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THE REACTION OF O(1D) WITH H₂O AND
THE REACTION OF OH WITH C₃H₆

by

R. Simonaitis and Julian Heicklen

September 5, 1972

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IONOSPHERE RESEARCH LABORATORY

University Park, Pennsylvania
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Project Supervisor

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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGEMENT</td>
<td>i</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>iii</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>iv</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>v</td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>EXPERIMENTAL</td>
<td>4</td>
</tr>
<tr>
<td>RESULTS</td>
<td>6</td>
</tr>
<tr>
<td>DISCUSSION</td>
<td>12</td>
</tr>
<tr>
<td>Determination of $k_1/k_4$</td>
<td>13</td>
</tr>
<tr>
<td>Determination of $k_2/k_3$</td>
<td>15</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>18</td>
</tr>
</tbody>
</table>
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. Competititive Reaction of ( O(1^D) ) with ( N_2O ) and ( H_2O ) at 25(^\circ)C</td>
<td>7</td>
</tr>
<tr>
<td>II. ( N_2O ) Photolysis at 2139A in the Presence of ( H_2O-CO-C_3H_6 ) Mixtures</td>
<td>8</td>
</tr>
<tr>
<td>III. Photolysis of ( N_2O ) at 2139A in the Presence of ( H_2O-TMP ) Mixtures at 10(^\circ)C</td>
<td>11</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Plot of $R{N_2}/R{CO_2} \left(1 + a\right)$ vs. $\left[N_2O\right]/\left[H_2O\right]$ in the photolysis of $N_2O$ in the presence of $H_2O$ and $CO$.</td>
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<td>2</td>
<td>Plot of $\Phi' {CO_2}^{-1}$ vs. $\left[C_3H_6\right]/\left[CO\right]$ in the photolysis of $N_2O$ in the presence of $H_2O$, $CO$, and $C_3H_6$.</td>
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Abstract

$\text{N}_2\text{O}$ was photolyzed at 2139 Å 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 $C_3H_6$.

$$OH + CO \rightarrow CO_2 + H$$
$$OH + C_3H_6 \rightarrow \text{products}$$

From the $CO_2$ yield, $k_3/k_2 = 75.0$ at $100^\circ C$ and $55.0$ at $200^\circ C$. 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 $25^\circ C$, $k_3$ extrapolates to $1.1 \times 10^{-11}$ cm$^3$/sec.
INTRODUCTION

The reaction between O(1D) and H₂O is the principle source of OH radicals in the stratosphere and it is one of the key reactions in assessing the effects on the O₃ layer of introducing H₂O into the stratosphere by supersonic aircraft. From laboratory measurements it is known that the reaction of O(1D) with H₂O gives OH radicals.

McGrath and Norrish⁴ demonstrated the presence of OH radicals in the flash photolysis of O₃-H₂O mixtures and proposed the reaction

\[ O(1D) + H₂O \rightarrow 2OH \]  
(1a)

In further experiments, Basco and Norrish⁵ demonstrated that up to 2 quants of vibrational energy could be present in the OH radical. More recently Biedenkapp, Hartzhorn, and Bair⁶ 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

\[ O(1D) + H₂O \rightarrow O(3P) + H₂O \]  
(1b)

\[ O(1D) + H₂O + M \rightarrow H₂O₂ + M \]  
(1c)

\[ O(1D) + H₂O \rightarrow H₂ + O₂ \]  
(1d)

A recent report⁷ has indicated that reaction 1b is unimportant.

The absolute total rate constant for the reaction of O(1D) with H₂O has been measured by Bair and coworkers⁸ by flash photolysis of ozone-H₂O mixtures to be 3.1 x 10⁻¹¹ cm³/sec. However, this number differs by an order of magnitude, when compared with the rate constant for O(1D) + N₂O, with the relative value of 1.5 obtained by Scott and Cvetanović⁹ and 2.2 obtained by Lissi and Heicklen.⁵

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 $O(1^D)$ atoms were generated by the photolysis of $N_2O$ at 2139Å radiation in the presence of $H_2O$, $CO$, and in some cases $C_3H_6$. The $O(1^D)$ 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

$$OH + G0 \rightarrow CO_2 + H$$

The resulting $CO_2$ production is therefore a measure of $OH$ production.

