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ON THE PRODUCTION OF N_2O FROM THE REACTION OF $O(^1D)$ WITH N_2

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R. Simonaitis, Eduardo Lissi and Julian Heicklen

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University Park, Pennsylvania

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ABSTRACT

Ozone was photolyzed at 2537 A and 25°C in the presence of 42-115 torr of O_2 and about 880 torr of N_2 to test the relative importance of the two reactions

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

$$O(^1D) + N_2 \rightarrow O(^3P) + N_2 \qquad 2$$

N_2O was not found as a product. Thus from our detectability limit for N_2O (0.3 μ), an upper limit to the efficiency of the first reaction relative to the second of 2.5×10^{-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 N_2O in the earth's upper atmosphere is still an unsolved problem. Some time ago Bates and Witherspoon[1] considered the reaction

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

but more recently Bates and Hayes[2] ignored this reaction because it was negligible compared to the deactivation of $O(^1D)$ by N_2.

$$O(^1D) + N_2 \rightarrow O(^3P) + N_2 \qquad 2$$

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_2O in the stratosphere.

There is experimental evidence that reaction 1 does occur. Groth and Schierholz[4] photolyzed O_2 at 1470 A 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_2O. However, Katakis and Taube[5] photolyzed O_3 at 2537 A 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_2O formation, $\Phi\{N_2O\}$, 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 A, $\Phi\{N_2O\} = 0.014$. 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 (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 $\leq 2.6 \times 10^{-6}$ compared to reaction 2. This upper limit for the efficiency for this reaction has thus been reduced by a factor of 40.

EXPERIMENTAL

Matheson O_2 and Prep. Grade N_2 were purified by passage over traps maintained at -196°C. Both the N_2 and O_2 contained each other as impurities but this is irrelevant. Ozone was prepared by passing an electric discharge through the O_2. The O_3 produced was collected at -196°C, and the excess O_2 pumped away. The O_3 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 O_3 were measured on a sulfuric acid manometer; N_2 and O_2 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 O_3 was monitored by light absorption. Dark decomposition of the O_3 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 A 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 N_2O 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 $\sim 0.2 - 0.3\,\mu$ of N_2O.

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 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.

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

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_2O above that present as background (0.3 μ) was observed. Consequently, the upper limit for the N_2O yield is $\sim$0.3 μ. In order to be certain that the small amount of N_2O is not lost during analysis control experiments were done in which several μ of N_2O were added to an identical gas mixture as in an actual run. Complete recovery of the added N_2O was achieved. Finally, 10.5 μ of N_2O 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_2O concentration to be certain that N_2O 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, 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 A and in the presence of O_2 and N_2 is the following:[7]

$O_3 + h\nu \rightarrow O_2(^1\Delta) + O(^1D)$		Rate = I_a
$O(^1D) + N_2 + M \rightarrow N_2O + M$		1
$O(^1D) + N_2 \rightarrow O(^3P) + N_2$		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
$O_2(^1\Delta),\ O_2(^1\Sigma)$ 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

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

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.

$$n\{O(^1D)\} = I_a' \int_0^{\infty} \frac{I_a}{I_o}\, dt \qquad \text{II}$$

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 $200 \pm 30\,\mu$/min from the photolysis of O_3 alone, where the quantum yield of O_3 disappearance is 5.5 for small conversions.[7] 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 $k_3/k_2 = 11.0$ [7,8] and $k_4/k_2 = 0.8$ [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°C and 1000 torr total pressure (87% N_2). If reaction 1 is entirely in the third order regime, then $k_1/k_2 \leq 0.8 \times 10^{-25}$ cm^3/particle. The known value for k_2 is 9×10^{-11} cm^3/particle-sec,[10] and is probably accurate to better than a factor of two. Thus $k_1 < 0.7 \times 10^{-35}$ cm^6/particle-sec. At stratospheric pressures of 30-50 torr, reaction 1 occurs no more than 2×10^{-7} as often as reaction 2. This is about a factor of 500 smaller than the value estimated by Nicolet[3] to be necessary for reaction 1 to be an important atmospheric source of N_2O.

