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Scientific Report No. 343

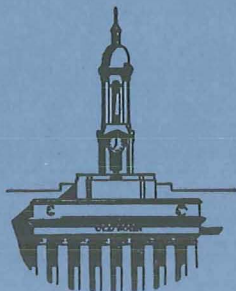
REACTION OF O(¹D) WITH N₂O

by

R. I. Greenberg and J. P. Heicklen

November 15, 1969

IONOSPHERE RESEARCH LABORATORY



University Park, Pennsylvania NASA Grant NGL-39-009-003

THE PENNSYLVANIA STATE UNIVERSITY
Ionosphere Research Laboratory

Errata Sheet

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"Reaction of $O(^1D)$ with N_2O "

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The conclusions were based on the assumption that each O_2 reacted with 2NO molecules before chemical analysis. Further checking revealed that actually each O_2 reacted with 4NO molecules. Therefore $\Phi_m \{O_2\} = \Phi \{O_2\} - \frac{1}{4} \Phi \{NO\}$ rather than $\Phi_m \{O_2\} = \Phi \{O_2\} - \frac{1}{2} \Phi \{NO\}$. The rate constant ratio of 1.12 ± 0.02 computed for k_2/k_3 should be changed to 0.59 ± 0.01 .

Ionospheric Research
NASA Grant NGL-39-009-003

Scientific Report

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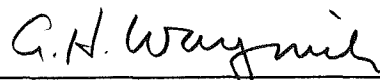
Ionosphere Research Laboratory

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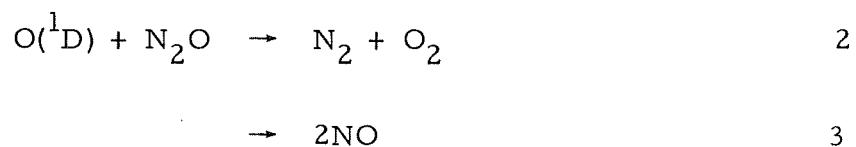
The Pennsylvania State University

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ABSTRACT

The reaction of $O(^1D)$, produced from the photolysis of N_2O at 2139 Å, reacts with N_2O via



We have used the method of chemical difference to obtain an accurate measure of $k_2/k_3 = 1.12 \pm 0.02$. Furthermore the quantum yield of production of $O(^3P)$, either from direct photolysis or deactivation of $O(^1D)$ by N_2O , is less than 0.02 and probably zero.

REACTION OF O(¹D) WITH N₂O

The photolysis of N₂O with either 1849 or 2139 Å^o radiation leads almost exclusively to the production of O(¹D)¹⁻⁵



The excited oxygen atom can then react further to produce O₂, NO, and additional N₂.



From the product quantum yields obtained in previous investigations with 1849 Å^o radiation, the ratio k_2/k_3 can be estimated based on a mechanism consisting solely of reactions 1-3. These estimates are listed in Table I. They vary from 0.5 to 1.44, and each estimate has considerable uncertainty. Furthermore Yamazaki and Cvetanovic² have also given evidence that at 1849 Å^o, about 20 percent of the primary decomposition might occur via



This reaction would complicate the analysis. However it should be much less important at 2139 Å^o, where there is barely sufficient energy for it to proceed.

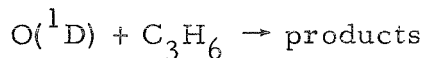
We have examined the photolysis of N_2O at $2139 \overset{\circ}{\text{A}}$, assumed reaction 4 to be negligible, and have used the method of chemical difference to accurately compute $k_2/k_3 = 1.12 \pm 0.02$.