The presence of small amounts of propylene scavenges any $O(3^P)$ atoms that may be formed in reaction 1b, thus preventing $CO_2$ formation via

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

Actually, the rate constant for reaction 3

$$OH + C_3H_6 \rightarrow \text{products}$$

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 $O(3^P)$. 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 $O(3^P)$ 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. 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 NO₂. The reaction between OH and olefins was studied by Wilson and Westenberg in a flow-discharge system using ESR detection, by Greiner using flash photolysis and ultraviolet absorption spectroscopy for OH detection, and by Morris, et al. in a discharge flow system using mass spectrometric detection. Avramenko and Kolesnikova have also studied OH reactions with olefins, but their water discharge method has been shown to be unsuitable for kinetic studies. 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, 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 \(\pm 1\)°C by a Cole-Parmer Proportio Null Regulator Series 1300.

The \(\text{N}_2\text{O}\) and CO used were Matheson C. P. grade. The \(\text{N}_2\text{O}\) was purified by passage over ascarite and degassed at \(-196\)°C. Gas chromatographic analysis indicated no detectable impurities. In particular \(\text{CO}_2\) and \(\text{N}_2\) 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 \(\text{CO}_2\) but contained 540 ppm of \(\text{N}_2\). The \(\text{N}_2\) yield in any photolysis experiment was appropriately corrected for this background \(\text{N}_2\). 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 \(\text{CO}_2\). 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 \(\text{H}_2\text{O}\) 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 \(\text{H}_2\text{O}\) pressures were not measured directly, but calculated assuming the perfect gas law. Our procedure was to introduce \(\text{H}_2\text{O}\) 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$_2$O pressure was calculated.

Irradiation was from a Phillips Zn resonance lamp Typ 93106E. The effective radiation was at 2139 Å. 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$_2$ ($\approx 0.03 \mu$/min.) was produced in the dark. At 200°C the dark reaction was somewhat larger ($\approx 0.15 \mu$/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$_3$H$_6$], appreciable amounts of C$_3$H$_6$ were consumed. The amount remaining was determined at the end of the run by gas chromatographic analysis and the average value of [C$_3$H$_6$] 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 \( \text{N}_2\text{O} \) and \( \text{H}_2\text{O} \) for the \( \text{O}(^1\text{D}) \) atom are presented in Table I. \( \text{N}_2\text{O} \) was irradiated in the presence of \( \text{H}_2\text{O} \) and CO. The products observed were \( \text{N}_2 \), \( \text{CO}_2 \), \( \text{O}_2 \), and \( \text{H}_2 \), but only the \( \text{N}_2 \) and \( \text{CO}_2 \) were measured. The ratio \( \text{R}\{\text{CO}_2\}/\text{R}\{\text{N}_2\} \) increases as the \( [\text{N}_2\text{O}]/[\text{H}_2\text{O}] \) ratio decreases, reaching a value of 1.71 at our lowest \( [\text{N}_2\text{O}]/[\text{H}_2\text{O}] \) ratio of 0.152. The \( \text{R}\{\text{CO}_2\}/\text{R}\{\text{N}_2\} \) ratio is otherwise independent of \( \text{N}_2\text{O} \) or \( \text{H}_2\text{O} \) 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 \( \text{C}_3\text{H}_6 \) were carried out in excess \( \text{H}_2\text{O} \) in order to minimize the deactivation of \( \text{O}(^1\text{D}) \) by \( \text{N}_2\text{O} \) and CO. Also, in order to achieve high pressures of \( \text{H}_2\text{O} \), the minimum temperature employed was 100°C. Some experiments were also performed at 200°C. The only products measured were \( \text{CO}_2 \) and \( \text{N}_2 \). The \( \text{R}\{\text{CO}_2\}/\text{R}\{\text{N}_2\} \) ratio is independent of the time of irradiation, the absorbed light intensity (changed by a factor of \( \sim 8 \)), the \( \text{N}_2\text{O} \) pressure or the \( [\text{N}_2\text{O}]/[\text{H}_2\text{O}] \) ratio. \( \text{R}\{\text{CO}_2\}/\text{R}\{\text{N}_2\} \) depends only on the \( [\text{C}_3\text{H}_6]/[\text{CO}] \) ratio and the temperature. It increases with a decreasing \( [\text{C}_3\text{H}_6]/[\text{CO}] \) ratio and reaches a value of 1.24 at our lowest \( [\text{C}_3\text{H}_6]/[\text{CO}] \) ratio of 0.0046. \( \text{R}\{\text{CO}_2\}/\text{R}\{\text{N}_2\} \) increases slightly as the temperature is raised from 100°C to 200°C. It should be evident that at large \( [\text{H}_2\text{O}]/[\text{N}_2\text{O}] \) ratios (> 10) \( \text{R}\{\text{CO}_2\}/\text{R}\{\text{N}_2\} \) is the quantum yield of \( \text{CO}_2 \), \( \Phi\{\text{CO}_2\} \), since in the primary photolytic act \( \Phi\{\text{N}_2\} = 1.00^{17-21} \) and all the \( \text{O}(^1\text{D}) \) atoms (> 95%) react with \( \text{H}_2\text{O} \).

