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THE REACTION OF $O(^1D)$ WITH H_2O AND THE REACTION OF OH WITH C_3H_6

by
R. Simonaitis and Julian Heicklen

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The Research in this document was supported by the National Science Foundation under Grant GA-12385 and in part by the National Aeronautics and Space Administration under Grant NGL 39-009-003.

IONOSPHERE RESEARCH LABORATORY

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Abstract

N_2O was photolyzed at 2139A to produce $O(^1D)$ atoms in the presence of H_2O and CO. The $O(^1D)$ atoms react with H_2O to produce HO radicals, as measured by CO_2 production from the reaction of OH with CO. The relative importance of the various possible $O(^1D)$-H_2O reactions is

$O(^1D) + H_2O \rightarrow 2OH$	> 90%
$\rightarrow O(^3P) + H_2O$	< 4%
$\rightarrow H_2O_2$	< 5%
$\rightarrow H_2 + O_2$	< 0.4%

The relative rate constant for $O(^1D)$ removal by H_2O compared to that by N_2O is 2.1 in good agreement with that found earlier in our laboratory.

In the presence of C_3H_6, the OH can be removed by reaction with either CO or C_3H_6.

$OH + CO \rightarrow CO_2 + H$	2
$OH + C_3H_6 \rightarrow$ products	3

From the CO_2 yield, $k_3/k_2 = 75.0$ at 100°C and 55.0 at 200°C. When these values are combined with the value of $k_2 = 7.0 \times 10^{-13} \exp(-1100/RT)$ cm^3/sec, $k_3 = 1.36 \times 10^{-11} \exp(-100/RT)$ cm^3/sec. At 25°C, k_3 extrapolates to 1.1×10^{-11} cm^3/sec.

INTRODUCTION

The reaction between $O(^1D)$ and H_2O is the principle source of OH radicals in the stratosphere and it is one of the key reactions in assessing the effects on the O_3 layer of introducing H_2O into the stratosphere by supersonic aircraft. From laboratory measurements it is known that the reaction of $O(^1D)$ with H_2O gives OH radicals.

McGrath and Norrish[1,2] demonstrated the presence of OH radicals in the flash photolysis of O_3-H_2O mixtures and proposed the reaction

$$O(^1D) + H_2O \rightarrow 2OH \qquad (1a)$$

In further experiments, Basco and Norrish[3] demonstrated that up to 2 quants of vibrational energy could be present in the OH radical. More recently Biedenkapp, Hartzhorn, and Bair[4] in a study of the same system also observed vibrationally excited OH. However, the efficiency of reaction (1a) is not known, although it is generally assumed to be high. Other possible reactions are

$$O(^1D) + H_2O \rightarrow O(^3P) + H_2O \qquad (1b)$$

$$O(^1D) + H_2O + M \rightarrow H_2O_2 + M \qquad (1c)$$

$$O(^1D) + H_2O \rightarrow H_2 + O_2 \qquad (1d)$$

A recent report[5] has indicated that reaction 1b is unimportant.

The absolute total rate constant for the reaction of $O(^1D)$ with H_2O has been measured by Bair and coworkers[4] by flash photolysis of ozone-H_2O mixtures to be 3.1×10^{-11} cm^3/sec. However, this number differs by an order of magnitude, when compared with the rate constant for $O(^1D)$ + N_2O, with the relative value of 1.5 obtained by Scott and Cvetanović[6] and 2.2 obtained by Lissi and Heicklen.[7]

In order to ascertain the relative importance of reactions 1a-1d, and to resolve the discrepancy in the rate measurements, we have carried

out a detailed study of this reaction.

The $O(^1D)$ atoms were generated by the photolysis of N_2O at 2139A radiation in the presence of H_2O, CO, and in some cases C_3H_6. The $O(^1D)$ atoms react with either N_2O or with H_2O and the resulting OH radicals from the latter reaction are scavenged by CO in accordance with reaction 2

