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The production of $O(^3P)$ and ground state OH in the reaction of hydrogen atoms with ozone

B. J. Finlayson-Pitts,^{a)} T. E. Kleindienst,^{b)} M. J. Ezell, and D. W. Toohey

Department of Chemistry, California State University, Fullerton, Fullerton, California 92634

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The production of significant concentrations of $O(^3P)$ in the gas phase reaction of hydrogen atoms with ozone in a fast flow discharge system at 1.1 ± 0.1 Torr total pressure in Ar and at room temperature has been reported earlier. These yields were observed to be independent of the concentration of known deactivators of $OH^{\dagger}$ ($v = 9$) such as O_2 and CO_2 . We report here the results of detailed studies of the yields of $O(^3P)$ and ground state $OH(X^2\pi_1, v=0)$ (OH) using resonance fluorescence under a wide variety of reaction conditions. It is shown that the highest yields of $O(^3P)$, $27 \pm 2\%$ of the calculated loss of O_3 , are observed when H is present in excess and the flow tube is coated with a halocarbon wax. The yields are substantially lower when O_3 is present in excess and increases as $[O_3]_0$ increases. In addition, in an excess of either reagent, the $O(^3P)$ yields are lower when the walls of the flow tube are coated with boric acid, which is known to deactivate the vibrationally excited $OH^{\dagger}$ produced in the initial reaction of H with O_3 . Addition of NO decreased the yield of $O(^3P)$, and increased the yield of OH. These results suggest that secondary reactions of $OH^{\dagger}$, likely with H and O_3 , are responsible for the production of $O(^3P)$, and that a second primary reaction channel, $H + O_3 \rightarrow HO_2 + O(^3P)$ [Eq. (1b)] accounts for $\leq 2\%$ of the net reaction.

INTRODUCTION

The reaction of hydrogen atoms with ozone is important in a number of areas including chemical dynamics,¹⁻⁴ the chemistry of the upper atmosphere,⁵⁻¹⁰ and in some oxidation and combustion systems.¹¹⁻¹³ It has been known for a number of years¹⁴⁻²⁰ that it produces the hydroxyl free radical in upper vibration-rotation levels of the ground electronic state:

Studies of this reaction have generally concentrated either on the product $OH(X^2\pi_1, v \leq 9)$ because of the unusual efficiency with which the reaction exothermicity is channeled into vibrational energy,^{1-3,21} or on the overall reaction kinetics^{22,23} which are important in establishing the role of this reaction in the upper stratosphere and mesosphere.

Until recently,²⁴ the alternate reaction path

apparently had not been considered. In our initial studies communicated earlier,²⁴ we reported the observation of significant concentrations of $O(^3P)$ in this system. The $O(^3P)$ was formed extremely rapidly and the yield was insensitive to the addition of such molecules as CO_2 and O_2 which are known²⁵ to deactivate $OH^{\dagger}(9)$ ²⁶ under these conditions, and which from the literature^{21,27} were expected to deactivate the lower vibrational levels as well. On this basis we suggested Reaction (1b) as one possible source of the $O(^3P)$, although rapid secondary reactions of the $OH^{\dagger}(v)$ produced in Reaction (1a) could not be excluded with certainty.

A subsequent direct search²⁸ for ground state $HO_2(^2A'')$, the second product in Reaction (1b), by laser magnetic resonance failed to detect this species and an upper lim-

it of 3% of the overall reaction of H with O_3 was established for the contribution of Reaction (1b). An indirect search²⁹ for HO_2 carried out simultaneously by another group by looking for $O_2(^1\Delta_g)$, which should have been produced by the reaction of H with HO_2 , placed an upper limit of 6% on the contribution of Reaction (1b) to the overall reaction.

We report here the results of detailed studies of the effects of changing the wall coating and the reaction conditions on the yields of $O(^3P)$. In addition, the yields of ground state OH were investigated and the effect of adding NO on both the OH and $O(^3P)$ yields studied. Finally, the decay of H with $[H]_0 \approx (2-3)[O_3]_0$ was followed. These results, taken in conjunction with work in this²⁵ and other laboratories^{21,30-33} on the reactions of $OH^{\dagger}(v)$, place an upper limit of 2% on the contribution of Reaction (1b) to the net reaction. The most likely sources of the $O(^3P)$ are the reactions of $OH^{\dagger}(v)$ with H, and under some conditions, with O_3 .

EXPERIMENTAL

The apparatus, described in detail elsewhere,^{25,34} is a conventional fast-flow discharge system with a double concentric movable inlet and fixed detection ports. Atomic hydrogen and oxygen, as well as ground state hydroxyl radicals, are detected using the resonance fluorescence technique as described earlier.^{25,34}

In the first series of experiments, where $O(^3P)$ was determined as a function of reaction time, the initial concentration of hydrogen atoms was first established by titration with an NO_2 /Ar mixture of known concentration by following the Lyman- α resonance fluorescence at 121.6 nm. The wavelength setting of the monochromator was then changed so that the net emission from the atomic oxygen triplet around 130.5 nm was detected. In order to convert the observed intensities into absolute concentrations of $O(^3P)$, the system was calibrated at the beginning and end of a series of runs by discharging N_2 and titrating the nitrogen atoms so produced with NO. Since the rate constant³⁵ for this reaction is 3.4×10^{-11}

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

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

FIG. 1. (a) Variation of $O(^3P)$ resonance fluorescence (I_F) as a function of reaction time with $[N_2]_0 = 1.7 \times 10^{15}$ and $[NO]_0 = 1.2 \times 10^{12}$. (b) Typical calibration plot for $O(^3P)$; $[N_2]_0 = 1.7 \times 10^{15}$.

$\text{cm}^3 \text{molecule}^{-1} \text{sec}^{-1}$,³⁶ it is $\geq 90\%$ complete at the maximum reaction time for titration of 49 msec, if $[N]_0 \geq 3 \times 10^{12}$ (Ref. 36) and $[NO]_0 \leq 1 \times 10^{12}$. While the initial concentration of nitrogen atoms was not determined directly in these studies, the following evidence indicates that this reaction was complete:

(1) As the reaction time between the point of addition of NO and the detection port decreased from ~ 50 msec, the signal from $O(^3P)$ remained constant at reaction times down to 25 msec [Fig. 1(a)] even at the lowest initial concentrations of N_2 used [$[N_2]_0$ was varied from 1.7 to 3.8×10^{15}]; this indicates that the initial concentration of atomic nitrogen was $\geq 3 \times 10^{12}$.

(2) Varying the flow of N_2 through the discharge by a factor of 2.3 with a constant (limiting) concentration of NO did not alter the observed fluorescence intensity; if the titration was not complete, increasing the concentration of N_2 (and hence presumably the nitrogen atoms) should have increased the conversion of NO to $O(^3P)$ and hence increased the observed $O(^3P)$ emission intensity.

