ON THE PRODUCTION OF N₂O FROM THE REACTION OF O(¹D) WITH N₂

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R. Simonaitis, Eduardo Lissi and Julian Heicklen
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ABSTRACT

Ozone was photolyzed at 2537 Å and 25°C in the presence of 42-115 torr of O₂ and about 880 torr of N₂ to test the relative importance of the two reactions

\[ \text{O}(^1\text{D}) + \text{N}_2 + \text{M} \rightarrow \text{N}_2\text{O} + \text{M} \]  
\[ \text{O}(^1\text{D}) + \text{N}_2 \rightarrow \text{O}^3\text{P} + \text{N}_2 \]

N₂O was not found as a product. Thus from our detectability limit for N₂O (0.3 μ), an upper limit to the efficiency of the first reaction relative to the second of \(2.5 \times 10^{-6}\) at 1000 torr total pressure was computed. This corresponds to \(k_1/k_2 < 0.8 \times 10^{-25}\) cm³/particle.
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INTRODUCTION

The source of $\text{N}_2\text{O}$ in the earth's upper atmosphere is still an unsolved problem. Some time ago Bates and Witherspoon\(^1\) considered the reaction

$$\text{O}(^1\text{D}) + \text{N}_2 + \text{M} \rightarrow \text{N}_2\text{O} + \text{M} \quad (1)$$

but more recently Bates and Hayes\(^2\) ignored this reaction because it was negligible compared to the deactivation of $\text{O}(^1\text{D})$ by $\text{N}_2$.

$$\text{O}(^1\text{D}) + \text{N}_2 \rightarrow \text{O}(^3\text{P}) + \text{N}_2 \quad (2)$$

However very recently Nicolet\(^3\) has again considered reaction 1, and has concluded that if it occurs $10^{-4}$ as often as reaction 2, it should be the principle source of $\text{N}_2\text{O}$ in the stratosphere.

There is experimental evidence that reaction 1 does occur. Groth and Schierholz\(^4\) photolyzed $\text{O}_2$ at 1470 A and 7 torr pressure in the presence of 419 torr of $\text{N}_2$ and found that about $10^{-4}$ of the oxygen atoms reacted with $\text{N}_2$ to produce $\text{N}_2\text{O}$. However, Katakis and Taube\(^5\) photolyzed $\text{O}_3$ at 2537 A at pressures of 10-100 torr in the presence of 300-500 torr of $\text{N}_2$, and could not find any oxides of nitrogen; under their conditions, the quantum yield of $\text{N}_2\text{O}$ formation, $\Phi\{\text{N}_2\text{O}\}$, was $< 10^{-4}$.

DeMore and Raper\(^6\) examined the photolysis of $\text{O}_3$ in liquid $\text{N}_2$ and found that for incident radiation between 2480 and 3000 A, $\Phi\{\text{N}_2\text{O}\} = 0.014$. This value is then the upper limiting value, since it was obtained in the condensed phase at -196\(^0\)C, conditions which tend to favor reaction 1 over reaction 2; in the gas phase at more elevated temperatures, the yield must be considerably smaller.
We have re-examined this problem in order to resolve the discrepancy between the results of Groth and Schierholz and of Katakis and Taube and to obtain a more accurate value for the efficiency of reaction 1 in the gas phase. At 1000 torr total pressure (N\textsubscript{2} + O\textsubscript{2}, mostly N\textsubscript{2}), we have found no evidence for N\textsubscript{2}O formation. Consequently the upper limit for the efficiency of reaction 1 at 1000 torr is $< 2.6 \times 10^{-6}$ compared to reaction 2. This upper limit for the efficiency for this reaction has thus been reduced by a factor of 40.
EXPERIMENTAL

Matheson O₂ and Prep. Grade N₂ were purified by passage over traps maintained at -196°C. Both the N₂ and O₂ contained each other as impurities but this is irrelevant. Ozone was prepared by passing an electric discharge through the O₂. The O₃ produced was collected at -196°C, and the excess O₂ pumped away. The O₃ was then distilled at -186°C, stored at -196°C, and degassed at this temperature before each run.