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

The resulting CO_2 production is therefore a measure of OH production. The presence of small amounts of propylene scavenges any $O(^3P)$ atoms that may be formed in reaction 1b, thus preventing CO_2 formation via

$$O\ (^3P) + CO + M \rightarrow CO_2 + M$$

Actually, the rate constant for reaction 3

$$OH + C_3H_6 \rightarrow \text{products} \qquad (3)$$

is much faster than for reaction 2. Consequently it is difficult to adjust the $[CO]/[C_3H_6]$ ratio such that CO scavenges only OH and propylene scavenges only $O(^3P)$. The procedure adopted therefore was to vary the $[C_3H_6]/[CO]$ ratio and extrapolate to zero. This procedure turns out to be useful in more ways than one, since the competition between reactions 2 and 3 may be studied. In order to obtain an accurate measure of reaction 1b, scavenging experiments with 2-trifluoromethylpropylene (TMP) were carried out. The reaction between TMP and $O(^3P)$ atoms is known to give only two addition products: 2-trifluoromethylpropionaldehyde (A), and 2-trifluoromethylpropylene oxide (E) with quantum yields of 0.40 and 0.60, respectively, independent of conditions.[8,9] Consequently measurement of these products should provide an accurate measure of reaction 1b providing that the reaction of OH with TMP does not give the same products. The importance of reaction 1d was determined by measuring the hydrogen

yield. A direct measure of reaction 1c by the present experiments was not possible.

The reaction between OH and olefin is of interest in photochemical smog. This reaction has been proposed as an important chain propagating step in the photochemical oxidation of NO to NO_2.[10] The reaction between OH and olefins was studied by Wilson and Westenberg[11] in a flow-discharge system using ESR detection, by Greiner[12] using flash photolysis and ultraviolet absorption spectroscopy for OH detection, and by Morris, et al.[13] in a discharge flow system using mass spectrometric detection. Avramenko and Kolesnikova[14] have also studied OH reactions with olefins, but their water discharge method has been shown to be unsuitable for kinetic studies.[15] In the above methods fast secondary reactions complicate the studies. These complications can be easily avoided in steady-state systems such as that employed in the present study. Unfortunately only relative rate constants may be obtained by this procedure. However, the rate constant for reaction 2 is well known,[16] thus absolute rate constants may be computed.

EXPERIMENTAL

A conventional high-vacuum line utilizing Teflon stopcocks with Viton "O" rings was used. The reaction vessel was a cylindrical quartz cell 10 cm long and 5 cm in diameter. The cell was enclosed in a wire-wound aluminum block furnace, the temperature of which was controlled to ± 1°C by a Cole-Parmer Proportio Null Regulator Series 1300.

The N_2O and CO used were Matheson C. P. grade. The N_2O was purified by passage over ascarite and degassed at -196°C. Gas chromatographic analysis indicated no detectable impurities. In particular CO_2 and N_2 were absent. The CO was purified by passage over glass beads and several traps at -196°C, degassing at -196°C and distillation from liquid Argon. The CO thus purified was free of CO_2 but contained 540 ppm of N_2. The N_2 yield in any photolysis experiment was appropriately corrected for this background N_2. The propylene (Matheson) was purified by degassing at -196°C. Small amounts of tap water were degassed at -96°C prior to use in order to remove dissolved air and CO_2. The 2-trifluoromethylpropene (TMP) was obtained from Peninsular ChemResearch Inc., and it was purified by distillation from a trap maintained at -130°C to a trap maintained at -160°C.

All gas pressures including H_2O below its room temperature vapor pressure were measured with either a McCloud gauge or a Hg manometer used in conjunction with a cathetometer. The high H_2O pressures were not measured directly, but calculated assuming the perfect gas law. Our procedure was to introduce H_2O below its room temperature vapor pressure into the line, measure its pressure on the Hg manometer, and condense it into the reaction vessel. The stopcock to the insulated reaction vessel was closed and the temperature raised to 100°C or 200°C. From

the known volume ratios the H_2O pressure was calculated.

Irradiation was from a Phillips Zn resonance lamp Typ 93106E. The effective radiation was at 2139A. After irradiation the noncondensables were collected with a Toepler pump and analyzed for N_2, and in a few cases for H_2, by gas chromatography using a 10-ft. long by 1/4 in. diameter column packed with 5A molecular sieves. The carrier gas for N_2 analysis was He, whereas for H_2 the carrier gas was Argon. A second fraction volatile at -96°C was removed and analyzed for CO_2 using a 24-ft. long by 1/4-in. column packed with Porapak Q operating at 25°C. In the runs with TMP this fraction was analyzed for 2-trifluoromethylpropion-aldehyde and 2-trifluoromethylpropylene oxide on a 1/4-in. diameter by 10-ft. long column at 30°C packed with 20% Kel-F oil No. 3 on chromosorb P.