Since the titration was complete, and since no wall loss of $O(^3P)$ was observed, the $O(^3P)$ concentration is equal to the initial concentration of NO. A typical calibration plot is shown in Fig. 1(b).

The production of ground state OH was also followed in some experiments. The initial concentrations of hydrogen atoms were determined by titration with NO_2 and

the OH produced was followed.³⁴ This titration also served to calibrate the OH resonance fluorescence intensity as a function of the absolute OH concentration, since the latter can be calculated from the initial concentrations of H and NO_2 if appropriate corrections are made for its loss processes. First order rate constants (k_w) for the OH wall loss were measured before and after each set of runs, and varied from 4 to 15 sec^{-1} . A reaction scheme of the important processes in the H + NO_2 system, including the wall loss and bimolecular reaction, was constructed and numerical integration of the rate equations carried out as described elsewhere.²⁵ The concentrations of OH predicted at the detection port then included corrections for all of its loss processes and these predicted concentrations were used to construct the calibration curves.

The purity of the tank gases and the purification procedures used are described elsewhere.²⁵ All experiments were carried out at 1.1 ± 0.1 Torr in Ar and at 300 ± 3 °K, with typical linear flow speeds of 1000 cm sec^{-1} .

RESULTS

Yields of $O(^3P)$

$O(^3P)$ was followed as a function of reaction time in both excess H and in excess O_3 , in flow tubes coated with either halocarbon wax³⁷ or boric acid. A typical time dependence of $O(^3P)$ in excess H in the wax coated tube is shown in Fig. 2. It is seen that $O(^3P)$ is formed very rapidly and in substantial concentrations.

Table I summarizes the results of a number of experi-

FIG. 2. Observed $O(^3P)$ concentration-time profile (●) in a typical run with $[H]_0 = 1.8 \times 10^{12}$ and $[O_3]_0 = 4.2 \times 10^{11}$ and predicted profiles under various assumptions: (a) $\beta = 0.30$, $k_4 = 1 \times 10^{-10}$; (b) $\beta = 0$, $k_4 = 6 \times 10^{-10}$; (c) $\beta = 0$, $k_4 = 1 \times 10^{-10}$. (Error bars represent $\pm 2\sigma$.)

TABLE I. Observed concentrations of $O(^3P)$ in the presence of excess H in a halocarbon wax coated tube.

Experiment number	$10^{-12} [H]_0$ (atoms cm^{-3})	$10^{-11} [O_3]_0$ (molecules cm^{-3})	Time t (msec)	$10^{-10} [O]_t^a$ ($\pm 2\sigma$) (atoms cm^{-3})	Estimated yield ^b	β^d
1	0.9	3.6	46	2.6 ± 1.6	0.13	0.11
2	1.0	2.7	44	3.1 ± 2.6	0.19	0.18
3	1.4	5.9	41	6.9 ± 0.9	0.17	0.17
4	1.4	5.7	39	11.1 ± 0.7	0.30	0.42
5		4.5		8.9 ± 0.7	0.29	0.42
6		3.1		6.4 ± 0.7	0.30	0.39
7	1.5	5.7	40	11.1 ± 0.6	0.28	0.27
8		4.6		9.6 ± 0.6	0.29	0.33
9		2.9		6.5 ± 0.5	0.30	0.30
10		2.1		4.6 ± 0.5	0.29	0.29
11	1.8	4.7	49	8.7 ± 1.5	0.22	0.27
12		4.2		8.4 ± 1.4	0.24	0.29
13		2.8		4.3 ± 1.9	0.18	0.21
14	2.2	6.3	35	13.1 ± 1.4	0.26	0.31
15		4.6		7.3 ± 1.4	0.19	0.21
16		3.2		4.8 ± 1.4	0.19	0.16
17	2.4	5.9	32	8.1 ± 3.0	0.17	0.18
18		5.2		9.2 ± 3.0	0.22	0.25
19		3.8		6.7 ± 3.7	0.22	0.24
20	2.4	5.0	30	9.4 ± 1.9	0.24	0.24
21		4.2		8.4 ± 1.9	0.25	0.25
22		3.1		4.3 ± 1.8	0.17	0.15
				Weighted mean ^c ($\pm 2\sigma_0$)	0.27 $\pm$ 0.02	0.31 $\pm$ 0.03
23	5.9	8.9	28	29.3 ± 1.3	0.34	0.42
24		5.3		19.5 ± 1.2	0.38	0.40
25		3.5		13.4 ± 1.2	0.39	0.41
26	9.7	11.9	16	53.2 ± 1.4	0.46	0.55
27		7.1		29.6 ± 1.3	0.43	0.48
28		4.1		13.6 ± 1.3	0.34	0.34

^aThe errors quoted were calculated using recommended procedures.⁴³⁻⁵¹ Thus, the standard deviations σ of the signal corresponding to the concentrations of $O(^3P)$ given were calculated using $\sigma_F = \sqrt{\sigma_T^2 + \sigma_{SL}^2}$, where subscripts F, T, and SL refer to the fluorescence, total, and scattered light, respectively. Assuming Poisson statistics for photon counting, $\sigma = \sqrt{I}$, where I = measured counts. Thus, $\sigma_F = \sqrt{I_T + I_{SL}}$. The relative error thus calculated was translated into the uncertainty in $[O]$ using the calibration curve for $O(^3P)$.

^bEstimated yield = $\Delta[O]/\Delta[O_3]$. $\Delta[O_3]$ was calculated from $[H]_0$, $[O_3]_0$, t , and $k_4 = (2.4 \pm 0.4) \times 10^{-11}$.

^cWeighted using $\omega = (1/\sigma_F^2)$ for each run as described in footnote a.

^d $\beta = (k_{5b} + k_{5b'})/k_5$ is the estimated fraction of Reactions (5) giving products $H_2 + O(^3P)$.

ments under these conditions. The yields of $O(^3P)$, i.e., $\Delta[O]/\Delta[O_3]$, were estimated from the observed $O(^3P)$ concentrations at longer reaction times and the calculated loss of O_3 . The latter was obtained from the initial concentrations using $k_1 = (2.4 \pm 0.4) \times 10^{-11}$.²³ It is seen that $O(^3P)$ formation accounts for $27\% \pm 2\%$ of the O_3 reacted, where the error represents $2\sigma_0$. Possible systematic errors are discussed below.

From studies²⁵ in this laboratory, CO_2 and O_2 are known to deactivate $OH(^9)$ under these conditions. Quenching studies of $OH(^9)$ by O_2 as a function of vibrational level (v) in other laboratories²¹ indicate that O_2 , at least, is also a relatively efficient deactivator

for all levels from $v \sim 5-9$. In addition, CO_2 might reasonably be expected to deactivate levels $v = 1-8$ as well as $v = 9$ in light of the fact that OH has been shown²⁷ recently to form a complex with CO_2 . Thus, the effects of addition of these deactivators on the $O(^3P)$ yield should provide an indication of whether OH^+ is a precursor to the $O(^3P)$. In the earlier studies,²⁴ O_2 and CO_2 were added in concentration ($\sim 10^{15}$) sufficient to reduce the $OH^+(9)$ Meinel band emission intensity to $\sim 60\%$ and 30% , respectively, of the unquenched value. No change in the $O(^3P)$ yield was observed. On the assumption that O_2 and CO_2 deactivate many of the vibrational levels with approximately the same efficiency as $v = 9$, then, these results suggested that $O(^3P)$ was not

TABLE II. $O(^3P)$ yields in the presence of excess H in a boric acid coated flow tube.

