PSU-IRL-SCI-411
Classification Numbers 1.9.2

N73-15388

THE PENNSYLVANIA
STATE UNIVERSITY

IONOSPHERIC RESEARCH

Scientific Report 411

PHOTOLYSIS OF O_3 AT 3130A

CASE FILE
COPY

by

R. Simonaitis, S. Braslavsky, Julian Heicklen,
and M. Nicolet

November 1, 1972

The research reported in this document has been sponsored by the National Science Foundation under Grants GA-12385 and GA-33446X and the National Aeronautics and Space Administration under Grant No. NGL-39-009-003.

IONOSPHERE RESEARCH LABORATORY

University Park, Pennsylvania

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)*

Ionosphere Research Laboratory

2a. REPORT SECURITY CLASSIFICATION

2b. GROUP

3. REPORT TITLE

Photolysis of O_3 at 3130A

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

Scientific Report

5. AUTHOR(S) *(First name, middle initial, last name)*

Simonaitis, Romualdas, S. Braslavsky, Julian Heicklen

6. REPORT DATE

November 1, 1972

7a. TOTAL NO. OF PAGES

9

7b. NO. OF REFS

8a. CONTRACT OR GRANT NO.

NSF GA-12385 and GA-33446X

NASA NGL-39-009-003

b. PROJECT NO.

c.

d.

9a. ORIGINATOR'S REPORT NUMBER(S)

PSU-IRL-SCI-411

9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*

10. DISTRIBUTION STATEMENT

Supporting Agency

11. SUPPLEMENTARY NOTES

12. SPONSORING MILITARY ACTIVITY

National Science Foundation
National Aeronautics and Space Administration

13. ABSTRACT

The photolysis of O_3 at 3130A and 25°C has been studied in the presence of a large excess of N_2O to react with any $O(^1D)$ atoms produced. From the N_2 produced, the quantum efficiency for $O(^1D)$ production was found to be 0.50 ± 0.03.

DD FORM 1 NOV 65 1473 (PAGE 1)

S/N 0101-807-6811

NONE

Security Classification

A-31408

PSU-IRL-SCI-411
Classification Numbers 1.9.2

Scientific Report 411

Photolysis of O_3 at 3130A

by

R. Simonaitis, S. Braslavsky, Julian Heicklen,

and M. Nicolet

November 1, 1972

The research reported in this document has been sponsored by the National Science Foundation under Grants GA-12385 and GA-33446X and the National Aeronautics and Space Administration under Grant No. NGL-39-009-003.

Submitted by: Julian Heicklen
Julian Heicklen, Professor of Chemistry
Project Supervisor

Approved by: Anthony J. Ferraro
Anthony J. Ferraro, Acting Director
Ionosphere Research Laboratory

Ionosphere Research Laboratory

The Pennsylvania State University

University Park, Pennsylvania 16802

ABSTRACT

The photolysis of O_3 at 3130A and 25°C has been studied in the presence of a large excess of N_2O to react with any $O(^1D)$ atoms produced. From the N_2 produced, the quantum efficiency for $O(^1D)$ production was found to be 0.50 ± 0.03.

Much of the solar radiation absorbed by the ozone in the stratosphere is in the range of 3000-3400A. Consequently, it is important to know the nature of the primary fragments produced in O_3 photolysis in this wavelength range if one is to understand the complex chemistry in the O_3 layer.

The photolysis of O_3 in the range of 2200-3000A, mainly at 2537A, has been extensively studied.[1] It is now accepted that the primary process is

$$O_3 + h\nu(<3000A) \rightarrow O_2(^1\Delta) + O(^1D) \qquad 1a$$

The electronically excited species react with O_3 as follows

$$O_2(^1\Delta) + O_3 \rightarrow 2O_2 + O(^3P) \qquad 2$$

$$O(^1D) + O_3 \rightarrow O_2 + O_2^* \qquad 3a$$

$$\rightarrow 2O_2 \qquad 3b$$

$$O(^3P) + O_3 \rightarrow 2O_2 \qquad 4$$

$$O_2^* + O_3 \rightarrow 2O_2 + O(^3P) \qquad 5$$

where O_2^* is one of the high-lying electronic states of O_2 (or even two $O(^3P)$ atoms, in which case reaction 5 is unnecessary). The rate coefficient ratio $k_{3a}/k_3 = 0.75 \pm 0.25$ where $k_3 \equiv k_{3a} + k_{3b}$.[1]

