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

by
R. Simonaitis, Eduardo Lissi and Julian Heicklen
February 22, 1972

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"On the Production of \( \text{N}_2\text{O} \) from the Reaction of \( \text{O}(^1\text{D}) \) with \( \text{N}_2 \)" \\
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ABSTRACT

Ozone was photolyzed at 2537Å 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

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

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

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 x 10⁻⁶ at 1000 torr total pressure was computed. This corresponds to \( k_1/k_2 < 0.8 \times 10^{-25} \text{ cm}^3/\text{particle} \).
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INTRODUCTION

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

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

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

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

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 N$_2$O in the stratosphere.

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

DeMore and Raper$^6$ examined the photolysis of O$_3$ in liquid N$_2$ and found that for incident radiation between 2480 and 3000 Å, $\Phi$\{N$_2$O\} = 0.014. This value is then the upper limiting value, since it was obtained in the condensed phase at -196$^\circ$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 (N₂ + O₂, mostly N₂), we have found no evidence for N₂O formation. Consequently the upper limit for the efficiency of reaction 1 at 1000 torr is \( \leq 2.6 \times 10^{-6} \) compared to reaction 2. This upper limit for the efficiency for this reaction has thus been reduced by a factor of 40.
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 alphatron 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 Å. Ozone at 5-12 torr pressure was photolyzed for 9-24 hours in the presence of 31 to 155 torr O$_2$ and 870-1050 torr N$_2$. The purpose of the added O$_2$ was to reduce the net rate of O$_3$ consumption by introducing reaction 3.

$$O(3P) + O_2 + M \rightarrow O_3 + M$$  \hspace{1cm} 3

Thus, for example, in the absence of added O$_2$, 2 torr of O$_3$ is completely consumed in 2 minutes; whereas, if 100 torr of O$_2$ is present it takes 24 hours to completely consume the ozone. Based on a total of 6 experiments, no N$_2$O above that present as background (0.3 μ) was observed. Consequently, the upper limit for the N$_2$O yield is ~0.3 μ. In order to be certain that the small amount of N$_2$O is not lost during analysis control experiments were done in which several μ of N$_2$O were added to an identical gas mixture as in an actual run. Complete recovery of the added N$_2$O was achieved. Finally, 10.5 μ of N$_2$O were added to a mixture of O$_3$ - O$_2$ - N$_2$ (13.5:42:880 torr) and photolyzed for 24 hours with no change in N$_2$O concentration to be certain that N$_2$O is not consumed by the O($^1D$) atoms produced from O$_3$ photolysis via the reactions

$$O(1D) + N_2O \rightarrow N_2 + O_2$$

$$O(1D) + N_2O \rightarrow 2NO$$
Consequently, N₂O consumption for N₂O pressures ≤ 10 μ via the above reactions is not important.

The known mechanism of O₃ photolysis at 2537 Å and in the presence of O₂ and N₂ is the following:⁷

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

where O₂* is an unspecified electronic state of O₂ (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 N₂O and O(¹D) atoms produced. \(n\{O(1D)\}\) is obtained by graphical integration from Eqn. II.

\[
n\{O(1D)\} = I_a \int_{t=0}^{t=\infty} \frac{I_a}{I_0} \, dt
\]
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 ± 30 \( \mu \)g/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. 1, values of \( k_3/k_2 = 11.0 \) and \( k_4/k_2 = 0.8 \) were used. These values are averages of those given in the references. In computing \( k_1[M]/k_2 \) from Eqn. 1, 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°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 \( 9 \times 10^{-11} \text{cm}^3/\text{particle-sec} \), 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 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).


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<tr>
<th>[O$_3$]$_0$, Torr</th>
<th>[O$_2$], Torr</th>
<th>[N$_2$], Torr</th>
<th>Irradiation Time, hrs. $^a$</th>
<th>n(O($^1$D)), Torr</th>
<th>$10^6 k_1 [M]/k_2$ $^b$</th>
</tr>
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<td>23</td>
<td>63</td>
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</tr>
<tr>
<td>6.80</td>
<td>47</td>
<td>900</td>
<td>12</td>
<td>65</td>
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</tr>
<tr>
<td>9.60</td>
<td>115</td>
<td>870</td>
<td>24</td>
<td>154</td>
<td>&lt; 2.5</td>
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$^a$ O$_3$ always completely consumed.

$^b$ upper limit calculated from Eqn. I and the upper limit for the N$_2$O yield of 0.3 μ.
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