Experiment number	$10^{-12} [\text{H}]_0$ (atoms cm^{-3})	$10^{-11} [\text{O}_3]_0$ (molecules cm^{-3})	Time t (msec)	$10^{-10} [\text{O}]_t^a$ ($\pm 2\sigma$) (atoms cm^{-3})	Estimated yield ^b
1	0.7	2.2	40	1.2 ± 0.2	0.12
2		1.3		0.8 ± 0.2	0.12
3	1.0	7.0	29	2.9 ± 1.1	0.10
4	1.3	6.8	40	4.5 ± 1.6	0.12
5		5.9		4.7 ± 1.6	0.12
6		4.3		3.1 ± 1.5	0.11
7	1.6	4.3	40	4.5 ± 0.2	0.14
8		2.4		2.5 ± 0.2	0.14
9		1.2		1.5 ± 0.2	0.16
10	1.8	5.7	40	3.5 ± 2.5	0.08
11	1.8	6.8	40	6.2 ± 1.2	0.12
12		4.1		3.9 ± 1.2	0.12
13		3.0		2.8 ± 1.2	0.12
14	2.1	5.8	42	7.3 ± 0.4	0.15
15		3.9		4.5 ± 0.4	0.13
16	2.5	7.5	40	6.1 ± 2.4	0.10
17		5.9		5.4 ± 2.2	0.11
18		2.9		3.7 ± 2.5	0.14
19	2.5	6.2	40	7.3 ± 1.0	0.13
20		4.7		6.1 ± 0.9	0.15
21		3.4		3.5 ± 0.8	0.15
22	2.6	7.1	29	9.6 ± 1.2	0.17
23		4.1		4.7 ± 1.2	0.14
24	3.5	6.2	35	10.0 ± 2.8	0.17
25		4.5		8.0 ± 2.8	0.19
26		2.8		4.7 ± 2.8	0.18
27	7.0	9.5	25	18.7 ± 1.5	0.20
28		6.8		16.7 ± 1.5	0.25
Weighted mean ^c 0.14 ± 0.01 ($2\sigma_0$)					

^aSee footnote a in Table I.^bSee footnote b in Table I.^cSee footnote c in Table I.

formed by secondary reactions of $OH^\dagger$ and that the most likely source was the second reaction channel (1b).

The products of such a primary reaction should not be sensitive to the nature of the flow tube wall coating. However, as seen from Table II, when the walls of the flow tube were coated with boric acid, the estimated yields of $O(^3P)$ in excess H fell by a factor of 2. Boric acid is known from studies in this²⁵ and other laboratories^{30,31} to deactivate $OH^\dagger$ rapidly. These results suggest then that, in contrast to the CO_2 and O_2 experiments, $O(^3P)$ is indeed formed in secondary reactions of the $OH^\dagger$ produced in Reaction (1a).

Furthermore, as seen in Table III, when these experiments are carried out in excess O_3 in the wax coated tube, the $O(^3P)$ yields are found to be substantially less than in excess H and to increase with the initial ozone concentration. In the boric acid coated tube under these conditions, the yields were $\leq 2\%$, which places an upper limit in the contribution of Reaction (1b) to Reactions (1) = (1a) + (1b).

Production of ground state OH

Determination of ground state OH yields is more difficult and less accurate than the $O(^3P)$ studies because of the need to measure, and correct for, the wall loss of OH in developing the resonance fluorescence calibration plots. The uncertainties in both the measurement and prediction (see below) of ground state OH concentrations are such that we prefer to emphasize not the absolute concentrations observed but the effect on them of adding CO_2 and NO. The addition of CO_2 at concentrations up to 2×10^{15} had no effect. As seen in Fig. 3, however, the addition of NO increased the observed concentrations at short reaction times and increased its rate of decay at longer times.

This is consistent with rapid quenching of $OH^\dagger$ to the ground state by NO, in competition with removal of $OH^\dagger$ by H. If $OH^\dagger$ is the precursor to $O(^3P)$, addition of NO should also decrease the $O(^3P)$ concentration under these conditions. Figure 4 shows the $O(^3P)$ yield as increasing concentrations of NO are added. It is seen that the yield falls with increasing concentrations of NO, suggesting

TABLE III. $O(^3P)$ yields in the presence of excess O_3 .

Experiment number	$10^{-11} [H]_0$ (atoms cm^{-3})	$10^{-12} [O_3]_0$ (molecules cm^{-3})	Time t (msec)	$10^{-10} [O]_t^a$ ($\pm 2\sigma$) (atoms cm^{-3})	Estimated yield ^b	
Halocarbon wax coated tube						
1	1.4	6.2	35	1.4 ± 0.9	0.10	
2	2.6	15.3	44	2.1 ± 0.2	0.08	
3		12.0		2.1 ± 0.2	0.08	
4		5.9		1.4 ± 0.2	0.05	
5		4.6		0.9 ± 0.2	0.03	
6	2.8	3.5	44	1.0 ± 0.2	0.04	
7		3.2		1.0 ± 0.2	0.04	
8		2.5		0.9 ± 0.2	0.04	
9		12.5		1.7 ± 0.1	0.06	
10		6.3		1.3 ± 0.1	0.05	
11		2.0		0.6 ± 0.1	0.03	
12		3.1	18.3	20	1.5 ± 0.2	0.05
13			14.0 ^c		1.2 ± 0.2	0.04
14	12.6		1.2 ± 0.2		0.04	
15	8.3		1.0 ± 0.2		0.03	
16	5.7		0.7 ± 0.2		0.02	
17	3.3	6.4	35	1.9 ± 1.0	0.06	
18	5.3	27.2 ^c	40	3.3 ± 0.2	0.06	
19		7.7 ^c		1.9 ± 0.2	0.04	
20		2.7 ^c		1.1 ± 0.2	0.02	
21	6.3	53.3 ^c	10	6.0 ± 0.2	0.10	
22		21.9 ^c	15	5.4 ± 0.2	0.09	
23		10.6 ^c	20	3.9 ± 0.2	0.06	
		5.5 ^c	30	2.7 ± 0.2	0.04	
Boric acid coated tube						
24	4.2	12.3	40	≤ 0.9	≤ 0.02	
25		8.7				
26		5.8				
27		4.1				
28		2.4				

^aSee footnote a in Table I.^bEstimated yield = $\Delta[O]/\Delta[H]$, where $\Delta[H]$ was calculated from $[H]_0$, $[O_3]_0$, t , and $k_1 = (2.4 \pm 0.4) \times 10^{-11}$.^c O_3 in O_2 used, rather than O_3 in He.

that $OH^\dagger$ is indeed the precursor to the $O(^3P)$ and is rapidly deactivated by NO.