A conventional high-vacuum line utilizing Teflon stopcocks with Viton "O" rings was used. Both mercury and stopcock grease were vigorously excluded. Pressures of O₃ were measured on a sulfuric acid manometer; N₂ and O₂ pressures, on a NRL alphantron gauge. The reaction cell was a cylindrical quartz cell 10 cm long and 5 cm in diameter. During a run the O₃ was monitored by light absorption. Dark decomposition of the O₃ was negligible.

A Hanovia flat-spiral low-pressure Hg resonance lamp Model No. Z1400-013 was used as a radiation source. A Corning 7-54 filter, which removes wavelengths below 2200 and above 4000 Å was used.

After irradiation, the mixture was passed through three traps at -196°C, the first trap being filled with glass wool. The non-condensable gases were removed. The remaining fraction was analyzed for N₂O by gas chromatography on a Porapak Q column, 1/4-inch in diameter by 24 ft. long operated at room temperature. Blank runs which were not irradiated gave ~0.2 - 0.3 μ of N₂O.
RESULTS AND DISCUSSION

Experiments were done in which the incident radiation was from a filtered mercury resonance lamp, so that the only effective wavelength was at 2537 A. Ozone at 5-12 torr pressure was photolyzed for 9-24 hours in the presence of 31 to 155 torr O₂ and 870-1050 torr N₂. The purpose of the added O₂ was to reduce the net rate of O₃ consumption by introducing reaction 3.

\[ O(^3P) + O₂ + M \rightarrow O₃ + M \]  

Thus, for example, in the absence of added O₂, 2 torr of O₃ is completely consumed in 2 minutes; whereas, if 100 torr of O₂ is present it takes 24 hours to completely consume the ozone. Based on a total of 6 experiments, no N₂O above that present as background (0.3 μ) was observed. Consequently, the upper limit for the N₂O yield is ∼0.3 μ.

In order to be certain that the small amount of N₂O is not lost during analysis control experiments were done in which several μ of N₂O were added to an identical gas mixture as in an actual run. Complete recovery of the added N₂O was achieved. Finally, 10.5 μ of N₂O were added to a mixture of O₃ - O₂ - N₂ (13.5:42:880 torr) and photolyzed for 24 hours with no change in N₂O concentration to be certain that N₂O is not consumed by the O(¹D) atoms produced from O₃ photolysis via the reactions

\[ O(¹D) + N₂O \rightarrow N₂ + O₂ \]
\[ O(¹D) + N₂O \rightarrow 2NO \]
Consequently, N\textsubscript{2}O consumption for N\textsubscript{2}O pressures \( \leq 10 \mu \) via the above reactions is not important.

The known mechanism of O\textsubscript{3} photolysis at 2537 Å and in the presence of O\textsubscript{2} and N\textsubscript{2} is the following:

\[
\begin{align*}
    O_3 + h\nu &\rightarrow O_2(\tilde{1}\Delta) + O(1D) & \text{Rate} = I_a \\
    O(1D) + N_2 + M &\rightarrow N_2O + M \quad 1 \\
    O(1D) + N_2 &\rightarrow O(3P) + N_2 \quad 2 \\
    O(1D) + O_3 &\rightarrow O_2 + O_2^* \quad 3a \\
    O(1D) + O_3 &\rightarrow 2O_2 \quad 3b \\
    O(1D) + O_2 &\rightarrow O(3P) + O_2 (1\Sigma) \quad 4 \\
    O_2(\tilde{1}\Delta), O_2 (1\Sigma) \text{ or } O_2^* + O_3 &\rightarrow 2O_2 + O(3P) \quad 5 \\
    O(3P) + O_3 &\rightarrow 2O_2 \quad 6 \\
    O(3P) + O_2 + M &\rightarrow O_3 + M \quad 7
\end{align*}
\]

where \( O_2^* \) is an unspecified electronic state of \( O_2 \) (see reference 7).