Some \( \text{CO}_2 \) was also produced from the reaction of \( \text{OH} \) with \( \text{C}_3\text{H}_6 \). At 100°C the quantum yield of \( \text{CO}_2 \), \( \Phi\{\text{CO}_2\} \), due to this reaction is 0.025 and at 200°C it is 0.048.
TABLE I: COMPETITIVE REACTION OF O(1D) WITH N₂O AND H₂O AT 25°C

<table>
<thead>
<tr>
<th>[N₂O]</th>
<th>[N₂O],</th>
<th>[H₂O],</th>
<th>[CO],</th>
<th>Irradiation</th>
<th>10⁹R</th>
<th>10⁹R</th>
<th>R(N₂)</th>
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<td>[H₂O]</td>
<td>Torr</td>
<td>Torr</td>
<td>Torr</td>
<td>Time, min.</td>
<td>M/Sec</td>
<td>M/Sec</td>
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a) This run done at 100°C.
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<th>[N(_2)O], Torr</th>
<th>[H(_2)O], Torr</th>
<th>[CO], Torr</th>
<th>[C(_3)H(_6)], Torr</th>
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</tr>
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<td>0.0094</td>
<td>12.9</td>
<td>340</td>
<td>53.0</td>
<td>0.50</td>
<td>85.0</td>
<td>0.84</td>
<td>0.92</td>
<td>0.92</td>
</tr>
</tbody>
</table>
TABLE II: N₂O PHOTOLYSIS AT 2139A IN THE PRESENCE OF H₂O-CO-C₃H₆ MIXTURES (concluded)

<table>
<thead>
<tr>
<th>[C₃H₆]²¹</th>
<th>[N₂O], Torr</th>
<th>[H₂O], Torr</th>
<th>[CO], Torr</th>
<th>[C₃H₆], Torr</th>
<th>Irradiation Time, min.</th>
<th>10⁹[R{CO₂}], M/sec</th>
<th>10⁹[R{N₂}], M/sec</th>
<th>R{CO₂} / R{N₂}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0062</td>
<td>30.0</td>
<td>400</td>
<td>106</td>
<td>0.65</td>
<td>45.0</td>
<td>4.92</td>
<td>5.62</td>
<td>0.88</td>
</tr>
<tr>
<td>0.0054</td>
<td>27.3</td>
<td>350</td>
<td>108</td>
<td>0.58</td>
<td>60.0</td>
<td>2.26</td>
<td>2.49</td>
<td>0.91</td>
</tr>
<tr>
<td>0.0046</td>
<td>8.90</td>
<td>520</td>
<td>117</td>
<td>0.54</td>
<td>90.0</td>
<td>2.68</td>
<td>2.16</td>
<td>1.24</td>
</tr>
</tbody>
</table>