Careful checks were carried out in these experiments to ensure that the concentration of H was not altered by the addition of NO, either by reaction with NO itself or with small amounts of NO_2 present as an impurity. Thus, no significant decrease in the hydrogen atom resonance fluorescence emission intensity was observed when NO was added at concentrations up to 3×10^{14} to initial concentrations of H which were sufficiently low ($\leq 1.5 \times 10^{12}$) that the resonance fluorescence intensity is linear with $[H]$. Similarly, the observed decrease in $O(^3P)$ cannot be due primarily to removal of O_3 by the NO since this reaction is slow ($k_{298} = 1.8 \times 10^{-14}$)³⁵ relative to that with H. For example, for the conditions of Fig. 4 only ~3% of the O_3 is removed by reaction with H for $[NO]_0 = 5 \times 10^{13}$.

To summarize, the effects of changing the reaction

conditions, the coating of the flow tube walls, and the addition of NO all suggest that $OH^\dagger$ is a precursor to the observed $O(^3P)$ in this system. The yields in excess O_3 in the boric acid coated flow tube place an upper limit of 2% on the contribution of Reaction (1b) to Reactions (1).

DISCUSSION

Possible sources of the $O(^3P)$ include the following:

FIG. 3. Observed OH concentration-time profiles in the absence and presence of NO with $[H]_0 = 2.3 \times 10^{12}$ and $[O_3]_0 = 5.9 \times 10^{11}$; $\bullet$: data with $[NO]_0 = 0.0$; $\circ$: data with $[NO]_0 = 1.8 \times 10^{14}$; (a) best fit to data in absence of NO with $\beta = 0.17$, $k_w = 11 \text{ sec}^{-1}$; (b) predicted OH profile for $\beta = 0.17$ in the presence of NO with $k_w = 11 \text{ sec}^{-1}$; (c) same as (b) except $k_w = 17 \text{ sec}^{-1}$ (error bars represent $\pm 2\sigma$).

In order to test these possible sources quantitatively a reaction scheme, described in detail elsewhere,²⁵ was applied. In this scheme, $OH^\dagger(9)$ is treated separately from the lower vibrational levels $OH^\dagger(1-8)$ which are lumped together as one species. Table IV gives the most important reactions for the present purposes and the rate constants used.

Reaction of $OH^\dagger$ with O_3

The results of a variety of kinetic studies^{21, 25, 30, 31} of $OH^\dagger(v)$ indicate that its reaction and/or deactivation by H is very rapid compared to that by O_3 . Reaction (2c), which requires 3 or more quanta of vibrational energy in the $OH^\dagger$ to overcome the endothermicity, is thus a feasible source of $O(^3P)$ only when O_3 is present in excess. If this reaction occurs in competition with other losses of $OH^\dagger$ (e.g., deactivation at the walls, or by the carrier gas), then the extent of Reactions (2) and hence the $O(^3P)$ yield will increase with $[O_3]_0$ in a manner at least qualitatively consistent with our observations. In excess O_3 then, Reaction (2c) is a feasible source of the $O(^3P)$.

TABLE IV. Important reactions and their rate constants in the $H + O_3$ system used to assess secondary sources of $O(^3P)$.

Reactions	k ($\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$)
(1a) $H + O_3 \rightarrow OH^\dagger(1-9) + O_2$	Overall 2.4×10^{-11} ; 45% of Reaction (1a) assumed to give $OH^\dagger(9)$ 55% to give $OH^\dagger(1-8)$ ^a
(2a) $OH^\dagger + O_3 \rightarrow HO_2 + O_2$ ($v \geq 0$)	See the text
(2b) $\rightarrow H + 2O_2$ ($v \geq 1$)	
(2c) $\rightarrow O + O_2 + OH$ ($v \geq 3$)	
(3a) $H + HO_2 \rightarrow 2OH$	$4.7 \times 10^{-11} \text{ b}$
(3b) $\rightarrow H_2 + O_2$	
(3c) $\rightarrow H_2O + O$	
(4) $OH^\dagger(n) + OH^\dagger(n) \rightarrow H_2O + O$	1.0×10^{-10} (see the text)
(5a) $OH^\dagger(9) + H \rightarrow OH^\dagger(1-8) + H$	$2 \times 10^{-10} \text{ c}$
(5a') $OH^\dagger(1-8) + H \rightarrow OH + H$	
(5b) $OH^\dagger(9) + H \rightarrow H_2 + O$	
(5b') $OH^\dagger(1-8) + H \rightarrow H_2 + O$	
(6) $OH + OH \rightarrow H_2O + O$	$1.7 \times 10^{-12} \text{ d}$
(7) $OH \xrightarrow{k_w} \text{loss at wall}$	$4-15 \text{ sec}^{-1}$ (see the text)
(8) $O + OH \rightarrow O_2 + H$	$4.2 \times 10^{-11} \text{ d}$
(9a) $OH^\dagger(9) + NO \rightarrow OH^\dagger(1-8) + NO$	See the text
(9b) $OH^\dagger(1-8) + NO \rightarrow OH + NO$	See the text

^aReferences 1-3.

^bReference 39.

^cReferences 25 and 31.

^dReference 35.

In excess H, $OH^\dagger$ is anticipated to be removed almost entirely by H rather than by O_3 , since the room temperature rate constants for the two processes are reported to be of the order of 10^{-10} and 10^{-11} , respectively.^{21, 30, 31} In any event, the low $O(^3P)$ yields in excess O_3 indicate that in excess H, where the O_3 concentrations are much

FIG. 4. Effect of NO on $O(^3P)$ concentrations-time profiles. $[H]_0 = 1.1 \times 10^{12}$, $[O_3]_0 = 5.7 \times 10^{11}$, and $[NO] = 0$ (a), 1.3×10^{13} (b), 5.0×10^{13} (c), 17.2×10^{13} (d), and 27.1×10^{13} (e).

lower than in Table III, Reaction (2c) must contribute even less than observed in excess O_3 , i. e., $\leq 2\%$.

Reaction of H with HO_2

Reactions (3) could be important if the channel (3c) forming $O(^3P)$ was significant and if substantial amounts of HO_2 are produced. The fraction of the overall $H + HO_2$ reaction which gives $O(^3P)$ is not well established. The most recent studies are those of Hack, Wagner, and Hoyer³⁸ in which 2% of the total reaction was found to proceed via channel (3c), 29% via channel (3b), and 69% via channel (3a), with an overall rate constant³⁹ k_3 at 298 °K of $(4.7 \pm 1.0) \times 10^{-11}$. These studies are supported by the earlier work⁴⁰ of Clyne and Thrush in which channel (3b) was found to account for 33% of the overall reaction. The small branching ratio into channel (3c) implies that even if HO_2 is produced in our system, its reaction with H is a negligible source of $O(^3P)$.

