus 23, 454 (1974).
 - ³⁷See for example, J. C. Polanyi and J. J. Sloan, Int. J. Chem. Kinet. Symp. 1, 51 (1975); P. E. Charters, R. G. MacDonald, and J. C. Polanyi, Appl. Opt. 10, 1747 (1971).
 - ³⁸G. E. Streit and H. S. Johnston, J. Chem. Phys. 64, 95 (1976) and references therein.
 - ³⁹A. W. Harrison and D. J. W. Kendall, Planet. Space Sci. 21, 1731 (1973); V. G. Velculescu, Z. Phys. 237, 69 (1970); R. E. Murphy, J. Chem. Phys. 54, 4852 (1971) and references therein.
 - ⁴⁰D. R. Bates and M. Nicolet, J. Geophys. Res. 55, 301 (1950).
 - ⁴¹J. D. McKinley, D. Garvin, and M. J. Boudart, J. Chem. Phys. 23, 784 (1955).
 - ⁴²T. M. Cawthorn, Jr. and J. D. McKinley, Jr., J. Chem. Phys. 25, 585 (1956).
 - ⁴³F. Kraus, Z. Naturforsch. Teil A 12, 479 (1957).
 - ⁴⁴D. Garvin, J. Am. Chem. Soc. 81, 3173 (1959).
 - ⁴⁵D. Garvin, H. P. Broida, and H. J. Kostkowski, J. Chem. Phys. 32, 880 (1960).
 - ⁴⁶A. E. Potter, Jr., R. N. Coltharp, and S. D. Worley, J. Chem. Phys. 54, 992 (1971).
 - ⁴⁷R. N. Coltharp, S. D. Worley, and A. E. Potter, Appl. Opt. 10, 1786 (1971).
 - ⁴⁸S. D. Worley, R. N. Coltharp, and A. E. Potter, J. Chem. Phys. 55, 2608 (1971).
 - ⁴⁹S. D. Worley, R. N. Coltharp, and A. E. Potter, Jr., J. Phys. Chem. 76, 1151 (1972).
 - ⁵⁰B. A. Blackwell, J. C. Polanyi, and J. J. Sloan, Chem. Phys. 24, 25 (1977) and references therein.
 - ⁵¹B. J. Finlayson-Pitts and T. E. Kleindienst, J. Chem. Phys. 70, 4804 (1979).
 - ⁵²C. J. Howard and B. J. Finlayson-Pitts, J. Chem. Phys. 72, 3842 (1980).
 - ⁵³B. J. Finlayson-Pitts and T. E. Kleindienst (unpublished data).
 - ⁵⁴B. J. Finlayson-Pitts, T. E. Kleindienst, M. J. Ezell, and D. W. Toohy, J. Chem. Phys. 74, 4533 (1981).
 - ⁵⁵The Einstein A factors A_{mn} for the transition from the m th to the n th level are related to the mean radiative lifetime of the m th level τ_m by $\tau_m^{-1} = \sum_{n=0}^{m-1} A_{mn}$.
 - ⁵⁶F. H. Mies, J. Mol. Spectrosc. 53, 150 (1974).
 - ⁵⁷F. Stuhl and H. Niki, J. Chem. Phys. 57, 3671 (1972).
 - ⁵⁸T. E. Kleindienst and B. J. Finlayson-Pitts, Chem. Phys. Lett. 61, 300 (1979) and references therein.
 - ⁵⁹M. A. A. Clyne and D. H. Stedman, Trans. Faraday Soc. 62, 2164 (1966).
 - ⁶⁰M. A. A. Clyne and B. A. Thrush, Discuss. Faraday Soc. 33, 139 (1962) and references therein.
 - ⁶¹P. P. Bemand and M. A. A. Clyne, J. Chem. Soc. Faraday Trans. 2 69, 1643 (1973).
 - ⁶²M. Griggs, J. Chem. Phys. 49, 857 (1968).
 - ⁶³R. V. Poirier and R. W. Carr, Jr., J. Phys. Chem. 75, 1593 (1971).
 - ⁶⁴M. F. R. Mulcahy, *Gas Kinetics* (Halsted, New York, 1973), Chap. 4 and references therein.
 - ⁶⁵J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954).
 - ⁶⁶R. L. Brown, J. Res. Natl. Bur. Stand. 83, 1 (1978).
 - ⁶⁷R. J. Cvetanovic, R. P. Overend, and G. Paraskevopoulos, Int. J. Chem. Kinet. Symp. 1, 249 (1975); R. J. Cvetanovic and D. L. Singleton, Int. J. Chem. Kinet. 9, 481, 1007 (1977); R. J. Cvetanovic, D. L. Singleton, and G. Paraskevopoulos, J. Phys. Chem. 83, 50 (1979) and references therein.
 - ⁶⁸P. R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences* (McGraw-Hill, New York, 1969) and references therein.
 - ⁶⁹E. M. Pugh and G. H. Winslow, *The Analysis of Physical Measurements* (Addison-Wesley, Reading, Mass., 1966) and references therein.
 - ⁷⁰L. F. Phillips and H. I. Schiff, J. Chem. Phys. 37, 1233 (1962).