At 100°C a very small amount of CO_2 ($\sim$ 0.03 μ/min.) was produced in the dark. At 200°C the dark reaction was somewhat larger ($\sim$ 0.15 μ/min.). The correction for the dark reaction was small, usually less than a few percent.

In most runs, particularly at the lower values of $[C_3H_6]$, appreciable amounts of C_3H_6 were consumed. The amount remaining was determined at the end of the run by gas chromatographic analysis and the average value of $[C_3H_6]$ was used in the computations. The amount of propylene consumed was never more than 30% of the initial amount and was usually less than 10%, so that the use of an average value introduces no appreciable error.

RESULTS

The results for the set of experiments carried out to determine the competition between N_2O and H_2O for the $O(^1D)$ atom are presented in Table I. N_2O was irradiated in the presence of H_2O and CO. The products observed were N_2, CO_2, O_2, and H_2, but only the N_2 and CO_2 were measured. The ratio $R\{CO_2\}/R\{N_2\}$ increases as the $[N_2O]/[H_2O]$ ratio decreases, reaching a value of 1.71 at our lowest $[N_2O]/[H_2O]$ ratio of 0.152. The $R\{CO_2\}/R\{N_2\}$ ratio is otherwise independent of N_2O or H_2O pressure, temperature (one run at 100°C), absorbed light intensity (changed by a factor of $\sim$ 7), and the time of irradiation.

The experiments in the presence of C_3H_6 were carried out in excess H_2O in order to minimize the deactivation of $O(^1D)$ by N_2O and CO. Also, in order to achieve high pressures of H_2O, the minimum temperature employed was 100°C. Some experiments were also performed at 200°C. The only products measured were CO_2 and N_2. The $R\{CO_2\}/R\{N_2\}$ ratio is independent of the time of irradiation, the absorbed light intensity (changed by a factor of $\sim$ 8), the N_2O pressure or the $[N_2O]/[H_2O]$ ratio. $R\{CO_2\}/R\{N_2\}$ depends only on the $[C_3H_6]/[CO]$ ratio and the temperature. It increases with a decreasing $[C_3H_6]/[CO]$ ratio and reaches a value of 1.24 at our lowest $[C_3H_6]/[CO]$ ratio of 0.0046. $R\{CO_2\}/R\{N_2\}$ increases slightly as the temperature is raised from 100°C to 200°C. It should be evident that at large $[H_2O]/[N_2O]$ ratios (> 10) $R\{CO_2\}/R\{N_2\}$ is the quantum yield of CO_2, $\Phi\{CO_2\}$, since in the primary photolytic act $\Phi\{N_2\} = 1.00$[17-21] and all the $O(^1D)$ atoms (> 95%) react with H_2O.

Some CO_2 was also produced from the reaction of OH with C_3H_6. At 100°C the quantum yield of CO_2, $\Phi\{CO_2\}$, due to this reaction is 0.025 and at 200°C it is 0.048.

TABLE I: COMPETITIVE REACTION OF $O(^1D)$ WITH N_2O AND H_2O AT 25°C

$\frac{[N_2O]}{[H_2O}$	$[N_2O]$, Torr	$[H_2O]$, Torr	[CO], Torr	Irradiation Time, min.	$10^9 R\{CO_2\}$, M/Sec	$10^9 R\{N_2\}$ M/Sec	$\frac{R\{CO_2\}}{R\{N_2\}}$
17.6	53.0	3.00	8.50	32.0	1.85	9.6	0.192
16.6	49.5	3.00	3.20	12.0	4.75	25.8	0.185
14.9	44.7	3.00	2.30	10.0	5.70	27.8	0.204
14.7	57.5	3.90	2.60	25.0	1.77	10.3	0.173
11.5	57.4	5.00	2.60	12.0	7.62	30.2	0.253
9.30	56.0	6.00	4.00	90.0	1.25	3.52	0.353
7.30	55.5	7.60	2.40	23.0	2.64	9.4	0.281
6.45	51.5	8.00	7.5	90.0	2.59	6.33	0.410
5.22	45.5	8.50	4.00	95.0	1.45	3.18	0.460
3.72[a]	59.5	16.0	10.5	51.0	2.11	4.11	0.510
3.33	55.0	16.5	8.5	10.0	4.93	8.25	0.600
3.30	53.0	16.0	10.0	30.0	4.61	9.5	0.488
0.193	3.25	16.8	10.5	180.0	0.98	0.604	1.64
0.152	2.85	18.7	10.5	172.0	1.03	0.606	1.71

a) This run done at 100°C.