The results of earlier studies⁴¹ by Westenberg and de Haas, however, indicate that channel (3c) may indeed account for a significant portion of Reactions (3). They derived relative rate constants for channels (3a), (3b), and (3c) from measured absolute concentrations of H and the steady state concentrations of OH and $O(^3P)$ in the $H-O_2-M$ system. Correcting their relative rate constants for more recent determinations³⁵ of the $O + OH$ and $OH + OH$ rate constants on which their relative values depend, 26%, 51%, and 23% of the reaction are predicted to proceed via channels (3a), (3b), and (3c), respectively.

However, even if this higher branching ratio for channel (3c) is assumed, in order for Reactions (3) to be a significant source of $O(^3P)$, one needs a substantial source of HO_2 . The only sources of HO_2 other than Reaction (1b) which, as discussed above, appears to be negligible are the reactions of OH and $OH^\dagger$ with O_3 and the recombination of H with O_2 either homogeneously or heterogeneously. Homogeneous third order formation of HO_2 is negligible under these experimental conditions since this reaction is slow³⁵ and only small concentrations of O_2 [i. e., that produced in Reaction (1a)] are present. However, to check that this or a faster heterogeneous recombination on the walls was not occurring, heated silver wool was inserted in the ozone line in one experiment to convert all of the O_3 in the helium stream to O_2 . This O_2/He mixture was then reacted with the excess hydrogen atoms. If heterogeneous formation of HO_2 was occurring in the system, the HO_2 should have been converted by the excess H into OH via Reaction (3a) and detectable amounts of OH should have been produced; in fact, none was observed.

Similarly, the reaction of OH and $OH^\dagger$ with O_3 to produce HO_2 is expected to contribute negligibly to HO_2 formation; the reaction of OH with O_3 is relatively slow ($k = 5.2 \times 10^{-14}$)⁴² and, as discussed above, $OH^\dagger + H$ appears to be approximately an order of magnitude faster than Reactions (2). However, given the substantial uncertainty²⁵ in the rate constants for $OH^\dagger$ reactions, an extreme worst case estimate of the importance of Reaction (2a) followed by channel (3c) was made by taking

$k_2 = k_{2a} = 6 \times 10^{-10}$, $k_{5b} = k_{5b'} = 0$, and $k_{5a} = k_{5a'} = 2 \times 10^{-10}$. (See Table IV for the definition of k_{5a} , $k_{5a'}$, k_{5b} , and $k_{5b'}$.) Assuming the reevaluated branching ratios of Westenberg and deHaas given above, the concentration of $O(^3P)$ formed in the reaction is anticipated for the conditions of Fig. 2 to be $\sim 16\%$ of that experimentally observed. Thus, the HO_2 from the reactions of OH and $OH^\dagger$ with O_3 cannot be responsible for the larger observed $O(^3P)$ concentrations.

Bimolecular reactions of $OH^\dagger$

Another potential source of $O(^3P)$ is the bimolecular Reaction (4) between the two hydroxyl radicals. If both are in the ground state, the rate constant³⁵ is 1.7×10^{-12} , too slow to be a significant source of $O(^3P)$ in our system.

The effect on this rate constant if one or both of the hydroxyl radicals is vibrationally excited is not known. However, if this were the source, a higher yield of $O(^3P)$ might be expected in excess O_3 compared to excess H since the latter appears to more rapidly remove $OH^\dagger$. In addition, a dependence of the $O(^3P)$ yield on the limiting reagent would be expected. Finally, the time dependence of the $O(^3P)$ would be expected to show an induction period at short reaction times. None of these effects are observed.

To test this more quantitatively, however, the reaction scheme in Table IV was used to predict the $O(^3P)$ concentrations expected if Reactions (5) do not produce $O(^3P) + H_2$, i. e., $k_5 = k_{5a} = k_{5a'} = 2 \times 10^{-10}$ and $k_{5b} = k_{5b'} = 0$. An extremely large rate constant $k_4 = 6 \times 10^{-10}$ was assumed to provide a worst case estimate of the contribution of Reaction (4). Curve (b) of Fig. 2 gives the predicted $O(^3P)$ concentrations under these conditions. It is seen that the yields of $O(^3P)$ are substantially lower than those observed. If an intermediate value of 1×10^{-10} is assumed for k_4 when at least one of the reacting hydroxyl radicals is vibrationally excited, then these reactions account for less than 10% of the observed $O(^3P)$ formed [curve (c) of Fig. 2]. Thus, Reaction (4) cannot be the major source of the $O(^3P)$.

Reaction of $OH^\dagger$ with H

The Reactions (5b) and (5b') of H with $OH^\dagger$ seems to be most consistent with our observations. Thus, the $O(^3P)$ yields are greatest in excess H. [As discussed above, the lower yields in excess O_3 are consistent with the reaction (2c) of $OH^\dagger$ with O_3 .] $OH^\dagger(v)$ in $v=1, 2$ has been shown³¹ to be deactivated rapidly by H, rather than reacting with it. As additional confirmation of this, we have observed in our system negligible concentrations of $O(^3P)$ from the reaction of H with NO_2 , which produces $OH^\dagger(v \leq 3)$; thus, the yield of $O(^3P)$ was observed to be $\leq 5\%$ of the NO_2 reacted. Since the $OH^\dagger$ is removed by H with a rate constant approximately ten times³¹ that for its deactivation by NO_2 ,^{31,33} and since H was present in great excess, most of the $OH^\dagger$ must have been removed by H. Thus, if Reaction (5b) is indeed the source of the $O(^3P)$, then the higher vibra-

tional levels $v > 3$ must be responsible.

Our observations can then be qualitatively explained in the following way: The reaction of H with O_3 is known to produce $OH^\dagger$ predominantly in the upper vibrational levels. From the work of Polanyi *et al.*¹⁻³ it is estimated that $\sim 45\%$ of the reaction produces $OH^\dagger$ in $v=9$, with the remainder producing $OH^\dagger$ mainly in $v=7, 8$. If CO_2 and O_2 are exceptionally good quenchers of $OH^\dagger(9)$ compared to the lower vibrational levels, then their addition would lead to increased concentrations of $OH^\dagger(1-8)$. If, however, in contrast to our original expectations based on the literature,^{21,27} $OH^\dagger(1-8)$ is not substantially quenched by CO_2 and O_2 , then the $OH^\dagger(1-8)$ would continue to produce $O(^3P)$ and the yield would not change, consistent with our observations. Boric acid and NO must deactivate all vibrational levels with comparable efficiency (although not necessarily with the same rate constants) so that their presence leads to increased yields of ground state OH and decreased yields of $O(^3P)$.