The photolyses were done in a quartz reaction cell 10 cm long by 5 cm in diameter. The effective radiation was at $2139 \overset{\circ}{\text{A}}$ from a Philips 93106 E Zn resonance lamp. After irradiation the products (N_2 , O_2 , NO) were collected in a Toepler pump and compressed before analysis. The compression induces the reaction



which goes to completion. The NO is completely consumed and was never detected, even though a thorough search was made (Pure NO in the absence of O_2 is easily detected). In this way the measured quantum yield of O_2 production, $\Phi_m \{O_2\}$, is really $\Phi \{O_2\} - (1/2) \Phi \{NO\}$. Since this is the quantity most useful in determining k_2/k_3 , this method of chemical difference reduces the experimental uncertainty by a factor of 10 or more. The products are then introduced, through a four-way stopcock, into a Gow-Mac 40-05D chromatograph utilizing a thermister detector and a 12 foot long $5 \overset{\circ}{\text{A}}$ molecular sieve column.

Actinometry was done by photolysis of N_2O in the presence of an excess of C_3H_6 to scavenge $O(^1D)$, $\Phi \{N_2\}$ drops to 1.00. In order to insure that sufficient C_3H_6 was used it was first necessary to obtain the rate constant ratio for the competition between reactions 2 plus 3 with



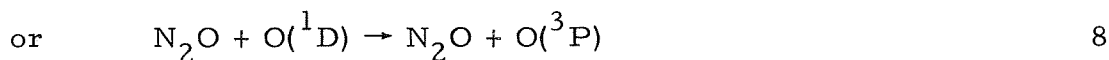
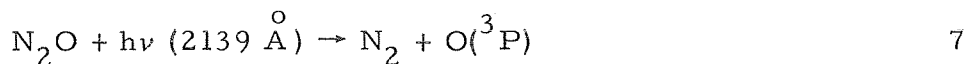
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Experiments were done with various mixtures of C_3H_6 and N_2O . The results are shown in Table II. As $[C_3H_6] / [N_2O]$ is raised both $\Phi\{N_2\}$ and $\Phi_m\{O_2\}$ drop; the former toward 1.00, the latter to zero. The rate of reaction 6, $R\{6\}$ is equal to $R\{2\} + R\{3\}$ when the drop is half-way. From the data in the Table, $k_6/(k_2 + k_3)$ can be estimated to be 8.0. Thus with $[C_3H_6] / [N_2O] \geq 2$, at least 94 percent of the excited oxygen atoms are scavenged by C_3H_6 , and absolute quantum yields can be computed.

The results of the photolyses of N_2O alone at $2139 \overset{\circ}{\text{A}}$ are shown in Table III. The pressure of N_2O was varied tenfold; I_a , by a factor of 14.5; and the extent of decomposition by a factor of 6. The results were completely invariant to any of these variations.

$\Phi\{N_2\} = 1.51 \pm 0.11$ and $\Phi_m\{O_2\} = 0.059 \pm 0.007$. Assuming that only Reactions 1, 2, 3 and 5 are important k_2/k_3 can be computed to be 1.04 ± 0.48 based on $\Phi\{N_2\}$ and 1.12 ± 0.02 based on $\Phi_m\{O_2\}$. It is clear that the uncertainty in the value based on $\Phi_m\{O_2\}$ is at least 20 times smaller than that based on $\Phi\{N_2\}$. This illustrates the advantage of obtaining differences between two quantities of similar value by chemical rather than analytical methods. Our result so obtained is in excellent agreement with that obtained by a similar method using NO_2 photolysis at $2139 \overset{\circ}{\text{A}}$ as a source of $O(^1D)$.¹⁰

In addition to the reactions of $O(^1D)$ it is necessary to consider the possibility of the presence of the $O(^3P)$ which might have been produced in one of two ways.



If present $\text{O}({}^3\text{P})$ would react with NO to ultimately produce O_2 via



No NO would be consumed, but some O_2 would have been produced in addition to that formed by Reaction 2. To check this possibility some experiments were done in the presence of 1 torr C_3H_6 to scavenge any $\text{O}({}^3\text{P})$. Under the conditions of the experiments the C_3H_6 removes less than 18 percent of the $\text{O}({}^1\text{D})$ atoms and usually much less. If any $\text{O}({}^3\text{P})$ had been present, $\Phi_m\{\text{O}_2\}$ would have been diminished. In fact for the six runs with 1 torr of C_3H_6 , $\Phi\{\text{N}_2\} = 1.48 \pm 0.15$ and $\Phi_m\{\text{O}_2\} = 0.059 \pm 0.009$ which are identical to the values found in the absence of C_3H_6 . It can be concluded that the quantum yield of $\text{O}({}^3\text{P})$ production is less than 0.02 and probably zero. The absence of $\text{O}({}^3\text{P})$ means that Reactions 7 and 8 are unimportant, and also requires that Reaction 4 be negligible, as it would be followed by