 - ⁷¹M. A. A. Clyne and P. B. Monkhouse, J. Chem. Soc. Faraday Trans. 2 73, 298 (1977).
 - ⁷²J. H. Lee, J. V. Michael, W. A. Payne, and L. J. Stief, J. Chem. Phys. 69, 350 (1978).
 - ⁷³L. F. Keyser, J. Phys. Chem. 83, 645 (1979).
 - ⁷⁴K. Cashion, J. Mol. Spectrosc. 10, 182 (1963).
 - ⁷⁵*Mathematical Methods for Digital Computers*, edited by A. Ralston and H. S. Wilf (Wiley, New York, 1960), pp. 95–109; A. Ralston, *Runge-Kutta Methods with Minimum Error Bounds* (MTAC, 1962), Vol. 16, ISS80.
 - ⁷⁶C. W. Gear, Commun. ACM 14, 1976 (1971).
 - ⁷⁷W. P. L. Carter, A. C. Lloyd, J. L. Sprung, and J. N.

- Pitts, Jr., *Int. J. Chem. Kinet.* **11**, 45 (1979).
- ⁷⁸J. E. Spencer and G. P. Glass, *Chem. Phys.* **15**, 35 (1976).
- ⁷⁹R. H. Frisbee and R. C. Millikan, *Chem. Phys. Lett.* **36**, 23 (1975).
- ⁸⁰M. Lev-on, W. E. Palke, and R. C. Millikan, *Int. J. Chem. Kinet.* **5**, 753 (1973); *Chem. Phys. Lett.* **24**, 59 (1974); D. C. Richman, M. Lev-on, and R. C. Millikan, *Int. J. Chem. Kinet.* **7**, 33 (1975).
- ⁸¹A. P. Force and J. R. Wiesenfeld, *J. Chem. Phys.* **74**, 1718 (1981).
- ⁸²N. Washida, H. Akimoto, and M. Okuda, *J. Chem. Phys.* **72**, 5781 (1980).
- ⁸³J. E. Spencer, H. Endo, and G. P. Glass, *16th Symposium (International) Combustion* (The Combustion Institute, Pittsburgh, 1977), pp. 829-839; J. E. Spencer and G. P. Glass, *Int. J. Chem. Kinet.* **11**, 97, 111 (1977).
- ⁸⁴"Reaction Rate and Photochemical Data for Atmospheric Chemistry-1977," edited by R. F. Hampson, Jr. and D. Garvin, *Natl. Bur. Stand. (U.S.) Spec. Publ.* **513** (1978) and references therein.
- ⁸⁵M. J. Kurylo, N. C. Peterson, and W. Braun, *J. Chem. Phys.* **54**, 943 (1971).
- ⁸⁶G. C. Pimentel (personal communication).
- ⁸⁷E. Cuellar, J. H. Parker, and G. C. Pimentel, *J. Chem. Phys.* **61**, 422 (1974); E. Cuellar and G. C. Pimentel, *ibid.* **71**, 1385 (1979).
- ⁸⁸T. L. Cottrell and A. J. Matheson, *Trans. Faraday Soc.* **58**, 2336 (1962); **59**, 824 (1963); T. L. Cottrell, R. C. Dobbie, J. McLain, and A. W. Read, *ibid.* **60**, 241 (1964).
- ⁸⁹C. B. Moore, *J. Chem. Phys.* **43**, 2979 (1965).
- ⁹⁰H. K. Shin, *J. Phys. Chem.* **75**, 1079 (1971).
- ⁹¹K. H. Welge, S. V. Filseth, and J. Davenport, *J. Chem. Phys.* **53**, 502 (1970).
- ⁹²J. J. Margitan, F. Kaufman, and J. G. Anderson, *Chem. Phys. Lett.* **34**, 485 (1975).
- ⁹³M. Quack and J. Troe, *Ber. Bunsenges. Phys. Chem.* **79**, 170 (1975); **81**, 160 (1977) and references therein.
- ⁹⁴R. P. Fernando and I. W. M. Smith, *Chem. Phys. Lett.* **66**, 218 (1979).
- ⁹⁵D. H. Jaffer and I. W. M. Smith, *Faraday Discuss. Chem. Soc.* **67**, 212 (1979).
- ⁹⁶G. Herzberg, *Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules* (Van Nostrand, Princeton, 1945).
- ⁹⁷W. F. J. Evans and E. J. Llewellyn, *J. Geophys. Res.* **78**, 323 (1973).
- ⁹⁸A. Fontijn, C. B. Meyer, and H. I. Schiff, *J. Chem. Phys.* **40**, 64 (1974); *Chemical Reactions in the Lower and Upper Atmosphere* (Interscience, New York, 1961), pp. 239-254.
- ⁹⁹M. Vanpee, K. D. Hill, and W. R. Kineyko, *AIAA J.* **9**, 135 (1971).
- ¹⁰⁰M. F. Golde, A. E. Roche, and F. Kaufman, *J. Chem. Phys.* **59**, 3953 (1973).
- ¹⁰¹K. H. Becker, W. Groth, and D. Thran, *Chem. Phys. Lett.* **15**, 215 (1972).