To test this hypothesis, the fraction of Reactions (5) leading to products rather than deactivation, i.e., $\beta = (k_{5b} + k_{5b'})/k_5$, where $k_5 = (k_a + k_{5a'} + k_{5b} + k_{5b'})$, was varied to obtain a best match to the $O(^3P)$ data in Fig. 2 and the OH data in Fig. 3. In these particular cases, $\beta = 0.30$ and 0.17 , respectively, gave the best match.

To predict the effect of NO on the OH concentrations (Fig. 3), the value of the rate constant k_9 (Table IV) is needed. For $v=1, 2$, k_9 is in the range^{31,33} $(0.15-1) \times 10^{-11}$ while the values for upper vibrational levels are unknown. To obtain an estimate of k_9 as an average over all nine vibrational levels present in these experiments, it was assumed that $k_9 = k_{9a} = k_{9b}$ and this value was varied to obtain a best fit to the $O(^3P)$ data of Fig. 4. The values of k_9 so obtained varied; thus $k_9 = 2 \times 10^{-11}$ gave a best fit to curve (b) of Fig. 4 while $k_9 = 5 \times 10^{-12}$ matched curve (d). (This variation in k_9 likely arises from assuming that $k_{9a} = k_{9b}$ and lumping all vibrational levels from $v=1-8$ together.) Taking $k_9 = 5 \times 10^{-12}$ as representative of the experimental conditions of Fig. 3 ($[NO]_0 = 1.8 \times 10^{14}$), and $k_w = 11 \text{ sec}^{-1}$, determined immediately before these runs, one predicts curve (b). While the fit to the data is poor, especially at long reaction times, a much better fit [curve (c)] resulted if it was assumed that k_w increased to 17 sec^{-1} in the presence of NO. We tested for an increased wall loss in the presence of NO by adding NO to the H + NO_2 reaction and measuring k_w . It was found that in both the wax tube and the boric acid coated tube, k_w increased by approximately a factor of 2 when NO was added at concentrations of $\sim 10^{14}$. Thus, the increased k_w needed to match the OH data in the presence of NO is reasonable.

In summary, then, our observations of the time dependences of $O(^3P)$ and OH appear consistent with Reaction (5b) as the source of $O(^3P)$ in excess H. Column 7 of Table I gives the values of β for each run which give the best fit to the observed $O(^3P)$ concentrations over the

reaction times studied. It is seen that for $[H]_0 \lesssim 3 \times 10^{12}$ and $[O_3]_0 \lesssim 6 \times 10^{11}$, $31\% \pm 3\%$ of the $OH^\dagger$ appears to react with H, where the quoted error is $2\sigma_0$. The experiments at higher $[H]_0$ $[(5-10) \times 10^{12}]$ appear to have somewhat higher $O(^3P)$ yields. However, for several of these, the $[O_3]_0$ was also somewhat higher than usual so that the bimolecular reaction (4) of $OH^\dagger$, or some other secondary reaction, may be contributing to the observed $O(^3P)$.

The estimated yields and values of β are not identical in each run because the yields were estimated from a typical $O(^3P)$ concentration at one reaction time while β was obtained by finding a best fit to the data over the entire range of reaction times studied. In addition, the computer predictions of β include other minor loss processes for $OH^\dagger$ in addition to Reactions (5).

In addition to the random errors, there are several possible sources of systematic errors. The most important one lies in assessing the contributions to $O(^3P)$ production of the bimolecular $OH^\dagger$ reactions. For the lack of any available information, we assumed here that $k_4 = 1 \times 10^{-10}$, in which case it contributes negligibly ($< 10\%$) to the $O(^3P)$ formation, as discussed above.

A second possible systematic error arises from the rate constant assumed for Reactions (5) (2×10^{-10}). Increasing k_5 to 6×10^{-10} increases the predicted $O(^3P)$ concentrations for a given value of β at low conversions, since it decreases the amount of reacted O_3 that exists as $OH^\dagger$ at any one time. As expected, the ultimate yields of $O(^3P)$ predicted using these two rate constants converge as all of the O_3 is consumed. However, at low concentrations of H and short reaction times where the extent of reaction is low, underestimating k_5 will lead to values of β which are too large. We estimate the possible error from this to be $\leq 15\%$.

A third possible source of systematic error is the effect of ignoring deactivation of $OH^\dagger$ at the walls and by the carrier gas Ar. We have shown²⁵ that in our system, under the conditions of the present experiments, $OH^\dagger(9)$ may be removed primarily by these two processes; deactivation by H becomes important as the concentration of H approaches 10^{13} . On the other hand, Spencer and Glass³¹ have shown that $OH^\dagger(1,2)$ is removed primarily by H under conditions (including nature of the wall coating) similar to the present experiments. The intermediate vibrational levels which appear to be the source of the $O(^3P)$ undoubtedly lie somewhere in between these two extremes. While including such deactivation will lead to increased values of β , no quantitative estimates of the possible error in β from this source are possible without knowing the actual rates of deactivation by the wall and Ar.

Two additional sources of systematic error are associated with measuring the initial O_3 concentrations, and to a lesser extent with establishing the calibration curves used to convert $O(^3P)$ fluorescence intensities into absolute concentrations. To minimize the error associated with measuring the initial O_3 concentrations, both the calibration of the rotometer and the linearity of the absorbance with concentration were checked carefully

several times during these experiments. We estimate the systematic error from this source to be $\leq 15\%$.

To minimize errors from the calibration for $O(^3P)$, the calibrations were typically carried out at several different N_2 flows at the beginning and end of each day. The calibration curve was generally quite stable and the systematic error associated with this is estimated to be $\leq 5\%$. Using the square root of the sum of the squares of these contributions, the total error in the measured $O(^3P)$ concentrations from these two last sources is estimated to be $\leq 16\%$.

If Reaction (5b) is the source of $O(^3P)$ in excess H, then ~ 1.3 molecules of H should be reacted for each molecule of O_3 in the wax coated tube. Thus, the concentration of H was also followed under conditions typical of Table I. Numerical integration of the rate equations in Table IV was carried out and β varied to produce a best fit to the H data in each run. A best match was found for six of eight runs by assuming that between 13% and 30% of the $OH^{\dagger}$ formed in Reaction (1a) reacted with H, the average being 25%; the other two runs gave a best match with 0%. While this is not compelling evidence for Reaction (5b), especially since the accuracy of the predictions of the H atom decay depends on the accuracy of k_1 , $[H]_0$, and $[O_3]_0$, it indicates at least that Reaction (5b) is a reasonable source of $O(^3P)$.