The dissociation enthalpy of O_3 at 0°K can be computed to be 24.2 kcal/mole from thermodynamic data.[2] From spectroscopic data, the electronic excitation energy in $O_2(^1\Delta)$ and $O(^1D)$ is 20.8 and 45.4 kcal/mole, respectively. Thus for wavelengths $>$ 3160A, there is insufficient energy (i.e. $<$ 90.4 kcal/mole) for reaction 1a to occur. The other possible primary processes are

$$O_3 + h\nu \rightarrow O_2(^3\Sigma) + O(^1D) \qquad 1b$$

$$\rightarrow O_2(^3\Sigma) + O(^3P) \qquad 1c$$

$$\rightarrow O_2(^1\Delta \text{ or } ^1\Sigma) + O(^3P) \qquad 1d$$

Whereas primary process 1a leads to a quantum yield of O_3 disappearance, $-\Phi\{O_3\}$, of 5.5 ± 0.5, processes 1b, 1c, and 1d predict $-\Phi\{O_3\} = 3.5 \pm 0.5$, 2.0, and 4.0, respectively.

Two groups have investigated the photodecomposition at 3340A by monitoring $-\Phi\{O_3\}$. Castellano and Schumacher[3] found $-\Phi\{O_3\} = 4.0$, and Jones and Wayne[4,5] found $-\Phi\{O_3\} = 3.6 \pm 0.4$. Furthermore Jones and Wayne[5] added H_2, found no increase of $-\Phi\{O_3\}$, and concluded that $O(^1D)$ was not produced. Thus the sole primary process at 3340A is reaction 1d.

Presumably the primary process changes from reaction 1a to reaction 1d near the energy threshold at 3160A. Thus at 3130A both processes may be occurring. The gas phase photolysis has been studied at 3130A by Castellano and Schumacher[6] and Jones and Wayne.[4,5] Both groups monitored $-\Phi\{O_3\}$, but the two groups obtained conflicting results. The former investigators found $-\Phi\{O_3\} = 6.0$ and concluded that reaction 1a was the sole reaction, whereas the latter investigators found $-\Phi\{O_3\}$ to be close to 4.0 and concluded that reaction 1d must be dominant. However Jones and Wayne[5] did add H_2, and found an enhancement in $-\Phi\{O_3\}$, so that some $O(^1D)$ must be produced.

Three studies have also been made in condensed phases at 3130A. Taube[7] studied the reaction in H_2O, whereas DeMore and Raper[8,9] studied the reaction in liquid Ar at 87°K. In these studies the efficiency of $O(^1D)$ production was monitored in three different ways. The results were all similar and DeMore and Raper[9] concluded that the efficiency of $O(^1D)$ production was 0.4 ± 0.15.

It is clear that the primary process at 3130A in the gas phase is not yet established. Therefore we have measured the efficiency of $O(^1D)$ production at room temperature by photolyzing O_3 in the presence of excess

N_2O. These experiments are similar to those of Goldman et al.[10] The only additional reactions are

$$O(^1D) + N_2O \rightarrow N_2 + O_2 \qquad 6a$$

$$\rightarrow 2NO \qquad 6b$$

The quantum efficiency for $O(^1D)$ production, $\phi\{O(^1D)\}$, is given by

$$\phi\{O(^1D)\} = \Phi\{N_2\}(k_6/k_{6a})(1 + k_3[O_3]/k_6[N_2O]) \qquad I$$

Thus the measurement of $\Phi\{N_2\}$ will give $\phi\{O(^1D)\}$ providing k_6/k_{6a} and k_3/k_6 are known. The ratio k_6/k_{6a} has been measured carefully.[11,12] For translationally equilibrated $O(^1D)$ atoms, as would be produced here, $k_6/k_{6a} = 2.1$. For thermal $O(^1D)$ atoms, k_3/k_6 is about 4.[1,10] This value is not very accurately known, but since $[O_3] << [N_2O]$, $k_3[O_3]/k_6[N_2O]$ contributes only slightly to the calculation.

