ON THE PRODUCTION OF N$_2$O FROM THE
REACTION OF O(1D) WITH N$_2$

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

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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

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

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

\[ \text{N}_2\text{O} \] was not found as a product. Thus from our detectability limit for \[ \text{N}_2\text{O} \] (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 $\text{N}_2\text{O}$ in the earth's upper atmosphere is still an unsolved problem. Some time ago Bates and Witherspoon\textsuperscript{1} considered the reaction

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

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

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

However very recently Nicolet\textsuperscript{3} has again considered reaction 1, and has concluded that if it occurs $\approx 10^{-4}$ 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. Gröth and Schierholz\textsuperscript{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\textsuperscript{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\textsuperscript{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°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 ($N_2 + O_2$, mostly $N_2$), we have found no evidence for $N_2O$ 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 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 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, $N_2O$ consumption for $N_2O$ pressures $\leq 10\mu$ via the above reactions is not important.

The known mechanism of $O_3$ photolysis at 2537 Å and in the presence of $O_2$ and $N_2$ is the following: 7

$$O_3 + hv \rightarrow O_2(1\Delta) + O(1D) \quad \text{Rate} = I_a$$

1

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

2

$$O(1D) + O_3 \rightarrow O_2 + O_2^*$$

3a

$$O(1D) + O_3 \rightarrow 2O_2$$

3b

$$O(1D) + O_2 \rightarrow O(3P) + O_2(1\Sigma)$$

4

$$O_2(1\Delta), O_2(1\Sigma) \text{ or } O_2^* + O_3 \rightarrow 2O_2 + O(3P)$$

5

$$O(3P) + O_3 \rightarrow 2O_2$$

6

$$O(3P) + O_2 + M \rightarrow O_3 + M$$

7

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 $N_2O$ and $O(1D)$ atoms produced. $n\{O(1D)\}$ is obtained by graphical integration from Eqn. II.

$$n\{O(1D)\} = I_a \int_0^\infty \frac{I_a}{T_o} \, dt$$

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 $200 \pm 30 \mu$min from the photolysis of $O_3$ alone, where the quantum yield of $O_3$ disappearance is 5.5 for small conversions. 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 $k_3/k_2 = 11.0$ 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. 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°C and 1000 torr total pressure (87% $N_2$). If reaction 1 is entirely in the third order regime, then $k_1/k_2 \leq 0.8 \times 10^{-25} \text{cm}^3/\text{particle}$. 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

The authors wish to thank Professor Marcel Nicolet who brought this problem to their attention. This work was supported by the National Aeronautics and Space Administration through Grant No. NGL-009-003 and the Atmospheric Sciences Section of The National Science Foundation through Grant No. GA-12385, for which we are grateful.
REFERENCES

7. For a recent review see E. Lissi and J. Heicklen, J. Photochem., in press (1972).
<table>
<thead>
<tr>
<th>$[O_3]_0$</th>
<th>$[O_2]$</th>
<th>$[N_2]$</th>
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<th>n(O$^1$D), Torr</th>
<th>$10^6 k_1 [M]/k_2$</th>
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<tr>
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<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>

a) $O_3$ always completely consumed

b) upper limit calculated from Eqn. I and the upper limit for the $N_2O$ yield of 0.3 μ.
FIGURE CAPTION

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