B

TABLE II: N_2O PHOTOLYSIS AT 2139A IN THE PRESENCE OF H_2O-CO-C_3H_6 MIXTURES

$\frac{[C_3H_6]^a}{[CO]}$	$[N_2O]$, Torr	$[H_2O]$, Torr	$[CO]$, Torr	$[C_3H_6]^a$, Torr	Irradiation Time, min.	$10^9 R\{CO_2\}$, M/sec	$10^9 R\{N_2\}$, M/sec	$\frac{R\{CO_2\}}{R\{N_2\}}$
			Temp = 100°C					
0.157	30.0	370	14.0	2.20	60.0	0.57	3.30	0.172
0.110	15.5	490	21.0	2.30	80.0	1.02	3.30	0.310
0.102	3.40	350	24.0	2.45	180.0	0.110	0.505	0.217
0.061	39.0	400	34.5	2.10	77.0	1.44	3.98	0.362
0.0605	10.8	490	43.0	2.60	90.0	0.88	2.39	0.368
0.0365	21.5	400	66.0	2.40	90.0	0.115	0.261	0.442
0.0520	5.10	357	53.5	2.80	210.0	0.93	1.87	0.500
0.025	9.90	490	100	2.50	90.0	1.45	2.20	0.661
0.0161	26.7	400	46.5	0.75	63.0	3.86	5.02	0.770
0.129	28.2	350	58.0	0.75	65.0	2.23	2.14	1.04
0.0122	27.2	350	59.0	0.72	60.0	2.67	2.62	1.02
0.0133	8.80	560	51.0	0.68	90.0	2.26	2.47	0.92
0.0108	16.2	725	60.0	0.65	89.0	1.32	1.50	0.88
0.0094	12.9	340	53.0	0.50	85.0	0.84	0.92	0.92

TABLE II: N_2O PHOTOLYSIS AT 2139A IN THE PRESENCE OF H_2O-CO-C_3H_6 MIXTURES (concluded)

$\frac{[C_3H_6]^a}{[CO]}$	$[N_2O]$, Torr	$[H_2O]$, Torr	[CO], Torr	$[C_3H_6]$, Torr[a]	Irradiation Time, min.	$10^9 R\{CO_2\}$, M/sec	$10^9 R\{N_2\}$, M/sec	$\frac{R\{CO_2\}}{R\{N_2\}}$
				Temp = 100°C				
0.0062	30.0	400	106	0.65	45.0	4.92	5.62	0.88
0.0054	27.3	350	108	0.58	60.0	2.26	2.49	0.91
0.0046	8.90	520	117	0.54	90.0	2.68	2.16	1.24
				Temp = 200°C				
0.151	32.1	440	18.5	2.80	80.0	0.53	1.85	0.288
0.058	28.2	486	46.5	2.70	91.0	1.14	2.08	0.555
0.0348	30.5	462	69	2.40	87.0	1.17	1.76	0.665
0.0212	33.5	440	108	2.30	90.0	1.51	1.84	0.820

a) Average pressure of C_3H_6 during run.

The results for the direct determination of the efficiency of reaction 1b are presented in Table III. The products measured in the presence of TMP are 2-trifluoromethylpropionaldehyde (A) and 2-trifluoromethylpropylene oxide (E). These same products are produced when $O(^3P)$ atoms add to TMP; however the ratio $\Phi\{E\}/\Phi\{A\} = 1.50$[8,9] in that system is very different from that observed in the present system.

Irradiation at 2139A of 75 torr of N_2O in the presence of 660 torr of H_2O at 100°C for 90 minutes gave traces of H_2. However the yield was so small that the quantum yield of 0.004 must be taken as an upper limit for reaction 1d, since it is difficult to exclude other minor sources of H_2.