Temp = 100°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         |

Temp = 200°C

a) Average pressure of C₃H₆ 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 2139Å of 75 torr of N$_2$O in the presence of 660 torr of H$_2$O 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 N₂O AT 2139Å IN THE PRESENCE OF H₂O-TMP MIXTURES AT 100°C

<table>
<thead>
<tr>
<th>[N₂O], Torr</th>
<th>[H₂O], Torr</th>
<th>[TMP], Torr</th>
<th>Irradiation Time, min.</th>
<th>( \frac{N₂}{R} )</th>
<th>( \frac{N₂}{M/sec} )</th>
<th>( \Phi{E}^a )</th>
<th>( \Phi{A}^a )</th>
<th>( \Phi{E} )</th>
<th>( \Phi{A} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>38.0</td>
<td>370</td>
<td>2.00</td>
<td>50.0</td>
<td>2.98</td>
<td>0.020</td>
<td>0.120</td>
<td>0.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>38.0</td>
<td>340</td>
<td>1.25</td>
<td>90.0</td>
<td>3.57</td>
<td>0.025</td>
<td>0.138</td>
<td>0.18</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) \( \Phi\{X\} = \frac{R\{X\}}{R\{N₂\}} \)
DISCUSSION

Photolysis of N$_2$O at 2139A in the presence of H$_2$O, CO and C$_3$H$_6$ can be analyzed by the following scheme:

\[ \text{N}_2\text{O} + \text{hv} \rightarrow \text{N}_2 + \text{O}^{(1D)} \]  
\[ \text{O}^{(1D)} + \text{H}_2\text{O} \rightarrow 2\text{OH} \]  
\[ \rightarrow \text{O}^{(3P)} + \text{H}_2\text{O} \]  
\[ \text{O}^{(1D)} + \text{H}_2\text{O} + \text{M} \rightarrow \text{H}_2\text{O}_2 + \text{M} \]  
\[ \text{O}^{(1D)} + \text{H}_2\text{O} \rightarrow \text{O}_2 + \text{H}_2 \]  
\[ \text{O}^{(1D)} + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}_2 \]  
\[ \text{O}^{(1D)} + \text{N}_2\text{O} \rightarrow 2\text{N}_2 \]  
\[ \text{O}^{(1D)} + \text{CO} \rightarrow \text{O}^{(3P)} + \text{CO} \]  
\[ \text{OH} + \text{C}_3\text{H}_6 \rightarrow \text{CO}_2 + \text{not CO}_2 \]  
\[ \rightarrow \text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H} \]  
\[ \text{O}^{(3P)} + \text{C}_3\text{H}_6 \rightarrow \text{Products} \]  
\[ \text{H} + \text{C}_3\text{H}_6 \rightarrow \text{Products} \]

The formation of O$^{(1D)}$ with unit efficiency in the photolysis of N$_2$O at 2139A is well known.$^{17-21}$ The reaction of O$^{(1D)}$ with N$_2$O 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$_2$O 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$_3$H$_6$ and CO have already been mentioned in the Introduction. The reaction of O$^{(3P)}$ with C$_3$H$_6$ 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 $R\{\text{CO}_2\}/R\{\text{N}_2\}$ with $[\text{N}_2\text{O}]/[\text{H}_2\text{O}]$ from experiments in the absence of $\text{C}_3\text{H}_6$. The relevant reactions are reactions 1 and 4 followed by reaction 2. The following expression is obtained from this scheme:

$$
\left( \frac{1}{1 + \alpha} \right) \frac{R\{\text{N}_2\}}{R\{\text{CO}_2\}} = \frac{1}{2} \frac{k_1}{k_{1a}} \left( 1 + \frac{k_4[\text{N}_2\text{O}]}{k_1[\text{H}_2\text{O}]} \right)
$$

where $\alpha = \frac{k_{4a}[\text{N}_2\text{O}]}{k_4[\text{N}_2\text{O}] + k_1[\text{H}_2\text{O}]}$

Actually in some runs reaction 5 may quench as much as 10% of the $\text{O}(^1\text{D})$, thus reducing the yield of $\text{CO}_2$. However, the reduction may be more than compensated by reformation of $\text{CO}_2$ via the $\text{O}(^3\text{P}) + \text{CO} + \text{M}$ reaction. An accurate correction for this effect could be made except for the fact that at low $\text{CO}$ pressures some of the $\text{O}(^3\text{P})$ atoms will be irreversibly lost at the walls.\textsuperscript{26} These effects probably nearly compensate so that the error introduced by neglecting the correction for $\text{O}(^1\text{D})$ deactivation by $\text{CO}$ cannot be more than 5%.