With the realization that reaction 1 is unimportant, the mechanism leads to the expression

\[
k_1[M]/k_2 = \frac{n\{N_2O\}}{n\{O(1D)\}} \left( 1 + \frac{k_3[O_3]}{k_2[N_2]} + \frac{k_4[O_2]}{k_2[N_2]} \right)
\]

where \( n\{N_2O\} \) and \( n\{O(1D)\} \) are the quantities of N\textsubscript{2}O and O(\textsuperscript{1}D) atoms produced. \( n\{O(1D)\} \) is obtained by graphical integration from Eqn. II.

\[
n\{O(1D)\} = I_a \int_{0}^{\infty} \frac{I_a}{t} \, dt \quad \text{II}
\]
where $I_a/I_o$ is the fraction of light absorbed, $I_a'$ is the absorbed light intensity for $I_a/I_o = 1.0$, and $t$ is the irradiation time.

A typical graph of $I_a/I_o$ vs. $t$ is shown in Figure 1. The quantity $I_a'$ was found to be $200 \pm 30 \mu\text{m/min}$ from the photolysis of $O_3$ alone, where the quantum yield of $O_3$ disappearance is 5.5 for small conversions. The values obtained for $n\{O(1D)\}$ are shown in Table I.

In order to compute $k_1[M]/k_2$ from Eqn. I, values of $k_3/k_2 = 11.0$ \textsuperscript{7,8} and $k_4/k_2 = 0.8$ \textsuperscript{9-11} were used. These values are averages of those given in the references. In computing $k_1[M]/k_2$ from Eqn. I, average values of $[O_3]$ were used, since the term $k_3[O_3]/k_2[N_2]$ is small. The value of $< 2.5 \times 10^{-6}$ for the experiment at the highest $O_2$ pressure can be taken as the upper limit for the efficiency of reaction 1 compared to reaction 2 at $25^\circ\text{C}$ and 1000 torr total pressure (87% $N_2$). If reaction 1 is entirely in the third order regime, then $k_1/k_2 < 0.8 \times 10^{-25}\text{cm}^3/\text{particle}$. The known value for $k_2$ is $9 \times 10^{-11}\text{cm}^3/\text{particle-sec}$,\textsuperscript{10} and is probably accurate to better than a factor of two. Thus $k_1 < 0.7 \times 10^{-35}\text{cm}^6/\text{particle-sec}$. At stratospheric pressures of 30-50 torr, reaction 1 occurs no more than $2 \times 10^{-7}$ as often as reaction 2. This is about a factor of 500 smaller than the value estimated by Nicolet\textsuperscript{3} to be necessary for reaction 1 to be an important atmospheric source of $N_2O$. 

ACKNOWLEDGEMENT

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REFERENCES

7. For a recent review see E. Lissi and J. Heicklen, J. Photochem., in press (1972).
TABLE I

<table>
<thead>
<tr>
<th>[O\textsubscript{3}]\textsubscript{0}, Torr</th>
<th>[O\textsubscript{2}], Torr</th>
<th>[N\textsubscript{2}], Torr</th>
<th>Irradiation Time, hrs.\textsuperscript{a}</th>
<th>n{O(\textsuperscript{1}D)}, Torr</th>
<th>(10^6k_1[M]/k_2) \textsuperscript{b}</th>
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<td>12.0</td>
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<tr>
<td>6.80</td>
<td>47</td>
<td>900</td>
<td>12</td>
<td>65</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>9.60</td>
<td>115</td>
<td>870</td>
<td>24</td>
<td>154</td>
<td>&lt; 2.5</td>
</tr>
</tbody>
</table>

\textsuperscript{a} O\textsubscript{3} always completely consumed.

\textsuperscript{b} upper limit calculated from Eqn. I and the upper limit for the N\textsubscript{2}O yield of 0.3 \textmu. 
FIGURE 1

Plot of the fraction of light absorbed vs. irradiation time for the photolysis at 2537 Å and 25°C of a mixture consisting initially of 9.6 torr O₃, 115 torr O₂, and 870 torr N₂.
Figure 1