TABLE III: PHOTOLYSIS OF N_2O AT 2139A IN THE PRESENCE OF H_2O-TMP MIXTURES AT 100°C

$[N_2O]$, Torr	$[H_2O]$, Torr	[TMP], Torr	Irradiation Time, min.	$10^9 \dot{R}\{N_2\}$ M/sec	$\Phi\{E\}^a$	$\Phi\{A\}^a$	$\frac{\Phi\{E\}}{\Phi\{A\}}$
38.0	370	2.00	50.0	2.98	0.020	0.120	0.17
38.0	340	1.25	90.0	3.57	0.025	0.138	0.18

a) $\Phi\{X\} = R\{X\}/R\{N_2\}$

DISCUSSION

Photolysis of N_2O at 2139A in the presence of H_2O, CO and C_3H_6 can be analyzed by the following scheme:

$$N_2O + h\nu \rightarrow N_2 + O(^1D)$$

$$O(^1D) + H_2O \rightarrow 2OH \quad \text{1a}$$

$$\rightarrow O(^3P) + H_2O \quad \text{1b}$$

$$O(^1D) + H_2O + M \rightarrow H_2O_2 + M \quad \text{1c}$$

$$O(^1D) + H_2O \rightarrow O_2 + H_2 \quad \text{1d}$$

$$O(^1D) + N_2O \rightarrow N_2 + O_2 \quad \text{4a}$$

$$O(^1D) + N_2O \rightarrow 2NO \quad \text{4b}$$

$$O(^1D) + CO \rightarrow O(^3P) + CO \quad \text{5}$$

$$OH + C_3H_6 \rightarrow CO_2 + \quad \text{3a}$$

$$\rightarrow \text{not } CO_2 \quad \text{3b}$$

$$OH + CO \rightarrow CO_2 + H \quad \text{2}$$

$$O(^3P) + C_3H_6 \rightarrow \text{Products} \quad \text{6}$$

$$H + C_3H_6 \rightarrow \text{Products} \quad \text{7}$$

The formation of $O(^1D)$ with unit efficiency in the photolysis of N_2O at 2139A is well known.[17-21] The reaction of $O(^1D)$ with N_2O has been extensively studied.[22,23] The exclusive reactions are 4a and 4b with $k_{4a}/k_{4b} = 0.67$[23] when the $O(^1D)$ atoms are produced from N_2O photolysis. Reaction 5 has been studied in this laboratory.[24] The ratio of rate coefficients $k_1/k_5 = 2.6 \exp(-1200/RT)$ where $k_1 \equiv k_{1a} + k_{1b} + k_{1c} + k_{1d}$, and R is in calories/mole-°K. The reactions of OH with C_3H_6 and CO have already been mentioned in the Introduction. The reaction of $O(^3P)$ with C_3H_6 can produce CO_2 a small fraction of the time.[25] However since $O(^3P)$ production turns out to be negligible, the amount of CO_2, if any, from Reaction 6 can be ignored.

Determination of k_1/k_4:

k_1/k_4 may be determined from the variation of $R\{CO_2\}/R\{N_2\}$ with $[N_2O]/[H_2O]$ from experiments in the absence of C_3H_6. The relevant reactions are reactions 1 and 4 followed by reaction 2. The following expression is obtained from this scheme:

$$\left(\frac{1}{1+\alpha}\right)\frac{R\{N_2\}}{R\{CO_2\}} = \frac{1}{2}\frac{k_1}{k_{1a}}\left(1+\frac{k_4[N_2O]}{k_1[H_2O]}\right) \qquad \text{I}$$

where $\alpha \equiv \dfrac{k_{4a}[N_2O]}{k_4[N_2O] + k_1[H_2O]}$

Actually in some runs reaction 5 may quench as much as 10% of the $O(^1D)$, thus reducing the yield of CO_2. However, the reduction may be more than compensated by reformation of CO_2 via the $O(^3P) + CO + M$ reaction. An accurate correction for this effect could be made except for the fact that at low CO pressures some of the $O(^3P)$ atoms will be irreversibly lost at the walls.[26] These effects probably nearly compensate so that the error introduced by neglecting the correction for $O(^1D)$ deactivation by CO cannot be more than 5%.