The present results and interpretation are consistent with the lack of detection^{28,29} of significant amounts of HO_2 in this system. However, the results of recent laser photolysis experiments⁴³ of O_3/H_2 mixtures support our original suggestion²⁴ of a second channel (1b) in the H + O_3 reaction. In the latter experiments, the $O(^1D_2)$ atoms produced in the photolysis of O_3 react with H_2 to produce H, which then reacts with the excess O_3 . The decay of H and the production of ground state $O(^3P)$ were followed and both found to be consistent with 40% of the H + O_3 reaction proceeding via Reaction (1b). However, the reaction of $OH^{\dagger}$ with O_3 could not be ruled out with certainty, although it would apparently have to proceed with a rate constant of $\sim 10^{-10}$ to be consistent with their observed $O(^3P)$ time dependence. As discussed above, previous experiments on the rate constant for $OH^{\dagger} + O_3$ indicate that the reaction is 1–2 orders of magnitude slower than this. Our own experiments²⁵ on $OH^{\dagger}(9) + O_3$ suggest that $OH^{\dagger}(9) + O_3$ is much slower than $OH^{\dagger} + H$, and if the latter has a rate constant of $\sim 10^{-10}$, then k_2 should indeed be $\leq 10^{-11}$. Thus, the most reasonable explanation for their results appears to be Reaction (1b) and the reason for the discrepancy between their results and the present ones is not clear.

If Reaction (5b) is indeed responsible for the $O(^3P)$ formation, it raises some interesting questions with regard to the effects of vibrational energy on the dynamics of the reaction of H with ground state OH:

This reaction is almost thermoneutral ($\Delta H_{298} = -1.9$ kcal/mole) and slow ($k_{298} = 3 \times 10^{-17}$),³⁵ with an activation energy of ~ 7 kcal. Thus, even $OH^{\dagger}(v=1)$, which is 10.2 kcal above $v=0$,⁴⁴ has enough vibrational energy to overcome the energy barrier. However, as discussed

above, $OH^{\dagger}(v=1-3)$ apparently is deactivated by H rather than reacting with it. Thus, large amounts of vibrational energy, well above the activation energy, are apparently needed for this reaction.

An additional interesting aspect of this reaction is that if the activation energy were lowered to zero, the rate constant predicted at 298 °K on the basis of the recommended³⁵ Arrhenius expression would be only 4×10^{-12} . However, the reaction producing $O(^3P)$ must be sufficiently fast compared to Reaction (1a) to mimic a primary process on a msec time scale, i.e., it must be $\sim 10^{-10}$, consistent with the observations in this²⁵ and other³¹ laboratories on H + $OH^{\dagger}$. Thus, the pre-exponential factor for this reaction must be increased compared to the reaction of ground state OH.

These results can be compared to those of Polanyi and co-workers⁴⁵ on a similar reaction

where the lower vibrational levels did react with Cl and the rate constant was found to increase by about a factor of 10 as v increased from 1 to 9. This reaction is similar to Reactions (5) in that it is also nearly thermoneutral ($\Delta H_0^{\circ} = -0.9$ kcal/mole) and also has an activation barrier of ~ 5 kcal/mole, much less than the energy of $v=1$. The difference between the two reactions may arise in part from the possibility of rapid deactivation of $OH^{\dagger}$ by H in addition to reaction. Thus, whether deactivation or reaction occurs when H approaches $OH^{\dagger}$ may depend on the direction of approach. For example, if H approaches from the oxygen atom end of $OH^{\dagger}$, deactivation via a quasi-intermediate water molecule may result:

whereas approach from the hydrogen atom end may lead to reaction:

In contrast, deactivation of the high vibrational levels of $OH^{\dagger}$ by Cl apparently accounts for less than 25% of the loss of the $OH^{\dagger}$.⁴⁵

Another relevant reaction which has been studied⁴⁶ is the reverse of Reactions (5):

This reaction is endothermic by ~ 2 kcal and has an activation energy of ~ 9 kcal. Putting one quantum of vibrational energy into the H_2 increases the rate constant by a factor of 2.6×10^3 .⁴⁶ In this case, however, efficient deactivation of the $H_2(v=1)$ by $O(^3P)$, comparable to Reaction (5a), seems less likely because formation of a highly excited water molecule intermediate would require insertion of the $O(^3P)$ into the H_2 .

The lack of participation of the lower vibrational levels of $OH^{\dagger}$ in $O(^3P)$ formation may result from the relative rates of Reactions (5a) and (5b) and their dependences on v . Thus, k_{5a} may even decrease with increasing v beyond a particular vibrational level; as the vibrational energy content of the $OH^{\dagger}(v)$ increases, the

energy of the intermediate (H-O-H)* also increases and its lifetime is expected to decrease. The lifetime may become sufficiently short that it rapidly decomposes back to the initial reactants rather than surviving long enough to scramble the initial vibrational energy of the O-H[†] bond, and form OH[†]($v' < v$). In this case, decreasing values of k_{5a} with v would result.

To test whether this explanation is feasible, RRKM theory⁴⁷ was used to estimate the decomposition rates of the intermediate (H-O-H)* as a function of the initial OH[†] vibrational energy. Although this theory is not strictly applicable, as it assumes randomization of energy throughout the molecule, crude estimates, at least, of the decomposition rates can be obtained. Taking the asymmetric stretch as the reaction coordinate, and the symmetric stretching and bending frequencies of the transition state to be 3652 and 797 cm⁻¹, respectively, the decomposition rate constants for the intermediate HOH are predicted to be 5×10^{12} sec⁻¹ for OH[†](1) and 7×10^{13} sec⁻¹ for OH[†](9). If the rate constant for intramolecular relaxation is of the order of 10^{12} – 10^{13} sec⁻¹, which is not unreasonable on the basis of Monte Carlo calculations,⁴⁸ then decomposition of the intermediate formed from the higher vibrational levels may indeed be sufficiently fast to lead to a net decrease in k_{5a} .

Reactions (5) may thus be unusual in that efficient deactivation channels are available as well as reactive ones, and these may show different qualitative as well as quantitative dependences on v . Clearly, much further work is needed to elucidate the detailed reaction dynamics, if indeed Reaction (5b) is the source of the observed O(³P). Further experiments are planned in this laboratory to confirm the source.