The experimental procedure was similar to that of Goldman et al.[10] The 3130A radiation was obtained from a 400 watt Hanovia medium pressure lamp. The radiation passed through an interference filter centered at ∿3150A with a 120A half-band-width. To be sure that the Hg line at 3020A was not contributing to the photolysis, the extinction coefficient for O_3 was measured and it agreed with that at 3130A. No more than 10% of the absorbed radiation could be at 3020A. Actinometry was obtained by measuring the N_2 produced in the photolysis of $CH_3N_2CH_3$ at matched absorbance, using an RCA 935 phototube to measure the absorbance. $\Phi\{N_2\}$ is known to be 1.0 in the $CH_3N_2CH_3$ photolysis.[13] Some N_2 was produced in unirradiated N_2O-O_3 mixtures, but this was only 5-10% of that produced during irradiation. Corrections for this background N_2 were made.

The results of the experiments are shown in Table I. It can be seen that $\phi\{O(^1D)\}$ is 0.50 ± 0.03 in good agreement with the liquid phase results.[7-9] Presumably at 3130A, the primary process is 50% reaction 1a and 50% reaction 1d. If so the predicted value for $-\Phi\{O_3\}$ is 4.8 ± 0.2. This value lies exactly between those found by Jones and Wayne[4,5] and Castellano and Schumacher.[6]

A value of 0.50 for the quantum efficiency at 3130A is an indication that there is production of $O(^1D)$ atoms not only in the stratosphere but also in the troposphere down to ground level. Then excited atoms which are not quenched by N_2 and O_2 will produce NO molecules by reaction with N_2O and OH radicals by reaction with H_2O, CH_4 and H_2 in the troposphere and stratosphere.

ACKNOWLEDGMENT

This work was supported by the Aeronomy Section of the National Science Foundation under Grant Nos. GA 12385 and GA 33446X and the National Aeronautics and Space Administration under Grant No. NGL-009-003, for which we are grateful.

Table I: Photolysis of O_3-N_2O Mixtures at 3130A and 25°C

$[O_3]$, Torr	$[N_2O]$, Torr	$\Phi\{N_2\}$	$\phi\{O(^1D)\}^a$
8.7	520	0.273	0.53
17.5	430	0.200	0.48
27.5	520	0.215	0.52
33.8	490	0.172	0.45
			Ave. = 0.50 ± 0.03

a) calculated from Eqn. I.

REFERENCES

1. For a review see E. Lissi and J. Heicklen, *J. Photochemistry*, *1*, 39 (1972).
2. J.A.N.A.F. Interim Thermochemical Tables, Edited by D. R. Stull, Dow Chemical Co., Midland, Mich. (1966).
3. E. Castellano and H. J. Schumacher, *Chem. Phys. Lettr.*, *13*, 625 (1972).
4. I. T. N. Jones and R. P. Wayne, *J. Chem. Phys.*, *51*, 3617 (1969).
5. I. T. N. Jones and R. P. Wayne, *Proc. Roy. Soc.*, *A 319*, 273 (1970).
6. E. Castellano and H. J. Schumacher, *Z. Physik. Chem.*, *65*, 62 (1969).
7. H. Taube, *Trans. Faraday Soc.*, *53*, 656 (1957).
8. W. DeMore and O. F. Raper, *J. Chem. Phys.*, *37*, 2048 (1962).
9. W. B. DeMore and O. F. Raper, *J. Chem. Phys.*, *44*, 1780 (1966).
10. C. S. Goldman, R. I. Greenberg, and J. Heicklen, *Intern. J. Chem. Kinetics*, *3*, 501 (1971).
11. P. M. Scott, K. F. Preston, R. J. Andersen, and L. M. Quick, *Canad. J. Chem.*, *49*, 1808 (1971).
12. R. Simonaitis, R. I. Greenberg, and J. Heicklen, *Intern. J. Chem. Kinetics*, *4*, 497 (1972).
13. J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons (1966), p. 463.