α may be computed by an iterative procedure from the known value k_{4a}/k_{4b} and from a rough initial value for k_1/k_4 obtained at low $[N_2O]/[H_2O]$. A plot of $[1/(1+\alpha)]R\{N_2\}/R\{CO_2\}$ vs. $[N_2O]/[H_2O]$ should be linear with an intercept of $k_1/2k_{1a}$ and a ratio of slope to intercept of k_4/k_1. The plot is presented in Figure 1. It is reasonably linear with an intercept of 0.50 and a slope of 0.236 independent of temperature in the range of 25°C - 100°C.

The value for k_1/k_4 found from the ratio of intercept to slope is 2.13. This value is in reasonable agreement with the value of 1.50 obtained by Scott and Cvetanović,[6] and in excellent agreement with the results of 2.2 found by Lissi and Heicklen.[7]

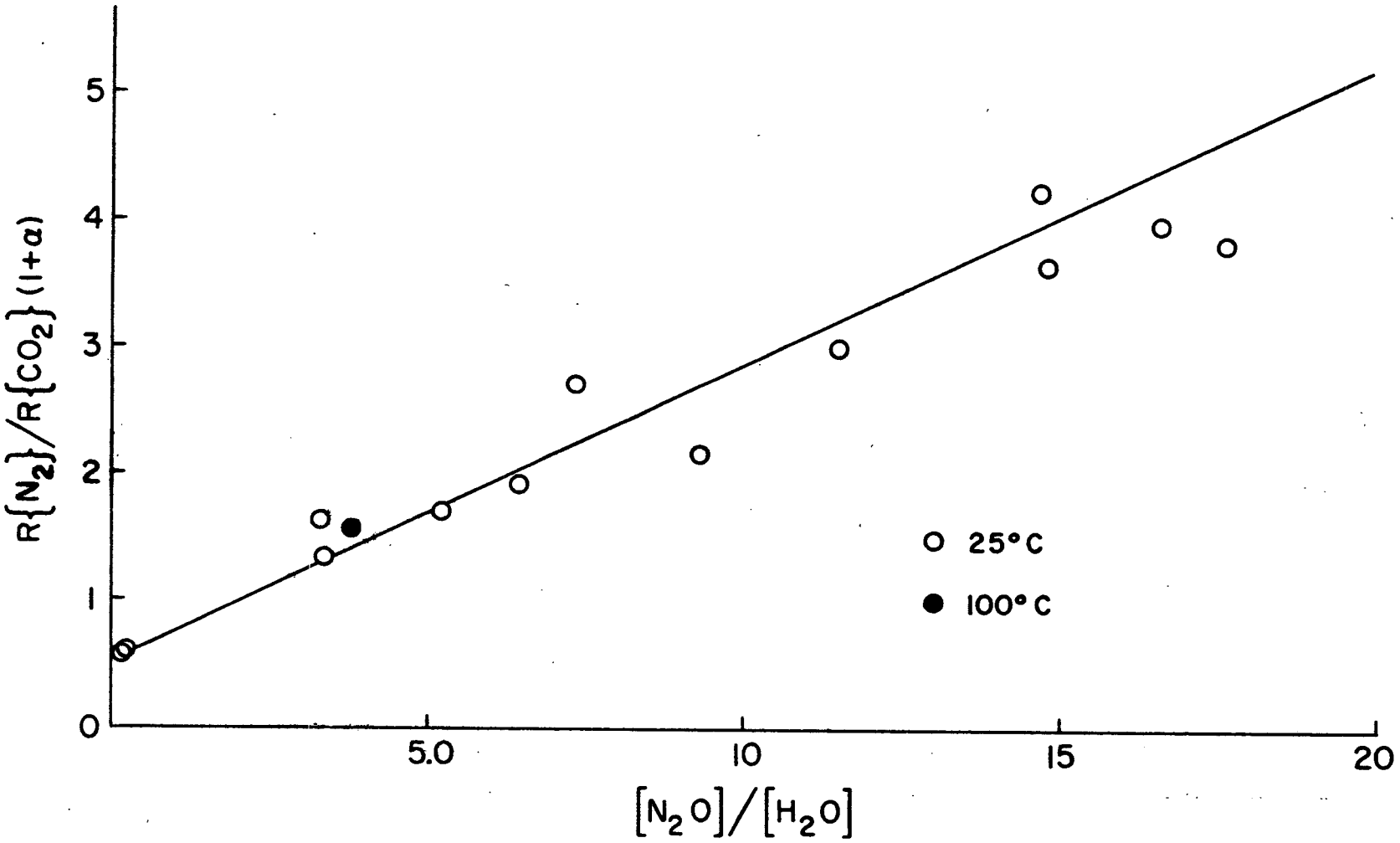

Figure 1

The intercept gives $k_{1a}/k_1 = 1.0$, so that reactions 1b, 1c, and 1d must be unimportant (<10% total). The quantum yields for A and E presented in Table III give an upper limit for reaction 1b. From the ratio of $\Phi\{E\}/\{A\} = 0.18$ it is clear that most of the aldehyde does not arise from $O(^3P)$ atom addition, but from the reaction with OH radicals, since this ratio is 1.50 for $O(^3P)$ atom addition.[8,9] Aldehydes are major products in the reaction of OH radicals with C_2H_4, C_3H_6 and presumably with other olefins.[13] The small yield of the epoxide however could come from $O(^3P)$ or from OH addition. From the epoxide quantum yield an upper limit for $\Phi\{O(^3P)\}$ is 0.040, in agreement with the findings of Paraskevopoulos and Cvetanović.[5]

The quantum yield of H_2 gives an upper limit of 0.004 for reaction 1d. A direct determination of H_2O_2 yield was not possible, but the fact that the intercept in Figure 1 is 1/2 and the fact that this is also the case in the presence of C_3H_6 (see below) indicate that the quantum yield for H_2O_2 production cannot be much greater than 0.05 and probably is zero.

Determination of k_2/k_3:

Based on the reaction scheme of reactions 1-7, the following expression can be obtained

$$\Phi'\{CO_2\}^{-1} = \frac{k_1}{2k_{1a}}\left(1 + \frac{k_3[C_3H_6]}{k_2[CO]}\right) \qquad \text{II}$$