$\alpha$ 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 $[\text{N}_2\text{O}]/[\text{H}_2\text{O}]$. A plot of $[1/(1 + \alpha)]R\{\text{N}_2\}/R\{\text{CO}_2\}$ vs. $[\text{N}_2\text{O}]/[\text{H}_2\text{O}]$ 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,\textsuperscript{6} and in excellent agreement with the results of 2.2 found by Lissi and Heicklen.\textsuperscript{7}
Figure 1

\[ \frac{R[N_2]}{R[CO_2]}(1+\alpha) \]

vs.

\[ \frac{[N_2O]}{[H_2O]} \]

- Open circles represent data at 25°C.
- Filled circles represent data at 100°C.
The intercept gives \( k_{1a}/k_1 = 1.0 \), so that reactions lb, lc, and ld must be unimportant (<10% total). The quantum yields for A and E presented in Table III give an upper limit for reaction lb. From the ratio of \( \Phi(E)/\{A\} = 0.18 \) it is clear that most of the aldehyde does not arise from \( \text{O}(^3\text{P}) \) atom addition, but from the reaction with OH radicals, since this ratio is 1.50 for \( \text{O}(^3\text{P}) \) atom addition.\(^8\),\(^9\) Aldehydes are major products in the reaction of OH radicals with \( \text{C}_2\text{H}_4, \text{C}_3\text{H}_6 \) and presumably with other olefins.\(^13\) The small yield of the epoxide however could come from \( \text{O}(^3\text{P}) \) or from OH addition. From the epoxide quantum yield an upper limit for \( \Phi\{\text{O}(^3\text{P})\} \) is 0.040, in agreement with the findings of Paraskevopoulos and Cvetanović.\(^5\)

The quantum yield of \( \text{H}_2 \) gives an upper limit of 0.004 for reaction ld. A direct determination of \( \text{H}_2\text{O}_2 \) 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 \( \text{C}_3\text{H}_6 \) see below) indicate that the quantum yield for \( \text{H}_2\text{O}_2 \) 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

\[
\Phi' \{\text{CO}_2\}^{-1} = \frac{k_1}{2k_{1a}} \left( 1 + \frac{k_3 \{\text{C}_3\text{H}_6\}}{k_2 \{\text{CO}\}} \right)
\]

where \( \Phi' \{\text{CO}_2\} = 2\Phi'\{\text{CO}_2\} - \gamma \).

\( \Phi' \{\text{CO}_2\} \) is essentially the quantum yield of \( \text{CO}_2 \), \( \Phi'\{\text{CO}_2\} \), corrected for some quenching of \( \text{O}(^1\text{D}) \) by \( \text{N}_2\text{O} \) and \( \text{CO} \) (\( \beta \)) and for the production of some \( \text{CO}_2 \) by reaction 3a (\( \gamma \)). Both corrections are small. The correction term \( \beta \) is given by:
\[ \beta = 1 + \frac{k_4}{k_1} \frac{[N_2O]}{[H_2O]} + \frac{k_5}{k_1} \frac{[CO]}{[H_2O]} \]

and \( \gamma \) is given by:

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

\( \beta \) 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.\(^{24} \) \( \gamma \) 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 \( \beta \) was never > 22%, and usually < 10%. The correction due to \( \gamma \) 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 \( \Phi^1 (CO_2)^{-1} \) vs. \([C_3H_6]/[CO]\) should be linear with an intercept of \( k_1/2k_{1a} \) and a slope of \( k_1 k_3 / 2k_{1a}k_2 \). 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 \( 1.7 \times 10^{-11} \) cm\(^3\)/sec obtained by Morris, et al.\(^13 \) using a discharge-flow method with mass spectrometric detection.
Figure 2
REFERENCES