ACKNOWLEDGEMENTS

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TABLE I

Values of k_2/k_3

<u>VALUE</u>	<u>BASIS</u>	<u>REFERENCE</u>
1.0	$\Phi \{O_2\} = 0.5$	MacDonald ⁶
0.7	$\Phi \{N_2\} = 1.4$	Noyes ⁷
0.5	$\Phi \{O_2\} = 0.35$	Noyes ⁷
1.56 (1.1 - 2.2)	$\Phi \{N_2\} = 1.61 \pm 0.08$	Zelikoff and Aschenbrand ⁸
1.38 (1.22 - 1.56)	$\Phi \{O_2\} = 0.58 \pm 0.03$	Zelikoff and Aschenbrand ⁸
0.78 (0.64 - 0.96)	$\Phi \{N_2\} = 1.44 \pm 0.05$	Castellion and Noyes ⁹
1.44	$\Phi \{NO\} = 0.82$	Castellion and Noyes ⁹
1.04 (0.67 - 1.63)	$\Phi \{N_2\} = 1.51 \pm 0.11$	This work
1.12 ± 0.02	$\Phi_m \{O_2\} = 0.059 \pm 0.007$	This work

TABLE II
 Photolysis of 300 Torr N₂O at 2139 Å and Room Temperature
 in the Presence of C₃H₆

<u>[C₃H₆], torr</u>	<u>I_a, μ/hr.</u>	<u>Exposure time, hrs.</u>	<u>Φ_m {O₂}^(a)</u>	<u>Φ {N₂}</u>
0.0	--	0.50	0.054	1.46 ^(b)
37.5	246	1.00	0.040	1.27
39	327	1.00	0.017	1.16
40	246	1.00	0.014	1.13
41	327	1.00	0.008	1.22
600	327	0.50	0.0	1.03

(a) $\Phi_m \{O_2\} = \Phi \{O_2\} - (1/2) \Phi \{NO\}$

(b) average value taken from Table III, C

TABLE III

Photolysis of Nitrous Oxide at 2139 Å^o
and Room Temperature

Exposure time, hrs.	I_a , μ /hr.	$\Phi\{N_2\}$	$\Phi_m\{O_2\}^{(a)}$
(A) 30 torr N ₂ O			
1.50	30.6	1.43	0.054
1.50	43.0	1.53	-
1.50	30.6	1.35	-
10.00	28.6	1.45	0.060
2.00	46.8	1.59	0.065
2.07	46.8	1.78	0.071
2.00	46.8	1.68	0.054
2.00	48.3	1.66	0.081 ^b
6.00	35.0	1.61	0.052
6.00	35.0	1.64	0.061
6.00	35.0	1.27	0.064 ^b
(B) 100 torr N ₂ O			
0.50	166	1.42	0.064
1.00	166	1.36	0.063
1.00	152	1.59	0.069
1.00	120	1.72	0.049 ^b
1.00	120	1.50	0.053 ^b
3.00	120	1.60	0.060
1.00	97	1.43	0.058
(C) 300 torr N ₂ O			
4.00	45.0	1.37	0.052
4.00	41.3	1.63	-
4.00	41.3	1.44	0.054
4.00	33.3	1.36	0.042
0.33	414	1.62	0.050
0.50	414	1.56	0.068
0.50	414	1.46	0.062
0.50	414	1.46	0.052
0.50	414	1.39	0.050 ^b
0.50	414	1.35	0.055 ^b

(a) $\Phi_m\{O_2\} = \Phi\{O_2\} - (1/2)\Phi\{NO\}$

(b) 1.0 ± 0.2 torr C₃H₆ present