where $\Phi'\{CO_2\} \equiv \beta\Phi\{CO_2\} - \gamma$.

$\Phi'\{CO_2\}$ is essentially the quantum yield of CO_2, $\Phi\{CO_2\}$, corrected for some quenching of $O(^1D)$ by N_2O and CO (β) and for the production of some CO_2 by reaction 3a (γ). Both corrections are small. The correction term β is given by:

$$\beta \equiv 1 + \frac{k_4}{k_1} \frac{[N_2O]}{[H_2O]} + \frac{k_5}{k_1} \frac{[CO]}{[H_2O]}$$

and γ is given by:

$$\gamma = \frac{2k_{1a}}{k_1} \frac{k_{3a}/k_3}{1 + k_2[CO]/k_3[C_3H_6]}$$

β may be readily evaluated using $k_4/k_1 = 0.425$ (see above) and $k_5/k_1 = 0.52$ at 100°C and 0.72 at 200°C.[24] γ may be computed by an iterative procedure using a rough initial value of k_2/k_3 and $k_{3a}/k_3 = 0.025$ at 100°C and 0.048 at 200°C obtained in experiments without added CO (see Results). The correction due to β was never > 22%, and usually < 10%. The correction due to γ was less than a few percent in most runs. However in a few runs, where $[C_3H_6]/[CO]$ was large, the correction amounted to about 20%.

A plot of $\Phi' \{CO_2\}^{-1}$ vs. $[C_3H_6]/[CO]$ should be linear with an intercept of $k_1/2k_{1a}$ and a slope of $\frac{k_1 \ k_3}{2k_1 a k_2}$. This plot is shown in Figure 2 for 100°C and 200°C. The plots are linear with an intercept of 1/2 and a slope of 37.5 at 100°C and an intercept of 1/2 and a slope of 27.4 at 200°C. Consequently $k_{1a}/k_1 = 1.0$ and $k_3/k_2 = 75.0$ at 100°C. At 200°C $k_{1a}/k_1 = 1.0$ and $k_3/k_2 = 55.0$. The Arrhenius expression from the data at the two temperatures may be obtained to be $k_3/k_2 = 293 \exp(+1000/RT)$. An absolute value for k_3 may be calculated from the known value of k_2, which has been the subject of many investigations. Baulch et al.[16] give $k_2 = 7.0 \times 10^{-13} \exp(-1100/RT)$ cm^3/sec based on a critical evaluation of all the determinations. The result is $k_3 = 1.36 \times 10^{-11} \exp(-100/RT)$ cm^3/sec. Thus at room temperature $k_3 = 1.1 \times 10^{-11}$ cm^3/sec. This value compares well the only other available value of 1.7×10^{-11} cm^3/sec obtained by Morris, et al.[13] using a discharge-flow method with mass spectrometric detection.