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TABLE I

$[O_3]_o$, Torr	$[O_2]$, Torr	$[N_2]$, Torr	Irradiation Time, hrs.[a]	$n\{O(^1D)\}$, Torr	$10^6 k_1 [M]/k_2$ [b]
12.0	42	890	23	63	< 5
6.80	47	900	12	65	< 5
9.60	115	870	24	154	< 2.5

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 A and 25°C of a mixture consisting initially of 9.6 torr O_3, 115 torr O_2, and 870 torr N_2.

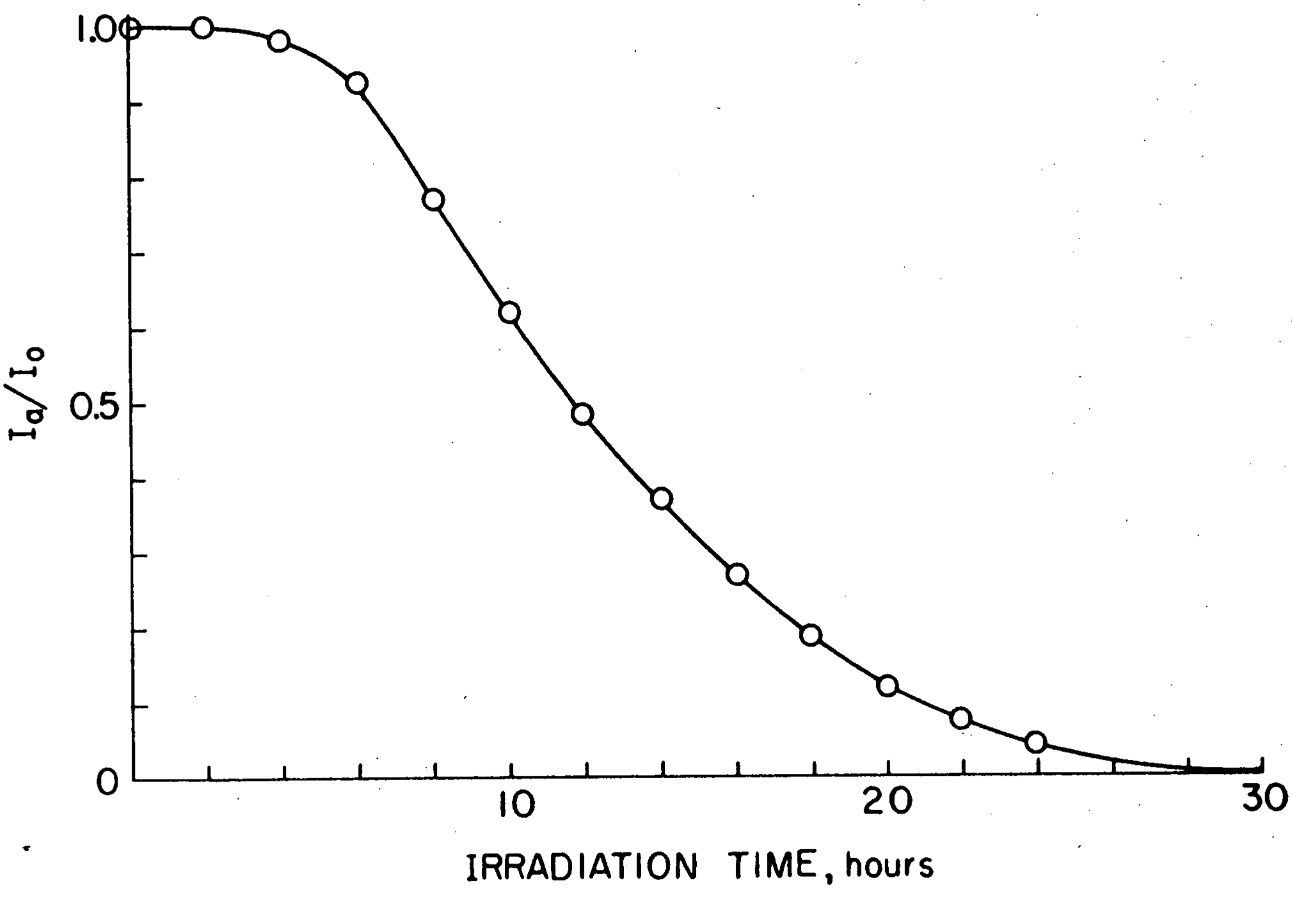

Figure 1