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- ¹See, for example, J. C. Polanyi and J. J. Sloan, *Int. J. Chem. Kinet. Symp.* 1, 51 (1975), and references therein.
- ²K. G. Anlauf, R. G. McDonald, and J. C. Polanyi, *Chem. Phys. Lett.* 1, 619 (1968).
- ³P. E. Charters, R. G. McDonald, and J. C. Polanyi, *Appl. Opt.* 10, 1747 (1971).
- ⁴F. Kaufman and R. D. Levine, *Chem. Phys. Lett.* 54, 407 (1978).
- ⁵J. Heicklen, *Atmospheric Chemistry* (Academic, New York, 1976), Chap. 2, and references therein.
- ⁶"Chlorofluoromethanes and the Stratosphere," edited by R. D. Hudson, NASA Ref. Publ. 1010 (1977), and references therein.
- ⁷A. F. Nagy, S. C. Liu, and D. J. Baker, *Geophys. Res. Lett.* 3, 731 (1976).
- ⁸G. E. Streit, G. Z. Whitten, and H. S. Johnston, *Geophys. Res. Lett.* 3, 521 (1976).
- ⁹E. J. Llewellyn and B. H. Long, *Can. J. Phys.* 56, 581 (1978); E. J. Llewellyn, B. H. Long, and B. H. Solheim, *Planet. Space Sci.* 26, 525 (1978) and references therein.
- ¹⁰H. Takahashi and P. P. Batista, *Planet. Space Sci.* 28, 559 (1980).
- ¹¹See, 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, in *Oxidation Combustion Reviews*, 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.
- ¹²B. 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. Publ.* 557 (1979); M. C. Dodge and R. R. Arnts, *Int. J. Chem. Kinet.* 11, 399 (1979).
- ¹³B. B. Krieger and R. H. Kummier, *J. Phys. Chem.* 81, 2493 (1977), and references therein.
- ¹⁴A. B. Meinel, *Astrophys. J.* 111, 207, 433, 555 (1950).
- ¹⁵D. R. Bates and M. Nicolet, *J. Geophys. Res.* 55, 301 (1950).
- ¹⁶J. D. McKinley, D. Garvin, and M. J. Boudart, *J. Chem. Phys.* 23, 784 (1955).
- ¹⁷T. M. Cawthon, Jr. and J. D. McKinley, Jr., *J. Chem. Phys.* 25, 585 (1956).
- ¹⁸F. Kraus, *Z. Naturforsch. Teil A* 12, 479 (1957).
- ¹⁹D. Garvin, *J. Am. Chem. Soc.* 81, 3173 (1959).
- ²⁰D. Garvin, H. P. Broida, and H. J. Kostkowski, *J. Chem. Phys.* 32, 880 (1960).
- ²¹G. E. Streit and H. S. Johnston, *J. Chem. Phys.* 64, 95 (1976), and references therein.
- ²²L. F. Phillips and H. I. Schiff, *J. Chem. Phys.* 37, 1233 (1962); M. A. A. Clyne and P. B. Monkhouse, *J. Chem. Soc. Faraday Trans. 2* 73, 298 (1977); J. H. Lee, J. V. Michael, W. A. Payne, and L. J. Stief, *J. Chem. Phys.* 69, 350 (1978); L. F. Keyser, *J. Phys. Chem.* 83, 645 (1979).
- ²³B. J. Finlayson-Pitts and T. E. Kleindienst (unpublished data).
- ²⁴B. J. Finlayson-Pitts and T. E. Kleindienst, *J. Chem. Phys.* 70, 4804 (1979).
- ²⁵B. J. Finlayson-Pitts and T. E. Kleindienst, *J. Chem. Phys.* (in press).
- ²⁶Throughout this paper vibrationally excited OH is designated as OH[†]. Where a specific vibrational level is discussed, it is written as OH[†](v). Ground state OH, i.e., $v=0$, is written as OH.
- ²⁷M. J. Kurylo and A. H. Laufer, *J. Chem. Phys.* 70, 2032 (1979).
- ²⁸C. J. Howard and B. J. Finlayson-Pitts, *J. Chem. Phys.* 72, 3842 (1980).
- ²⁹N. Washida, H. Akimoto, and M. Okuda, *J. Chem. Phys.* 72, 5781 (1980).
- ³⁰A. E. Potter, Jr., R. N. Coltharp, and S. D. Worley, *J. Chem. Phys.* 54, 992 (1971); R. N. Coltharp, S. D. Worley, and A. E. Potter, *Appl. Opt.* 10, 1786 (1971); S. D. Worley, R. N. Coltharp, and A. E. Potter, *J. Chem. Phys.* 55, 2608 (1971); S. D. Worley, R. N. Coltharp, and A. E. Potter, Jr., *J. Phys. Chem.* 76, 1151 (1972), and references therein.
- ³¹J. E. Spencer and G. P. Glass, *Chem. Phys.* 15, 35 (1976).
- ³²J. E. Spencer, H. Endo, and G. P. Glass, *16th Symposium (International) on Combustion* (The Combustion Institute, Pittsburgh, 1977), pp. 339–348; J. E. Spencer and G. P. Glass, *Int. J. Chem. Kinet.* 11, 97, 111 (1977).
- ³³D. H. Jaffer and I. W. M. Smith, *Faraday Discuss. Chem. Soc.* 67, 212 (1979).
- ³⁴T. E. Kleindienst and B. J. Finlayson-Pitts, *Chem. Phys. Lett.* 61, 300 (1979), and references therein.
- ³⁵R. F. Hampson, "Chemical Kinetic and Photochemical Data Sheets for Atmospheric Reactions," Report No. FAA-EE-

- 80-17, U. S. Department of Transportation, Federal Aviation Administration, Office of Environment and Energy, High Altitude Pollution Program, Washington, D.C. 20591, April 1980, and references therein.
- ³⁶Concentrations and second order rate constants are given throughout in units of molecules, atoms, or radicals cm^{-3} and $\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$, respectively.
- ³⁷R. B. Badachhape, P. Kamarchik, A. P. Conroy, G. P. Glass, and J. L. Margrave, *Int. J. Chem. Kinet.* **8**, 23 (1976).
- ³⁸W. Hack, H. Gg. Wagner, and K. Hoyer mann, *Ber. Bunsenges. Phys. Chem.* **82**, 713 (1978).
- ³⁹W. Hack, A. W. Preuss, H. Gg. Wagner, and K. Hoyer mann, *Ber. Bunsenges. Phys. Chem.* **83**, 212 (1979).
- ⁴⁰M. A. A. Clyne and B. A. Thrush, *Proc. R. Soc. London Ser. A* **275**, 559 (1963).
- ⁴¹A. A. Westenberg and N. deHaas, *J. Phys. Chem.* **76**, 1586 (1972).
- ⁴²J. G. Anderson and F. Kaufman, *Chem. Phys. Lett.* **19**, 483 (1973).
- ⁴³A. P. Force and J. R. Wiesenfeld, *J. Chem. Phys.* **74**, 1718 (1981).
- ⁴⁴V. I. Krassovsky, N. N. Shefov, and V. I. Yarin, *Planet. Space Sci.* **9**, 883 (1962).
- ⁴⁵B. A. Blackwell, J. C. Polanyi, and J. J. Sloan, *Chem. Phys.* **24**, 25 (1977).
- ⁴⁶G. C. Light, *J. Chem. Phys.* **68**, 2831 (1978).
- ⁴⁷P. J. Robinson and K. A. Holbrook, *Unimolecular Reactions* (Wiley-Interscience, New York, 1972).
- ⁴⁸D. L. Bunker, *J. Chem. Phys.* **40**, 1946 (1964).
- ⁴⁹R. 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.
- ⁵⁰P. R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences* (McGraw-Hill, New York, 1969), and references therein.
- ⁵¹E. M. Pugh and G. H. Winslow, *The Analysis of Physical Measurements* (Addison-Wesley, Reading, Mass., 1966), and references therein.