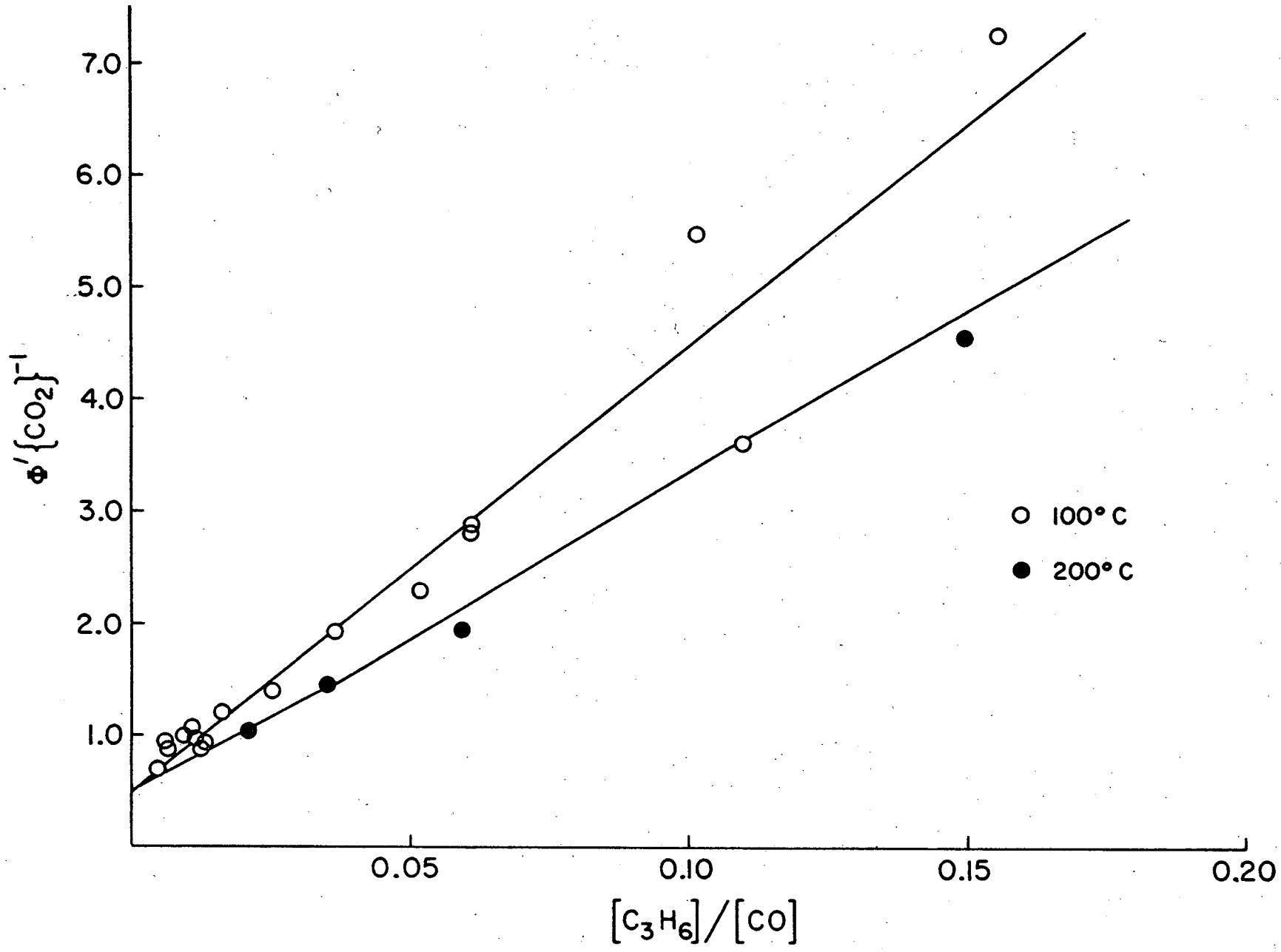

Figure 2

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